09/12/2021

1. Hardness
2. Corrosion
3. Fuel & Consumption
4. Spectroscopy
    - → UV Visible
    - → Infra Red
    - → Micro Wave
5. Nano materials

C_8H_{18}

$(C_2H_5)_4Pb$ TEL (Tetra ethyl lead)

Leaded Petrol

Book - Engineering Chem. By Jain & Jain. - 16th

—x—

Stearic acid - saturated fatty acid - 18 C-chain - IUPAC: Octadecanoic acid.

$C_{18}H_{36}O_2$ or $C_{17}H_{35}CO_2H$ - The salts & esters of stearic acid → stearates. It is a Waxy Solid.

Palmitic acid - saturated fatty acid - 16 - C - backbone (straight chain) Hexadecanoic acid

$CH_3(CH_2)_{14}COOH$ or $C_{16}H_{32}O_2$

$$\underset{\text{sodium stearate SOAP}}{2C_{17}H_{35}COONa} + \underset{\text{Hardness causing substance}}{CaCl_2} \longrightarrow \underset{\text{Calcium Stearate (insoluble) white ppt}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2NaCl$$

MODULE - II

Water Treatments

① Types of Hardness - Units.

② Alkalinity of water & its significance.

③ Softening methods & numerical problems based on these methods.

④ Membrane-based processes.

⑤ Dissolved Oxygens.

⑥ Problems with Boiler feed water & its treatments.

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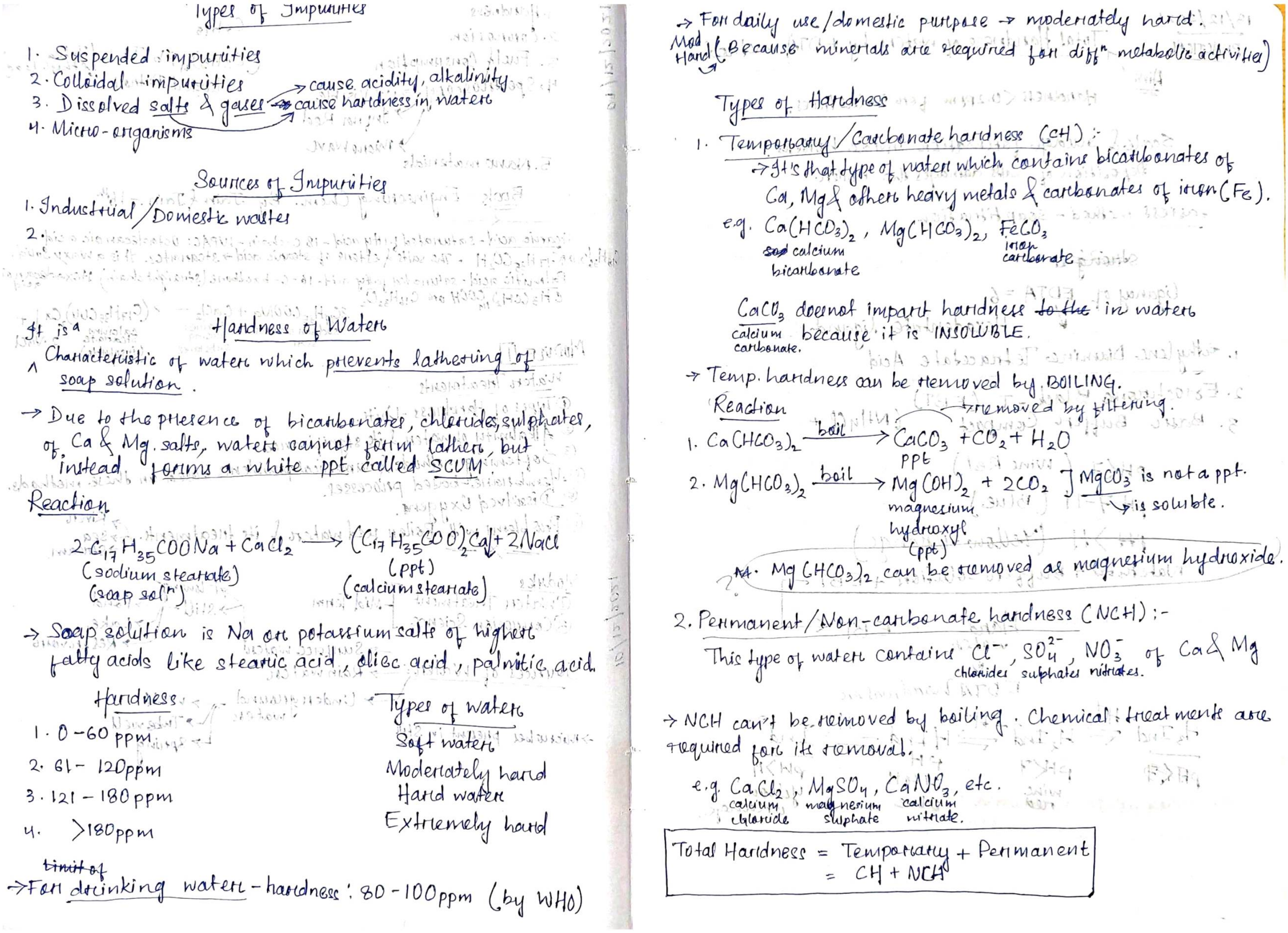
10/12/2021

Modules

①Water Treatment
②Corrosion Science
} Mid Term

Sources of Water
- → Surface water
    - → Flowing
        - → River
        - → Sea
        - → Stream
    - → Still
        - → Pond
        - → Lake
        - → Reservoirs
- → Rain water
- → Underground water
    - → well
    - → Tube well
    - → Spring

→ Microbes present in Still



Types of Impurities

1. Suspended impurities
2. Colloidal impurities → cause acidity, alkalinity
3. Dissolved salts & gases → cause hardness in water
4. Micro-organisms

Sources of Impurities

1. Industrial / Domestic wastes
2.

Hardness of Water

It is a Characteristic of water which prevents lathering of soap solution.

→ Due to the presence of bicarbonates, chlorides, sulphates, of Ca & Mg. salts, water cannot form lather, but instead forms a white ppt. called SCUM.

Reaction

$$\underset{\substack{\text{(sodium stearate)}\\ \text{(soap sol}^n\text{)}}}{2C_{17}H_{35}COONa} + CaCl_2 \longrightarrow \underset{\substack{\text{(ppt)}\\ \text{(calcium stearate)}}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2NaCl$$

→ Soap solution is Na or potassium salts of higher fatty acids like stearic acid, oliec acid, palmitic acid.

Hardness	Types of water
1. 0 – 60 ppm	Soft water
2. 61 – 120 ppm	Moderately hard
3. 121 – 180 ppm	Hard water
4. >180 ppm	Extremely hard

→ For drinking water – ~~limit of~~ hardness : 80 - 100 ppm (by WHO)

→ For daily use / domestic purpose → moderately hard.

Mod Hard (Because minerals are required for diff^n metabolic activities)

Types of Hardness

1. Temporary / Carbonate hardness (CH) :-

→ It's that type of water which contains bicarbonates of Ca, Mg & other heavy metals & carbonates of iron (Fe).

e.g. $\underset{\text{calcium bicarbonate}}{Ca(HCO_3)_2}$, $Mg(HCO_3)_2$, $\underset{\text{iron carbonate}}{FeCO_3}$

$\underset{\text{calcium carbonate.}}{CaCO_3}$ doesnot impart hardness ~~to the~~ in water because it is INSOLUBLE.

→ Temp. hardness can be removed by BOILING.

Reaction

$$1.\ Ca(HCO_3)_2 \xrightarrow{\text{boil}} \underset{\text{ppt}}{CaCO_3} + CO_2 + H_2O$$

→ removed by filtering.

$$2.\ Mg(HCO_3)_2 \xrightarrow{\text{boil}} \underset{\substack{\text{magnesium}\\ \text{hydroxyl}\\ \text{(ppt)}}}{Mg(OH)_2} + 2CO_2$$

$MgCO_3$ is not a ppt. → is soluble.

$Mg(HCO_3)_2$ can be removed as magnesium hydroxide.

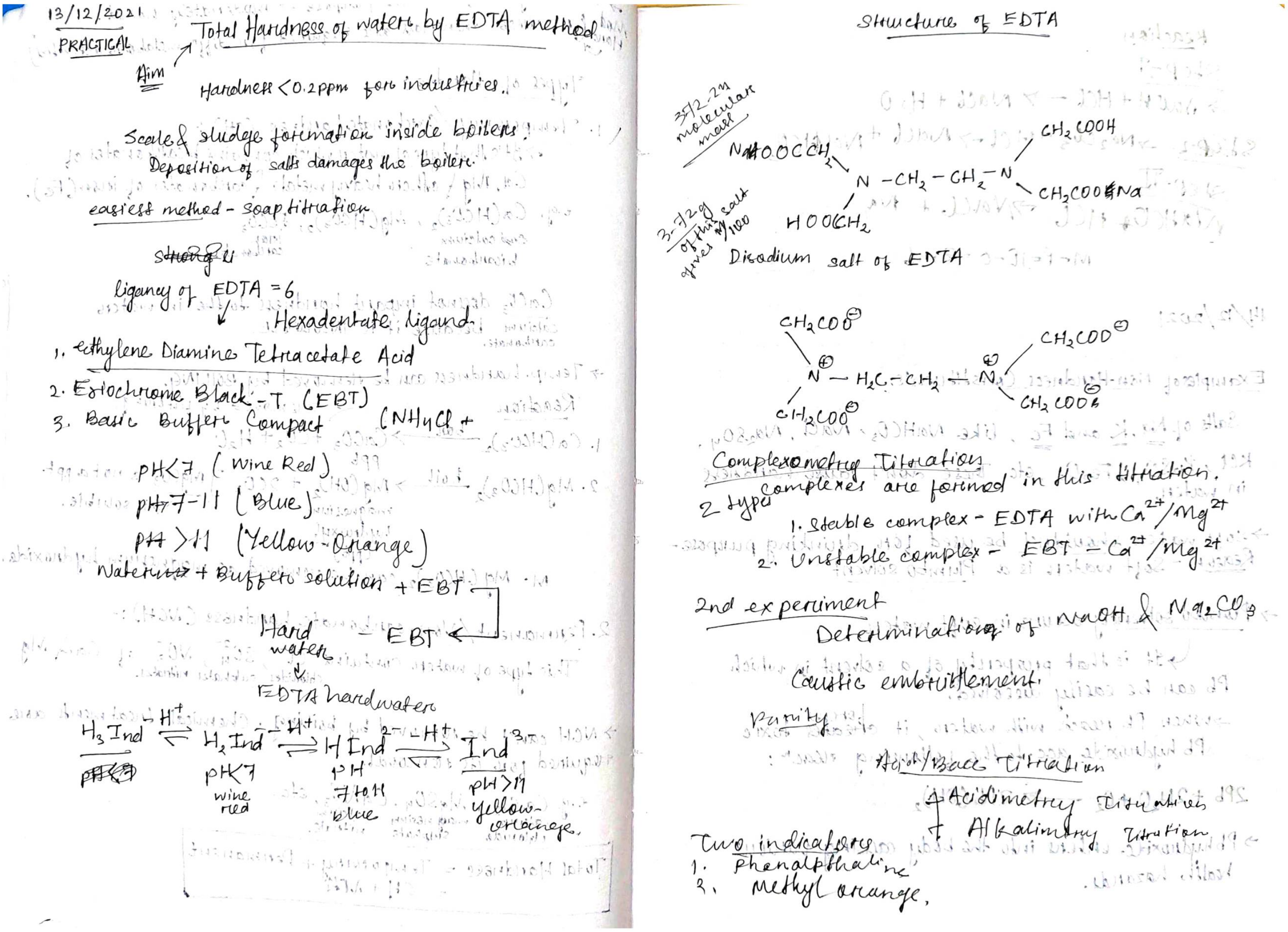
2. Permanent / Non-carbonate hardness (NCH) :-

This type of water contains $\underset{\text{chlorides}}{Cl^-}$, $\underset{\text{sulphates}}{SO_4^{2-}}$, $\underset{\text{nitrates.}}{NO_3^-}$ of Ca & Mg

→ NCH can't be removed by boiling. Chemical treatments are required for its removal.

e.g. $\underset{\text{calcium chloride}}{CaCl_2}$, $\underset{\text{magnesium sulphate}}{MgSO_4}$, $\underset{\text{calcium nitrate.}}{CaNO_3}$, etc.

$$\boxed{\begin{aligned}\text{Total Hardness} &= \text{Temporary} + \text{Permanent}\\ &= CH + NCH\end{aligned}}$$



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PRACTICAL

Aim ↗ Total Hardness of water by EDTA method

Hardness < 0.2ppm for industries.

Scale & sludge formation inside boilers.
Deposition of salts damages the boiler.

easiest method - soap titration

~~strong~~ Li

ligancy of EDTA = 6
↓
Hexadentate ligand.

1. ethylene Diamine Tetracetate Acid
2. Eriochrome Black - T (EBT)
3. Basic Buffer Compact (NH$_4$Cl +

pH<7 (Wine Red)
pH 7-11 (Blue)
pH >11 (Yellow-Orange)

~~Water~~ + Buffer solution + EBT

Hard water − EBT
↓
EDTA hardwater

$H_3Ind \underset{}{\overset{-H^+}{\rightleftharpoons}} H_2Ind^- \overset{-H^+}{\rightleftharpoons} HInd^{2-} \overset{-H^+}{\rightleftharpoons} Ind^{3-}$

H$_3$Ind: ~~pH<7~~
H$_2$Ind$^-$: pH<7, wine red
HInd^{2-}: pH 7 to 11, blue
Ind^{3-}: pH>11, yellow-orange.

Structure of EDTA

372.24 molecular mass

3.72g of this salt gives M/100

Disodium salt of EDTA

Complexometry Titration

2 types complexes are formed in this titration.

1. Stable complex - EDTA with Ca^{2+}/Mg^{2+}
2. Unstable complex - EBT − Ca^{2+}/Mg^{2+}

2nd experiment

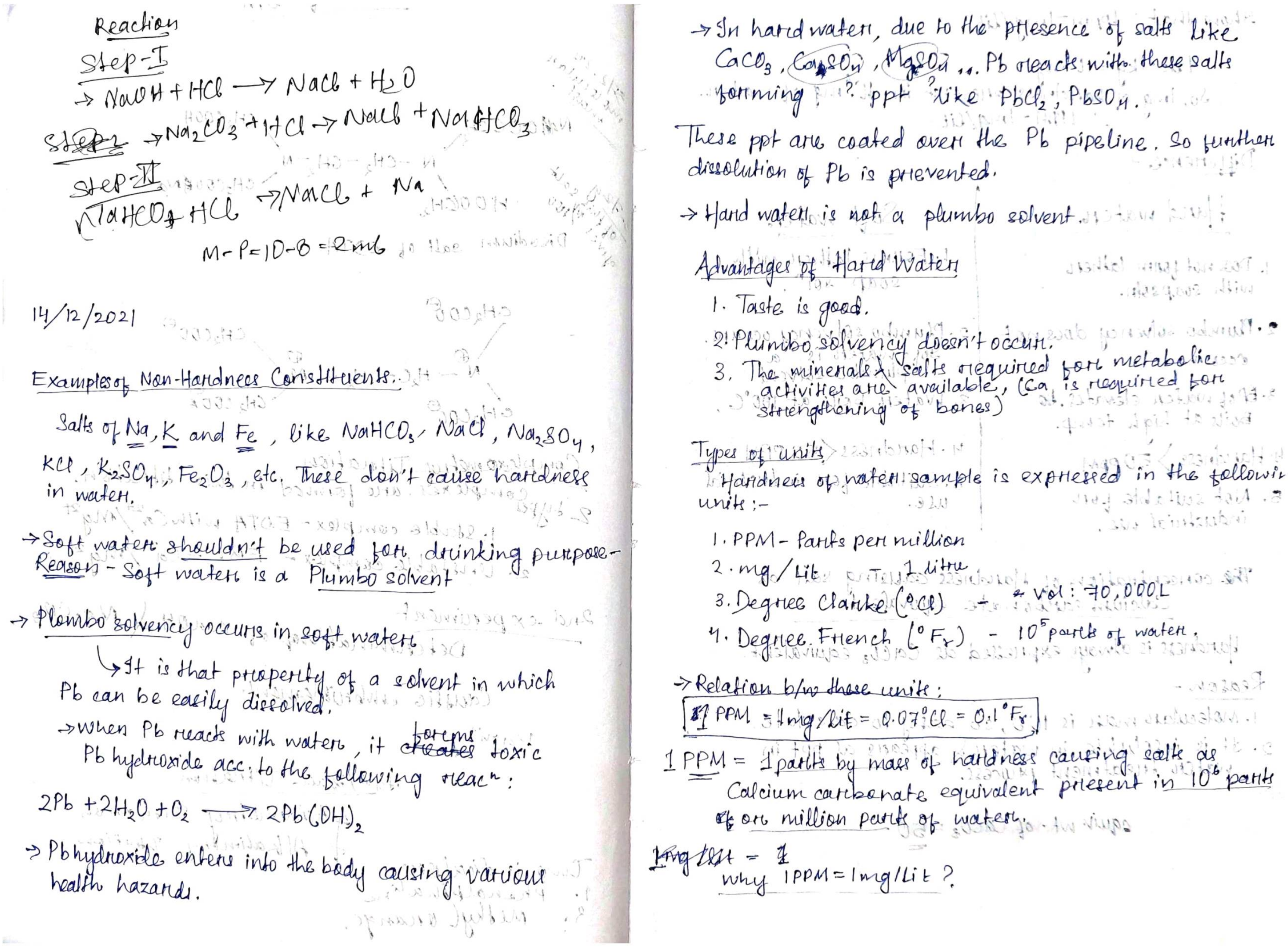
Determination of NaOH & Na$_2$CO$_3$

Caustic embrittlement.

Purity

Acid/Base Titration
- Acidimetry Titration
- Alkalimetry Titration

Two indicators
1. Phenalpthaline
2. Methyl orange.



Reaction

Step-I

→ $NaOH + HCl \longrightarrow NaCl + H_2O$

Step-2 → $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

Step-III

$NaHCO_3 + HCl \rightarrow NaCl + Na$

M-P = 10-8 = 2 ml

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Examples of Non-Hardness Constituents:

Salts of Na, K and Fe, like $NaHCO_3$, $NaCl$, Na_2SO_4, KCl, K_2SO_4, Fe_2O_3, etc. These don't cause hardness in water.

→ Soft water shouldn't be used for drinking purpose-

Reason - Soft water is a Plumbo solvent

→ Plumbo solvency occurs in soft water

↳ It is that property of a solvent in which Pb can be easily dissolved.

→ When Pb reacts with water, it ~~creates~~ forms toxic Pb hydroxide acc. to the following reacⁿ:

$$2Pb + 2H_2O + O_2 \longrightarrow 2Pb(OH)_2$$

→ Pb hydroxide enters into the body causing various health hazards.

→ In hard water, due to the presence of salts like $CaCO_3$, $CaSO_4$, $MgSO_4$ .. Pb reacts with these salts forming ? ppt ?like $PbCl_2$, $PbSO_4$.

These ppt are coated over the Pb pipeline. So further dissolution of Pb is prevented.

→ Hard water is not a plumbo solvent.

Advantages of Hard Water

1. Taste is good.
2. Plumbo solvency doesn't occur.
3. The minerals & salts required for metabolic activities are available, (Ca is required for strengthening of bones)

Types of units

Hardness of water sample is expressed in the following units:-

1. PPM - Parts per million
2. mg/Lit — 1 litre
3. Degree Clarke (°Cl) — vol: 70,000L
4. Degree French (°Fr) - 10^5 parts of water.

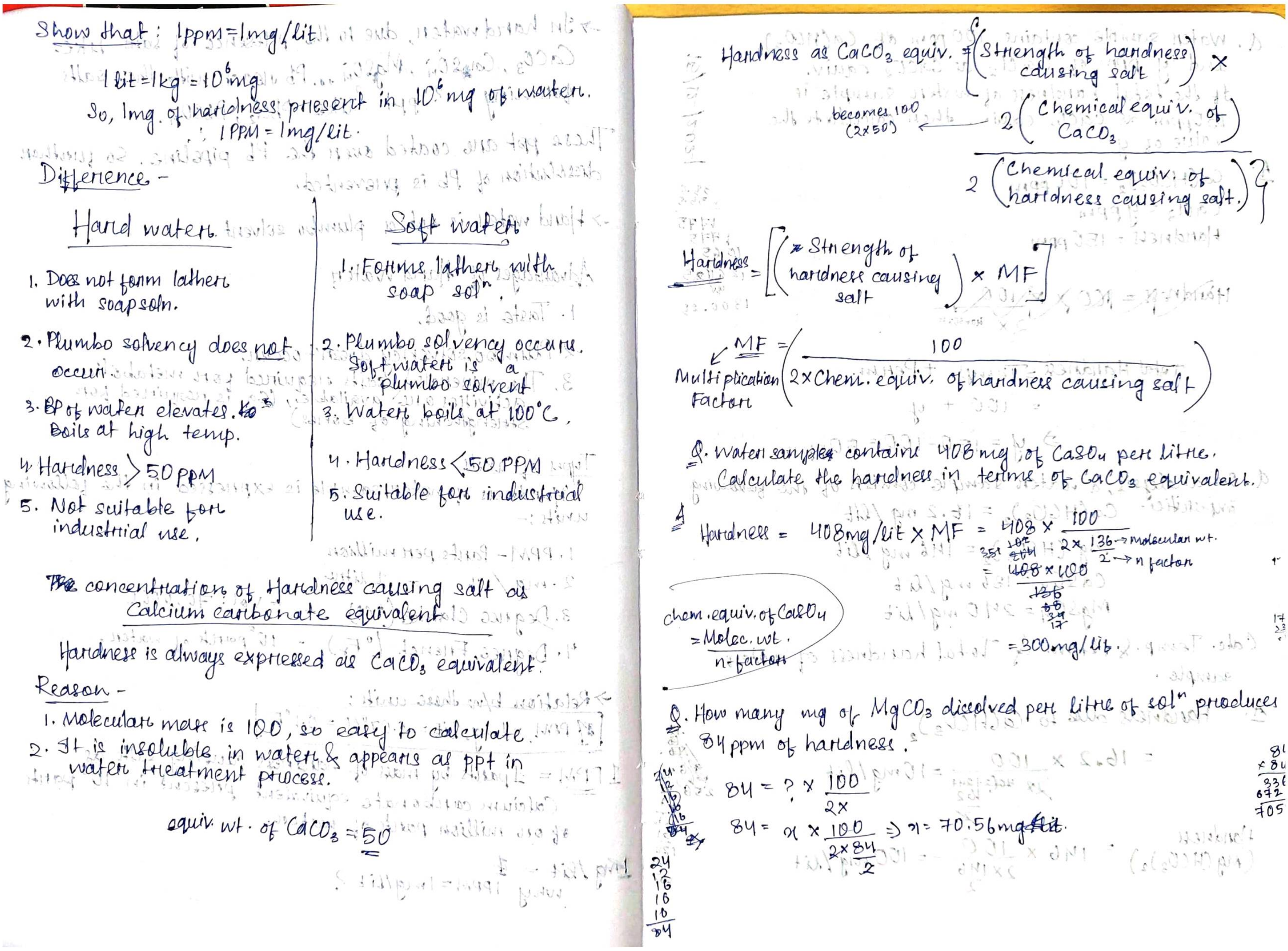
→ Relation b/w these units:

$$\boxed{1\ PPM = 1mg/lit = 0.07°Cl = 0.1°Fr}$$

1 PPM = 1 parts by mass of hardness causing salts as Calcium carbonate equivalent present in 10^6 parts or one million parts of water.

1mg/Lit = 1

why 1PPM = 1mg/Lit?



Show that: 1ppm = 1mg/lit.

1 lit = 1kg = 10^6mg

So, 1mg. of hardness present in 10^6 mg of water.

∴ 1PPM = 1mg/lit.

Difference -

Hard water.	Soft water
1. Does not form lather with soapsoln.	1. Forms lather with soap sol^n.
2. Plumbo solvency does not occur.	2. Plumbo solvency occurs. Soft water is a plumbo solvent
3. BP of water elevates. ~~to~~ Boils at high temp.	3. Water boils at 100°C.
4. Hardness > 50 PPM	4. Hardness < 50 PPM
5. Not suitable for industrial use.	5. Suitable for industrial use.

~~The~~ concentration of Hardness causing salt as Calcium carbonate equivalent

Hardness is always expressed as $CaCO_3$ equivalent.

Reason -

1. Molecular mass is 100, so easy to calculate.
2. It is insoluble in water & appears as ppt in water treatment process.

equiv. wt. of $CaCO_3$ = 50

$$\text{Hardness as } CaCO_3 \text{ equiv.} = \left\{ \left(\begin{array}{c}\text{Strength of hardness}\\ \text{causing salt}\end{array}\right) \times \frac{2\left(\begin{array}{c}\text{Chemical equiv. of}\\ CaCO_3\end{array}\right)}{2\left(\begin{array}{c}\text{Chemical equiv. of}\\ \text{hardness causing salt.}\end{array}\right)} \right\}$$

becomes 100 (2×50) ←

$$\text{Hardness} = \left[\left(\begin{array}{c}\text{Strength of}\\ \text{hardness causing}\\ \text{salt}\end{array}\right) \times MF \right]$$

$$MF = \left(\frac{100}{2 \times \text{Chem. equiv. of hardness causing salt}} \right)$$

↙ Multiplication Factor

Q. Water samples contains 408 mg of $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalent.

A

$$\text{Hardness} = 408\text{mg/lit} \times MF = 408 \times \frac{100}{2 \times \frac{136}{2}}$$

136 → molecular wt.

2 → n factor

$$= \frac{408 \times 100}{136}$$

= 300mg/lit.

chem. equiv. of $CaSO_4$ = $\frac{\text{Molec. wt.}}{\text{n-factor}}$

Q. How many mg of $MgCO_3$ dissolved per litre of sol^n produces 84 ppm of hardness.

$$84 = ? \times \frac{100}{2x}$$

$$84 = x \times \frac{100}{2 \times \frac{84}{2}} \Rightarrow x = 70.56\text{mg}~~\text{lit}~~.$$

24
12
16
16
16
84

84
× 84
336
672
7056

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Q. Water sample contains 100 ppm of $Ca(HCO_3)_2$ and 'y' ppm of $CaCl_2$ as $CaCO_3$ equiv. If the total hardness of water sample is 150ppm as $CaCO_3$ equiv. then calculate the value of y.

A: $Ca(HCO_3)_2 = 100$ppm

$CaCl_2 = y$ ppm

Hardness = 150 ppm

~~Hardness = 100 × M 100 / 2 × 40+35×35~~

35.5
× 35.5
1775
1775
1065
126025
1300.25

Total Hardness = Temp. + Perm.

= 100 + y

⇒ y = 150 − 100 = 50ppm

Q. On analysis, a water sample consists of the following impurities- $Ca(HCO_3)_2$ = 16.2 mg/lit

$Mg(HCO_3)_2$ = 146 mg/lit

$CaSO_4$ = 136 mg/lit

$MgSO_4$ = 240 mg/lit

Calc. Temp. & Perm. & Total hardness of water sample.

A. Hardness due to $Ca(HCO_3)_2$

$$= 16.2 \times \frac{100}{\cancel{2\times} \frac{\cancel{40+(2+24)}\ 162}{\cancel{2}}} = 10 \text{ mg/lit}$$

Hardness ($Mg(HCO_3)_2$) $= 146 \times \frac{100}{2\times\frac{146}{2}} = 100$ mg/lit

122
40
162

Hardness ($CaSO_4$) $= 136 \times \frac{100}{\cancel{2}\times\frac{136}{\cancel{2}}} = 100$ mg/lit

Hardness ($MgSO_4$) $= 240 \times \frac{100}{2\times\frac{\cancel{240}\ 120}{2}} = 200$ mg/lit

Temp. H = 110

Perm. H = 300

T. Hardness = 410 ppm

Q. Water sample on analysis was found to contain the following impurities: Na_2SO_4 = 100mg/lit

KCl = 200mg/lit

$CaCl_2$ = 333 mg/lit

$CaSO_4$ = 13.6 mg/lit

Calc. Temp., Perm., Total Hardness of water sample.

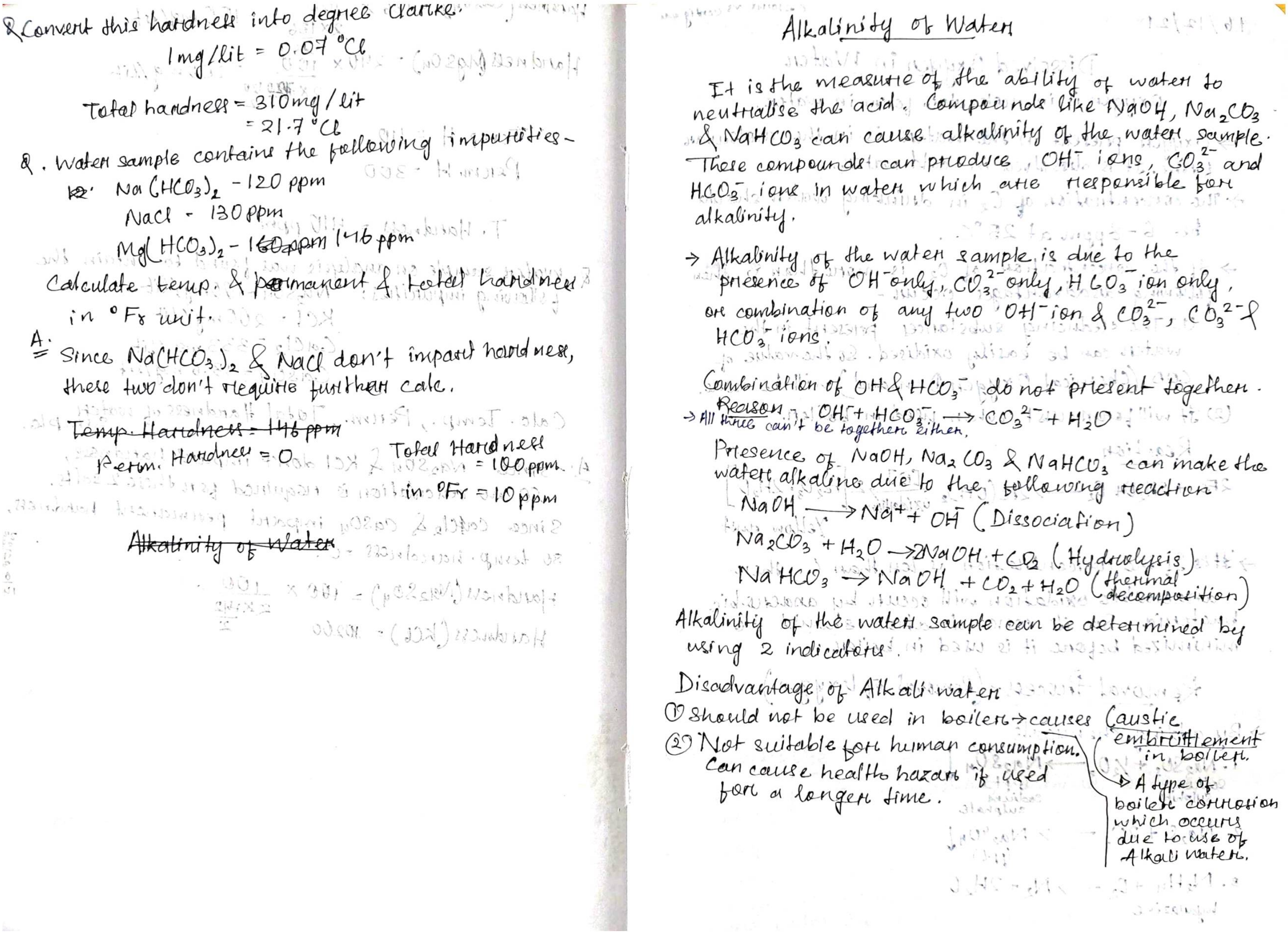
A. Since Na_2SO_4 & KCl don't impart hardness, so no calculation is required for these 2 salts.

Since $CaCl_2$ & $CaSO_4$ impart permanent hardness, so temp. hardness = 0.

23
23
46
32
64
142

Hardness (Na_2SO_4) $= \cancel{100} \times \frac{100}{\cancel{2\times}\frac{142}{\cancel{2}}}$

Hardness (KCl) = ~~10~~200



Q. Convert this hardness into degree Clarke.

$1 mg/lit = 0.07 °Cl$

Total hardness $= 310 mg/lit$
$= 21.7 °Cl$

Q. Water sample contains the following impurities –
~~1.~~ $Na(HCO_3)_2$ – 120 ppm
$NaCl$ – 130 ppm
$Mg(HCO_3)_2$ – ~~160 ppm~~ 146 ppm
Calculate temp. & permanent & total hardness in °Fr unit.

A. Since $Na(HCO_3)_2$ & $NaCl$ don't impart hardness, these two don't require further calc.

~~Temp. Hardness = 146 ppm~~

Perm. Hardness = 0

Total Hardness = 100 ppm
in °Fr = 10 ppm

~~Alkalinity of Water~~

Alkalinity of Water

It is the measure of the ability of water to neutralise the acid. Compounds like $NaOH$, Na_2CO_3 & $NaHCO_3$ can cause alkalinity of the water sample. These compounds can produce OH^- ions, CO_3^{2-} and HCO_3^- ions in water which are responsible for alkalinity.

→ Alkalinity of the water sample is due to the presence of OH^- only, CO_3^{2-} only, HCO_3^- ion only, or combination of any two OH^- ion & CO_3^{2-}, CO_3^{2-} & HCO_3^- ions.

Combination of OH & HCO_3^- do not present together.
Reason – $OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$
→ All three can't be together either.

Presence of $NaOH$, Na_2CO_3 & $NaHCO_3$ can make the water alkaline due to the following reaction

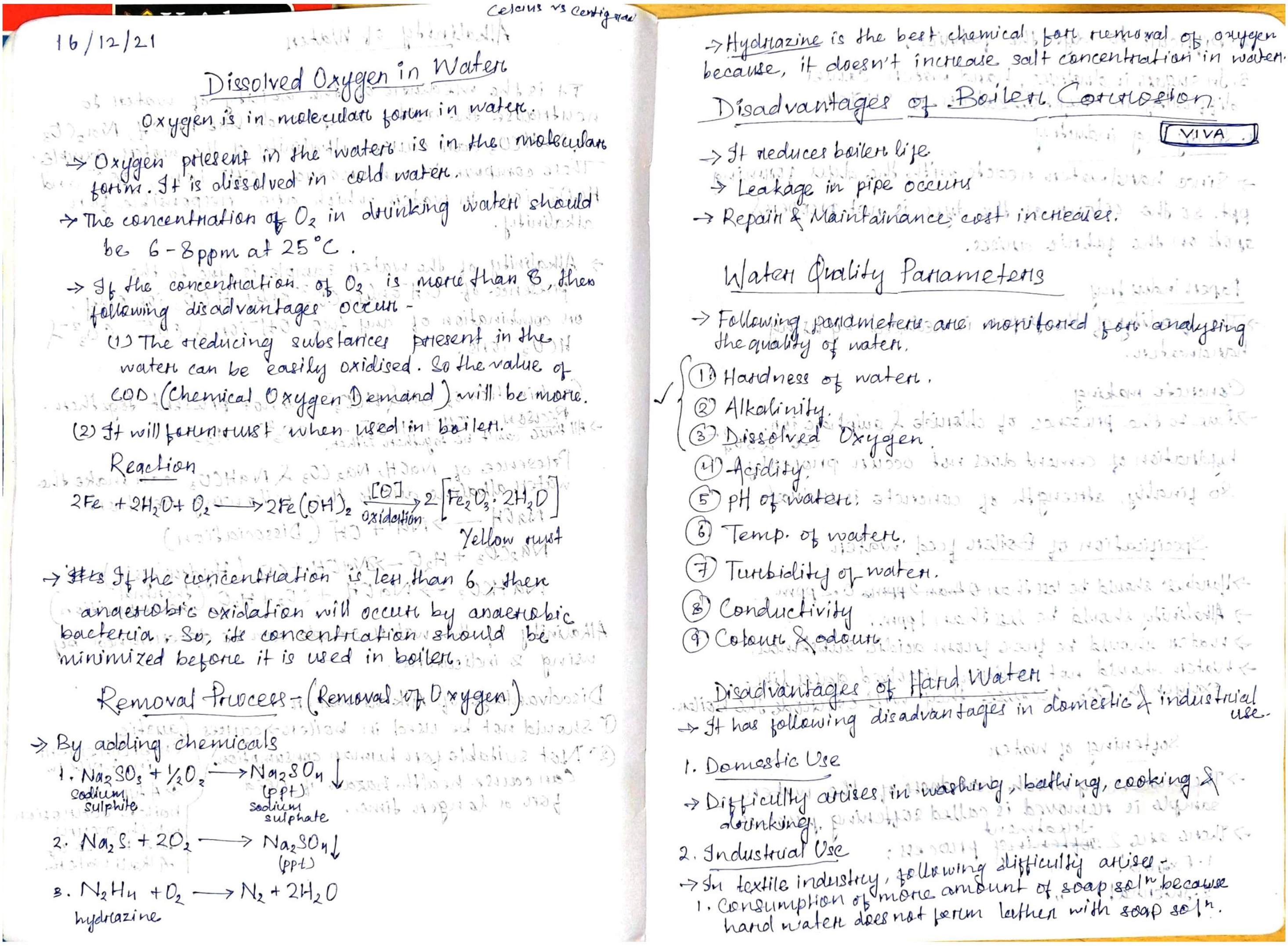
$NaOH \longrightarrow Na^+ + OH^-$ (Dissociation)

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$ (Hydrolysis)

$NaHCO_3 \rightarrow NaOH + CO_2 + H_2O$ (thermal decomposition)

Alkalinity of the water sample can be determined by using 2 indicators.

Disadvantage of Alkali water
① Should not be used in boiler → causes Caustic embrittlement in boiler.
→ A type of boiler corrosion which occurs due to use of Alkali water.
② Not suitable for human consumption. Can cause health hazard if used for a longer time.



Celcius vs Centigrade

16/12/21

Dissolved Oxygen in Water

Oxygen is in molecular form in water.

→ Oxygen present in the water is in the molecular form. It is dissolved in cold water.

→ The concentration of O_2 in drinking water should be 6-8ppm at 25°C.

→ If the concentration of O_2 is more than 8, then following disadvantages occur -

(1) The reducing substances present in the water can be easily oxidised. So the value of COD (Chemical Oxygen Demand) will be more. ✓

(2) It will form rust when used in boiler.

Reaction

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2 \xrightarrow[\text{oxidation}]{[O]} 2\left[Fe_2O_3 \cdot 2H_2O\right]$$

Yellow rust

→ ~~Its~~ If the concentration is less than 6, then anaerobic oxidation will occur by anaerobic bacteria. So, its concentration should be minimized before it is used in boiler.

Removal Process - (Removal of Oxygen)

→ By adding chemicals

1. $Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 \downarrow$
   sodium sulphite → (ppt) sodium sulphate
2. $Na_2S + 2O_2 \longrightarrow Na_2SO_4 \downarrow$ (ppt)
3. $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
   hydrazine

→ Hydrazine is the best chemical for removal of oxygen because, it doesn't increase salt concentration in water.

Disadvantages of Boiler Corrosion

VIVA

→ It reduces boiler life.

→ Leakage in pipe occurs

→ Repair & Maintainance cost increases.

Water Quality Parameters

→ Following parameters are monitored for analysing the quality of water.

✓
① Hardness of water.
② Alkalinity.
③ Dissolved Oxygen.
④ Acidity.
⑤ pH of water.
⑥ Temp. of water.
⑦ Turbidity of water.
⑧ Conductivity
⑨ Colour & odour.

Disadvantages of Hard Water

→ It has following disadvantages in domestic & industrial use.

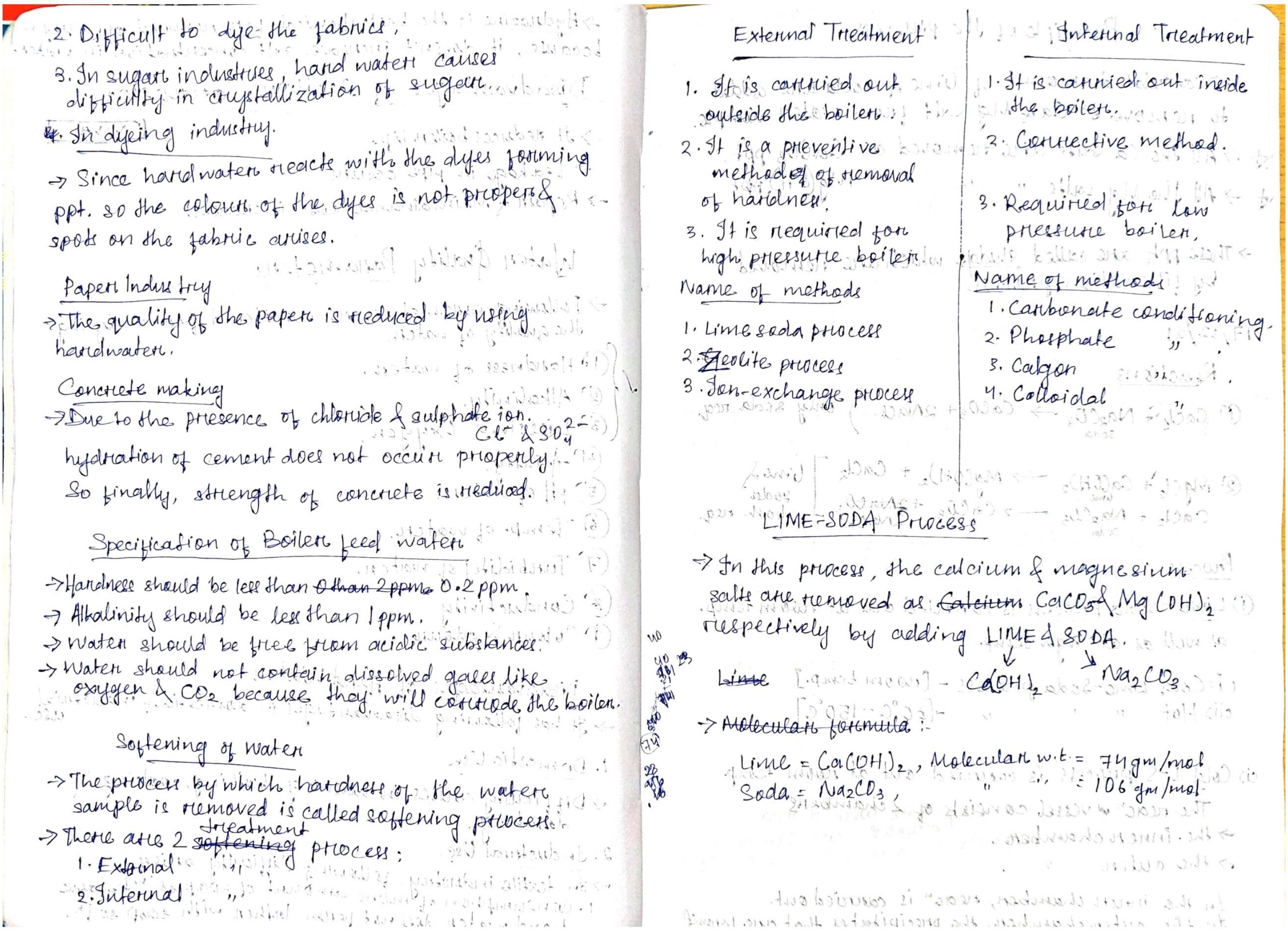
1. Domestic Use

→ Difficulty arises in washing, bathing, cooking & drinking.

2. Industrial Use

→ In textile industry, following difficulty arises -

1. Consumption of more amount of soap solⁿ because hard water does not form lather with soap solⁿ.



2. Difficult to dye the fabrics,
3. In sugar industries, hard water causes difficulty in crystallization of sugar.
~~4.~~ In dyeing industry.

→ Since hardwater reacts with the dyes forming ppt. so the colour of the dyes is not proper & spots on the fabric arises.

Paper Industry

→ The quality of the paper is reduced by using hardwater.

Concrete making

→ Due to the presence of chloride & sulphate ion. $Cl^- \& SO_4^{2-}$ hydration of cement does not occur properly. So finally, strength of concrete is reduced.

Specification of Boiler feed water

→ Hardness should be less than ~~0 than 2ppm~~ 0.2 ppm.
→ Alkalinity should be less than 1 ppm.
→ Water should be free from acidic substances.
→ Water should not contain dissolved gases like oxygen & CO_2 because they will corrode the boiler.

Softening of water

→ The process by which hardness of the water sample is removed is called softening process.
→ There are 2 ~~softening~~ treatment process:
1. External ,,
2. Internal ,,

External Treatment	Internal Treatment
1. It is carried out outside the boiler.	1. It is carried out inside the boiler.
2. It is a preventive method of removal of hardness.	3. Corrective method.
3. It is required for high pressure boiler.	3. Required for low pressure boiler.
Name of methods	Name of methods
1. Lime soda process	1. Carbonate conditioning.
2. Zeolite process	2. Phosphate ,,
3. Ion-exchange process	3. Calgon
	4. Colloidal ,,

LIME-SODA Process

→ In this process, the calcium & magnesium salts are removed as ~~Calcium~~ $CaCO_3$ & $Mg(OH)_2$ respectively by adding LIME & SODA.

~~Lime~~ $Ca(OH)_2$ Na_2CO_3

→ ~~Molecular formula~~ :-

Lime = $Ca(OH)_2$, Molecular w.t = 74 gm/mol
Soda = Na_2CO_3, " " = 106 gm/mol

Principle of the process

→ Calculated amount of lime & soda are added to remove Ca & Mg salt from water sample.

☆ → All the Ca salts are removed as $CaCO_3$ ppt.

☆ → All the Mg salts " " " $Mg(OH)_2$ ppt

→ These ppt$_s$ are called sludge which are removed by filteration process.

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Reactions

① $CaCl_2 + \underset{soda}{Na_2CO_3} \rightarrow CaCO_3 + 2NaCl$) only soda req.

② $MgCl_2 + \underset{lime}{Ca(OH)_2} \longrightarrow Mg(OH)_2 + CaCl_2$
$CaCl_2 + \underset{soda}{Na_2CO_3} \longrightarrow CaCO_3 + \cancel{2NaCO_3}\ 2NaCl$] lime & soda both req.

Process

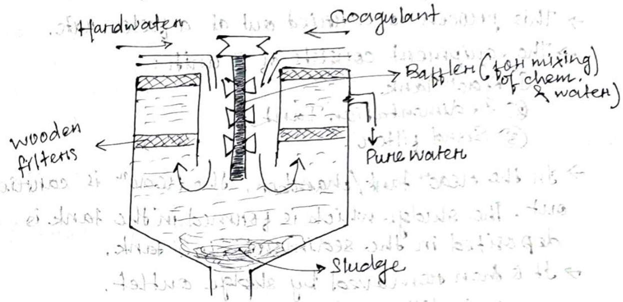
① Lime-Soda Process is carried out at room temp. as well as at high temp.

(i) Cold Lime-Soda process - [room temp.]
(ii) Hot " " " -[80°C - 150°C]

(i) Cold L-S process is carried out at room temp.
The reac^n vessel consists of 2 chambers
→ the inner chamber.
→ the outer " .

In the inner chamber, reac^n is carried out.
In the outer chamber, the precipitates that are formed in the inner chamber are deposited as sludge.

→ Since, the reac^n is carried out at room temp, the precipitates don't settle down easily, so ~~COAGULANTS~~ coagulants are required for the settling down of the ppt$_s$.



→ Coagulants are added for settling down of the precipitates.

Examples of coagulants-

Alum = $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Sodium Aluminate = $NaAlO_2$

→ Since, this process is carried out at room temp., the ppt$_s$ don't settledown easily, so coagulants are added for settling down of the ppts.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

→ $Al(OH)_3$ traps all the ppts forming a bigger size particle.

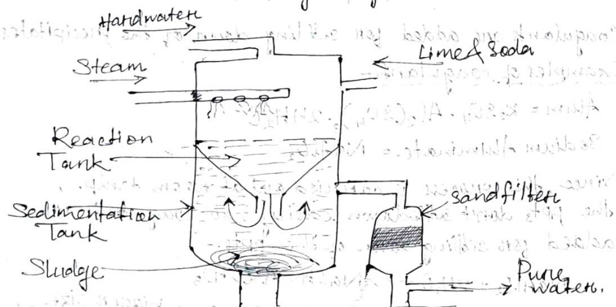
→ So, the ppt easily settles down.

Disadvantage of this process-

→ Hardness is reduced to 50-60 ppm, so it is not suitable for boiler.
→ The process is very slow.
→ Coagulants are required.
→ It is difficult to remove sludge.

(ii) **Hot-Lime Soda Process** is carried out at a temp. of 80°C - 150°C.

- → Since it is carried out at high temp., ppt's settle down easily.
- → This process is carried out at a faster rate.
- → The equipment consists of 3 units :
  - ① Reac^n Tank.
  - ② Sedimentation Tank.
  - ③ Sand filter.
- → In the reac^n tank/chamber, the reac^n is carried out. The sludge which is formed in the tank is deposited in the sedimentation tank.
- → It is then removed by sludge outlet.



Advantages -

- → It is a ~~faster p~~ faster process.
- → Hardness is reduced to 15-30 ppm
- → Micro organisms are removed.
- → Coagulants are not required, since it is carried out at higher temp.

Calculation for Lime and Soda

① **Reactions**

① $Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3$ ✗

Since ($NaHCO_3$) is present in water, & makes the water alkaline, which is not suitable for boiler. So, we can't use Na_2CO_3 for the removal of $Ca(HCO_3)_2$

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

Requirement: 1L (1 mole of lime)

② **Reactions** - $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$

$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + \cancel{Ca(HCO_3)_2}$

$\cancel{Ca(HCO_3)_2} + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$

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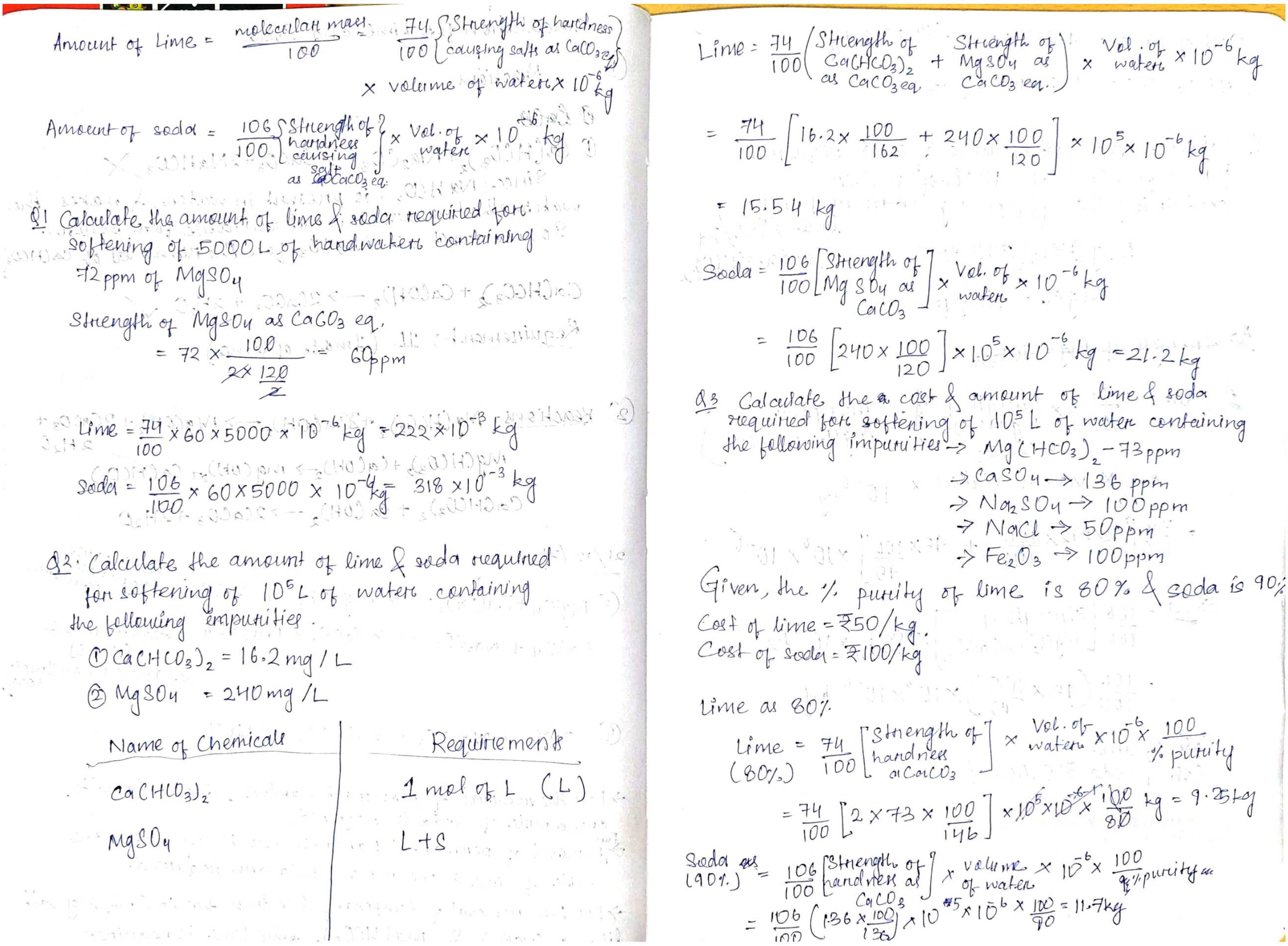
③ $MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$ → will cause hardness once more.

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$

requirement (L+S) i.e. (1 mole lime + 1 mole soda)

④ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

- → For the removal of permanent hardness due to Ca salts, one mole of soda is required.
- → For Removal of permanent hardness due to Mg salts, one mole of lime & one mole of soda are required.
- → For the removal of temporary hardness due to Ca & Mg salts like $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$ only lime is required.



Amount of Lime = $\frac{\text{molecular mass}}{100} = \frac{74}{100}\begin{Bmatrix}\text{Strength of hardness}\\ \text{causing salts as } CaCO_3 \text{ eq}\end{Bmatrix}$ $\times$ volume of water $\times 10^{-6}$ kg

Amount of soda = $\frac{106}{100}\begin{Bmatrix}\text{Strength of}\\ \text{hardness}\\ \text{causing}\\ \text{salt}\\ \text{as } CaCO_3 \text{ eq.}\end{Bmatrix} \times$ Vol. of water $\times 10^{-6}$ kg

Q1 Calculate the amount of lime & soda required for softening of 5000L of hardwater containing 72 ppm of $MgSO_4$

Strength of $MgSO_4$ as $CaCO_3$ eq.

$= 72 \times \frac{100}{\cancel{2}\times \frac{120}{\cancel{2}}} = 60$ ppm

Lime $= \frac{74}{100} \times 60 \times 5000 \times 10^{-6}$ kg $= 222 \times 10^{-3}$ kg

Soda $= \frac{106}{100} \times 60 \times 5000 \times 10^{-4}$ kg $= 318 \times 10^{-3}$ kg

Q2. Calculate the amount of lime & soda required for softening of 10^5 L of water containing the following impurities.

① $Ca(HCO_3)_2 = 16.2$ mg / L

② $MgSO_4 = 240$ mg /L

Name of Chemical	Requirements
$Ca(HCO_3)_2$	1 mol of L (L)
$MgSO_4$	L+S

Lime $= \frac{74}{100}\begin{pmatrix}\text{Strength of}\\ Ca(HCO_3)_2\\ \text{as } CaCO_3 \text{ eq}\end{pmatrix} + \begin{pmatrix}\text{Strength of}\\ MgSO_4 \text{ as}\\ CaCO_3 \text{ eq.}\end{pmatrix} \times$ Vol. of water $\times 10^{-6}$ kg

$= \frac{74}{100}\left[16.2 \times \frac{100}{162} + 240 \times \frac{100}{120}\right] \times 10^5 \times 10^{-6}$ kg

$= 15.54$ kg

Soda $= \frac{106}{100}\begin{bmatrix}\text{Strength of}\\ MgSO_4 \text{ as}\\ CaCO_3\end{bmatrix} \times$ Vol. of water $\times 10^{-6}$ kg

$= \frac{106}{100}\left[240 \times \frac{100}{120}\right] \times 10^5 \times 10^{-6}$ kg $= 21.2$ kg

Q3 Calculate the ~~a~~ cost & amount of lime & soda required for softening of 10^5 L of water containing the following impurities →

→ $Mg(HCO_3)_2$ – 73ppm
→ $CaSO_4$ → 136 ppm
→ Na_2SO_4 → 100ppm
→ $NaCl$ → 50ppm
→ Fe_2O_3 → 100ppm

Given, the % purity of lime is 80% & soda is 90%

Cost of lime = ₹50/kg.

Cost of soda = ₹100/kg

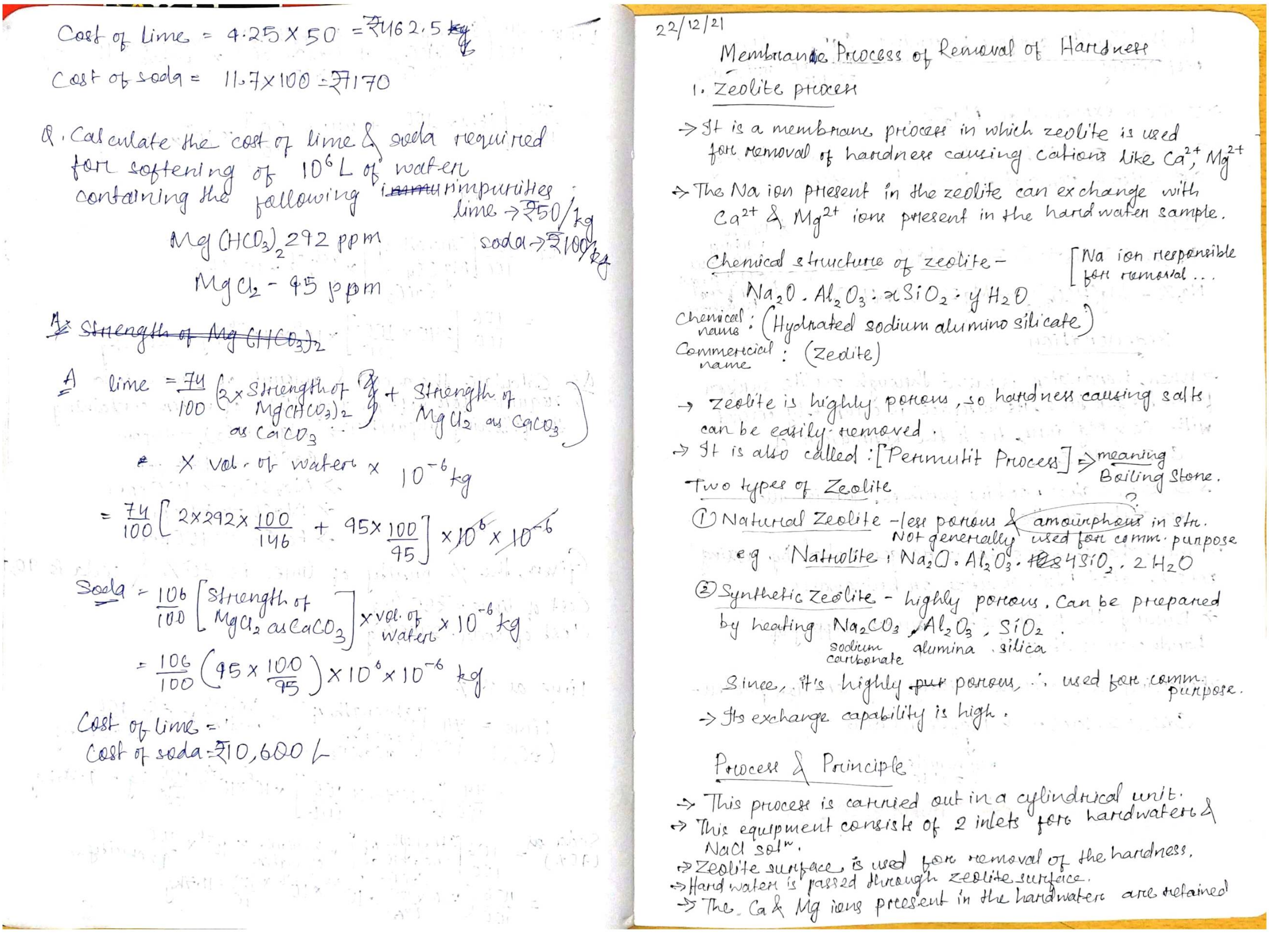
Lime as 80%

Lime (80%) $= \frac{74}{100}\begin{bmatrix}\text{Strength of}\\ \text{hardness}\\ \text{as } CaCO_3\end{bmatrix} \times$ Vol. of water $\times 10^{-6} \times \frac{100}{\%\text{ purity}}$

$= \frac{74}{100}\left[2 \times 73 \times \frac{100}{146}\right] \times 10^5 \times 10^{-6} \times \frac{100}{80}$ kg $= 9.25$ kg

Soda (90%) $= \frac{106}{100}\begin{bmatrix}\text{Strength of}\\ \text{hardness as}\\ CaCO_3\end{bmatrix} \times$ volume of water $\times 10^{-6} \times \frac{100}{\%\text{ purity}}$

$= \frac{106}{100}\left(136 \times \frac{100}{136}\right) \times 10^5 \times 10^{-6} \times \frac{100}{90} = 11.7$ kg



Cost of lime = 4.25 × 50 = ₹462.5 ~~kg~~

Cost of soda = 11.7 × 100 = ₹1170

Q. Calculate the cost of lime & soda required for softening of 10^6 L of water containing the following ~~immu~~ impurities

lime → ₹50/kg
soda → ₹100/kg

$Mg(HCO_3)_2$ 292 ppm

$MgCl_2$ - 95 ppm

~~A. Strength of $Mg(HCO_3)_2$~~

A lime $= \frac{74}{100}\left[2\times \text{Strength of } Mg(HCO_3)_2 \text{ as } CaCO_3 + \text{Strength of } MgCl_2 \text{ as } CaCO_3\right]$ × vol. of water × 10^{-6} kg

$= \frac{74}{100}\left[2\times 292\times \frac{100}{146} + 95\times\frac{100}{95}\right]\times \cancel{10^6}\times\cancel{10^{-6}}$

Soda $= \frac{106}{100}\left[\text{Strength of } MgCl_2 \text{ as } CaCO_3\right]\times \text{vol. of water} \times 10^{-6}$ kg

$= \frac{106}{100}\left(95\times\frac{100}{95}\right)\times 10^6 \times 10^{-6}$ kg

Cost of lime =

Cost of soda = ₹10,600 /-

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Membrane Process of Removal of Hardness

1. Zeolite process

→ It is a membrane process in which zeolite is used for removal of hardness causing cations like Ca^{2+}, Mg^{2+}

→ The Na ion present in the zeolite can exchange with Ca^{2+} & Mg^{2+} ions present in the hardwater sample.

Chemical structure of zeolite - [Na ion responsible for removal...

$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$

Chemical name : (Hydrated sodium alumino silicate)

Commercial name : (Zeolite)

→ zeolite is highly porous, so hardness causing salts can be easily removed.

→ It is also called : [Permutit Process] ⇒ meaning Boiling Stone.

Two types of Zeolite

① Natural Zeolite - less porous & amourphous in str. Not generally used for comm. purpose

e.g. Natrolite : $Na_2O \cdot Al_2O_3 \cdot \cancel{10}\,4SiO_2 \cdot 2H_2O$

② Synthetic Zeolite - highly porous. Can be prepared by heating Na_2CO_3 (sodium carbonate), Al_2O_3 (alumina), SiO_2 (silica).

Since, it's highly ~~pur~~ porous, ∴ used for comm. purpose.

→ Its exchange capability is high.

Process & Principle

→ This process is carried out in a cylindrical unit.

→ This equipment consists of 2 inlets for hardwater & NaCl solⁿ.

→ Zeolite surface is used for removal of the hardness.

→ Hard water is passed through zeolite surface.

→ The Ca & Mg ions present in the hardwater are retained

by the Zeolite surface forming $CaZe$ & $MgZe$ respectively.
calcium zeolite magnesium zeolite.

→ Zedite is expressed as Na_2Ze.

→ There are 2 outlets in the equipment for collecting soft water & removal of the waste water.

Reaction

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$$

$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$

★ When writing principles don't forget to append reactions.

Regeneration

→ When, hardwater is passed through zeolite surface for a longer time, its surface is completely covered with Ca & Mg ions, due to the formation of $CaZe$ & $MgZe$.

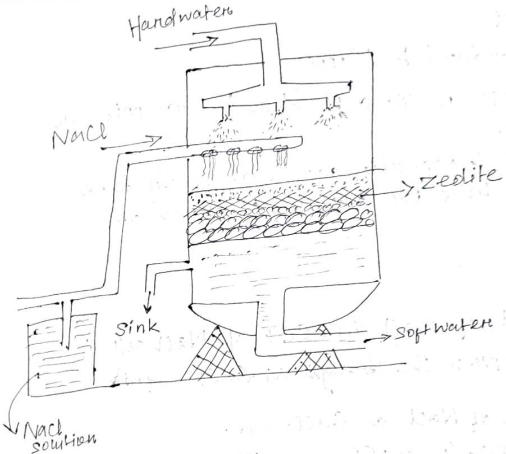
→ So, zeolite stops working further. This is called exhausted zeolite.

→ This exhausted zeolite is re-generated by passing concentrated NaCl solution or brinewater.

→ During the regeneration process, supply of hardwater is stopped.

→ Following reacn occurs during regeneration process -

$$CaZe + 2NaCl \longrightarrow \underset{\substack{\downarrow \\ \text{regenerated zeolite}}}{Na_2Ze} + CaCl_2$$



Limitations of Zeolite -

① Water should not be turbid because suspended particle will choke the pores of zeolite surface making it inactive.

② The ions like Mn^{2+}, Fe^{2+} should be removed from the hard water before it is used in the zeolite process, because $MnZe$ & $FeZe$ cannot be generated easily.

③ Acidic substances must be removed from the water because acid will destroy the zeolite surface. Acid should be neutralized with calculated amount of soda.

④ Hot water should not be used because Zeolite will be dissolved in hotwater.

⑤ The anions present in the hardwater must be removed first before it is used in zeolite process. This is because anions like bicarbonate will form $NaHCO_3$ during the softening process. $NaHCO_3$ will produce NaOH at high temperature. So this type of water is not suitable for boiler use.

$$NaHCO_3 \xrightarrow{\Delta} NaOH + CO_2$$

Advantages

① Hardness is reduced to 10 ppm.

② Sludge disposal is not a problem because ppts are not formed.

③ Maintainance & operation can be ~~as~~ easily done.

④ It takes less time for softening of hardwater.

23/12/21

Q. The strength of NaCl in 200L of NaCl soln is 150g/L. Express the strength as $CaCO_3$ equiv.

A

Strength of NaCl as $CaCO_3$ eqv.

$$= 150g/L \times \frac{100}{2 \times 58.5} \times 200$$

$$= 25{,}641\,g = 2.5641 \times 10^7\,mg.$$

~~= 25641×~~

Q. The hardness of 10,000 L of a sample of water was removed by passing it through a zeolite softener. The softener then requires ~~200ml~~ of 200L of NaCl solution containing 150g/L of NaCl for regeneration. Calculate the hardness of water sample.

A Strength of NaCl as $CaCO_3$ eqv.

$$= 150g/L \times \frac{100}{2 \times 58.5} \times 200 = 25641\,g$$

Amount of NaCl is eqv. to the hardness present in the water sample.

Hardness present in 10000 L of water is 25641

" " " 1 L of " $= \frac{25641}{10000}$

Hardness of water sample $\Rightarrow 2.5641 \times 10^3\,mg/L$

Q. An exhausted zeolite softener was regenerated by passing 150L of NaCl solution having a strength of 150g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener if the hardness of water is 500ppm = 500mg/L.

A

Strength of NaCl in 150L of NaCl solution as $CaCO_3$ eqv. $= 150g/L \times \frac{100}{2 \times 58.5} \times 150$

~~= 19230 ... mg/L~~

$$= 19230.76\,\cancel{g} \times 10^3\,mg$$

$$= 1.923076 \times 10^7\,mg$$

~~500g~~ 500mg of hardness is present in 1L of water.

1.923×10^7 mg " " " "

$$\frac{1.923 \times 10^7}{500}$$

$$= 38461.5\,L$$

—×—

ION-EXCHANGE PROCESS

This is also called Demineralization process or Deionization process.

→ In this process, the salts are completely removed from water.

→ For this process - Ion-exchange resins are used.

→ Ion-exchange resins are insoluble, cross-linked, have higher molecular weight, organic polymers with porous structures.

→ The functional groups like H^+/OH^- ions present in the polymer are capable of exchange with cations & anions present in water sample.

→ There are 2 types of ion-exchange resins.
① Cation ~~ions~~ exchange resins.
② Anion " " .

Cation Exchange Resins

→ It is represented as $\bar{R}\overset{+}{H}$ or RH → functional group.
(R: stands for resin matrix)

→ It is prepared by mixing styrene with divinyl benzene. This copolymer is treated with either HCl or H_2SO_4.

→ The H^+ ion present is capable of exchanging with hardness causing cations. It is also called cationic exchanger.

→ Anion Exchange Resins → $\overset{+}{R}\bar{OH}$ → functional group
(R: stands for resin matrix)

→ It is prepared by mixing styrene with divinyle benzene & a little amount of ammonia solⁿ.

→ This copolymer is treated with dilute NaOH solⁿ.

→ The OH group present in this copolymer is responsible for exchange with anions present in the water. It is also called anion exchanger.

Principle.

The hardwater sample is passed through cation & anion exchange resins. Following reactions are carried out during the softening process.

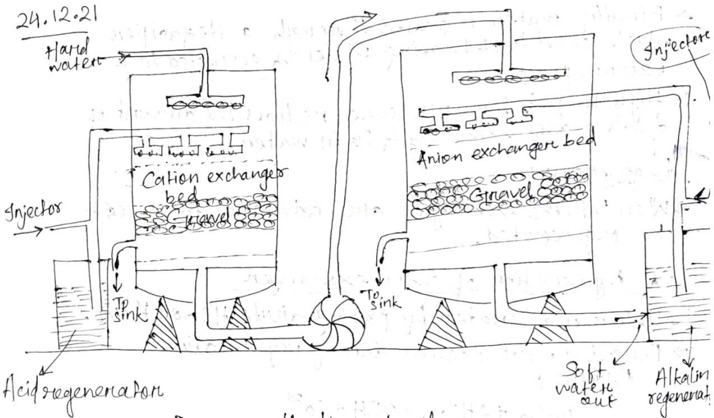
① $2\bar{R}\overset{+}{H} + Ca^{2+} \rightleftharpoons R_2Ca + 2H^+$

② $2\overset{+}{R}\bar{OH} + SO_4^{2-} \rightleftharpoons R_2SO_4 + 2\bar{OH}$

③ $2H^+ + 2\bar{OH} \longrightarrow 2H_2O$.

Diagram - refer book

24.12.21



Demineralization of water.

~~Diagm~~

24.12.21

→ In this process, cation exchange resins and anion exchange resins are placed in separate containers.

→ The hardwater is passed through cation exchange resins where all the cations like Ca^{2+}, Mg^{2+}, etc. are removed from water and equiv. amount of H^+ ions are released to the water.

→ After this, the water is passed through, anion exchange resin, where all the anions like, SO_4^{2-}, Cl^-, etc. are removed from hardwater & equiv. amount of OH^- ions are released to the water.

→ So, the water collected from the container is free from all the ions.

→ Finally, water is passed through a degasifier which consists of heating plates & connected to a vacuum pump.

→ High temp. & low pressure reduces the amount of dissolved gases, like CO_2 & O_2 in water.

Regeneration

→ When both the exchangers are exhausted, they need to be regenerated.

★ Regeneration of cation exchanger

→ This is regenerated by passing dilute HCl or H_2SO_4.

→ Following reac^n occurs during regeneration -

Reaction:-

$$R_2Ca + 2H^+ \longrightarrow 2RH + Ca^{2+}$$

→ The waste water is removed through the bottom outlet.

→ During the regeneration process, supply of hardwater is stopped.

★ Regeneration of anion exchanger -

→ This is regenerated by passing dilute NaOH solution.

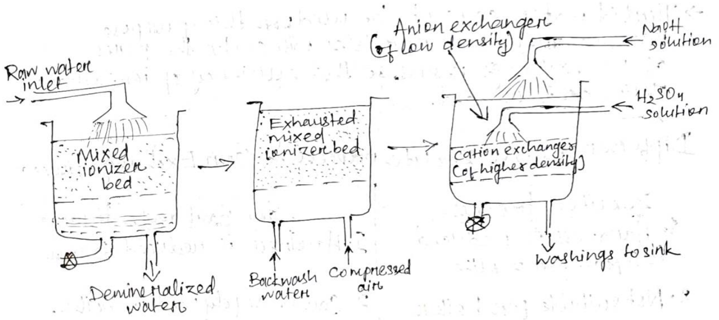
→ Following reaction occurs during regeneration -

$$R_2SO_4 + 2OH^- \longrightarrow 2ROH + SO_4^{2-}$$

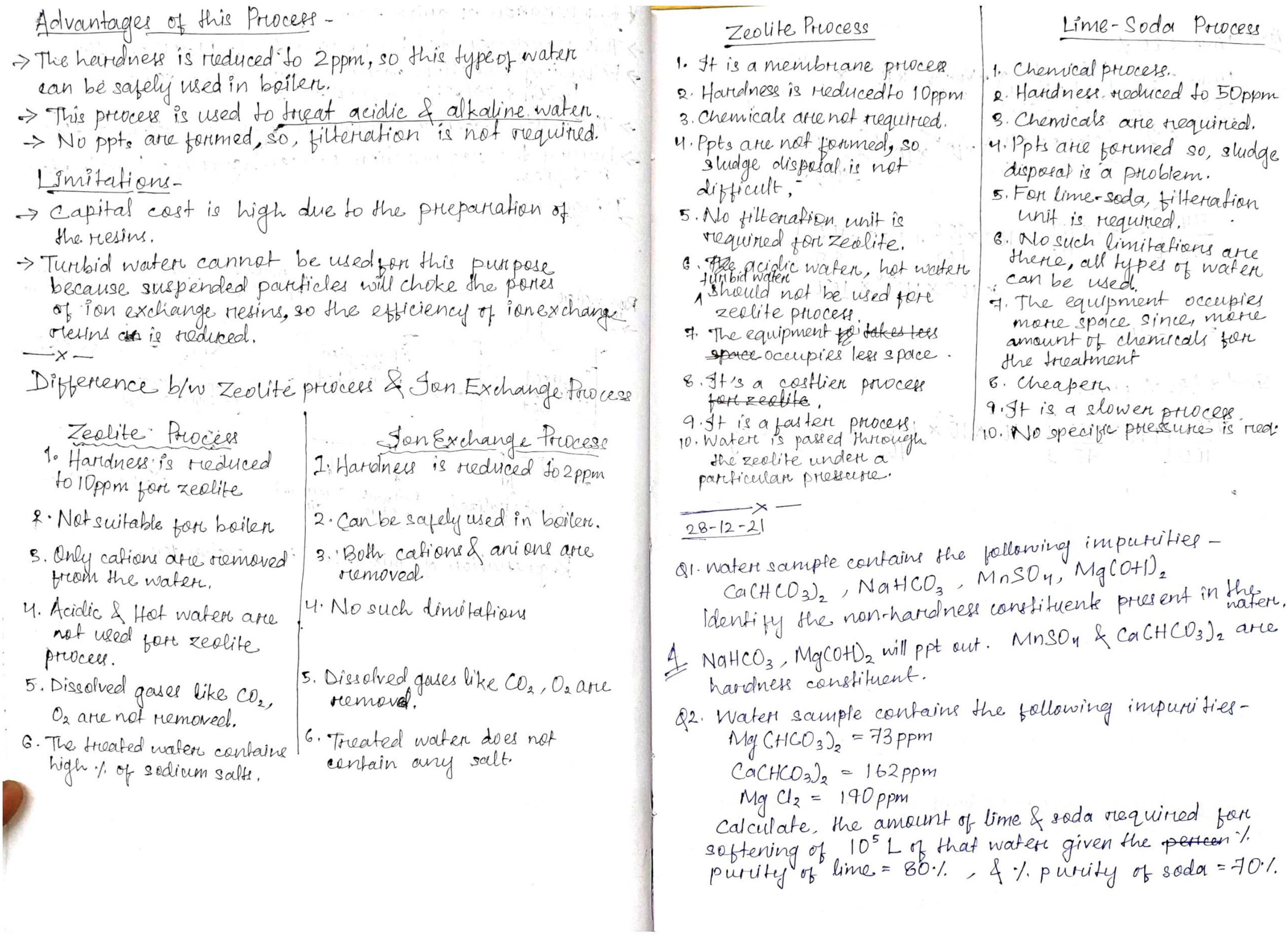
→ The waste water is removed through the bottom outlet.

→ During the regeneration process, supply of hardwater is stopped.

Diagram-



Regeneration of mixed-bed ion exchanger.



Advantages of this Process -

- → The hardness is reduced to 2ppm, so this type of water can be safely used in boiler.
- → This process is used to treat acidic & alkaline water.
- → No ppts are formed, so, filteration is not required.

Limitations-

- → Capital cost is high due to the preparation of the resins.
- → Turbid water cannot be used for this purpose because suspended particles will choke the pores of ion exchange resins, so the efficiency of ion exchange resins ~~as~~ is reduced.

—x—

Difference b/w Zeolite process & Ion Exchange Process

Zeolite Process	Ion Exchange Process
1. Hardness is reduced to 10ppm for zeolite	1. Hardness is reduced to 2ppm
2. Not suitable for boiler	2. Can be safely used in boiler.
3. Only cations are removed from the water.	3. Both cations & anions are removed.
4. Acidic & Hot water are not used for zeolite process.	4. No such limitations
5. Dissolved gases like CO_2, O_2 are not removed.	5. Dissolved gases like CO_2, O_2 are removed.
6. The treated water contains high % of sodium salts.	6. Treated water does not contain any salt.

Zeolite Process	Lime-Soda Process
1. It is a membrane process	1. Chemical process.
2. Hardness is reduced to 10ppm	2. Hardness reduced to 50ppm
3. Chemicals are not required.	3. Chemicals are required.
4. Ppts are not formed, so sludge disposal is not difficult,	4. Ppts are formed so, sludge disposal is a problem.
5. No filteration unit is required for zeolite.	5. For lime-soda, filteration unit is required.
6. ~~The~~ acidic water, hot water turbid water should not be used for zeolite process.	6. No such limitations are there, all types of water can be used.
7. The equipment ~~[illegible]~~ ~~takes less space~~ occupies less space.	7. The equipment occupies more space since, more amount of chemicals for the treatment
8. It's a costlier process ~~for zeolite~~.	8. Cheaper.
9. It is a faster process.	9. It is a slower process.
10. Water is passed through the zeolite under a particular pressure.	10. No specific pressure is req.

—x—

28-12-21

Q1. Water sample contains the following impurities - $Ca(HCO_3)_2$, $NaHCO_3$, $MnSO_4$, $Mg(OH)_2$. Identify the non-hardness constituents present in the water.

A. $NaHCO_3$, $Mg(OH)_2$ will ppt out. $MnSO_4$ & $Ca(HCO_3)_2$ are hardness constituent.

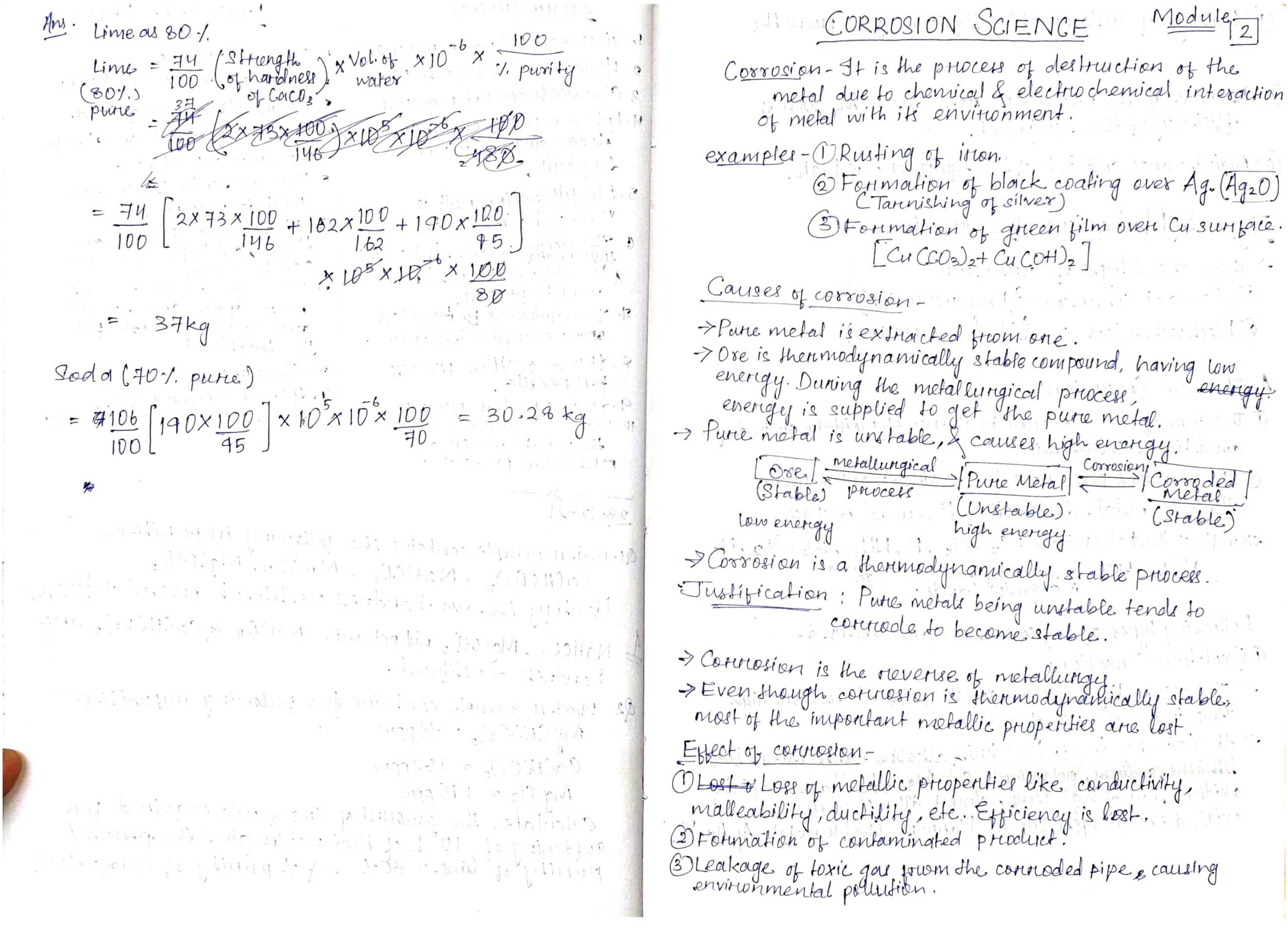
Q2. Water sample contains the following impurities-

$Mg(HCO_3)_2 = 73$ ppm

$Ca(HCO_3)_2 = 162$ ppm

$MgCl_2 = 190$ ppm

Calculate the amount of lime & soda required for softening of 10^5 L of that water given the ~~percen~~ % purity of lime = 80%, & % purity of soda = 70%.



Ans. Lime as 80%.

Lime (80% pure) $= \frac{74}{100}\left(\text{Strength of hardness of } CaCO_3\right) \times \text{Vol. of water} \times 10^{-6} \times \frac{100}{\%\ \text{purity}}$

~~$= \frac{37}{100}\left(2\times 73\times\frac{100}{146}\right)\times 10^{5}\times 10^{-6}\times\frac{100}{480}$~~

$= \frac{74}{100}\left[2\times 73\times\frac{100}{146} + 162\times\frac{100}{162} + 190\times\frac{100}{95}\right] \times 10^{5}\times 10^{-6}\times\frac{100}{80}$

$= 37\,kg$

Soda (70% pure)

$= \frac{106}{100}\left[190\times\frac{100}{95}\right]\times 10^{5}\times 10^{-6}\times\frac{100}{70} = 30.28\ kg$

CORROSION SCIENCE

Module $\boxed{2}$

Corrosion - It is the process of destruction of the metal due to chemical & electrochemical interaction of metal with its environment.

examples - ① Rusting of iron.
② Formation of black coating over Ag. (Ag_2O) (Tarnishing of silver)
③ Formation of green film over Cu surface. [$Cu(CO_3)_2 + Cu(OH)_2$]

Causes of corrosion -

→ Pure metal is extracted from ore.

→ Ore is thermodynamically stable compound, having low ~~energy.~~ energy. During the metallurgical process, energy is supplied to get the pure metal.

→ Pure metal is unstable, & causes high energy.

$$\begin{tikzcd}
\boxed{\text{Ore}} \arrow[r, shift left, "\text{metallurgical}"] & \boxed{\text{Pure Metal}} \arrow[l, shift left, "\text{process}"] \arrow[r, shift left, "\text{Corrosion}"] & \boxed{\text{Corroded Metal}} \arrow[l, shift left]
\end{tikzcd}$$

(Stable) low energy — (Unstable) high energy — (Stable)

→ Corrosion is a thermodynamically stable process.

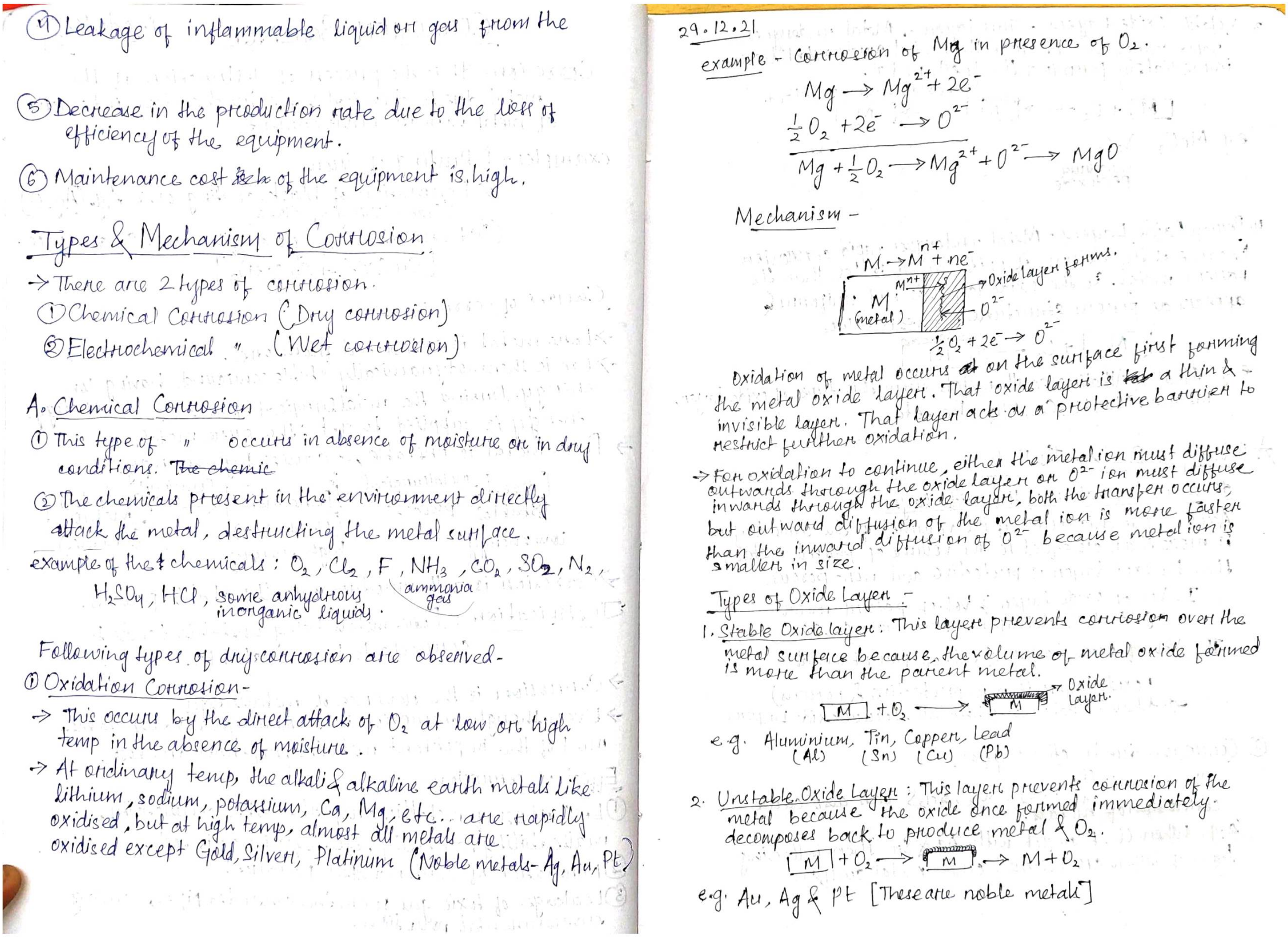
Justification : Pure metals being unstable tends to corrode to become stable.

→ Corrosion is the reverse of metallurgy.

→ Even though corrosion is thermodynamically stable, most of the important metallic properties are lost.

Effect of corrosion -

① ~~Lost o~~ Loss of metallic properties like conductivity, malleability, ductility, etc. Efficiency is lost.
② Formation of contaminated product.
③ Leakage of toxic gas from the corroded pipe, causing environmental pollution.



④ Leakage of inflammable liquid or gas from the

⑤ Decrease in the production rate due to the loss of efficiency of the equipment.

⑥ Maintenance cost [illegible] of the equipment is high.

Types & Mechanism of Corrosion

→ There are 2 types of corrosion.

① Chemical Corrosion (Dry corrosion)

② Electrochemical " (Wet corrosion)

A. Chemical Corrosion

① This type of " occurs in absence of moisture or in dry conditions. ~~The chemic~~

② The chemicals present in the environment directly attack the metal, destructing the metal surface.

example of the ~~t~~ chemicals : O_2, Cl_2, F, NH_3 (ammonia gas), CO_2, SO_2, N_2, H_2SO_4, HCl, some anhydrous inorganic liquids.

Following types of dry corrosion are observed-

① Oxidation Corrosion-

→ This occurs by the direct attack of O_2 at low or high temp in the absence of moisture.

→ At ordinary temp, the alkali & alkaline earth metals like lithium, sodium, potassium, Ca, Mg, etc.. are rapidly oxidised, but at high temp, almost all metals are oxidised except Gold, Silver, Platinum (Noble metals- Ag, Au, Pt)

29.12.21

example - Corrosion of Mg in presence of O_2.

$$Mg \rightarrow Mg^{2+} + 2e^-$$
$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$
$$Mg + \frac{1}{2}O_2 \rightarrow Mg^{2+} + O^{2-} \rightarrow MgO$$

Mechanism -

$M \rightarrow M^{n+} + ne^-$

M^{n+}

M (metal)

Oxide layer forms.

O^{2-}

$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

Oxidation of metal occurs ~~at~~ on the surface first forming the metal oxide layer. That oxide layer is ~~[illegible]~~ a thin & invisible layer. That layer acts as a protective barrier to restrict further oxidation.

→ For oxidation to continue, either the metal ion must diffuse outwards through the oxide layer or O^{2-} ion must diffuse inwards through the oxide layer, both the transfer occurs, but outward diffusion of the metal ion is more faster than the inward diffusion of O^{2-} because metal ion is smaller in size.

Types of Oxide Layer -

1. Stable Oxide layer : This layer prevents corrosion over the metal surface because the volume of metal oxide formed is more than the parent metal.

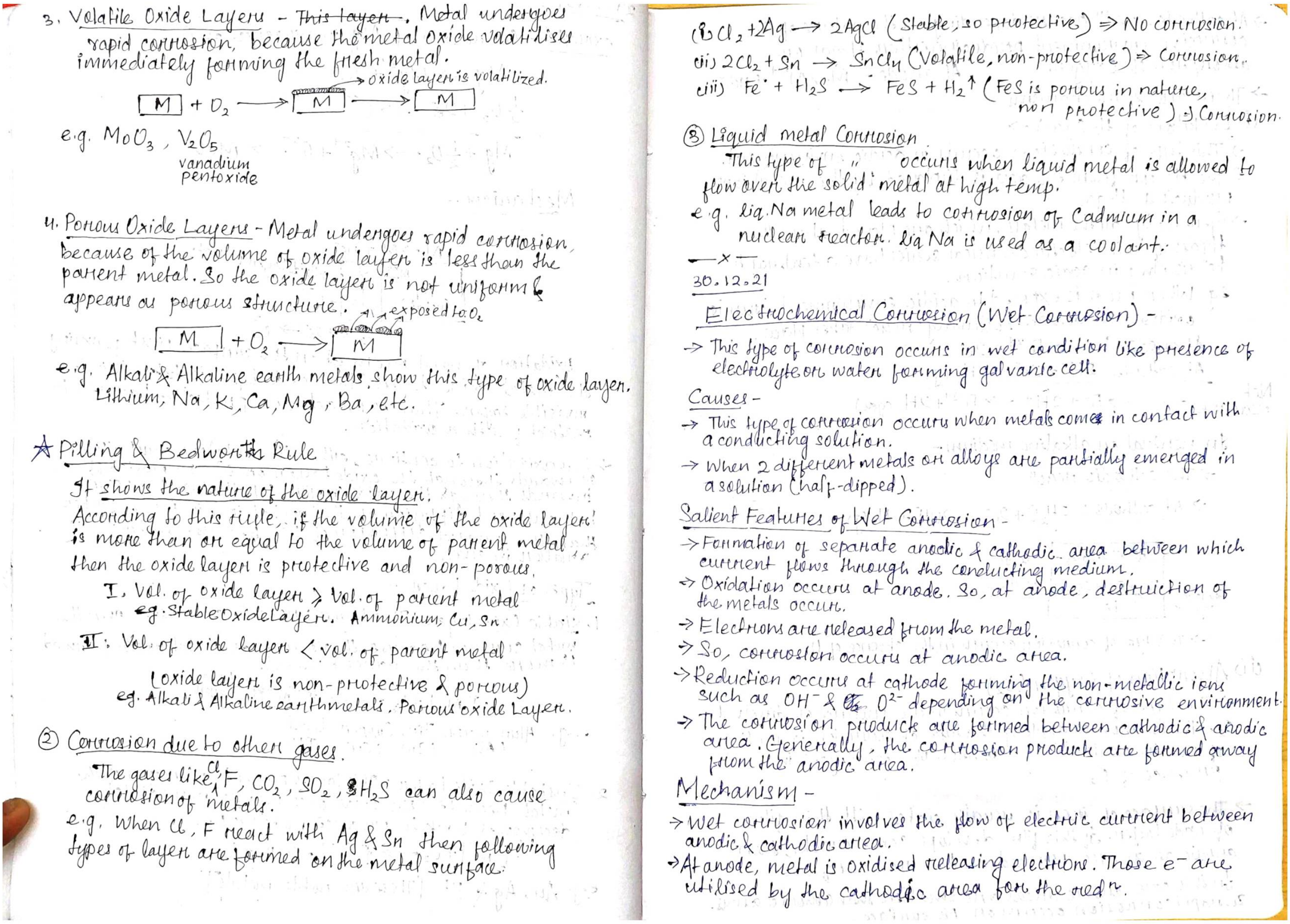
$\boxed{M} + O_2 \longrightarrow \boxed{M}$ Oxide layer.

e.g. Aluminium (Al), Tin (Sn), Copper (Cu), Lead (Pb)

2. Unstable Oxide Layer : This layer prevents corrosion of the metal because the oxide once formed immediately decomposes back to produce metal & O_2.

$\boxed{M} + O_2 \longrightarrow \boxed{M} \rightarrow M + O_2$

e.g. Au, Ag & Pt [These are noble metals]



3. Volatile Oxide Layers - ~~This layer~~. Metal undergoes rapid corrosion, because the metal oxide volatilises immediately forming the fresh metal.

$$\boxed{M} + O_2 \longrightarrow \boxed{M} \longrightarrow \boxed{M}$$

e.g. MoO_3, V_2O_5 vanadium pentoxide

4. Porous Oxide Layers - Metal undergoes rapid corrosion because of the volume of oxide layer is less than the parent metal. So the oxide layer is not uniform & appears as porous structure.

$$\boxed{M} + O_2 \longrightarrow \boxed{M}$$

e.g. Alkali & Alkaline earth metals show this type of oxide layer. Lithium, Na, K, Ca, Mg, Ba, etc.

★ Pilling & Bedworth Rule

It shows the nature of the oxide layer.
According to this rule, if the volume of the oxide layer is more than or equal to the volume of parent metal then the oxide layer is protective and non-porous.

I. Vol. of oxide layer ⩾ Vol. of parent metal
eg. Stable Oxide Layer. Ammonium, Cu, Sn

II. Vol. of oxide layer < vol. of parent metal
(oxide layer is non-protective & porous)
eg. Alkali & Alkaline earth metals. Porous oxide Layer.

② Corrosion due to other gases.

The gases like Cl, F, CO_2, SO_2, H_2S can also cause corrosion of metals.
e.g. When Cl, F react with Ag & Sn then following types of layer are formed on the metal surface.

(i) $Cl_2 + 2Ag \rightarrow 2AgCl$ (Stable, so protective) ⇒ No corrosion.
(ii) $2Cl_2 + Sn \rightarrow SnCl_4$ (Volatile, non-protective) ⇒ Corrosion.
(iii) $Fe + H_2S \rightarrow FeS + H_2\uparrow$ (FeS is porous in nature, non protective) ⇒ Corrosion.

③ Liquid metal Corrosion

This type of " occurs when liquid metal is allowed to flow over the solid metal at high temp.
e.g. liq. Na metal leads to corrosion of Cadmium in a nuclear reactor. liq Na is used as a coolant.

—×—

30.12.21

Electrochemical Corrosion (Wet Corrosion) -

→ This type of corrosion occurs in wet condition like presence of electrolyte or water forming galvanic cell.

Causes -
→ This type of corrosion occurs when metals comes in contact with a conducting solution.
→ When 2 different metals or alloys are partially emerged in a solution (half-dipped).

Salient Features of Wet Corrosion -
→ Formation of separate anodic & cathodic area between which current flows through the conducting medium.
→ Oxidation occurs at anode. So, at anode, destruction of the metals occur.
→ Electrons are released from the metal.
→ So, corrosion occurs at anodic area.
→ Reduction occurs at cathode forming the non-metallic ions such as OH^- & O^{2-} depending on the corrosive environment.
→ The corrosion products are formed between cathodic & anodic area. Generally, the corrosion products are formed away from the anodic area.

Mechanism -
→ Wet corrosion involves the flow of electric current between anodic & cathodic area.
→ At anode, metal is oxidised releasing electrons. Those e^- are utilised by the cathodic area for the red^n.

→ At cathode, redn occurs depending on the nature of the corrosive environment producing either H-gas or absorption of Oxygen. At anode - $M \rightarrow M^{n+} + ne^-$.

→ There are 2 mechanisms

(i) Evolution of H_2 (gas) →

→ This type of corrosion occurs in acidic environment.

→ The H^+ ion from the acid is displaced, by the metal ions producing H-gas.

→ Generally, all the metals, which are placed above the Hydrogen in electrochemical series have a tendency to be dissolved in acidic solution.

e.g. When iron is exposed to acidic environment, iron is oxidised at anode. Following reacn takes place.

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

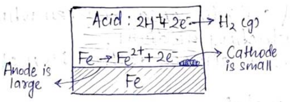
At cathode: $2H^+ + 2e^- \rightarrow H_2 (g)$

Net reaction $\longrightarrow Fe + 2H^+ \rightarrow Fe^{2+} + 2H_2$ (gas)

In neutral or alkaline medium -

→ The cathodic reacn

→ At cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$



→ This type of corrosion occurs in the absence of O_2.

(ii) Absorption of Oxygen (O_2) -

→ This type of corrosion occurs in the presence of dissolved O_2. The common example of this type of corrosion is rusting of iron in neutral (?) solution of electrolytes in presence of O_2.

→ The surface of iron is usualy coated with thin film of oxide layer. If this film develops some cracks, then anodic areas are formed on the iron surface.

In this case, anodic areas are smaller than cathodic areas. So, rapid corrosion occurs on Fe surface.

Reaction

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

At cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Net reacn: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$

→ In presence of more amount of O_2, $Fe(OH)_2$ is oxidised to produced Ferric Hydroxide, acc. to the following reacn.

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3$$

or

$$2[Fe_2O_3 \cdot 3H_2O]$$

Yellow Rust.

→ In absence of less amount of O_2, corrosion product is black due to the formation of anhydrous magnetite (Fe_3O_4).

→ Effect of Oxygen.

→ Increase of oxygen accelerates the cathodic reaction producing more amount of OH^- ions.

→ Increase of O_2 requires more electrons, so, oxidation of metal occurs at a faster rate.

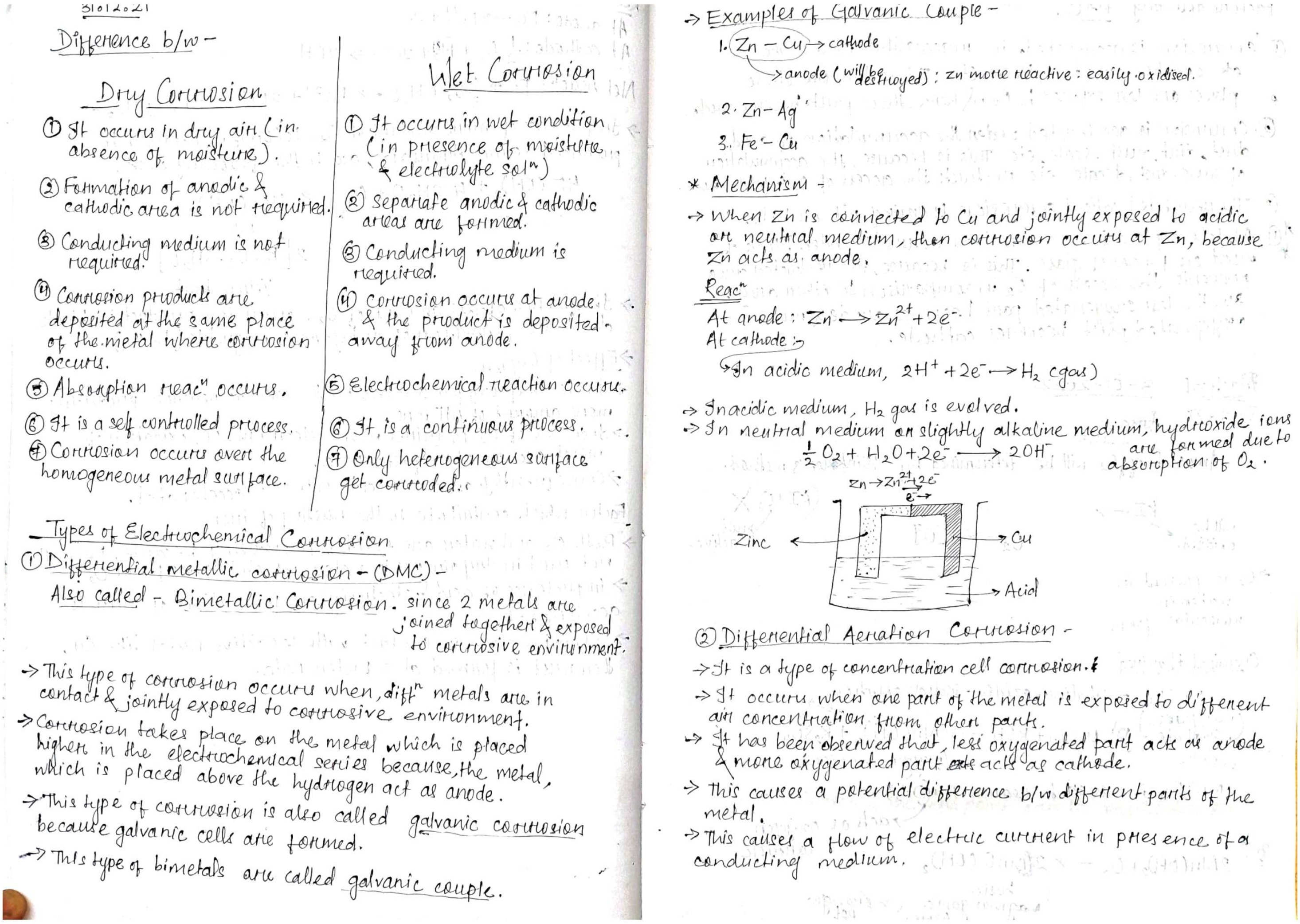
→ Consequently, anodic reaction is also accelerated.

Factors which contribute to the rusting of iron.

→ Both O_2 and water are essential for rusting because, Fe will not rust in dry air or in water, which is free from O_2.

→ In presence of acid & electrolytes, formation of rust is acceleriated.

→ When Fe comes in contact with less active metal like Cu, then rust is formed at a faster rate.



31/01/2021

Difference b/w -

Dry Corrosion	Wet Corrosion
① It occurs in dry air (in absence of moisture).	① It occurs in wet condition (in presence of moisture & electrolyte solⁿ)
② Formation of anodic & cathodic area is not required.	② Separate anodic & cathodic areas are formed.
③ Conducting medium is not required.	③ Conducting medium is required.
④ Corrosion products are deposited at the same place of the metal where corrosion occurs.	④ Corrosion occurs at anode & the product is deposited away from anode.
⑤ Absorption reacⁿ occurs.	⑤ Electrochemical reaction occurs.
⑥ It is a self controlled process.	⑥ It, is a continuous process.
⑦ Corrosion occurs over the homogeneous metal surface.	⑦ Only heterogeneous surface get corroded.

Types of Electrochemical Corrosion

① Differential metallic corrosion - (DMC) -

Also called - Bimetallic Corrosion. since 2 metals are joined together & exposed to corrosive environment.

-> This type of corrosion occurs when, diffⁿ metals are in contact & jointly exposed to corrosive environment.

-> Corrosion takes place on the metal which is placed higher in the electrochemical series because, the metal, which is placed above the hydrogen act as anode.

-> This type of corrosion is also called galvanic corrosion because galvanic cells are formed.

-> This type of bimetals are called galvanic couple.

-> Examples of Galvanic Couple -

1. Zn – Cu -> cathode
   -> anode (will be destroyed) : Zn more reactive : easily oxidised.
2. Zn – Ag
3. Fe – Cu

* Mechanism -

-> When Zn is connected to Cu and jointly exposed to acidic or neutral medium, then corrosion occurs at Zn, because Zn acts as anode.

Reacⁿ

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode :->

-> In acidic medium, $2H^+ + 2e^- \longrightarrow H_2$ (gas)

-> In acidic medium, H_2 gas is evolved.

-> In neutral medium or slightly alkaline medium, hydroxide ions are formed due to absorption of O_2.

$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

② Differential Aeration Corrosion -

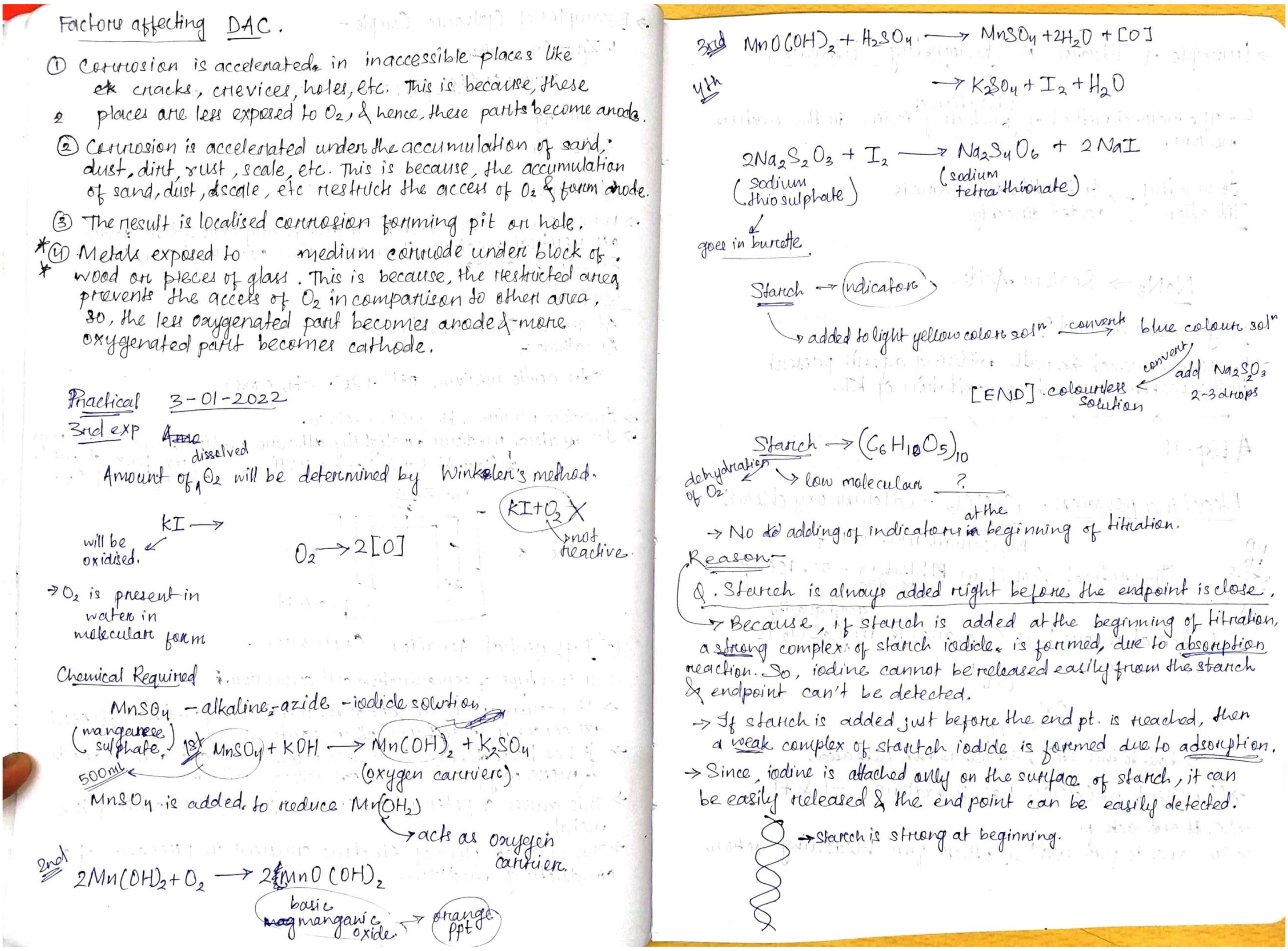
-> It is a type of concentration cell corrosion.

-> It occurs when one part of the metal is exposed to different air concentration from other parts.

-> It has been observed that, less oxygenated part acts as anode & more oxygenated part ~~acts~~ acts as cathode.

-> this causes a potential difference b/w different parts of the metal.

-> This causes a flow of electric current in presence of a conducting medium.



Factors affecting DAC.

① Corrosion is accelerated in inaccessible places like ~~ek~~ cracks, crevices, holes, etc. This is because, these places are less exposed to O_2, & hence, these parts become anode.

② Corrosion is accelerated under the accumulation of sand, dust, dirt, rust, scale, etc. This is because, the accumulation of sand, dust, scale, etc restricts the access of O_2 & form anode.

③ The result is localised corrosion forming pit or hole.

* ④ Metals exposed to medium corrode under block of wood or pieces of glass. This is because, the restricted area prevents the access of O_2 in comparison to other area, so, the less oxygenated part becomes anode & more oxygenated part becomes cathode.

Practical 3-01-2022

3rd exp ~~Amo~~

Amount of dissolved O_2 will be determined by Winkler's method.

KI →
will be oxidised.

$O_2 \rightarrow 2[O]$

$KI + O_2$ ✗ → not reactive.

→ O_2 is present in water in molecular form

Chemical Required

$MnSO_4$ – alkaline-azide – iodide solution
(manganese sulphate, 500ml)

1st $MnSO_4 + KOH \longrightarrow Mn(OH)_2 + K_2SO_4$
(oxygen carrier)

$MnSO_4$ is added to reduce $Mn(OH_2)$ → acts as oxygen carrier.

2nd $2Mn(OH)_2 + O_2 \longrightarrow 2MnO(OH)_2$
basic ~~mag~~ manganic oxide → orange ppt

3rd $MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$

4th $\longrightarrow K_2SO_4 + I_2 + H_2O$

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
(sodium thiosulphate) (sodium tetrathionate)
↓
goes in burette

Starch → indicator
↳ added to light yellow colour sol^n $\xrightarrow{\text{convert}}$ blue colour sol^n
add $Na_2S_2O_3$ 2-3 drops $\xrightarrow{\text{convert}}$ colourless solution [END]

Starch → $(C_6H_{10}O_5)_{10}$
dehydration of O_2
↳ low molecular ?

→ No ~~do~~ adding of indicators ~~in~~ at the beginning of titration.

Reason–

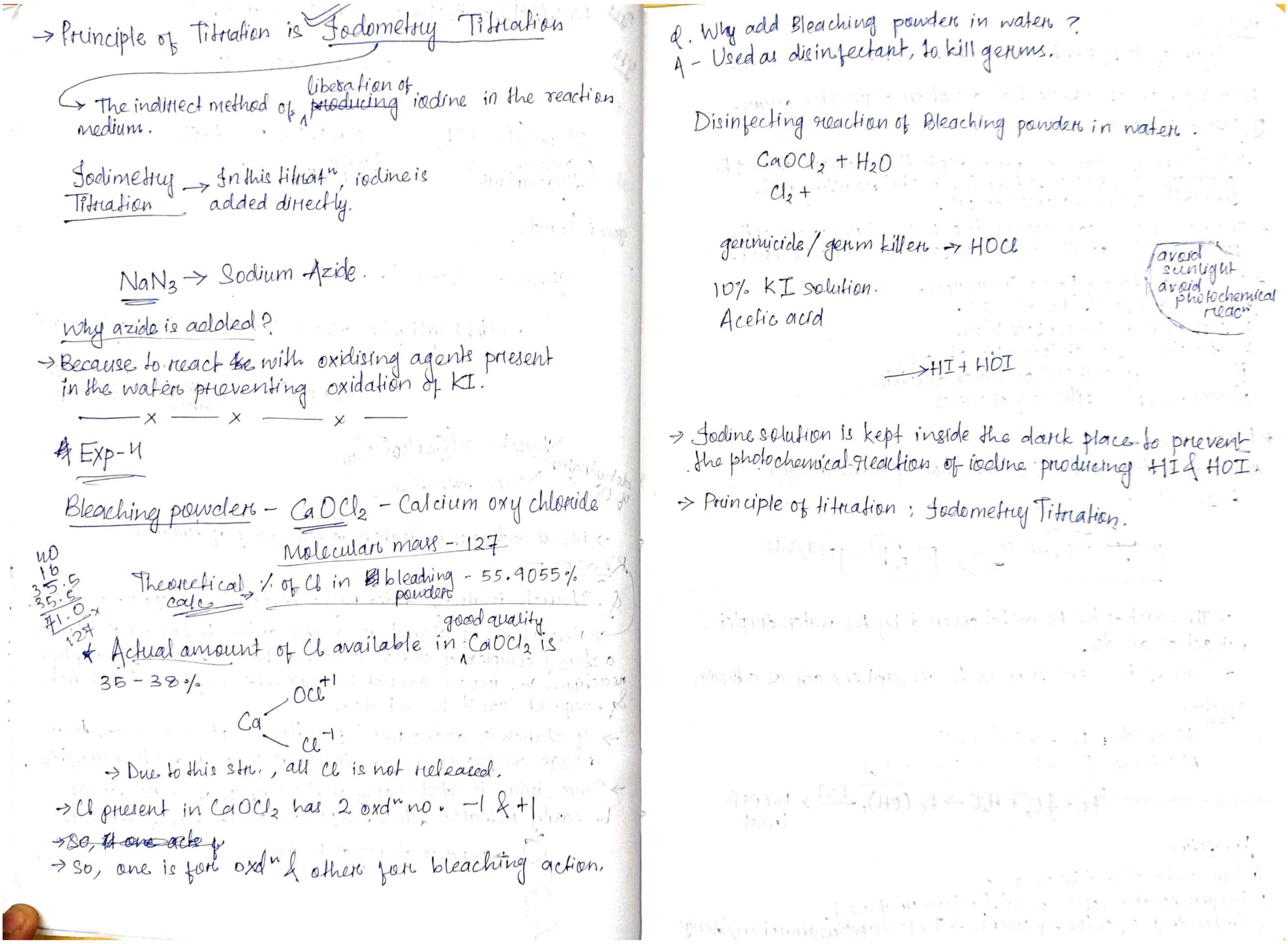
Q. Starch is always added right before the endpoint is close.

→ Because, if starch is added at the beginning of titration, a strong complex of starch iodide is formed, due to absorption reaction. So, iodine cannot be released easily from the starch & endpoint can't be detected.

→ If starch is added just before the end pt. is reached, then a weak complex of starch iodide is formed due to adsorption.

→ Since, iodine is attached only on the surface of starch, it can be easily released & the end point can be easily detected.

→ Starch is strong at beginning.



→ Principle of Titration is Iodometry Titration

→ The indirect method of ~~producing~~ liberation of iodine in the reaction medium.

Iodimetry Titration → In this titratⁿ, iodine is added directly.

NaN_3 → Sodium Azide.

Why azide is added?

→ Because to react ~~the~~ with oxidising agents present in the water preventing oxidation of KI.

——— × ——— × ——— × ———

~~A~~ Exp-4

Bleaching powder – $CaOCl_2$ – Calcium oxy chloride

Molecular mass - 127

40
16
35.5
35.5
71.0
127

Theoretical calc → % of Cl in ~~B~~ bleaching powder - 55.9055 %

★ Actual amount of Cl available in good quality $CaOCl_2$ is 35 - 38%

$Ca(OCl^{+1})(Cl^{-1})$

→ Due to this str., all Cl is not released.

→ Cl present in $CaOCl_2$ has 2 oxdⁿ no. −1 & +1

~~→So, it one acts~~

→ So, one is for oxdⁿ & other for bleaching action.

Q. Why add Bleaching powder in water?

A - Used as disinfectant, to kill germs.

Disinfecting reaction of Bleaching powder in water.

$CaOCl_2 + H_2O$

$Cl_2 +$

germicide / germ killer → HOCl

10% KI solution.

Acetic acid

avoid sunlight
avoid photochemical reacⁿ

$\longrightarrow HI + HOI$

→ Iodine solution is kept inside the dark place to prevent the photochemical reaction of iodine producing HI & HOI.

→ Principle of titration : Iodometry Titration.

4.01.22

Types of Differential Aeration Corrosion: DAC

Following types of differential aeration corrosion occurs -

[1] Pitting Corrosion

→ This type of corrosion occurs due to the localised attack of the corrosive environment on the metal resulting in the formation of holes, cavities or pit.

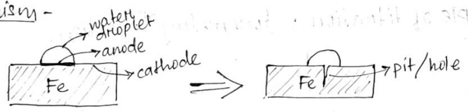
→ This type of corrosion occurs due to the breakdown of the protective film on the metal surface at a specific point.

→ Factors affecting Pitting Corrosion -
① Uneven surface. (Roughness).
② Scratches on the surface film.
③ Deposition of dust/sand/rust, etc.
④ " of salt solⁿ or water droplets.
⑤ Non-uniform polishing of metal.

★ Mechanism -

Rusting of Iron due to the deposition of water droplets -

Mechanism -



→ The part of the Fe metal covered by the water droplet will act as anode.

→ Part of Fe metal exposed to atmosphere acts as cathode.

Reaction

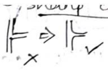
At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

At cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\bar{O}H$

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \xrightarrow{[O]} \underset{\text{(rust)}}{Fe(OH)_3}$$

Prevention

① Pure metal should be used.
② Proper polishing of the metal (Uniform polishing).
③ Proper designing of the equipment. → T & L-shape construction/design should be avoided, because they have sharp corners.
U-shaped corners >> Best.



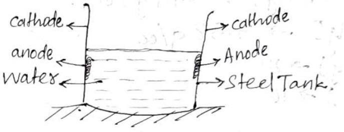
[2] Waterline Corrosion

→ When water is kept stagnant in a steel tank for a long time, then corrosion occurs below the water level.

→ This is because, the conc: of oxygen above the water line is more than below the water line.

→ This results in difference in air concentration at different parts of the steel tank.

→ So, corrosion of steel tank occurs below the water level because that part acts as anode.



Reaction

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$

At cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2\bar{O}H$

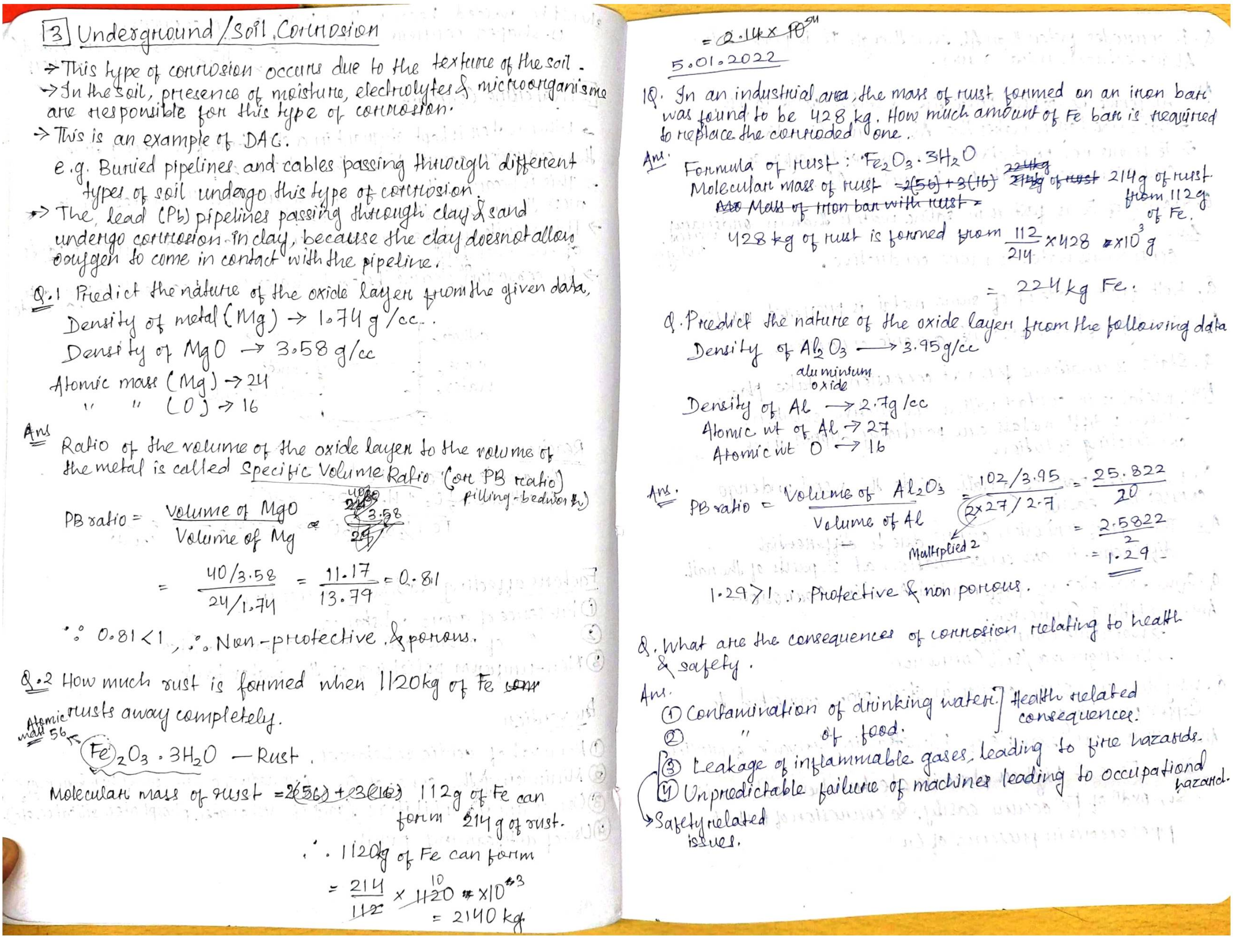
$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \xrightarrow{[O]} \underset{\text{(rust)}}{Fe(OH)_3}$$

Factors affecting Waterline Corrosion

① Presence of acidic substances.
② " of more amount of oxygen in water.
③ Non-uniform polishing of the water tank.

Prevention

① Removal of acidic substances.
② Minimising the conc. of O_2. (no adding chem. only boil & remove O_2)
③ Use of anodic inhibitors (salts of carbonates, phosphates, silicates, etc).
④ Use of antifoaming paints.



3 Underground / Soil Corrosion

- → This type of corrosion occurs due to the texture of the soil.
- → In the soil, presence of moisture, electrolytes & microorganisms are responsible for this type of corrosion.
- → This is an example of DAC.

e.g. Buried pipelines and cables passing through different types of soil undergo this type of corrosion.

- → The lead (Pb) pipelines passing through clay & sand undergo corrosion in clay, because the clay does not allow oxygen to come in contact with the pipeline.

Q.1 Predict the nature of the oxide layer from the given data,

Density of metal (Mg) → 1.74 g/cc.
Density of MgO → 3.58 g/cc
Atomic mass (Mg) → 24
" " (O) → 16

Ans Ratio of the volume of the oxide layer to the volume of the metal is called Specific Volume Ratio (or PB ratio) (Pilling-bedworth)

$$\text{PB ratio} = \frac{\text{Volume of MgO}}{\text{Volume of Mg}}$$

$$= \frac{40/3.58}{24/1.74} = \frac{11.17}{13.79} = 0.81$$

∵ 0.81 < 1, ∴ Non-protective & porous.

Q.2 How much rust is formed when 1120 kg of Fe ~~con~~ rusts away completely.

Atomic mass 56 ← $Fe_2O_3 \cdot 3H_2O$ — Rust.

Molecular mass of rust = 2(56) + 3(16)

112 g of Fe can form 214 g of rust.

∴ 1120 kg of Fe can form

$$= \frac{214}{\cancel{112}} \times \overset{10}{\cancel{1120}} \times 10^3$$

= 2140 kg.

~~= 2.14 × 10^{?}~~

5.01.2022

1Q. In an industrial area, the mass of rust formed on an iron bar was found to be 428 kg. How much amount of Fe bar is required to replace the corroded one.

Ans. Formula of rust : $Fe_2O_3 \cdot 3H_2O$

Molecular mass of rust ~~= 2(56) + 3(16)~~ ~~224 kg 214 kg of rust~~ 214 g of rust from 112 g of Fe.

~~Mass of iron bar with rust =~~

428 kg of rust is formed from $\frac{112}{214} \times 428 \times 10^3$ g

= 224 kg Fe.

Q. Predict the nature of the oxide layer from the following data

Density of Al_2O_3 (aluminium oxide) → 3.95 g/cc
Density of Al → 2.7 g/cc
Atomic wt of Al → 27
Atomic wt O → 16

Ans.

$$\text{PB ratio} = \frac{\text{Volume of } Al_2O_3}{\text{Volume of Al}} = \frac{102/3.95}{2 \times 27/2.7} = \frac{25.822}{20} = \frac{2.5822}{2} = 1.29$$

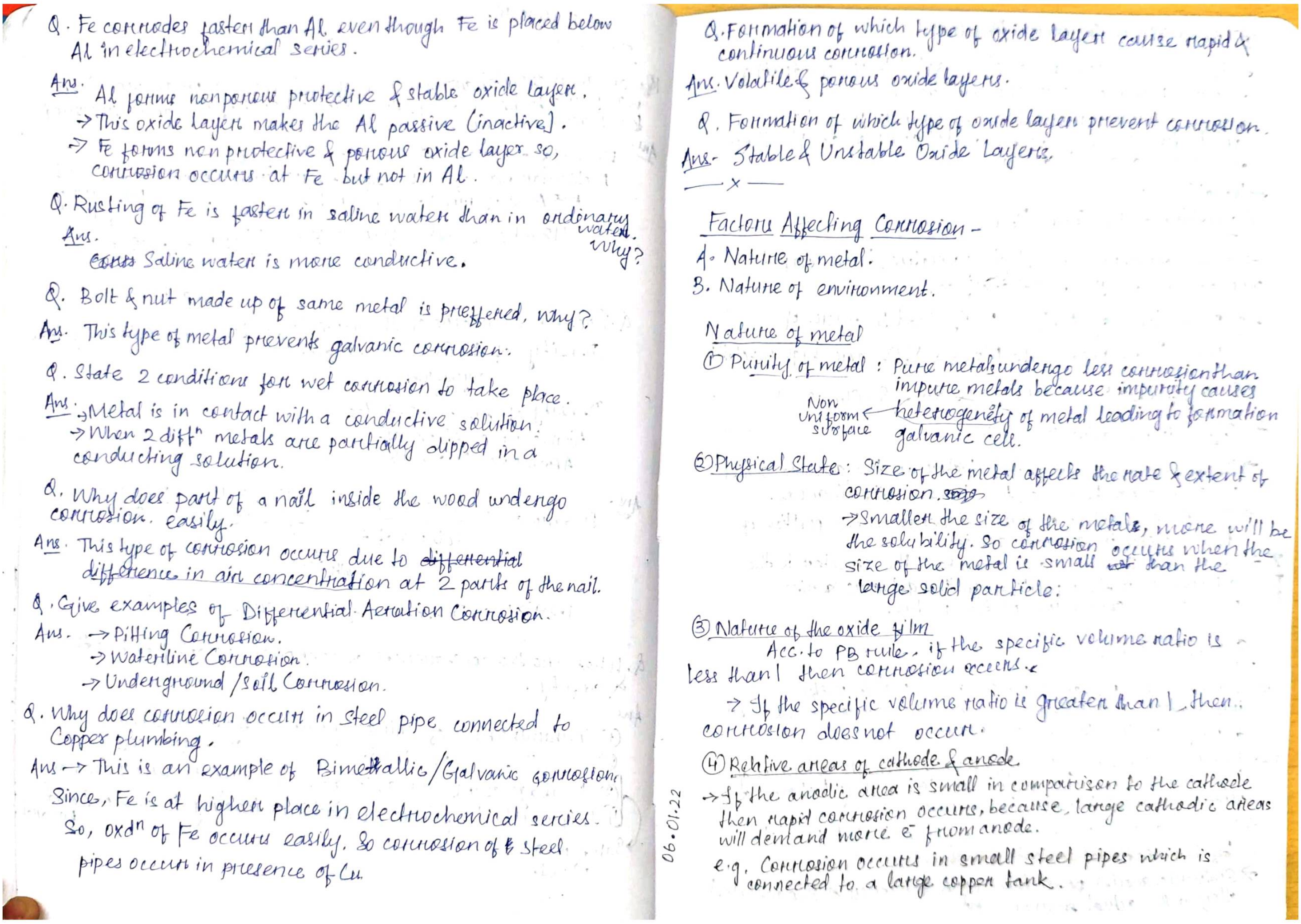
Multiplied 2

1.29 > 1 ∴ Protective & non porous.

Q. What are the consequences of corrosion relating to health & safety.

Ans.

① Contamination of drinking water.] Health related consequences.
② " of food.
③ Leakage of inflammable gases, leading to fire hazards.
④ Unpredictable failure of machines leading to occupational hazard.
→ Safety related issues.



Q. Fe corrodes faster than Al even though Fe is placed below Al in electrochemical series.

Ans. Al forms nonporous protective & stable oxide layer.
→ This oxide layer makes the Al passive (inactive).
→ Fe forms non protective & porous oxide layer so, corrosion occurs at Fe but not in Al.

Q. Rusting of Fe is faster in saline water than in ordinary water. Why?

Ans.
Saline water is more conductive.

Q. Bolt & nut made up of same metal is preffered, why?

Ans. This type of metal prevents galvanic corrosion.

Q. State 2 conditions for wet corrosion to take place.

Ans. → Metal is in contact with a conductive solution.
→ When 2 diff^n metals are partially dipped in a conducting solution.

Q. Why does part of a nail inside the wood undergo corrosion easily.

Ans. This type of corrosion occurs due to ~~differential~~ difference in air concentration at 2 parts of the nail.

Q. Give examples of Differential Aeration Corrosion.

Ans. → Pitting Corrosion.
→ Waterline Corrosion.
→ Underground / Soil Corrosion.

Q. Why does corrosion occur in steel pipe connected to Copper plumbing.

Ans → This is an example of Bimetallic / Galvanic corrosion.
Since, Fe is at higher place in electrochemical series.
So, oxd^n of Fe occurs easily. So corrosion of steel pipes occurs in presence of Cu.

06.01.22

Q. Formation of which type of oxide layer cause rapid & continuous corrosion.

Ans. Volatile & porous oxide layers.

Q. Formation of which type of oxide layer prevent corrosion.

Ans- Stable & Unstable Oxide Layers.

— x —

Factors Affecting Corrosion -

A. Nature of metal.

B. Nature of environment.

Nature of metal

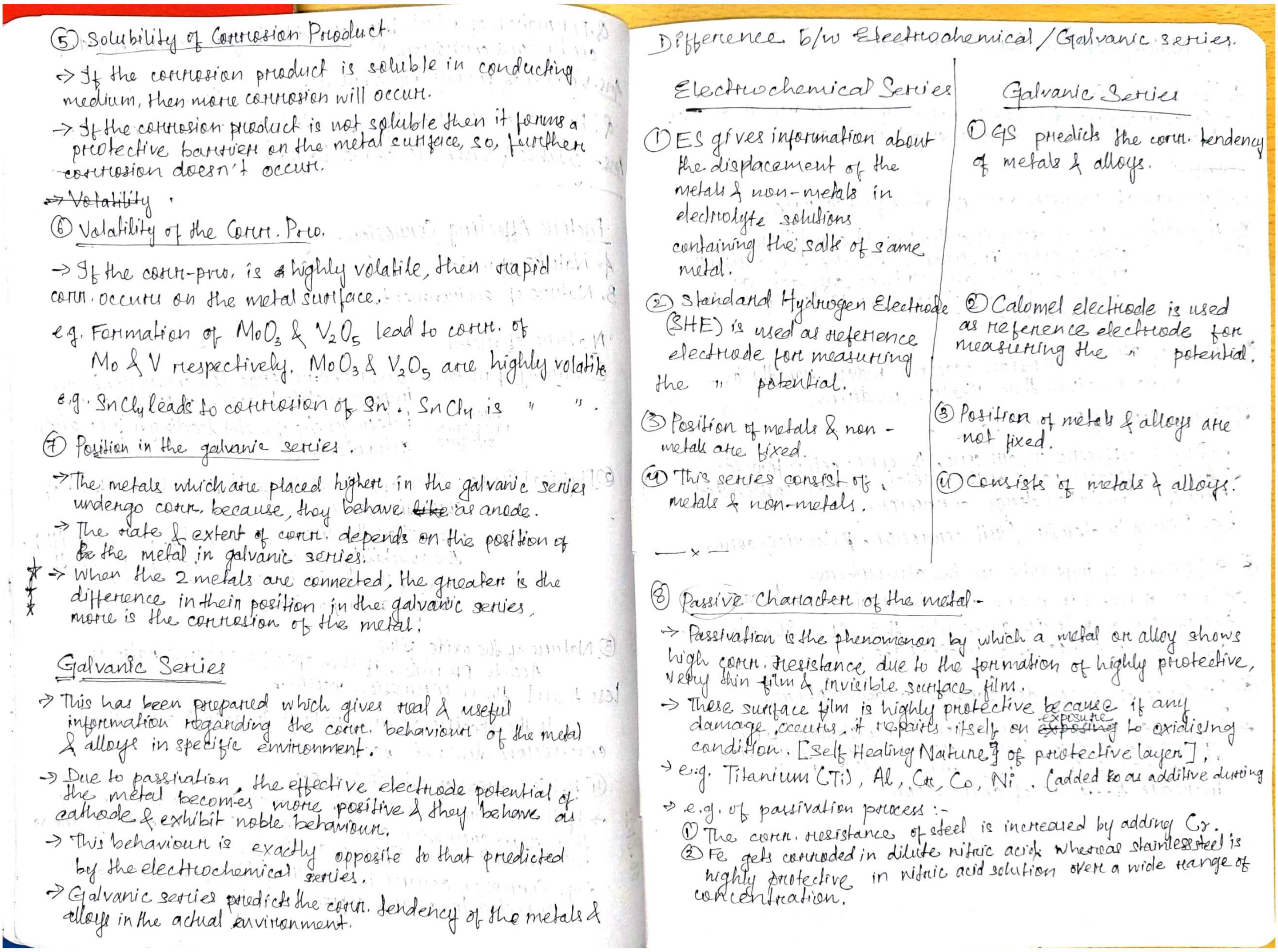
① Purity of metal : Pure metals undergo less corrosion than impure metals because impurity causes heterogeneity of metal leading to formation galvanic cell.

Non uniform surface ← heterogeneity

② Physical State : Size of the metal affects the rate & extent of corrosion.
→ Smaller the size of the metals, more will be the solubility. So corrosion occurs when the size of the metal is small than the large solid particle.

③ Nature of the oxide film
Acc. to PB rule, if the specific volume ratio is less than 1 then corrosion occurs.
→ If the specific volume ratio is greater than 1, then corrosion does not occur.

④ Relative areas of cathode & anode
→ If the anodic area is small in comparison to the cathode then rapid corrosion occurs, because large cathodic areas will demand more e^- from anode.
e.g. Corrosion occurs in small steel pipes which is connected to a large copper tank.



⑤ Solubility of Corrosion Product.

-> If the corrosion product is soluble in conducting medium, then more corrosion will occur.

-> If the corrosion product is not soluble then it forms a protective barrier on the metal surface, so, further corrosion doesn't occur.

~~=> Volatility~~.

⑥ Volatility of the Corr. Pro.

-> If the corr-pro. is ~~a~~ highly volatile, then rapid corr. occurs on the metal surface.

e.g. Formation of MoO_3 & V_2O_5 lead to corr. of Mo & V respectively. MoO_3 & V_2O_5 are highly volatile.

e.g. $SnCl_4$ leads to corrosion of Sn. $SnCl_4$ is " ".

⑦ Position in the galvanic series.

-> The metals which are placed higher in the galvanic series undergo corr. because, they behave ~~like~~ as anode.

-> The rate & extent of corr. depends on the position of ~~Be~~ the metal in galvanic series.

★★★ -> When the 2 metals are connected, the greater is the difference in their position in the galvanic series, more is the corrosion of the metal.

Galvanic Series

-> This has been prepared which gives real & useful information regarding the corr. behaviour of the metal & alloys in specific environment.

-> Due to passivation, the effective electrode potential of the metal becomes more positive & they behave as cathode & exhibit noble behaviour.

-> This behaviour is exactly opposite to that predicted by the electrochemical series.

-> Galvanic series predicts the corr. tendency of the metals & alloys in the actual environment.

Difference b/w Electrochemical / Galvanic series.

Electrochemical Series	Galvanic Series
① ES gives information about the displacement of the metals & non-metals in electrolyte solutions containing the salts of same metal.	① GS predicts the corr. tendency of metals & alloys.
② Standard Hydrogen Electrode (SHE) is used as reference electrode for measuring the " potential.	② Calomel electrode is used as reference electrode for measuring the " potential.
③ Position of metals & non-metals are fixed.	③ Position of metals & alloys are not fixed.
④ This series consist of metals & non-metals.	④ Consists of metals & alloys.

—x—

⑧ Passive Character of the metal -

-> Passivation is the phenomenon by which a metal or alloy shows high corr. resistance due to the formation of highly protective, very thin film & invisible surface film.

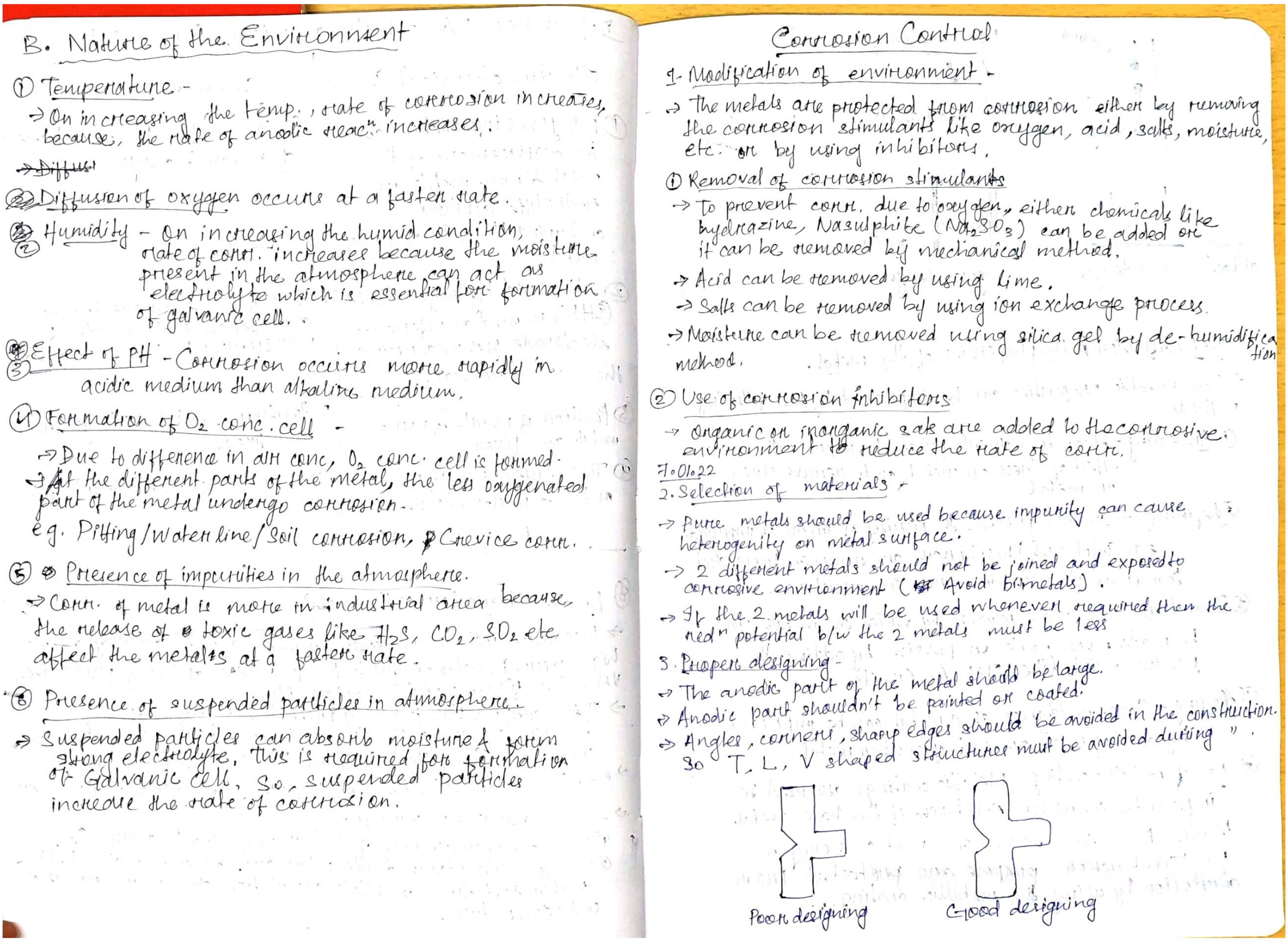
-> These surface film is highly protective because if any damage occurs, it repairs itself on ~~exposing~~ exposure to oxidising condition. [Self Healing Nature] of protective layer].

-> e.g. Titanium (Ti), Al, Cr, Co, Ni. (added ~~to~~ as additive during

-> e.g. of passivation process :-

① The corr. resistance of steel is increased by adding Cr.

② Fe gets corroded in dilute nitric acid whereas stainless steel is highly protective in nitric acid solution over a wide range of concentration.



B. Nature of the Environment

① Temperature -

→ On increasing the temp., rate of corrosion increases, because, the rate of anodic reac^n increases.

~~→ Diffusi~~

Diffusion of oxygen occurs at a faster rate.

② Humidity - On increasing the humid condition, rate of corr. increases because the moisture present in the atmosphere can act as electrolyte which is essential for formation of galvanic cell.

③ Effect of PH - Corrosion occurs more rapidly in acidic medium than alkaline medium.

④ Formation of O_2 conc. cell -

→ Due to difference in air conc, O_2 conc. cell is formed.

→ At the different parts of the metal, the less oxygenated part of the metal undergo corrosion.

e.g. Pitting / Water line / Soil corrosion, Crevice corr.

⑤ Presence of impurities in the atmosphere.

→ Corr. of metal is more in industrial area because, the release of toxic gases like H_2S, CO_2, SO_2 etc affect the metals at a faster rate.

⑥ Presence of suspended particles in atmosphere.

→ Suspended particles can absorb moisture & form strong electrolyte, this is required for formation of Galvanic cell, So, suspended particles increase the rate of corrosion.

Corrosion Control

1- Modification of environment -

→ The metals are protected from corrosion either by removing the corrosion stimulants like oxygen, acid, salts, moisture, etc. or by using inhibitors.

① Removal of corrosion stimulants

→ To prevent corr. due to oxygen, either chemicals like hydrazine, Na sulphite (Na_2SO_3) can be added or it can be removed by mechanical method.

→ Acid can be removed by using lime.

→ Salts can be removed by using ion exchange process.

→ Moisture can be removed using silica gel by de-humidification method.

② Use of corrosion inhibitors

→ Organic or inorganic salts are added to the corrosive environment to reduce the rate of corr.

7.01.22

2. Selection of materials -

→ Pure metals should be used because impurity can cause heterogenity on metal surface.

→ 2 different metals should not be joined and exposed to corrosive environment (Avoid bimetals).

→ If the 2 metals will be used whenever required then the red^n potential b/w the 2 metals must be less

3. Proper designing -

→ The anodic part of the metal should be large.

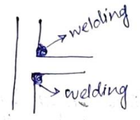
→ Anodic part shouldn't be painted or coated.

→ Anodic part should be avoided in the construction.

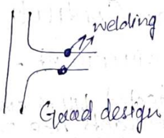
→ Angles, corners, sharp edges should be avoided during ".
So T, L, V shaped structures must be avoided

Poor designing

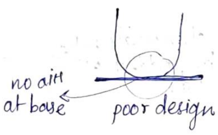
Good designing



poor design



Good design



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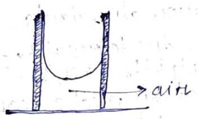


good design

4. Modification in the properties of the metal.

→ The metallic properties can be improved by the following methods.

① **Annealing** - Heat treatment process to improve the effect of stress on metal or to remove stress on metal.

② **Refining** - In this process, the purity of metal is improved. e.g. Sulphur & Phosphorous are removed from steel to improve its ~~corossion~~ corrosion resistance.

③ **Passivation** - This is the process by which the metals can be made more noble or passive by adding the passive metals like 'Ti', Al, Cr, etc.

④ **Alloying** - Corr. resistance of a metal can be improved by adding small amount of another metal

⑤ **Use of metallic coating** - Metallic coatings are used to improve the corrosion resistance of the base metal. Usually, Fe & Steel which are most commonly used for construction purpose are protected from corrosion by using the metallic coatings.

→ The metals which are used for coating are Al, Zn, Ca, Cr, Ni, etc

→ There are 2 types of coating:-

(i) **Anodic coating** - Prevents the base metal. The metallic coating acts as anode & the base " acts as cathode e.g. Al, Cadmium, Zn on steel surface.

→ The coating of Zn on Fe surface is called **Galvanization**.

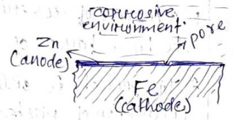
→ In this process, Zn is coated over the Fe surface in hot condition.

→ The temp. is maintained at 425 to 500°C.

→ In this method, Zn protects Fe because Zn acts as anode in comparison to Fe metal.

→ This type of coating is effective even if the surface is having pores, cracks and damage.

→ Fe is protected till all the Zn is consumed.



$Zn \rightarrow Zn^{2+} + 2e^-$

(ii) **Cathodic Coating** - Protects the base metal due to their noble behaviour & high corr. resistance.

→ In such coating, the effective electrode potential of coating material is more than the base metal.

→ This type of coating is effective when the coatings are uniform & free from pores, cracks or damage.

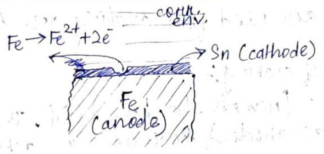
→ If there is any breakage over the coating surface, then the base metal will be corroded rapidly.

e.g. of metals which can show such coatings, Sn, Al..

→ When Sn is coated over Fe surface, it is called Tinning of Fe.

→ Since, the effective electrode potential of Sn is more than Fe, Sn protects the Fe metal being cathodic.

→ If any damage occurs on Sn coating then, rapid corr. occurs on Fe because, Fe is more anodic than Sn.



→ Hence, Galvanization is always preferable ~~to~~ than Tinning.

Q. Why are galvanized utensils are not used?

Ans. Zn of galvanized utensil is dissolved in dilute acid present in food forming toxic compound. ~~Hence~~ Hence, it is avoided to keep & prepare food.

13.01.22

Distinguish b/w Galvanization & Tinning.

Galvanization	Tinning
1. A process of covering the surface of iron by a layer of zinc (Zn).	1. A process of covering the Fe by a layer of tin.
2. Zinc protects the Fe by both sacrificially & formation of protective oxide layer.	2. Tin protects Fe only by formation of protective oxide layer.
3. Double protection layer.	3. Single protection route.
4. Galvanized iron containers not safe to store food ~~&~~ because it reacts with Zn to form toxic masses causing food poisoning	4. Tin coated containers are safe to store food.

→ Zn is anodic to Fe, so when ZnO film is damaged, Zn is attacked by the corrosive environment to form $Zn(OH)_2$ & Fe is protected (Zn is oxidised).

→ Used for Anodic coating → Zn, Al

→ Used for cathodic coating → Sn, Pb

Cathodic / Electrochemical Protection

→ Reduces corrosion of underground metallic structures by forcing it to behave like a Cathode

2 types
→ Sacrificial anodic protection ✓
→ Impressed current protection ✗ Not in syllabus

Sacrificial Protection

→ Metal will be consumed protecting the other metal.

→ wet/electrochemical corr. occurs due to formation of separate anode & cathode.

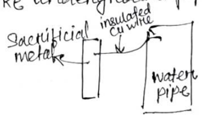
→ The existence of potential difference b/w anode and cathode causes loss of electrons (oxidation) at anode.

→ So, without cathodic protection, active metal suffers from corr. If a more active metal is connected via an insulated Cu-wire to a metallic structure which is undergoing corr. then corr. occurs at more active metal & the metallic structure can be protected.

→ As the more active metal is sacrificed in the process of protecting the metallic structure, it is known as sacrificial anode.

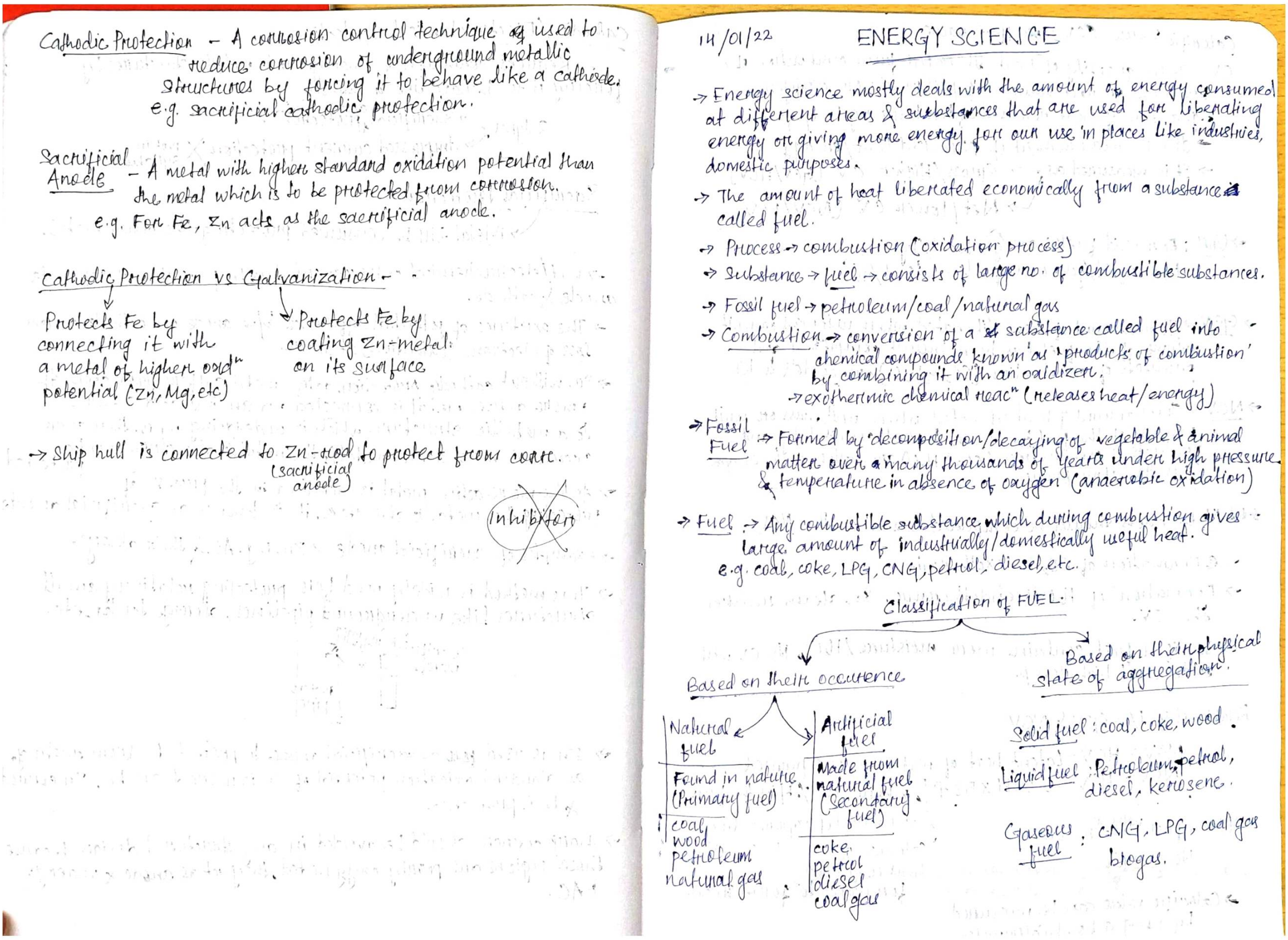
→ examples of sacrificial anode → Zn, Mg, Al & their alloys.

→ This method is widely used for protecting relatively small structures like underground pipelines, storage tanks, etc.



→ Zn is used ~~for~~ as sacrificial anode to protect Fe from rusting, as standard oxidation potential of Zn is more than Fe, Zn corrodes & Fe is protected.

→ Sharp corners should be avoided in any structural design because those regions are poorly oxygenated, they act as anode & undergo DAC.



Cathodic Protection – A corrosion control technique ~~as~~ used to reduce corrosion of underground metallic structures by forcing it to behave like a cathode.
e.g. sacrificial cathodic protection.

Sacrificial Anode – A metal with higher standard oxidation potential than the metal which is to be protected from corrosion.
e.g. For Fe, Zn acts as the sacrificial anode.

Cathodic Protection vs Galvanization –

Cathodic Protection	Galvanization
Protects Fe by connecting it with a metal of higher oxid^n potential (Zn, Mg, etc)	Protects Fe by coating Zn-metal on its surface

→ Ship hull is connected to Zn-rod (sacrificial anode) to protect from corr.

~~Inhibitor~~

14/01/22

ENERGY SCIENCE

→ Energy science mostly deals with the amount of energy consumed at different areas & substances that are used for liberating energy or giving more energy for our use in places like industries, domestic purposes.

→ The amount of heat liberated economically from a substance ~~is~~ called fuel.

→ Process → combustion (oxidation process)

→ Substance → fuel → consists of large no. of combustible substances.

→ Fossil fuel → petroleum/coal/natural gas

→ **Combustion** → conversion of a ~~st~~ substance called fuel into chemical compounds known as 'products of combustion' by combining it with an oxidizer.
→ exothermic chemical reac^n (releases heat/energy)

→ **Fossil Fuel** → Formed by decomposition/decaying of vegetable & animal matter over ~~a~~ many thousands of years under high pressure & temperature in absence of oxygen (anaerobic oxidation)

→ **Fuel** → Any combustible substance which during combustion gives large amount of industrially/domestically useful heat.
e.g. coal, coke, LPG, CNG, petrol, diesel, etc.

Classification of FUEL

Based on their occurence

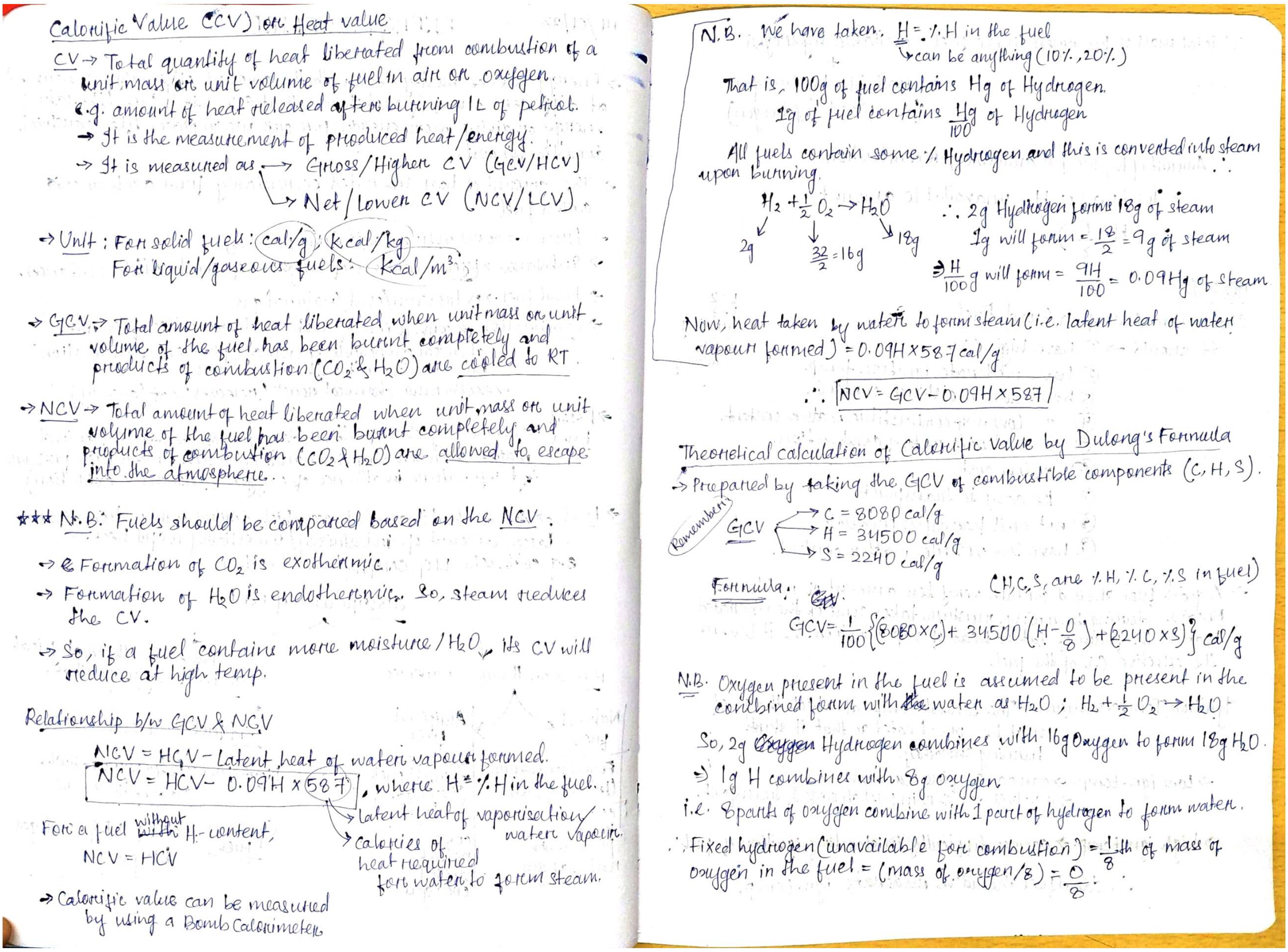
Natural fuel	Artificial fuel
Found in nature (Primary fuel)	Made from natural fuel (Secondary fuel)
coal wood petroleum natural gas	coke petrol diesel coal gas

Based on their physical state of aggregation.

Solid fuel : coal, coke, wood.

Liquid fuel : Petroleum, petrol, diesel, kerosene.

Gaseous fuel : CNG, LPG, coal gas biogas.



Calorific Value (CV) or Heat value

CV → Total quantity of heat liberated from combustion of a unit mass or unit volume of fuel in air or oxygen.

e.g. amount of heat released after burning 1L of petrol.

- → It is the measurement of produced heat/energy.
- → It is measured as → Gross/Higher CV (GCV/HCV)
  - → Net/Lower CV (NCV/LCV).

→ Unit : For solid fuels: cal/g ; Kcal/kg
For liquid/gaseous fuels: Kcal/m^3

→ GCV → Total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2 & H_2O) are cooled to RT.

→ NCV → Total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2 & H_2O) are allowed to escape into the atmosphere.

*** N.B: Fuels should be compared based on the NCV.

- → Formation of CO_2 is exothermic.
- → Formation of H_2O is endothermic. So, steam reduces the CV.
- → So, if a fuel contains more moisture/H_2O, its CV will reduce at high temp.

Relationship b/w GCV & NCV

NCV = HCV − Latent heat of water vapour formed.

$$\boxed{NCV = HCV - 0.09H \times 587}$$

, where H = % H in the fuel.

587 → latent heat of vaporisation/water vapour.
→ Calories of heat required for water to form steam.

For a fuel ~~with~~ without H-content,
NCV = HCV

→ Calorific value can be measured by using a Bomb Calorimeter

N.B. We have taken, H = % H in the fuel
↳ can be anything (10%, 20%)

That is, 100g of fuel contains Hg of Hydrogen.
1g of fuel contains $\frac{H}{100}$g of Hydrogen

All fuels contain some % Hydrogen and this is converted into steam upon burning.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

2g, $\frac{32}{2} = 16g$, 18g

∴ 2g Hydrogen forms 18g of steam
1g will form = $\frac{18}{2} = 9g$ of steam
⇒ $\frac{H}{100}g$ will form = $\frac{9H}{100} = 0.09H$g of steam

Now, heat taken by water to form steam (i.e. latent heat of water vapour formed) = 0.09H × 587 cal/g

$$\therefore \boxed{NCV = GCV - 0.09H \times 587}$$

Theoretical calculation of Calorific Value by Dulong's Formula

→ Prepared by taking the GCV of combustible components (C, H, S).

Remember

GCV → C = 8080 cal/g
→ H = 34500 cal/g
→ S = 2240 cal/g

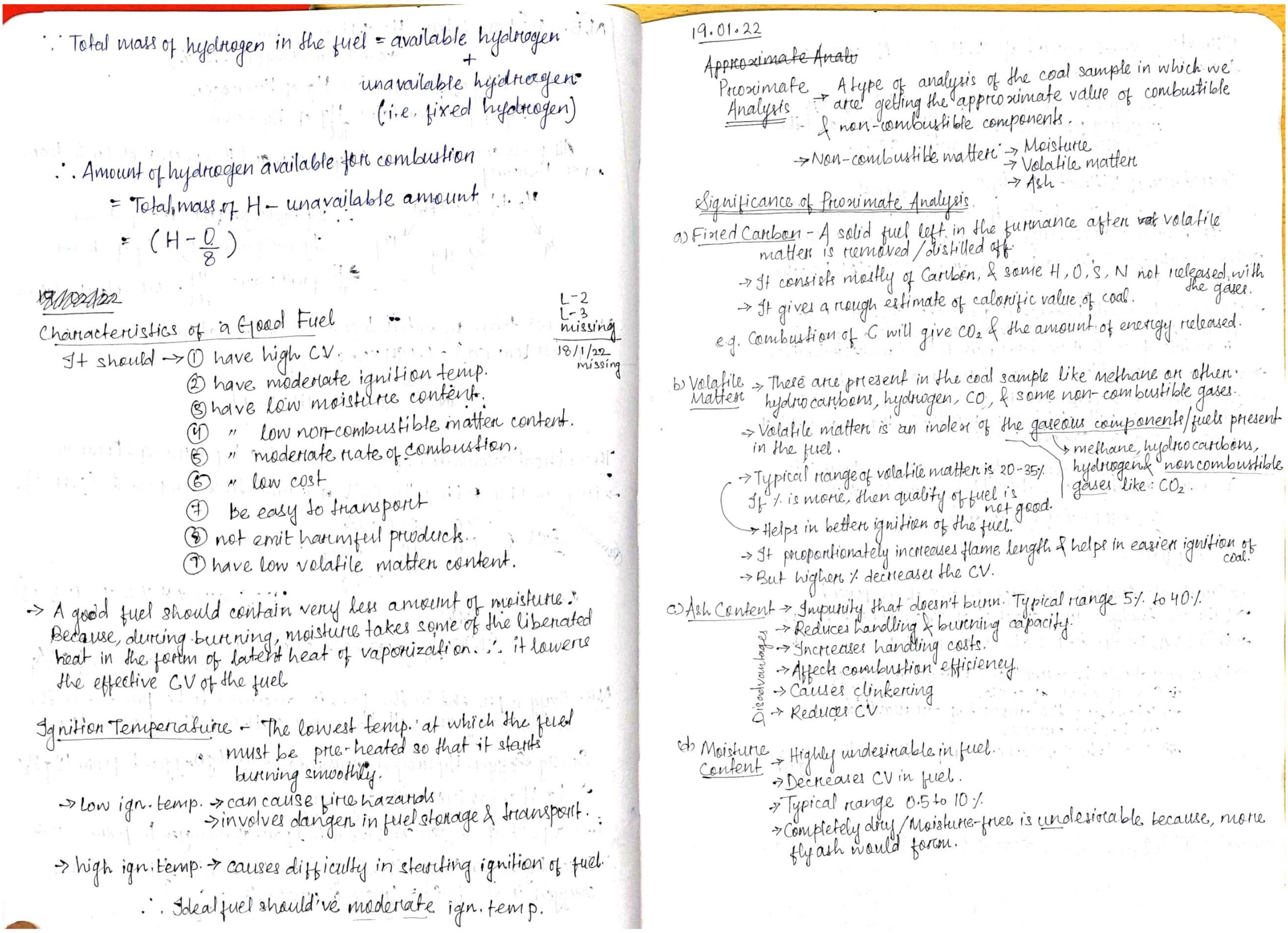
Formula: ~~GCV~~ (H, C, S, are % H, % C, % S in fuel)

$$GCV = \frac{1}{100}\left\{(8080 \times C) + 34500\left(H - \frac{O}{8}\right) + (2240 \times S)\right\} cal/g$$

N.B. Oxygen present in the fuel is assumed to be present in the combined form with ~~the~~ water as H_2O ; $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

So, 2g ~~Oxygen~~ Hydrogen combines with 16g Oxygen to form 18g H_2O.
⇒ 1g H combines with 8g oxygen
i.e. 8 parts of oxygen combine with 1 part of hydrogen to form water.

∴ Fixed hydrogen (unavailable for combustion) = $\frac{1}{8}$th of mass of oxygen in the fuel = (mass of oxygen/8) = $\frac{O}{8}$.



∵ Total mass of hydrogen in the fuel = available hydrogen + unavailable hydrogen (i.e. fixed hydrogen)

∴ Amount of hydrogen available for combustion

= Total mass of H − unavailable amount

$= (H - \frac{O}{8})$

[illegible]

L-2
L-3
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18/1/22
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Characteristics of a Good Fuel

It should →
① have high CV.
② have moderate ignition temp.
③ have low moisture content.
④ " low non-combustible matter content.
⑤ " moderate rate of combustion.
⑥ " low cost
⑦ be easy to transport
⑧ not emit harmful products.
⑨ have low volatile matter content.

→ A good fuel should contain very less amount of moisture. Because, during burning, moisture takes some of the liberated heat in the form of latent heat of vaporization. ∴ it lowers the effective CV of the fuel

Ignition Temperature – The lowest temp. at which the fuel must be pre-heated so that it starts burning smoothly.

→ Low ign. temp. → can cause fire hazards
→ involves danger in fuel storage & transport.

→ high ign. temp. → causes difficulty in starting ignition of fuel.

∴ Ideal fuel should've moderate ign. temp.

19.01.22

~~Approximate Analo~~

Proximate Analysis → A type of analysis of the coal sample in which we are getting the approximate value of combustible & non-combustible components.

→ Non-combustible matter → Moisture
→ Volatile matter
→ Ash

Significance of Proximate Analysis

a) Fixed Carbon – A solid fuel left in the furnance after ~~vol~~ volatile matter is removed / distilled off.

→ It consists mostly of Carbon, & some H, O, S, N not released with the gases.
→ It gives a rough estimate of calorific value of coal.

e.g. Combustion of C will give CO_2 & the amount of energy released.

b) Volatile Matter → There are present in the coal sample like methane or other hydrocarbons, hydrogen, CO, & some non-combustible gases.

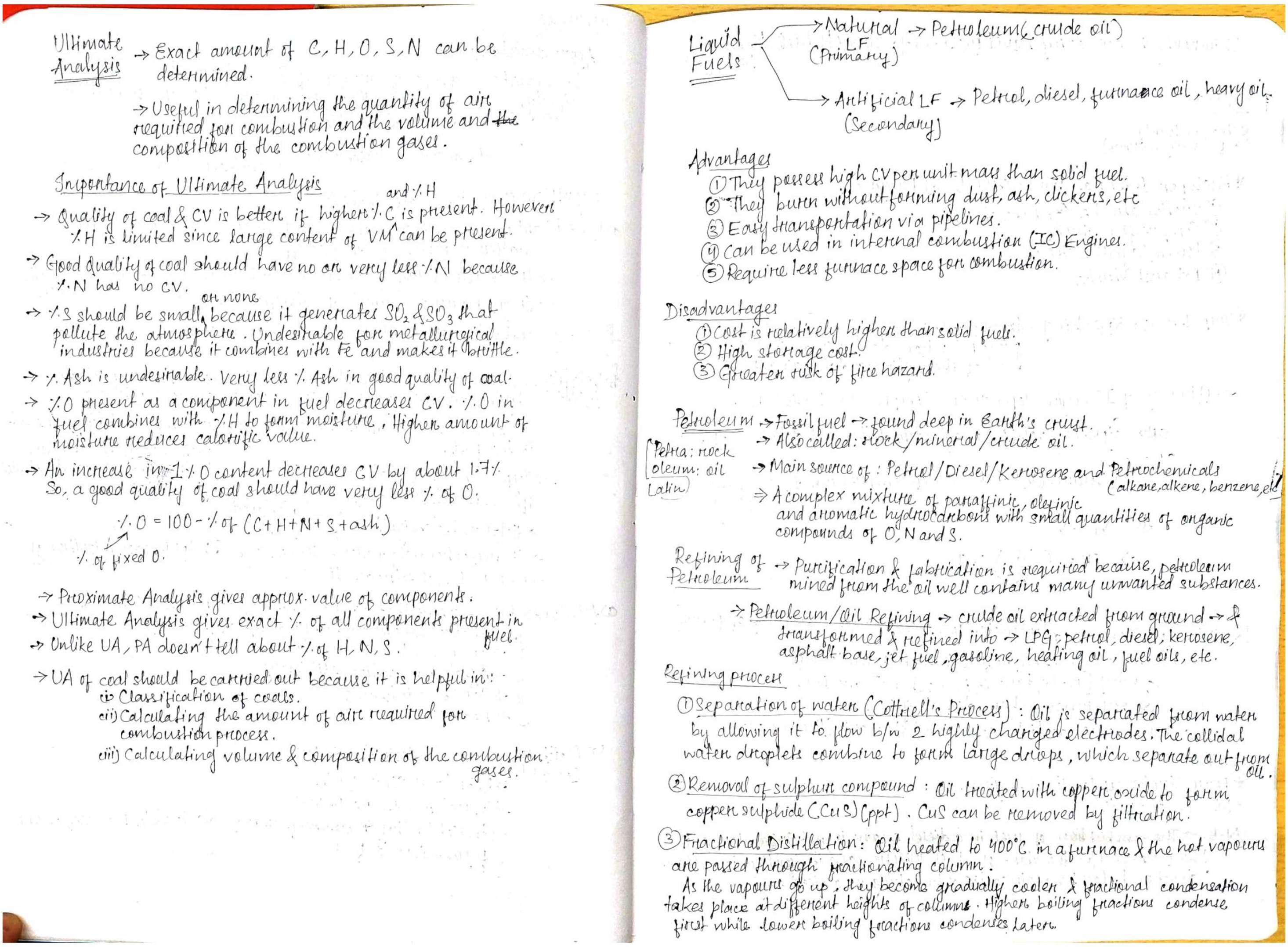
→ Volatile matter is an index of the gaseous components/fuels present in the fuel.
↳ methane, hydrocarbons, hydrogen & non combustible gases like : CO_2.

→ Typical range of volatile matter is 20-35%
If % is more, then quality of fuel is not good.
→ Helps in better ignition of the fuel.
→ It proportionately increases flame length & helps in easier ignition of coal.
→ But higher % decreases the CV.

c) Ash Content → Impurity that doesn't burn. Typical range 5% to 40%.

Disadvantages
→ Reduces handling & burning capacity.
→ Increases handling costs.
→ Affects combustion efficiency.
→ Causes clinkering
→ Reduces CV

d) Moisture Content → Highly undesirable in fuel.
→ Decreases CV in fuel.
→ Typical range 0.5 to 10%.
→ Completely dry/Moisture-free is undesirable because, more fly ash would form.



Ultimate Analysis → Exact amount of C, H, O, S, N can be determined.

→ Useful in determining the quantity of air required for combustion and the volume and ~~the~~ composition of the combustion gases.

Importance of Ultimate Analysis

→ Quality of coal & CV is better if higher %C and %H is present. However %H is limited since large content of VM can be present.

→ Good quality of coal should have no or very less %N because %N has no CV.

→ %S should be small or none because it generates SO_2 & SO_3 that pollute the atmosphere. Undesirable for metallurgical industries because it combines with Fe and makes it brittle.

→ % Ash is undesirable. Very less % Ash in good quality of coal.

→ %O present as a component in fuel decreases CV. %O in fuel combines with %H to form moisture. Higher amount of moisture reduces calorific value.

→ An increase in 1% O content decreases CV by about 1.7%. So, a good quality of coal should have very less % of O.

$$\%O = 100 - \% \text{ of } (C+H+N+S+ash)$$

% of fixed O.

→ Proximate Analysis gives approx. value of components.

→ Ultimate Analysis gives exact % of all components present in fuel.

→ Unlike UA, PA doesn't tell about % of H, N, S.

→ UA of coal should be carried out because it is helpful in:
- (i) Classification of coals.
- (ii) Calculating the amount of air required for combustion process.
- (iii) Calculating volume & composition of the combustion gases.

Liquid Fuels
- → Natural LF (Primary) → Petroleum (crude oil)
- → Artificial LF (Secondary) → Petrol, diesel, furnace oil, heavy oil.

Advantages
1. They possess high CV per unit mass than solid fuel.
2. They burn without forming dust, ash, clickers, etc
3. Easy transportation via pipelines.
4. Can be used in internal combustion (IC) Engines.
5. Require less furnace space for combustion.

Disadvantages
1. Cost is relatively higher than solid fuels.
2. High storage cost.
3. Greater risk of fire hazard.

Petroleum → Fossil fuel → found deep in Earth's crust.

(Petra: rock
oleum: oil
Latin)

→ Also called: rock/mineral/crude oil.

→ Main source of: Petrol/Diesel/Kerosene and Petrochemicals (alkane, alkene, benzene, etc)

⇒ A complex mixture of paraffinic, olefinic and aromatic hydrocarbons with small quantities of organic compounds of O, N and S.

Refining of Petroleum → Purification & fabrication is required because, petroleum mined from the oil well contains many unwanted substances.

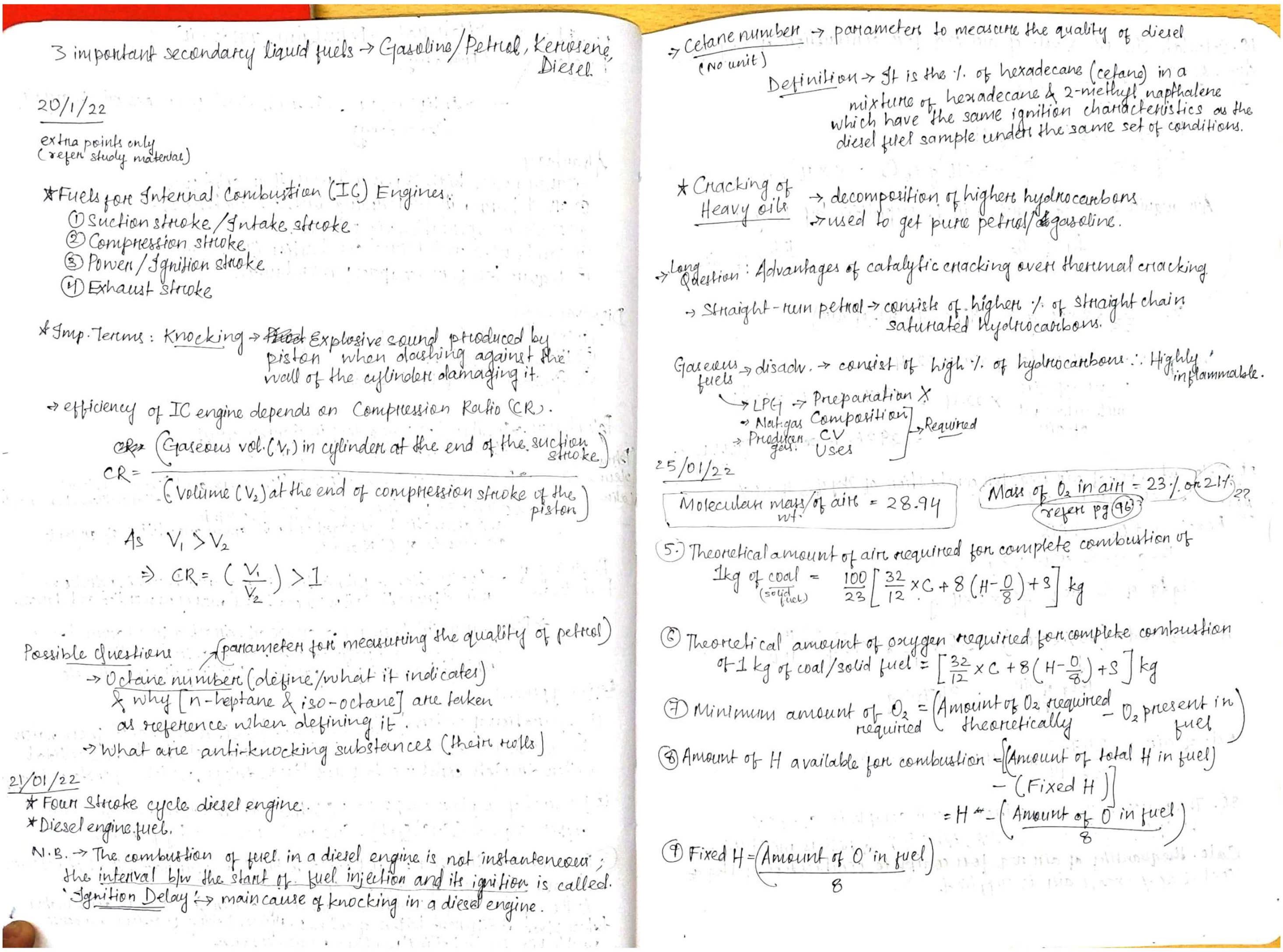
→ Petroleum/Oil Refining → crude oil extracted from ground → & transformed & refined into → LPG, petrol, diesel, kerosene, asphalt base, jet fuel, gasoline, heating oil, fuel oils, etc.

Refining process

① Separation of water (Cottrell's Process): Oil is separated from water by allowing it to flow b/w 2 highly charged electrodes. The collidal water droplets combine to form large drops, which separate out from oil.

② Removal of sulphur compound: Oil treated with copper oxide to form copper sulphide (CuS) (ppt). CuS can be removed by filtration.

③ Fractional Distillation: Oil heated to 400°C in a furnace & the hot vapours are passed through fractionating column.
As the vapours go up, they become gradually cooler & fractional condensation takes place at different heights of columns. Higher boiling fractions condense first while lower boiling fractions condenses later.



3 important secondary liquid fuels → Gasoline/Petrol, Kerosene, Diesel.

20/1/22

extra points only
(refer study material)

★Fuels for Internal Combustion (IC) Engines.
① Suction stroke/Intake stroke
② Compression stroke
③ Power/Ignition stroke
④ Exhaust stroke

★Imp. Terms : Knocking → ~~Prod~~ Explosive sound produced by piston when dashing against the wall of the cylinder damaging it.

→ efficiency of IC engine depends on Compression Ratio (CR).

$$CR = \frac{(\text{Gaseous vol.}(V_1) \text{ in cylinder at the end of the suction stroke})}{(\text{Volume }(V_2) \text{ at the end of compression stroke of the piston})}$$

As $V_1 > V_2$

$$\Rightarrow CR = \left(\frac{V_1}{V_2}\right) > 1$$

Possible Questions
→ Octane number (parameter for measuring the quality of petrol) (define/what it indicates)
& why [n-heptane & iso-octane] are taken as reference when defining it.
→ What are anti-knocking substances (their roles)

21/01/22

★ Four Stroke cycle diesel engine.
★ Diesel engine fuel.

N.B. → The combustion of fuel in a diesel engine is not instanteneous; the interval b/w the start of fuel injection and its ignition is called 'Ignition Delay' → main cause of knocking in a diesel engine.

→ Cetane number → parameter to measure the quality of diesel
(No unit)
Definition → It is the % of hexadecane (cetane) in a mixture of hexadecane & 2-methyl napthalene which have the same ignition characteristics as the diesel fuel sample under the same set of conditions.

★ Cracking of Heavy oils → decomposition of higher hydrocarbons
→ used to get pure petrol/gasoline.

→ Long Question : Advantages of catalytic cracking over thermal cracking.

→ Straight-run petrol → consists of higher % of straight chain saturated hydrocarbons.

Gaseous fuels → disadv. → consist of high % of hydrocarbons ∴ Highly inflammable.
→ LPG → Preparation ✗
→ Nat. gas Composition
→ Producer gas. CV
Uses
→ Required

25/01/22

Molecular mass/wt. of air = 28.94

Mass of O_2 in air = 23% or 21% ?? refer pg (96)

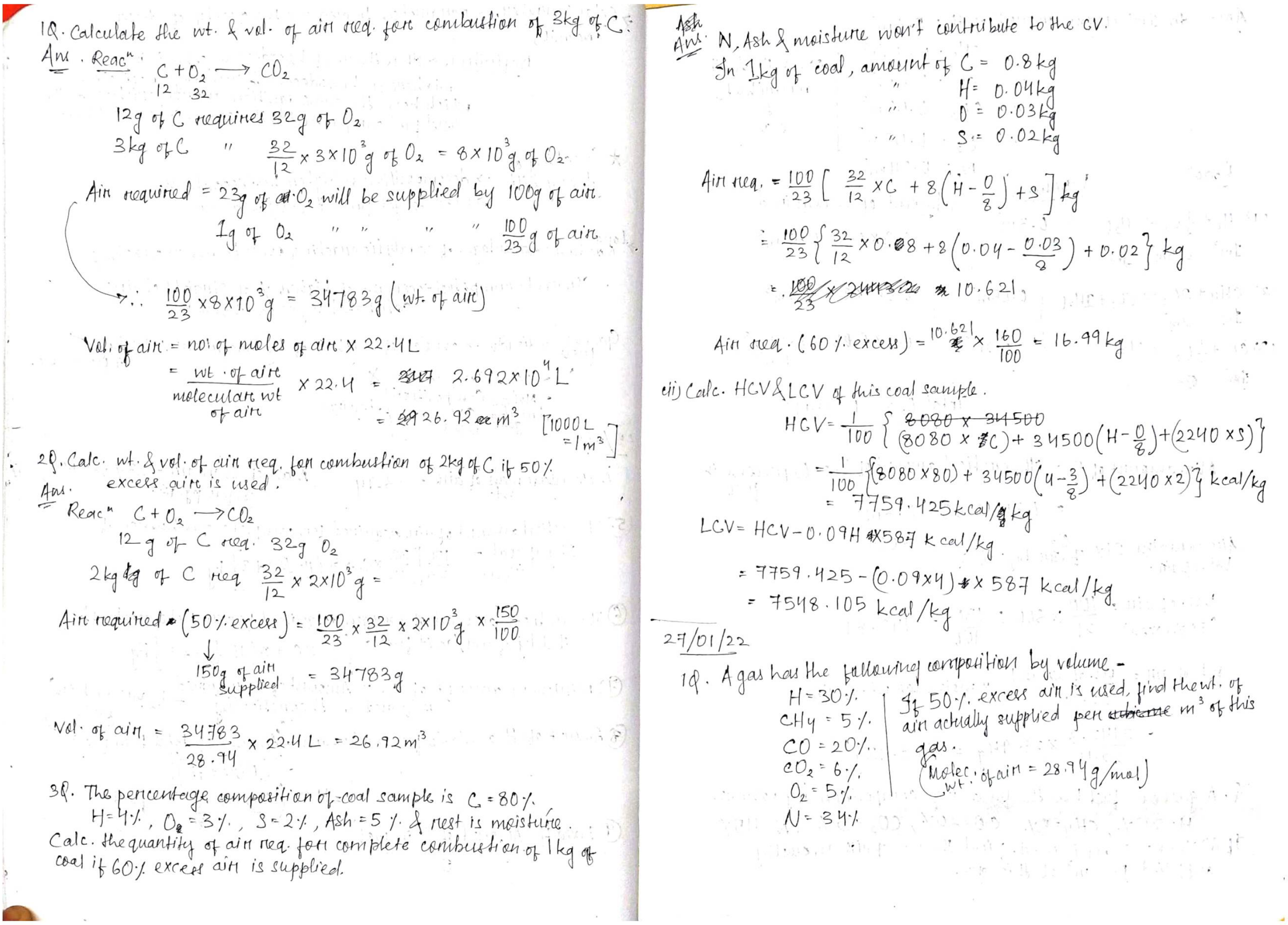
⑤ Theoretical amount of air required for complete combustion of 1kg of coal (solid fuel) $= \frac{100}{23}\left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S\right]$ kg

⑥ Theoretical amount of oxygen required for complete combustion of 1 kg of coal/solid fuel $= \left[\frac{32}{12} \times C + 8\left(H - \frac{O}{8}\right) + S\right]$ kg

⑦ Minimum amount of O_2 required = (Amount of O_2 required theoretically − O_2 present in fuel)

⑧ Amount of H available for combustion = [(Amount of total H in fuel) − (Fixed H)]
$= H - \left(\frac{\text{Amount of O in fuel}}{8}\right)$

⑨ Fixed H = $\left(\frac{\text{Amount of 'O' in fuel}}{8}\right)$



1Q. Calculate the wt. & vol. of air req. for combustion of 3kg of C.

Ans. Reacⁿ: $C + O_2 \longrightarrow CO_2$ (12, 32)

12g of C requires 32g of O_2

3kg of C " $\frac{32}{12} \times 3\times10^3$ g of O_2 = 8×10^3 g of O_2

Air required = 23g of ~~air~~ O_2 will be supplied by 100g of air

1g of O_2 " " " " $\frac{100}{23}$ g of air

∴ $\frac{100}{23} \times 8\times10^3$ g = 34783g (wt. of air)

Vol. of air = no. of moles of air × 22.4L

= $\frac{\text{wt. of air}}{\text{molecular wt of air}} \times 22.4$ = ~~3447~~ 2.692×10^4 L

= ~~29~~ 26.92 ~~cc~~ m^3 [1000 L = 1 m^3]

2Q. Calc. wt. & vol. of air req. for combustion of 2kg of C if 50% excess air is used.

Ans.

Reacⁿ $C + O_2 \longrightarrow CO_2$

12 g of C req. 32g O_2

2kg ~~kg~~ of C req $\frac{32}{12} \times 2\times10^3$ g =

Air required (50% excess) = $\frac{100}{23} \times \frac{32}{12} \times 2\times10^3 g \times \frac{150}{100}$

↓

150g of air supplied = 34783g

Vol. of air = $\frac{34783}{28.94} \times 22.4$ L = 26.92m^3

3Q. The percentage composition of coal sample is C = 80%, H = 4%, O_2 = 3%, S = 2%, Ash = 5% & rest is moisture. Calc. the quantity of air req. for complete combustion of 1kg of coal if 60% excess air is supplied.

Ans. N, Ash & moisture won't contribute to the CV.

In 1kg of coal, amount of C = 0.8kg
" H = 0.04kg
" O = 0.03kg
" S = 0.02kg

Air req. = $\frac{100}{23}\left[\frac{32}{12}\times C + 8\left(H - \frac{O}{8}\right) + S\right]$ kg

= $\frac{100}{23}\left\{\frac{32}{12}\times 0.08 + 8\left(0.04 - \frac{0.03}{8}\right) + 0.02\right\}$ kg

= ~~$\frac{100}{23} \times 2.443226$~~ 10.621

Air req. (60% excess) = $10.621 \times \frac{160}{100}$ = 16.99 kg

(ii) Calc. HCV & LCV of this coal sample.

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

= $\frac{1}{100}\left\{(8080\times80) + 34500\left(4 - \frac{3}{8}\right) + (2240\times2)\right\}$ kcal/kg

= 7759.425 kcal/kg

LCV = HCV − 0.09H × 587 kcal/kg

= 7759.425 − (0.09×4) × 587 kcal/kg

= 7548.105 kcal/kg

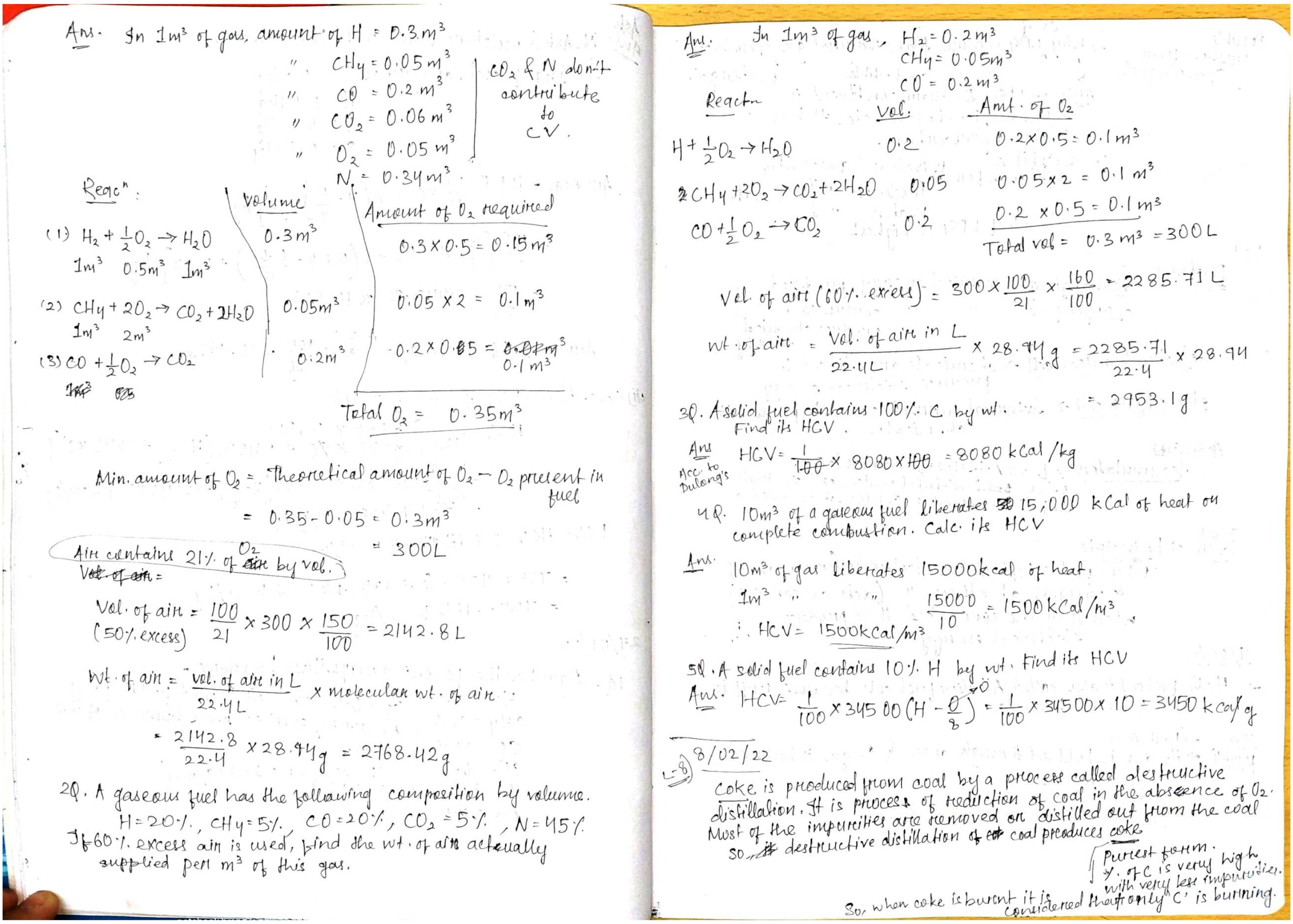
27/01/22

1Q. A gas has the following composition by volume -

H = 30%
CH_4 = 5%
CO = 20%
CO_2 = 6%
O_2 = 5%
N = 34%

If 50% excess air is used, find the wt. of air actually supplied per ~~cubic~~ m^3 of this gas.

(Molec. wt. of air = 28.94 g/mol)



Ans. In $1 m^3$ of gas, amount of H = $0.3 m^3$

" $CH_4 = 0.05 m^3$

" $CO = 0.2 m^3$

" $CO_2 = 0.06 m^3$

" $O_2 = 0.05 m^3$

$N = 0.34 m^3$

CO_2 & N don't contribute to CV.

Reacⁿ:	Volume	Amount of O_2 required
(1) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $1m^3$ $0.5m^3$ $1m^3$	$0.3m^3$	$0.3 \times 0.5 = 0.15 m^3$
(2) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $1m^3$ $2m^3$	$0.05m^3$	$0.05 \times 2 = 0.1 m^3$
(3) $CO + \frac{1}{2}O_2 \rightarrow CO_2$	$0.2m^3$	$0.2 \times 0.~~0~~5 = ~~0.01m^3~~$ $0.1 m^3$

Total O_2 = $0.35m^3$

Min. amount of O_2 = Theoretical amount of O_2 − O_2 present in fuel

= $0.35 - 0.05 = 0.3m^3$

= 300L

Air contains 21% of O_2 ~~air~~ by vol.

~~Vol. of air~~ =

Vol. of air (50% excess) = $\frac{100}{21} \times 300 \times \frac{150}{100} = 2142.8 L$

Wt. of air = $\frac{\text{Vol. of air in L}}{22.4L}$ × molecular wt. of air

= $\frac{2142.8}{22.4} \times 28.94g = 2768.42g$

2Q. A gaseous fuel has the following composition by volume.
H = 20%, CH_4 = 5%, CO = 20%, CO_2 = 5%, N = 45%
If 60% excess air is used, find the wt. of air actually supplied per m^3 of this gas.

Ans. In $1m^3$ of gas, $H_2 = 0.2 m^3$

$CH_4 = 0.05m^3$

$CO = 0.2 m^3$

Reactn	Vol.	Amt. of O_2
$H + \frac{1}{2}O_2 \rightarrow H_2O$	0.2	$0.2 \times 0.5 = 0.1 m^3$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	0.05	$0.05 \times 2 = 0.1 m^3$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	0.2	$0.2 \times 0.5 = 0.1 m^3$

Total vol = $0.3 m^3$ = 300 L

Vol. of air (60% excess) = $300 \times \frac{100}{21} \times \frac{160}{100} = 2285.71 L$

Wt. of air = $\frac{\text{Vol. of air in L}}{22.4L} \times 28.94 g = \frac{2285.71}{22.4} \times 28.94$

= 2953.1 g

3Q. A solid fuel contains 100% C by wt.
Find its HCV.

Ans
Acc. to Dulong's

HCV = $\frac{1}{\cancel{100}} \times 8080 \times \cancel{100}$ = 8080 kCal/kg

4Q. $10m^3$ of a gaseous fuel liberates ~~50~~ 15,000 kCal of heat on complete combustion. Calc. its HCV

Ans. $10m^3$ of gas liberates 15000kcal of heat.

$1m^3$ " " $\frac{15000}{10}$ = 1500 kCal/m^3

∴ HCV = 1500kCal/m^3

5Q. A solid fuel contains 10% H by wt. Find its HCV

Ans. HCV = $\frac{1}{100} \times 34500 \left(H - \frac{\overset{\rightarrow 0}{O}}{8}\right) = \frac{1}{100} \times 34500 \times 10 = 3450$ kcal/g

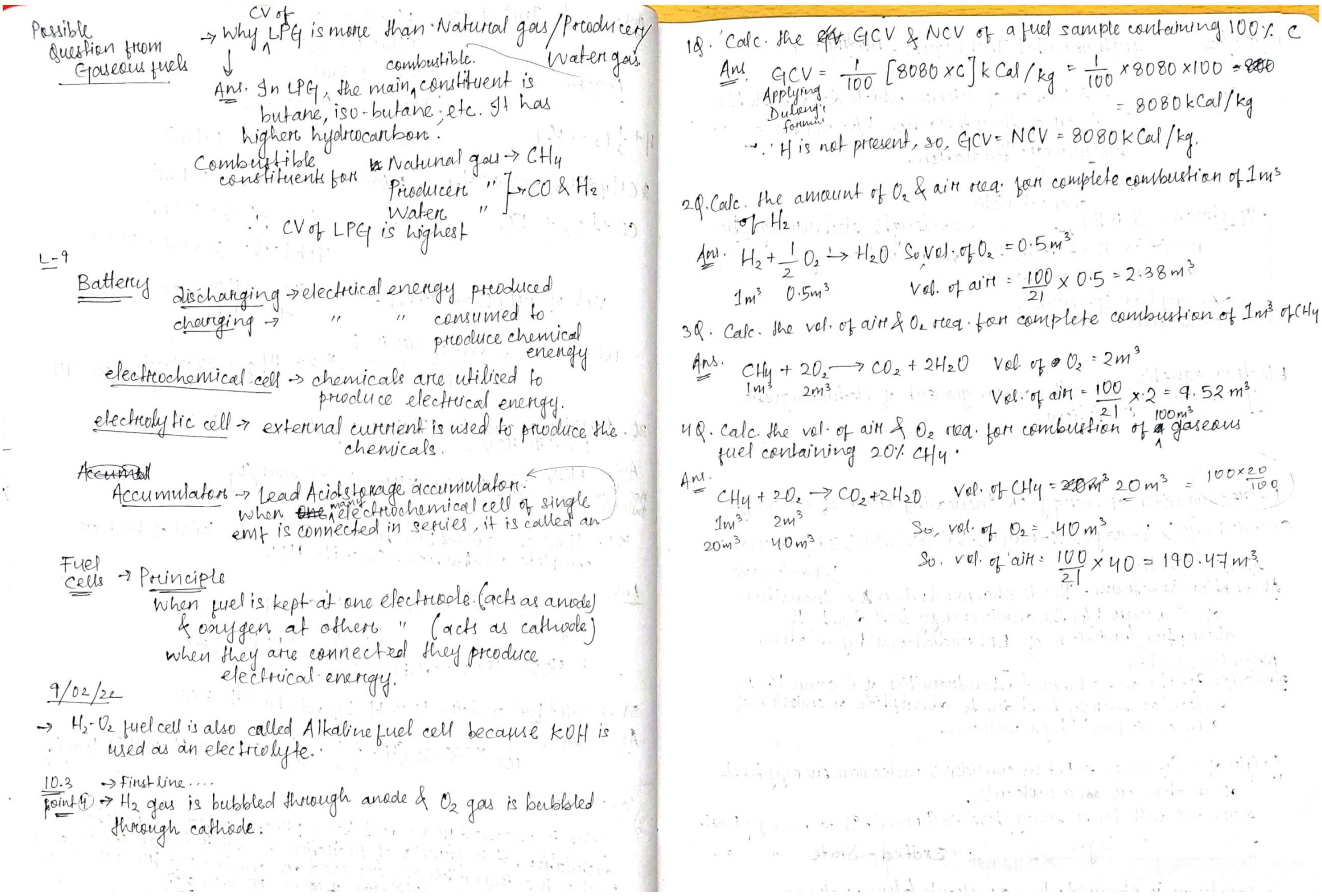
L-8) 8/02/22

Coke is produced from coal by a process called destructive distillation. It is process of reduction of coal in the absence of O_2. Most of the impurities are removed or distilled out from the coal

So, ~~it~~ destructive distillation of ~~coal~~ coal produces coke

Purest form.
% of C is very high
with very less impurities.

So, when coke is burnt it is considered that only 'C' is burning.



Possible Question from Gaseous fuels → Why CV of LPG is more than Natural gas/Producer/Water gas.

Ans. In LPG, the main combustible constituent is butane, iso-butane, etc. It has higher hydrocarbon.

Combustible constituents for ~~x~~ Natural gas → CH_4
Producer "] → CO & H_2
Water "]

∴ CV of LPG is highest

L-9

Battery discharging → electrical energy produced
charging → " " consumed to produce chemical energy

electrochemical cell → chemicals are utilised to produce electrical energy.

electrolytic cell → external current is used to produce the chemicals.

~~Accumul~~

Accumulator → Lead Acid storage accumulator.
when ~~one~~ many electrochemical cell of single emf is connected in series, it is called an

Fuel Cells → Principle
when fuel is kept at one electrode (acts as anode) & oxygen at other " (acts as cathode) when they are connected they produce electrical energy.

9/02/22

→ H_2-O_2 fuel cell is also called Alkaline fuel cell because KOH is used as an electrolyte.

10.3 → First line....
point ④ → H_2 gas is bubbled through anode & O_2 gas is bubbled through cathode.

1Q. Calc. the ~~gcv~~ GCV & NCV of a fuel sample containing 100% C

Ans. $GCV = \frac{1}{100}[8080 \times C]$ kCal/kg $= \frac{1}{100} \times 8080 \times 100$ = ~~800~~
Applying Dulong's formula
$= 8080$ kCal/kg

∵ H is not present, so, GCV = NCV = 8080 kCal/kg.

2Q. Calc. the amount of O_2 & air req. for complete combustion of $1 m^3$ of H_2.

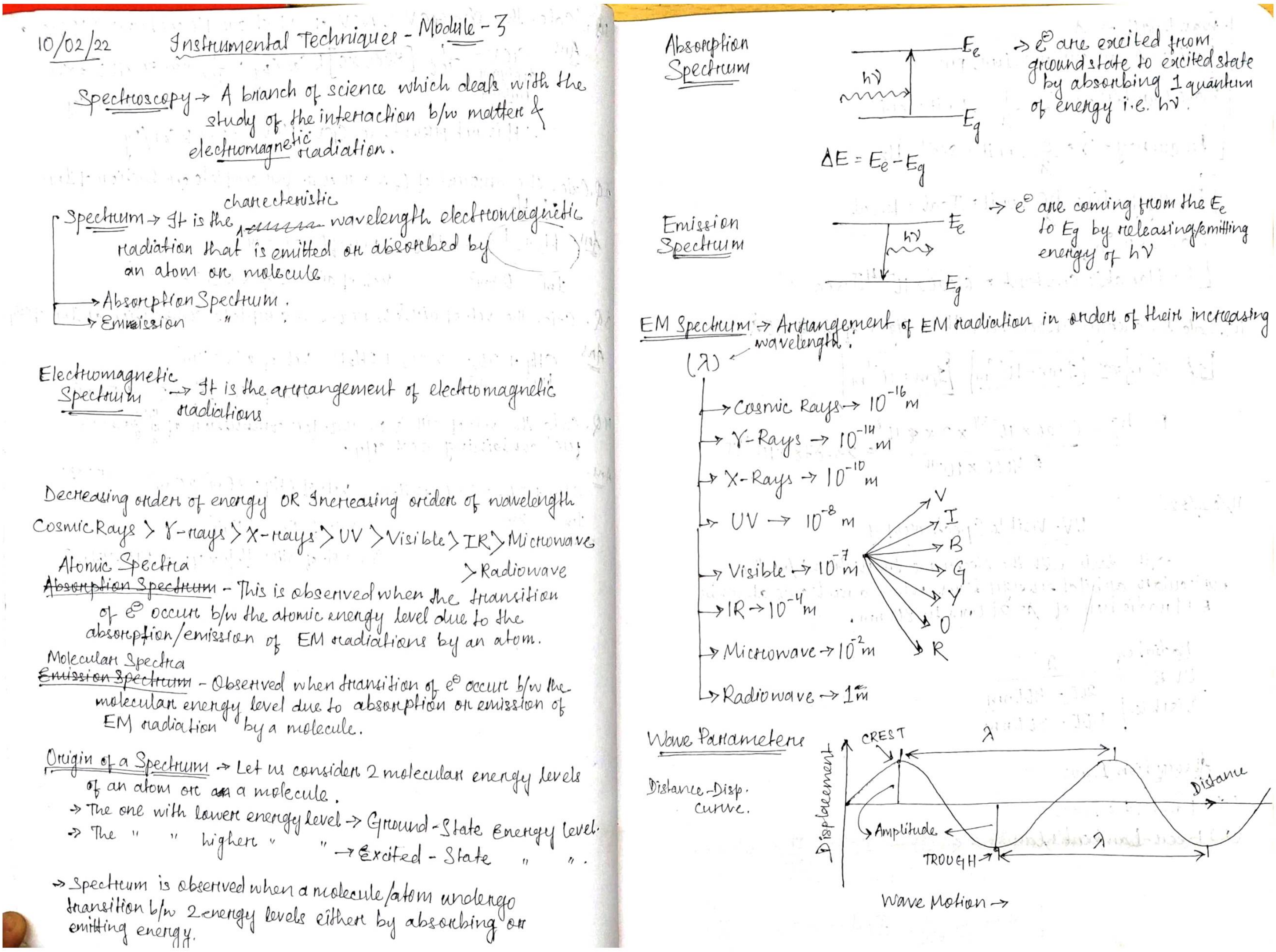
Ans. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ So vol. of $O_2 = 0.5 m^3$
$1 m^3$ $0.5 m^3$
Vol. of air $= \frac{100}{21} \times 0.5 = 2.38 m^3$

3Q. Calc. the vol. of air & O_2 req. for complete combustion of $1 m^3$ of CH_4

Ans. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ Vol. of $O_2 = 2 m^3$
$1 m^3$ $2 m^3$
Vol. of air $= \frac{100}{21} \times 2 = 9.52 m^3$

4Q. Calc. the vol. of air & O_2 req. for combustion of ~~a~~ $100 m^3$ gaseous fuel containing 20% CH_4.

Ans. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ Vol. of CH_4 = ~~20 m^3~~ $20 m^3$ $= 100 \times \frac{20}{100}$
$1 m^3$ $2 m^3$
$20 m^3$ $40 m^3$
So, vol. of $O_2 = 40 m^3$
So. vol. of air $= \frac{100}{21} \times 40 = 190.47 m^3$



10/02/22

Instrumental Techniques - Module - 3

Spectroscopy → A branch of science which deals with the study of the interaction b/w matter & electromagnetic radiation.

Spectrum → It is the characteristic ~~[illegible]~~ wavelength electromagnetic radiation that is emitted or absorbed by an atom or molecule

→ Absorption Spectrum.

→ Emission "

Electromagnetic Spectrum → It is the arrangement of electromagnetic radiations

Decreasing order of energy OR Increasing order of wavelength

Cosmic Rays > γ-rays > X-rays > UV > Visible > IR > Microwave > Radiowave

Atomic Spectra ~~Absorption Spectrum~~ - This is observed when the transition of $e^{\ominus}$ occur b/w the atomic energy level due to the absorption/emission of EM radiations by an atom.

Molecular Spectra ~~Emission Spectrum~~ - Observed when transition of $e^{\ominus}$ occur b/w the molecular energy level due to absorption or emission of EM radiation by a molecule.

Origin of a Spectrum → Let us consider 2 molecular energy levels of an atom or ~~an~~ a molecule.

→ The one with lower energy level → Ground-State Energy level.

→ The " " higher " " → Excited - State " ".

→ Spectrum is observed when a molecule/atom undergo transition b/w 2 energy levels either by absorbing or emitting energy.

Absorption Spectrum

E_e

$h\nu$

E_g

→ $e^{\ominus}$ are excited from ground state to excited state by absorbing 1 quantum of energy i.e. $h\nu$.

$$\Delta E = E_e - E_g$$

Emission Spectrum

E_e

$h\nu$

E_g

→ $e^{\ominus}$ are coming from the E_e to E_g by releasing/emitting energy of $h\nu$

EM Spectrum → Arrangement of EM radiation in order of their increasing wavelength.

(λ)

→ Cosmic Rays → 10^{-16} m

→ γ-Rays → 10^{-14} m

→ X-Rays → 10^{-10} m

→ UV → 10^{-8} m

→ Visible → 10^{-7} m → V, I, B, G, Y, O, R

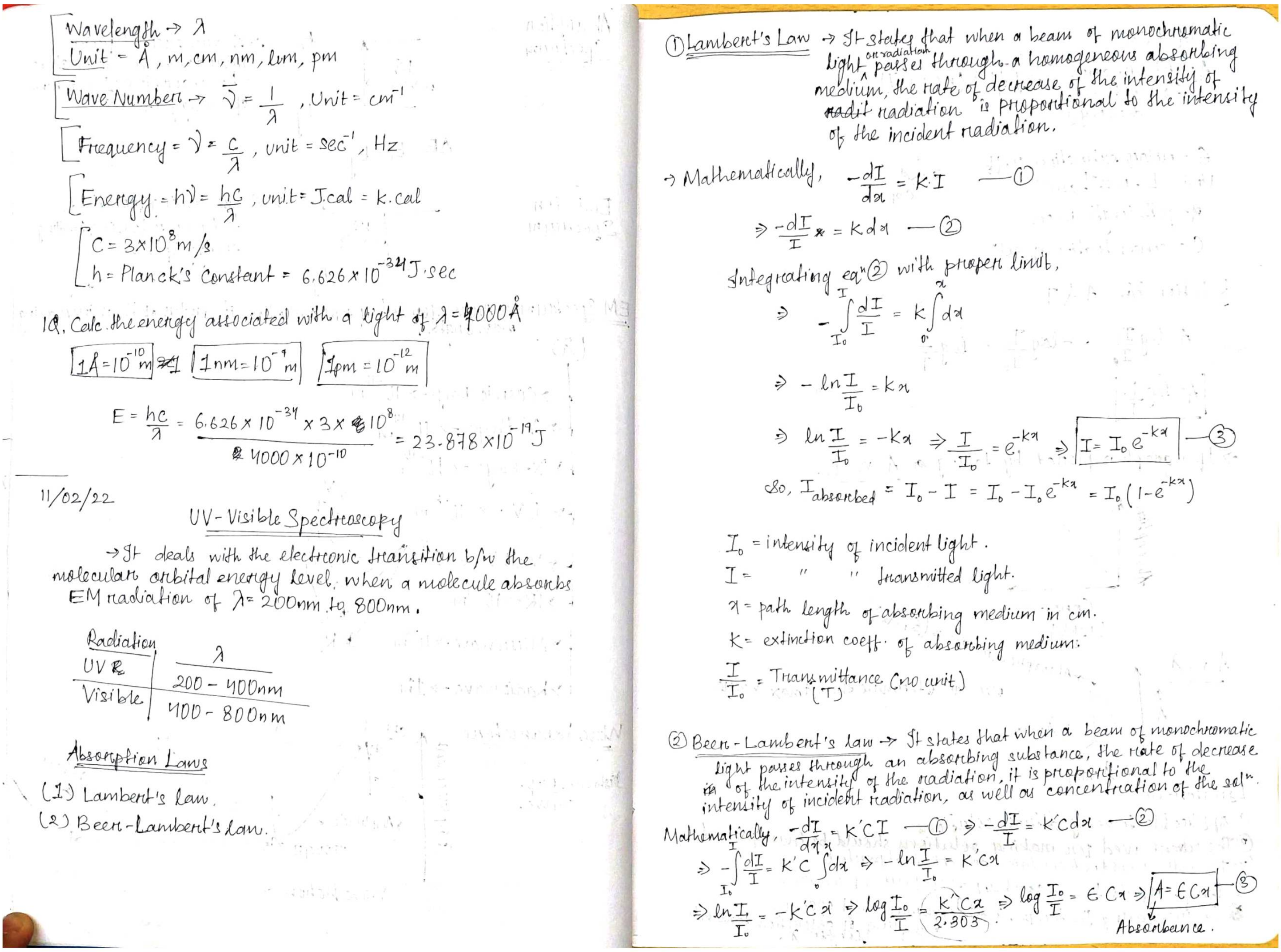
→ IR → 10^{-4} m

→ Microwave → 10^{-2} m

→ Radiowave → 1 m

Wave Parameters

Distance-Disp. curve.



Wavelength → λ
Unit = Å, m, cm, nm, μm, pm

Wave Number → $\bar{\nu} = \frac{1}{\lambda}$, Unit = cm^{-1}

Frequency = $\nu = \frac{c}{\lambda}$, unit = sec^{-1}, Hz

Energy = $h\nu = \frac{hc}{\lambda}$, unit = J.cal = k.cal

$C = 3 \times 10^8 m/s$
h = Planck's Constant = 6.626×10^{-34} J.sec

1Q. Calc the energy associated with a light of $\lambda = 4000$Å

$\boxed{1Å = 10^{-10} m}$ ~~≠1~~ $\boxed{1nm = 10^{-9} m}$ $\boxed{1pm = 10^{-12} m}$

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}} = 23.878 \times 10^{-19} J$$

11/02/22

UV-Visible Spectroscopy

→ It deals with the electronic transition b/w the molecular orbital energy level, when a molecule absorbs EM radiation of λ = 200nm to 800nm.

Radiation	λ
UV	200 - 400nm
Visible	400 - 800nm

Absorption Laws

(1) Lambert's law.
(2) Beer-Lambert's law.

① **Lambert's Law** → It states that when a beam of monochromatic light or radiation passes through a homogeneous absorbing medium, the rate of decrease of the intensity of ~~radit~~ radiation is proportional to the intensity of the incident radiation.

→ Mathematically, $-\frac{dI}{dx} = k \cdot I$ —①

$\Rightarrow \frac{-dI}{I} = k\,dx$ —②

Integrating eqn ② with proper limit,

$\Rightarrow -\int_{I_0}^{I} \frac{dI}{I} = k \int_{0}^{x} dx$

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

$\Rightarrow \ln \frac{I}{I_0} = -kx \Rightarrow \frac{I}{I_0} = e^{-kx} \Rightarrow \boxed{I = I_0 e^{-kx}}$ —③

So, $I_{absorbed} = I_0 - I = I_0 - I_0 e^{-kx} = I_0(1 - e^{-kx})$

I_0 = intensity of incident light.
I = " " transmitted light.
x = path length of absorbing medium in cm.
k = extinction coeff. of absorbing medium.
$\frac{I}{I_0}$ = Transmittance (T) (no unit)

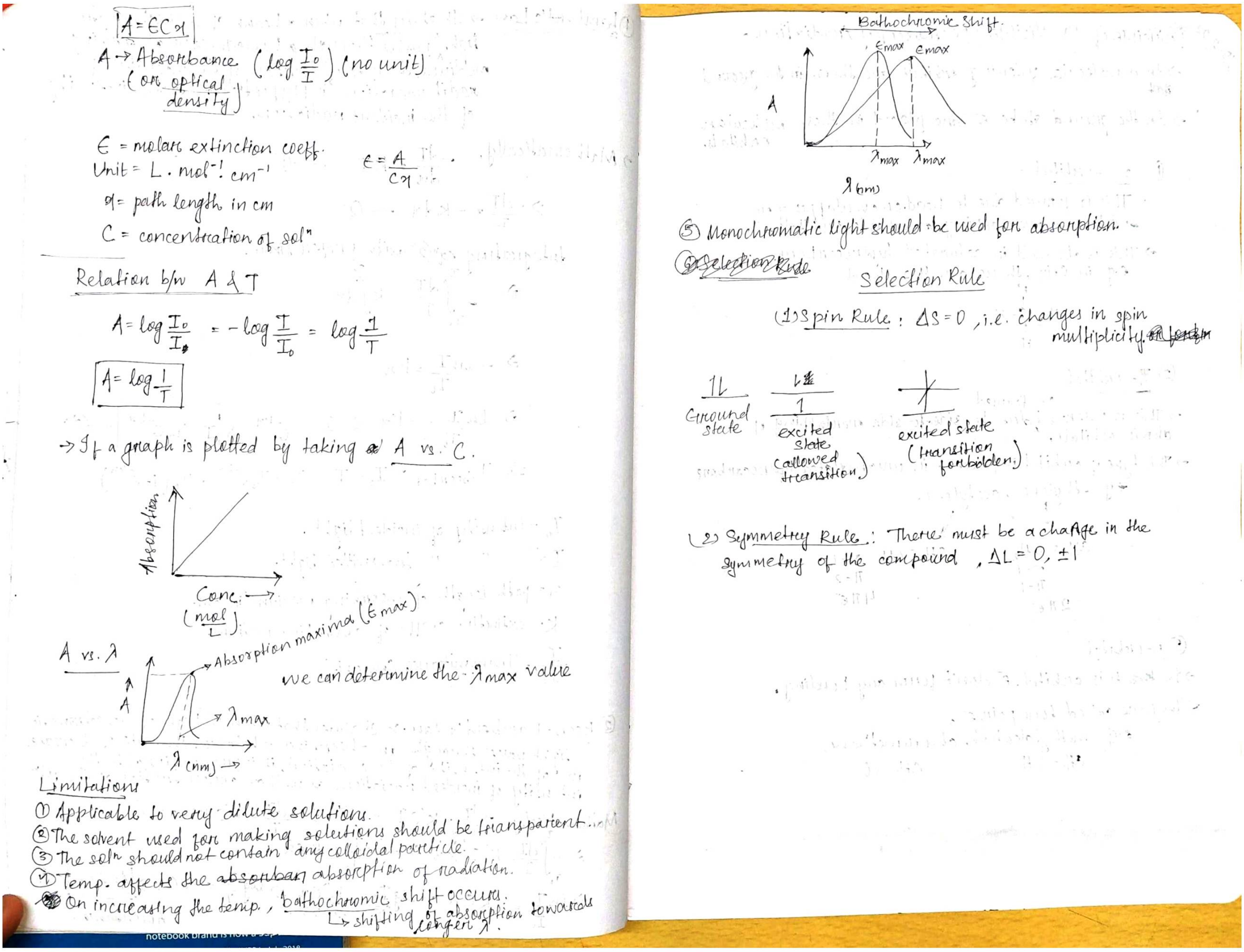
② **Beer-Lambert's law** → It states that when a beam of monochromatic light passes through an absorbing substance, the rate of decrease ~~in~~ of the intensity of the radiation, it is proportional to the intensity of incident radiation, as well as concentration of the soln.

Mathematically, $-\frac{dI}{dx} = k'CI$ —① $\Rightarrow -\frac{dI}{I} = k'C\,dx$ —②

$\Rightarrow -\int_{I_0}^{I} \frac{dI}{I} = k'C \int_{0}^{x} dx \Rightarrow -\ln \frac{I}{I_0} = k'Cx$

$\Rightarrow \ln \frac{I}{I_0} = -k'Cx \Rightarrow \log \frac{I_0}{I} = \frac{k'Cx}{2.303} \Rightarrow \log \frac{I_0}{I} = \epsilon Cx \Rightarrow \boxed{A = \epsilon Cx}$ —③

Absorbance.



$\boxed{A = \epsilon C x}$

A → Absorbance $\left(\log \frac{I_0}{I}\right)$ (no unit)
(or optical density)

ϵ = molar extinction coeff.
Unit = L . mol⁻¹. cm⁻¹
x = path length in cm
C = concentration of solⁿ

$\epsilon = \frac{A}{Cx}$

Relation b/w A & T

$A = \log \frac{I_0}{I} = -\log \frac{I}{I_0} = \log \frac{1}{T}$

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

→ If a graph is plotted by taking ~~a~~ A vs. C.

Absorption
Conc. →
(mol/L)

A vs. λ

→ Absorption maxima (ε max)
A
→ λmax
λ (nm) →

we can determine the λmax value

Limitations
① Applicable to very dilute solutions.
② The solvent used for making solutions should be transparent.
③ The solⁿ should not contain any colloidal particle.
④ Temp. affects the ~~absorban~~ absorption of radiation.
On increasing the temp., bathochromic shift occurs.
↳ shifting of absorption towards longer λ.

Bathochromic Shift
εmax εmax
A
λmax λmax
λ (nm)

⑤ Monochromatic light should be used for absorption.
~~6) Selection Rule~~

Selection Rule

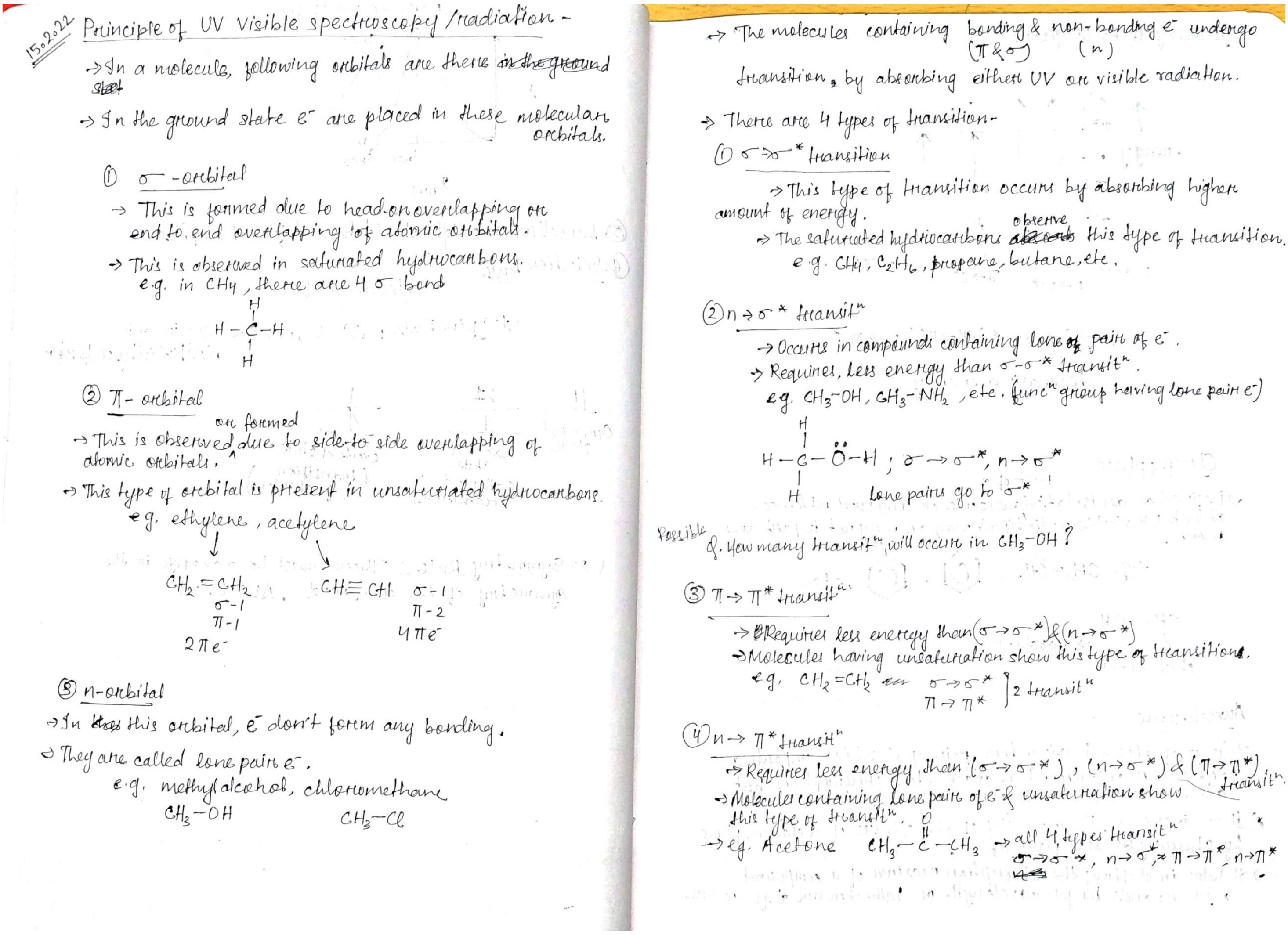
(1) Spin Rule : ΔS = 0 , i.e. changes in spin multiplicity. ~~or [illegible]~~

↑↓
Ground state

↓
↑
excited state (allowed transition)

excited state (transition forbidden)

(2) Symmetry Rule : There must be a change in the symmetry of the compound , ΔL = 0, ±1



15.2.22

Principle of UV Visible spectroscopy / radiation -

→ In a molecule, following orbitals are there ~~in the ground state~~

→ In the ground state e^- are placed in these molecular orbitals.

① σ - orbital

→ This is formed due to head-on overlapping or end to end overlapping of atomic orbitals.

→ This is observed in saturated hydrocarbons.
e.g. in CH_4, there are 4 σ bond

$$\begin{array}{ccc} & H & \\ & | & \\ H - & C & - H \\ & | & \\ & H & \end{array}$$

② π - orbital

→ This is observed or formed due to side-to side overlapping of atomic orbitals.

→ This type of orbital is present in unsaturated hydrocarbons.
e.g. ethylene, acetylene

$CH_2 = CH_2$
σ - 1
π - 1
$2\pi e^-$

$CH \equiv CH$
σ - 1
π - 2
$4\pi e^-$

③ n-orbital

→ In ~~thes~~ this orbital, e^- don't form any bonding.

→ They are called lone pair e^-.
e.g. methyl alcohol, chloromethane
CH_3-OH CH_3-Cl

→ The molecules containing bonding (π & σ) & non-bonding e^- (n) undergo transition, by absorbing either UV or visible radiation.

→ There are 4 types of transition -

① $\sigma \rightarrow \sigma^*$ transition

→ This type of transition occurs by absorbing higher amount of energy.

→ The saturated hydrocarbons ~~absorb~~ observe this type of transition.
e.g. CH_4, C_2H_6, propane, butane, etc.

② $n \rightarrow \sigma^*$ transit^n

→ Occurs in compounds containing lone ~~of~~ pair of e^-.

→ Requires, less energy than $\sigma - \sigma^*$ transit^n.
e.g. CH_3-OH, CH_3-NH_2, etc. (func^n group having lone pair e^-)

$$\begin{array}{ccccc} & H & & & \\ & | & & & \\ H - & C & - \ddot{O} & - H & ;\ \sigma \rightarrow \sigma^*,\ n \rightarrow \sigma^* \\ & | & & & \\ & H & & & \end{array}$$

lone pairs go to σ^*

Possible Q. How many transit^n will occur in CH_3-OH?

③ $\pi \rightarrow \pi^*$ transit^n

→ Requires less energy than ($\sigma \rightarrow \sigma^*$) & ($n \rightarrow \sigma^*$)

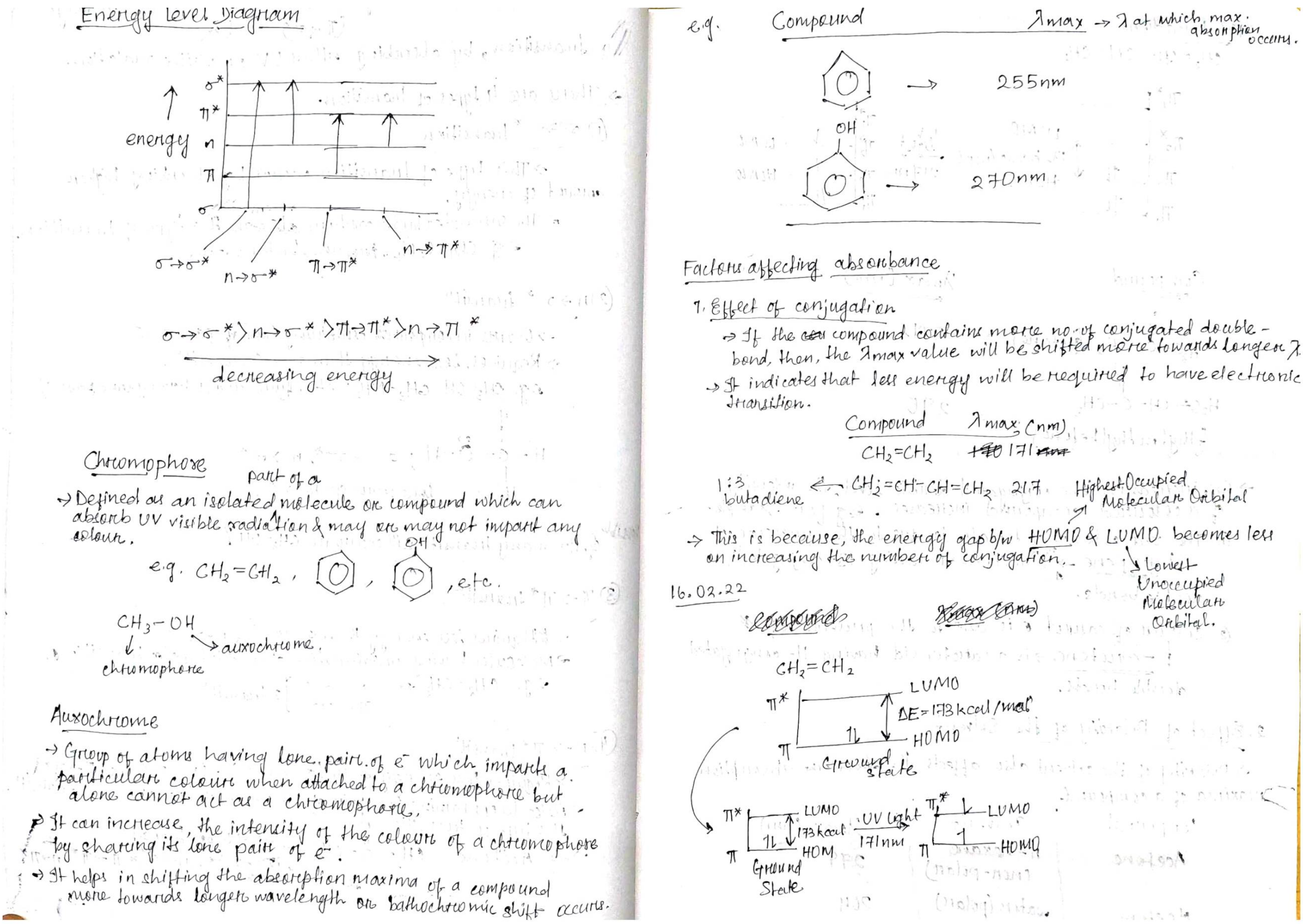
→ Molecules having unsaturation show this type of transitions.
e.g. $CH_2 = CH_2$ $\left.\begin{array}{c} \sigma \rightarrow \sigma^* \\ \pi \rightarrow \pi^* \end{array}\right]$ 2 transit^n

④ $n \rightarrow \pi^*$ transit^n

→ Requires less energy than ($\sigma \rightarrow \sigma^*$), ($n \rightarrow \sigma^*$) & ($\pi \rightarrow \pi^*$) transit^n.

→ Molecules containing lone pair of e^- & unsaturation show this type of transit^n.

→ e.g. Acetone $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$ → all 4 types transit^n
$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$



Energy Level Diagram

$$\sigma\to\sigma^* > n\to\sigma^* > \pi\to\pi^* > n\to\pi^*$$

decreasing energy

Chromophore

→ Defined as an isolated part of a molecule or compound which can absorb UV visible radiation & may or may not impart any colour.

e.g. $CH_2=CH_2$, , , etc.

CH_3-OH

CH_3 ↓ chromophore

OH → auxochrome.

Auxochrome

→ Group of atoms having lone pair of e^- which imparts a particular colour when attached to a chromophore but alone cannot act as a chromophore.

→ It can increase the intensity of the colours of a chromophore by sharing its lone pair of e^-.

→ It helps in shifting the absorption maxima of a compound more towards longer wavelength or bathochromic shift occurs.

e.g. Compound — λmax → λ at which max. absorption occurs.

→ 255nm

→ 270nm

Factors affecting absorbance

1. Effect of conjugation

→ If the ~~cou~~ compound contains more no. of conjugated double-bond, then, the λmax value will be shifted more towards longer λ.

→ It indicates that less energy will be required to have electronic transition.

Compound	λmax (nm)
$CH_2=CH_2$	~~170~~ 171 ~~nm~~
1:3 butadiene ← $CH_2=CH-CH=CH_2$	217

→ This is because, the energy gap b/w HOMO & LUMO becomes less on increasing the number of conjugation.

HOMO → Highest Occupied Molecular Orbital

LUMO → Lowest Unoccupied Molecular Orbital.

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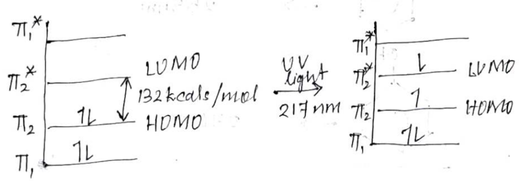
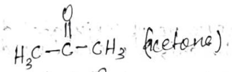
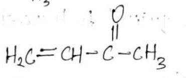
~~Compound~~ ~~λmax (nm)~~

$CH_2=CH_2$

1:3 butadiene

$CH_2=CH-CH=CH_2$



Compound	λmax (nm)
 $H_3C-\overset{\overset{O}{\parallel}}{C}-CH_3$ (acetone) →	279
 $H_2C=CH-\overset{\overset{O}{\parallel}}{C}-CH_3$ (ethyl methyl ketone) →	290

→ On increasing the conjugated double bond, the intensity of a coloured compound increases. ~~e.g~~ for example-

① The red colour of tomato is due to the presence of Lycopene → is a carotenoid having 13-conjugated double bonds.

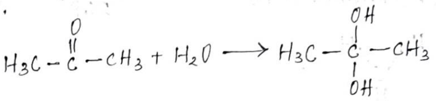
② colour of carrot ~~e~~ is due to the presence of ~~β~~ β-carotene → is a carotenoid having 11-conjugated double bonds.

2. Effect of Polarity of the Solvent.

→ Polarity of the solvent also affects the ~~absorbtin~~ absorption maxima of a compound.

Compound	Solvent	λmax (nm)
Acetone	n-hexane (non-polar)	279
Acetone	water (polar)	264

→ Due to the hydrolysis of acetone, the no. of conjugations are removed.



$$H_3C-\overset{\overset{O}{\parallel}}{C}-CH_3+H_2O\longrightarrow H_3C-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

3. Effect of auxochrome

→ Due to the presence of the auxochrome, the λmax value of a compound shift more towards longer wavelength.

e.g.

Compound	λmax (nm)
	255
	270

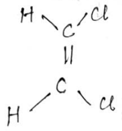
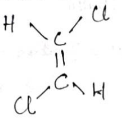
4. Steric Effect

→ Steric effect of a compound changes the geometry of a compound. This affects the position of conjugation. So, the λmax value shifts more towards shorter wavelength.

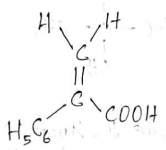
e.g. The λmax value for a ~~cis~~ cis-compound shifts more towards shorter wavelength. ~~λmax (nm)~~

~~e.g. cis 1-2 dichloroethane →~~

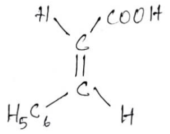
~~H~~

	λmax (nm)
cis 1-2 dichloroethylene 	261
trans 1-2 dichloroethylene 	274

cis - cinnamic acid 268



trans- cinnamic acid



~~271~~ 272.

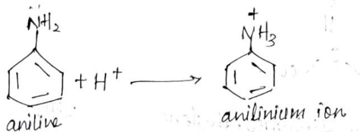
5. Absorption and Intensity Shift

1. Hypsochromic Shift (blue shift) -

→ This type of shifting occurs when the λ_{max} value is shifting more towards shorter wavelength.

→ This is due to the removal of conjugation or changes in polarity of the solvent.

→ λ_{max} value occurs at 280nm in aniline due to the presence of lone pair of e^- in conjugation with π bond system. of the benzene. But in acidic solution, λ_{max} value occurs at 265nm due to the formation of anilinium ion. & removal of conjugation.



aniline $\lambda_{max} = 280nm$

anilinium ion $\lambda_{max} = 265 nm$

2. Bathochromic Shift (Red Shift) -

→ It is an effect due to which, the absorption maxima is shifted more towards longer wavelength, due to presence of auxochrome or change in polarity of the solvent.

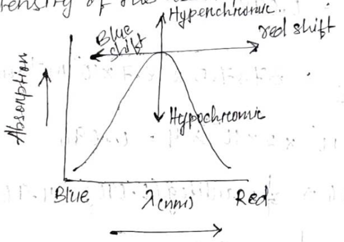
e.g. Acetone in n-hexane and water.
Benzene & phenol.

3. Hyperchromic Shift -

→ In this case, intensity of the absorption increases.

4. Hypochromic Shift -

→ Intensity of the absorption decreases.



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Applications of UV Visible spectroscopy

main 5 points.

→ It is useful to determine the kinetics of a chemical reaction.

→ Impurities can be easily detected.

→ Functional group of a compound can be identified.

→ Molecular weight of compound can be determined by using Beer - Lambert's law.

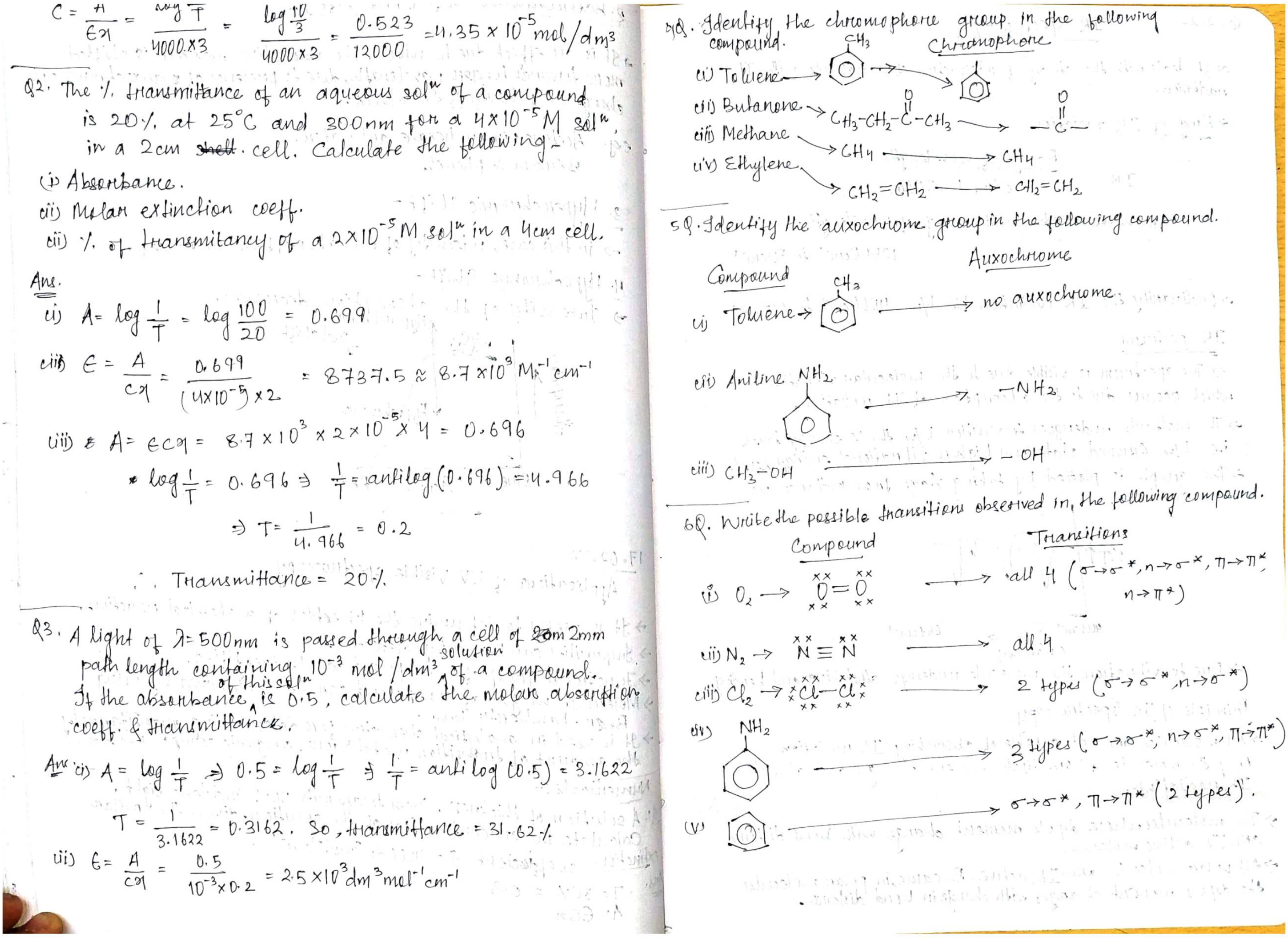
→ It is used in analytical chemistry for determining quantitatively the amount of transition metal ions, organic compounds, etc.

Numericals :-

Q1. A solution of thickness, 3cm transmits 30% incident light. Calculate the concentration of the solution. given the molar extinction coefficient $\epsilon = 4000 dm^3 mol^{-1} cm^{-1}$.

Ans. $T = 30\% = 0.3$

$A = \epsilon C x$



$C = \frac{A}{\varepsilon x} = \frac{\log \frac{1}{T}}{4000 \times 3} = \frac{\log \frac{10}{3}}{4000 \times 3} = \frac{0.523}{12000} = 4.35 \times 10^{-5}$ mol/dm^3

Q2. The % transmittance of an aqueous solⁿ of a compound is 20% at 25°C and 300nm for a 4×10^{-5} M solⁿ, in a 2cm ~~shell~~. cell. Calculate the following-

(i) Absorbance.

(ii) Molar extinction coeff.

(iii) % of transmitancy of a 2×10^{-5} M solⁿ in a 4cm cell.

Ans.

(i) $A = \log \frac{1}{T} = \log \frac{100}{20} = 0.699$

(ii) $\varepsilon = \frac{A}{cx} = \frac{0.699}{(4 \times 10^{-5}) \times 2} = 8737.5 \approx 8.7 \times 10^{3}\ M^{-1} cm^{-1}$

(iii) $A = \varepsilon c x = 8.7 \times 10^{3} \times 2 \times 10^{-5} \times 4 = 0.696$

$\log \frac{1}{T} = 0.696 \Rightarrow \frac{1}{T} = \text{antilog}(0.696) = 4.966$

$\Rightarrow T = \frac{1}{4.966} = 0.2$

∴ Transmittance = 20%.

Q3. A light of $\lambda = 500$nm is passed through a cell of ~~2cm~~ 2mm path length containing 10^{-3} mol/dm^3 solution of a compound. If the absorbance of this solⁿ is 0.5, calculate the molar absorption coeff. & transmittance.

Ans (i) $A = \log \frac{1}{T} \Rightarrow 0.5 = \log \frac{1}{T} \Rightarrow \frac{1}{T} = \text{anti}\log(0.5) = 3.1622$

$T = \frac{1}{3.1622} = 0.3162$. So, transmittance = 31.62%

(ii) $\varepsilon = \frac{A}{cx} = \frac{0.5}{10^{-3} \times 0.2} = 2.5 \times 10^{3}\ dm^{3} mol^{-1} cm^{-1}$

4Q. Identify the chromophore group in the following compound.

Chromophore

(i) Toluene →

(ii) Butanone → $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ → $-\overset{O}{\overset{\|}{C}}-$

(iii) Methane → CH_4 → CH_4

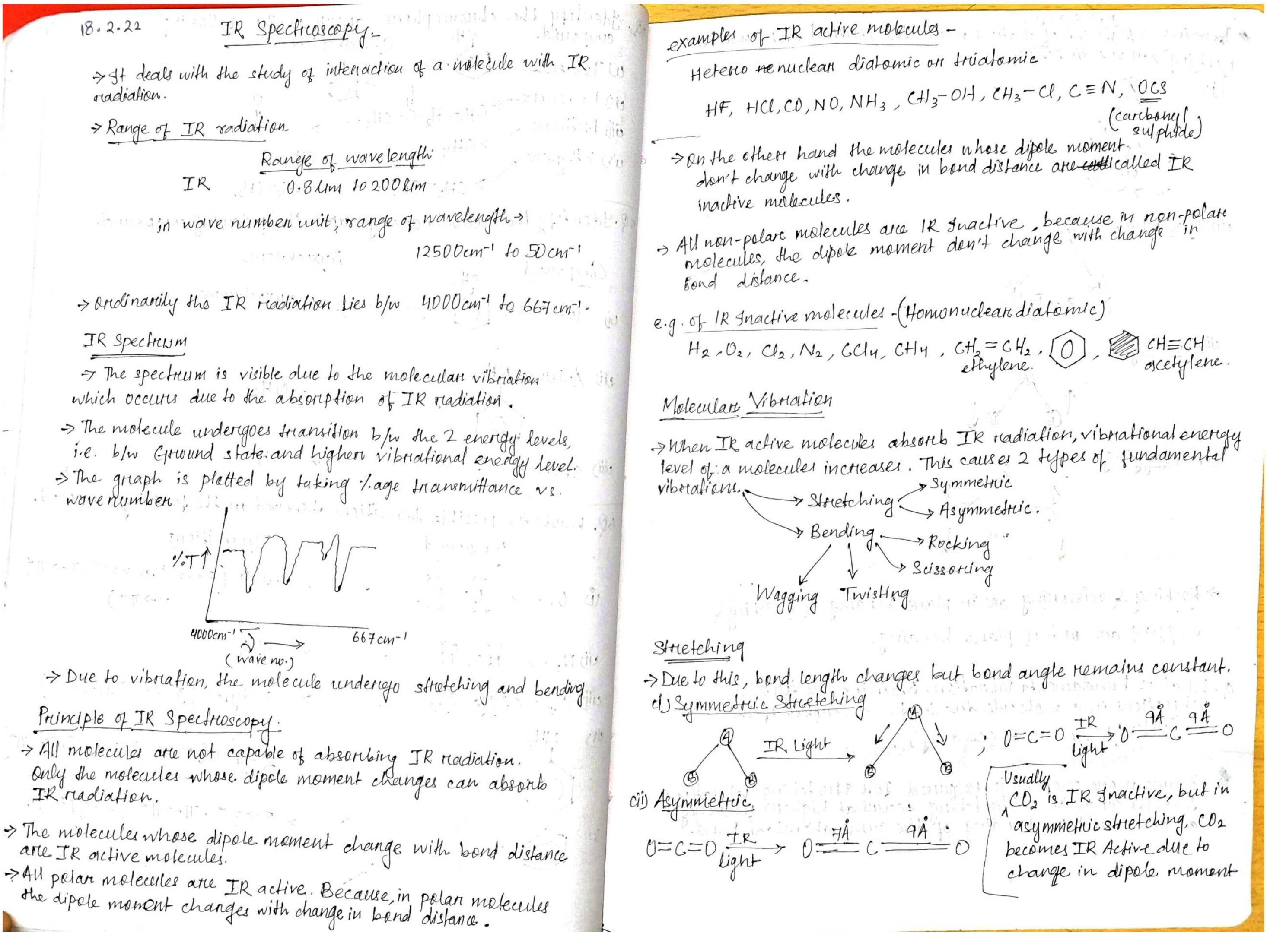
(iv) Ethylene → $CH_2=CH_2$ → $CH_2=CH_2$

5Q. Identify the auxochrome group in the following compound.

Compound	Auxochrome
(i) Toluene →	no auxochrome.
(ii) Aniline	$-NH_2$
(iii) CH_3-OH	$-OH$

6Q. Write the possible transitions observed in the following compound.

Compound	Transitions
(i) $O_2 \rightarrow \ddot{\underset{\times\times}{O}}=\ddot{\underset{\times\times}{O}}$	all 4 ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$)
(ii) $N_2 \rightarrow \ddot{N} \equiv \ddot{N}$	all 4
(iii) $Cl_2 \rightarrow :\ddot{\underset{\times\times}{Cl}}-\ddot{\underset{\times\times}{Cl}}:$	2 types ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$)
(iv) NH_2	3 types ($\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$)
(v)	$\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ (2 types).



18.2.22

IR Spectroscopy.

→ It deals with the study of interaction of a molecule with IR radiation.

→ Range of IR radiation

	Range of wavelength
IR	0.8 μm to 200 μm

in wave number unit, range of wavelength →
$12500\ cm^{-1}$ to $50\ cm^{-1}$

→ Ordinarily the IR radiation lies b/w $4000\ cm^{-1}$ to $667\ cm^{-1}$.

IR Spectrum

→ The spectrum is visible due to the molecular vibration which occurs due to the absorption of IR radiation.

→ The molecule undergoes transition b/w the 2 energy levels, i.e. b/w Ground state and higher vibrational energy level.

→ The graph is plotted by taking %age transmittance vs. wave number.

→ Due to vibration, the molecule undergo stretching and bending.

Principle of IR Spectroscopy.

→ All molecules are not capable of absorbing IR radiation. Only the molecules whose dipole moment changes can absorb IR radiation.

→ The molecules whose dipole moment change with bond distance are IR active molecules.

→ All polar molecules are IR active. Because, in polar molecules the dipole moment changes with change in bond distance.

examples of IR active molecules –

Hetero ~~ne~~ nuclear diatomic or triatomic

HF, HCl, CO, NO, NH_3, CH_3-OH, CH_3-Cl, $C\equiv N$, OCS (carbonyl sulphide)

→ On the other hand the molecules whose dipole moment don't change with change in bond distance are ~~call~~ called IR inactive molecules.

→ All non-polar molecules are IR inactive, because in non-polar molecules, the dipole moment don't change with change in bond distance.

e.g. of IR inactive molecules – (Homonuclear diatomic)

H_2, O_2, Cl_2, N_2, CCl_4, CH_4, $CH_2=CH_2$ ethylene, , , $CH\equiv CH$ acetylene.

Molecular Vibration

→ When IR active molecules absorb IR radiation, vibrational energy level of a molecules increases. This causes 2 types of fundamental vibrations.

- Stretching
  - Symmetric
  - Asymmetric.
- Bending
  - Rocking
  - Scissoring
  - Wagging
  - Twisting

Stretching

→ Due to this, bond length changes but bond angle remains constant.

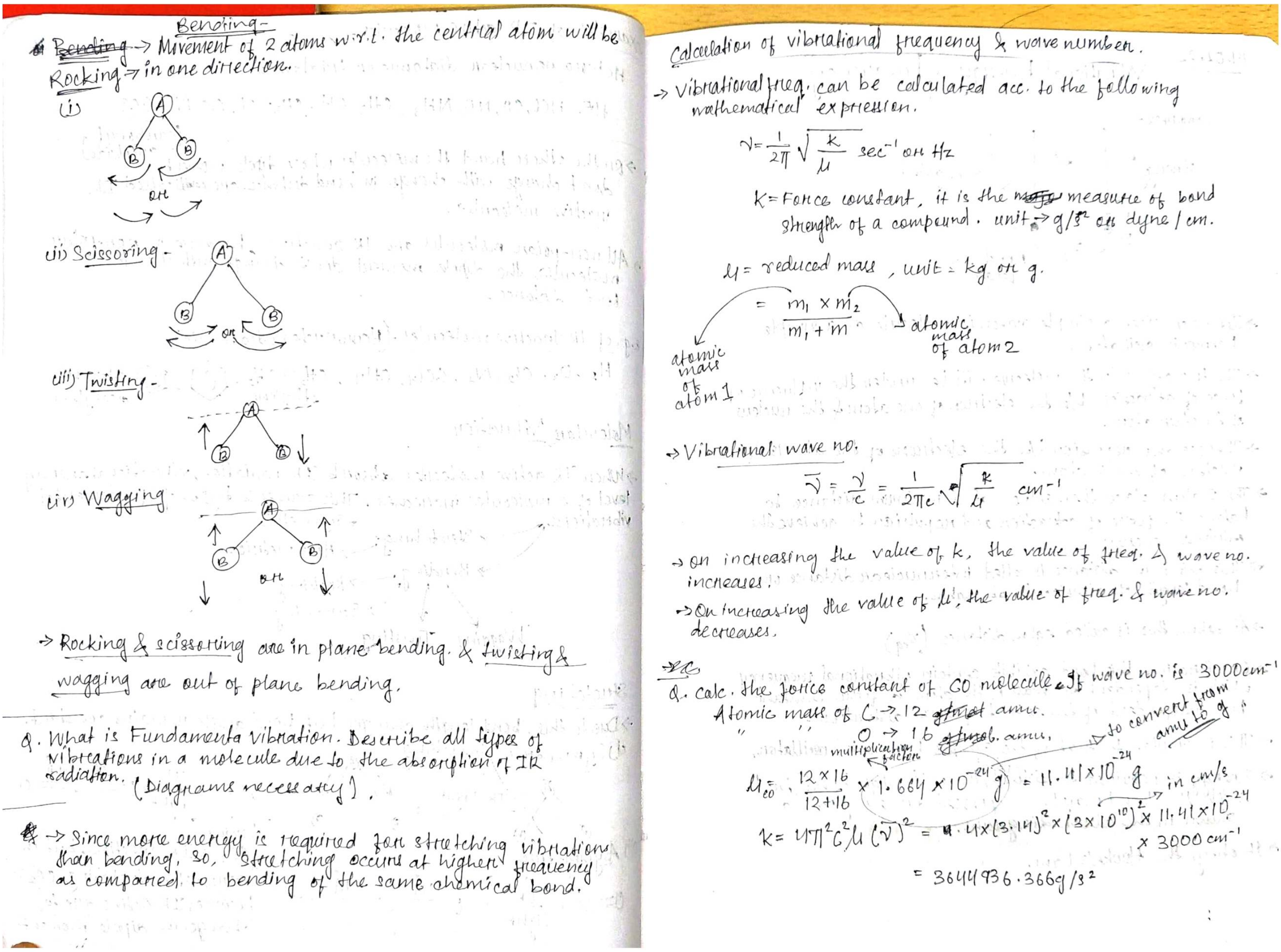
(i) Symmetric Stretching

; $O=C=O \xrightarrow[\text{light}]{IR} O \overset{9Å}{=\!=} C \overset{9Å}{=\!=} O$

(ii) Asymmetric.

$O=C=O \xrightarrow[\text{light}]{IR} O \overset{7Å}{=\!=} C \overset{9Å}{=\!=} O$

Usually CO_2 is IR inactive, but in asymmetric stretching, CO_2 becomes IR Active due to change in dipole moment



Bending-

~~Bending~~ → Movement of 2 atoms w.r.t. the central atom will be

Rocking → in one direction.

(i)

(ii) Scissoring -

(iii) Twisting -

(iv) Wagging

→ Rocking & scissoring are in plane bending. & twisting & wagging are out of plane bending.

Q. What is Fundamenta vibration. Describe all types of vibrations in a molecule due to the absorption of IR radiation. (Diagrams necessary).

→ Since more energy is required for stretching vibrations than bending, so, stretching occurs at higher frequency as compared to bending of the same chemical bond.

Calculation of vibrational frequency & wave number.

→ Vibrational freq. can be calculated acc. to the following mathematical expression.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ sec}^{-1} \text{ or Hz}$$

K = Force constant, it is the ~~mass~~ measure of bond strength of a compound. unit → g/s^2 or dyne / cm.

μ = reduced mass, unit = kg or g.

$$= \frac{m_1 \times m_2}{m_1 + m}$$

atomic mass of atom 1

atomic mass of atom 2

→ Vibrational wave no.

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

→ On increasing the value of k, the value of freq. & wave no. increases.

→ On increasing the value of μ, the value of freq. & wave no. decreases.

Q. Calc. the force constant of CO molecule. If wave no. is $3000 cm^{-1}$

Atomic mass of C → 12 ~~g/mol~~ amu.

" " O → 16 ~~g/mol~~ amu.

multiplication factor

to convert from amu to g

$$\mu_{co} = \frac{12 \times 16}{12 + 16} \times 1.664 \times 10^{-24} g = 11.41 \times 10^{-24} g$$

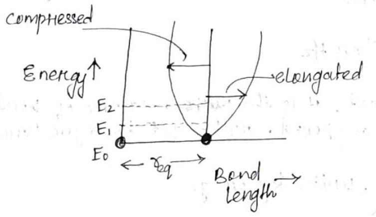
in cm/s

$$k = 4\pi^2 c^2 \mu (\bar{\nu})^2 = 4 \times (3.14)^2 \times (3 \times 10^{10})^2 \times 11.41 \times 10^{-24} \times 3000 \text{ cm}^{-1}$$

$$= 3644936.366 g/s^2$$

19.02.22

Vibrational Energy & Frequency



- → Let us consider a simple diatomic molecule as a simple harmonic oscillator.
- → The two atoms in the molecule will be under the influence of force of attraction b/w the electron of one atom & the nucleus of the other atom.
- → There's also repulsion b/w the electrons of the atoms & nucleus of the 2 atom.
- → The 2 atoms place themselves at a minimum distance to balance the force of attraction and repulsion to achieve the minimum energy
- → This minimum distance is called internuclear distance or bond length of a molecule ~~at eqbm~~.
- → At eqbm, this is called eqbm distance (r_{eq}).
- → On vibration, this bond exhibits certain vibrational frequency which is dependent on mass of the atom & force constant but independent of the extent of small distortion.
- → This is similar to that of the simple harmonic oscillator,
- → Energy is required to ~~disturb~~ distort the molecular bond due to which the bond may be compressed or elongated as shown in the above diagram.
- → It obeys the Hooke's Law.

Vibrational Energy

→ It can be calculated by using the equation :

$$\text{Vibrational energy} \rightarrow E_{vib} = \left(v + \frac{1}{2}\right) h\nu \ \mathrm{J}$$

ν → Frequency of vibration (Hz or sec^{-1})

v → vibrational quantum no. $= 0, 1, 2, 3, \ldots$

h → Planck's Constant $= 6.626 \times 10^{-34}$ J sec

Energy difference b/w the 2 successive vibrational energy level

→ The 'v' varies from $0 \rightarrow 1$; In ground state → 0
; In next higher level → 1
⋮
2

$$\Delta E_{vib} = E_1 - E_0 = \left(1+\frac{1}{2}\right)h\nu - \left(0+\frac{1}{2}\right)h\nu$$

~~$= \left(1+\frac{1}{2}\right) - \left(0+\frac{1}{2}\right)$~~ $= \underline{h\nu}$ J

~~Energy diffⁿ b/w the~~

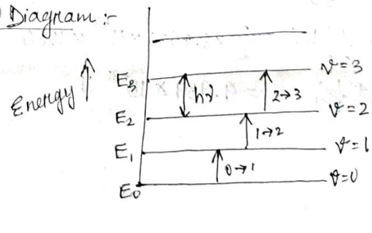
When 'v' varies from $1 \rightarrow 2$

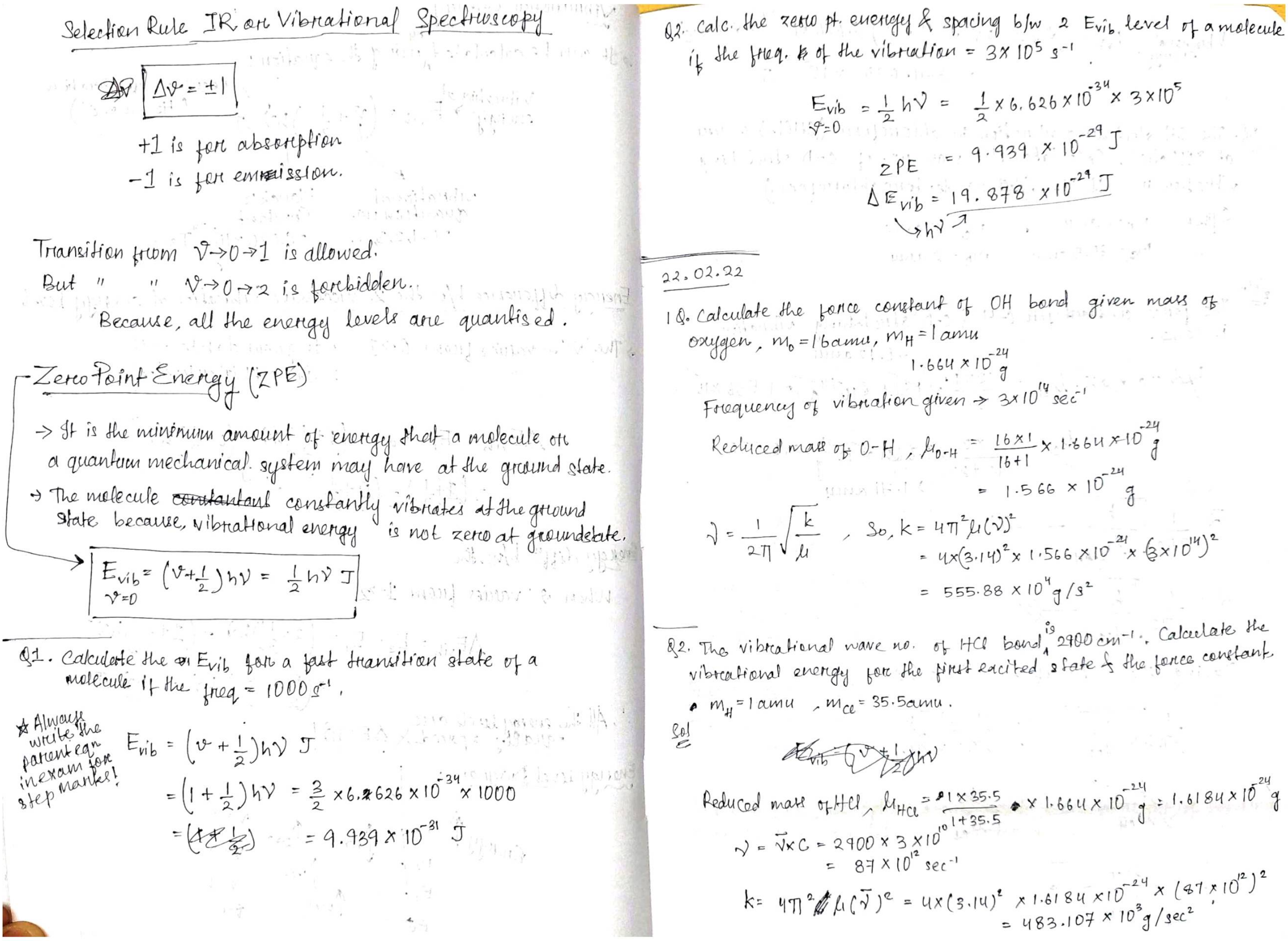
$$\Delta E_{vib} = E_2 - E_1 = \left(2+\frac{1}{2}\right)h\nu - \left(1+\frac{1}{2}\right)h\nu$$

$$= \left(\frac{5}{2} - \frac{3}{2}\right)h\nu = \underline{h\nu} \ \mathrm{J}.$$

∴ All the energy levels are equally spaced. & $\boxed{\Delta E = h\nu}$

Energy level Diagram :-





Selection Rule IR or Vibrational Spectroscopy

~~Δv~~ $\boxed{\Delta v = \pm 1}$

+1 is for absorption

−1 is for emission.

Transition from $v \to 0 \to 1$ is allowed.

But " " $v \to 0 \to 2$ is forbidden.

Because, all the energy levels are quantised.

Zero Point Energy (ZPE)

→ It is the minimum amount of energy that a molecule or a quantum mechanical system may have at the ground state.

→ The molecule ~~contantant~~ constantly vibrates at the ground state because, vibrational energy is not zero at groundstate.

$$\boxed{\underset{v=0}{E_{vib}} = (v+\tfrac{1}{2})h\nu = \tfrac{1}{2}h\nu \text{ J}}$$

Q1. Calculate the ~~or~~ E_{vib} for a fast transition state of a molecule if the freq = 1000 s^{-1}.

★ Always write the parent eqn in exam for step marks!

$$E_{vib} = (v + \tfrac{1}{2})h\nu \text{ J}$$

$$= (1 + \tfrac{1}{2})h\nu = \tfrac{3}{2} \times 6.626 \times 10^{-34} \times 1000$$

$$= \cancel{(1+\tfrac{1}{2})} = 9.939 \times 10^{-31} \text{ J}$$

Q2. Calc. the zero pt. energy & spacing b/w 2 E_{vib} level of a molecule if the freq. ~~k~~ of the vibration = $3 \times 10^5\ s^{-1}$.

$$\underset{v=0}{E_{vib}} = \tfrac{1}{2}h\nu = \tfrac{1}{2} \times 6.626 \times 10^{-34} \times 3 \times 10^{5}$$

$$ZPE = 9.939 \times 10^{-29} \text{ J}$$

$$\underset{\hookrightarrow h\nu}{\Delta E_{vib}} = 19.878 \times 10^{-29} \text{ J}$$

22.02.22

1Q. Calculate the force constant of OH bond given mass of oxygen, $m_o = 16$ amu, $m_H = 1$ amu
1.664×10^{-24} g

Frequency of vibration given → $3 \times 10^{14}\ sec^{-1}$

Reduced mass of O−H, $\mu_{O-H} = \frac{16 \times 1}{16+1} \times 1.664 \times 10^{-24}$ g

$$= 1.566 \times 10^{-24} \text{ g}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}, \quad \text{So, } k = 4\pi^2 \mu (\nu)^2$$

$$= 4 \times (3.14)^2 \times 1.566 \times 10^{-24} \times (3 \times 10^{14})^2$$

$$= 555.88 \times 10^{4} \text{ g/s}^2$$

Q2. The vibrational wave no. of HCl bond is 2900 cm^{-1}. Calculate the vibrational energy for the first excited state & the force constant.

- $m_H = 1$ amu, $m_{Cl} = 35.5$ amu.

Sol

$\cancel{E_{vib} = (v + \tfrac{1}{2})h\nu}$

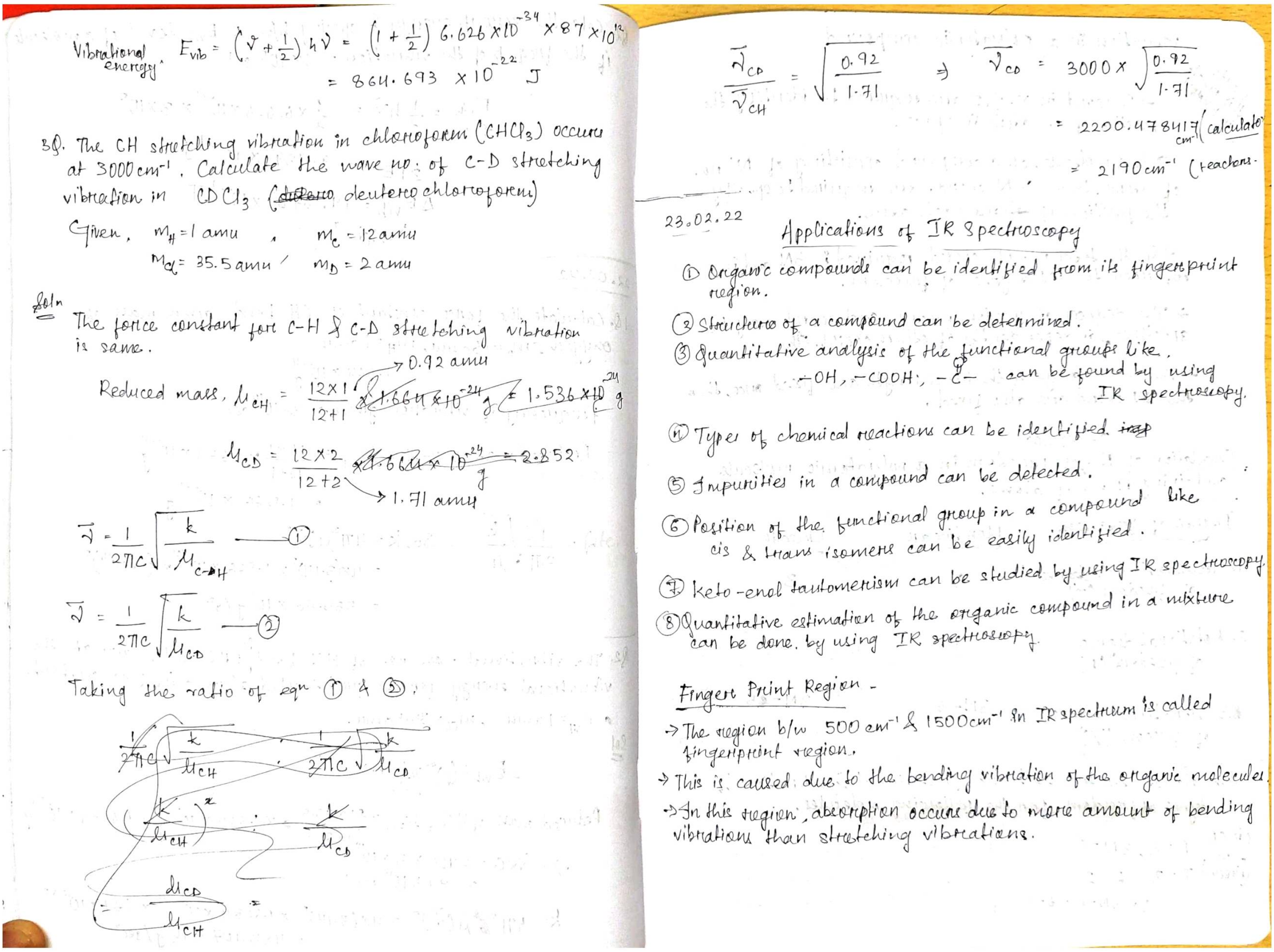
Reduced mass of HCl, $\mu_{HCl} = \frac{1 \times 35.5}{1+35.5} \times 1.664 \times 10^{-24}$ g $= 1.6184 \times 10^{-24}$ g

$$\nu = \bar{\nu} \times C = 2900 \times 3 \times 10^{10}$$

$$= 87 \times 10^{12}\ sec^{-1}$$

$$k = 4\pi^2 \mu (\bar{\nu})^2 = 4 \times (3.14)^2 \times 1.6184 \times 10^{-24} \times (87 \times 10^{12})^2$$

$$= 483.107 \times 10^{3} \text{ g/sec}^2$$



Vibrational energy, $E_{vib} = (\bar{\nu} + \frac{1}{2}) h\nu = (1 + \frac{1}{2}) 6.626 \times 10^{-34} \times 87 \times 10^{12}$

$= 864.693 \times 10^{-22}$ J

3Q. The CH stretching vibration in chloroform ($CHCl_3$) occurs at 3000 cm⁻¹. Calculate the wave no: of C-D stretching vibration in $CDCl_3$ (~~deutero~~ deutero chloroform)

Given, $m_H = 1$ amu , $m_C = 12$ amu

$m_{Cl} = 35.5$ amu , $m_D = 2$ amu

Soln

The force constant for C-H & C-D stretching vibration is same.

$$\text{Reduced mass, } \mu_{CH} = \frac{12 \times 1}{12+1} \cancel{\times 1.664 \times 10^{-24} g = 1.536 \times 10^{-24} g} \rightarrow 0.92 \text{ amu}$$

$$\mu_{CD} = \frac{12 \times 2}{12+2} \cancel{\times 1.664 \times 10^{-24} g = 2.852} \rightarrow 1.71 \text{ amu}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{C-H}}} \text{ --- ①}$$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{CD}}} \text{ --- ②}$$

Taking the ratio of eqⁿ ① & ②,

$$\frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{CH}}} : \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{CD}}}$$

$$\left(\frac{k}{\mu_{CH}}\right)^2 : \frac{k}{\mu_{CD}}$$

$$= \frac{\mu_{CD}}{\mu_{CH}} =$$

$$\frac{\bar{\nu}_{CD}}{\bar{\nu}_{CH}} = \sqrt{\frac{0.92}{1.71}} \Rightarrow \bar{\nu}_{CD} = 3000 \times \sqrt{\frac{0.92}{1.71}}$$

$= 2200.478417$ cm⁻¹ (calculator

$= 2190$ cm⁻¹ (teachers.

23.02.22

Applications of IR Spectroscopy

① Organic compounds can be identified from its fingerprint region.

② Structure of a compound can be determined.

③ Quantitative analysis of the functional groups like $-OH$, $-COOH$, $-\overset{O}{C}-$ can be found by using IR spectroscopy.

④ Types of chemical reactions can be identified. ~~imp~~

⑤ Impurities in a compound can be detected.

⑥ Position of the functional group in a compound like cis & trans isomers can be easily identified.

⑦ Keto-enol tautomerism can be studied by using IR spectroscopy.

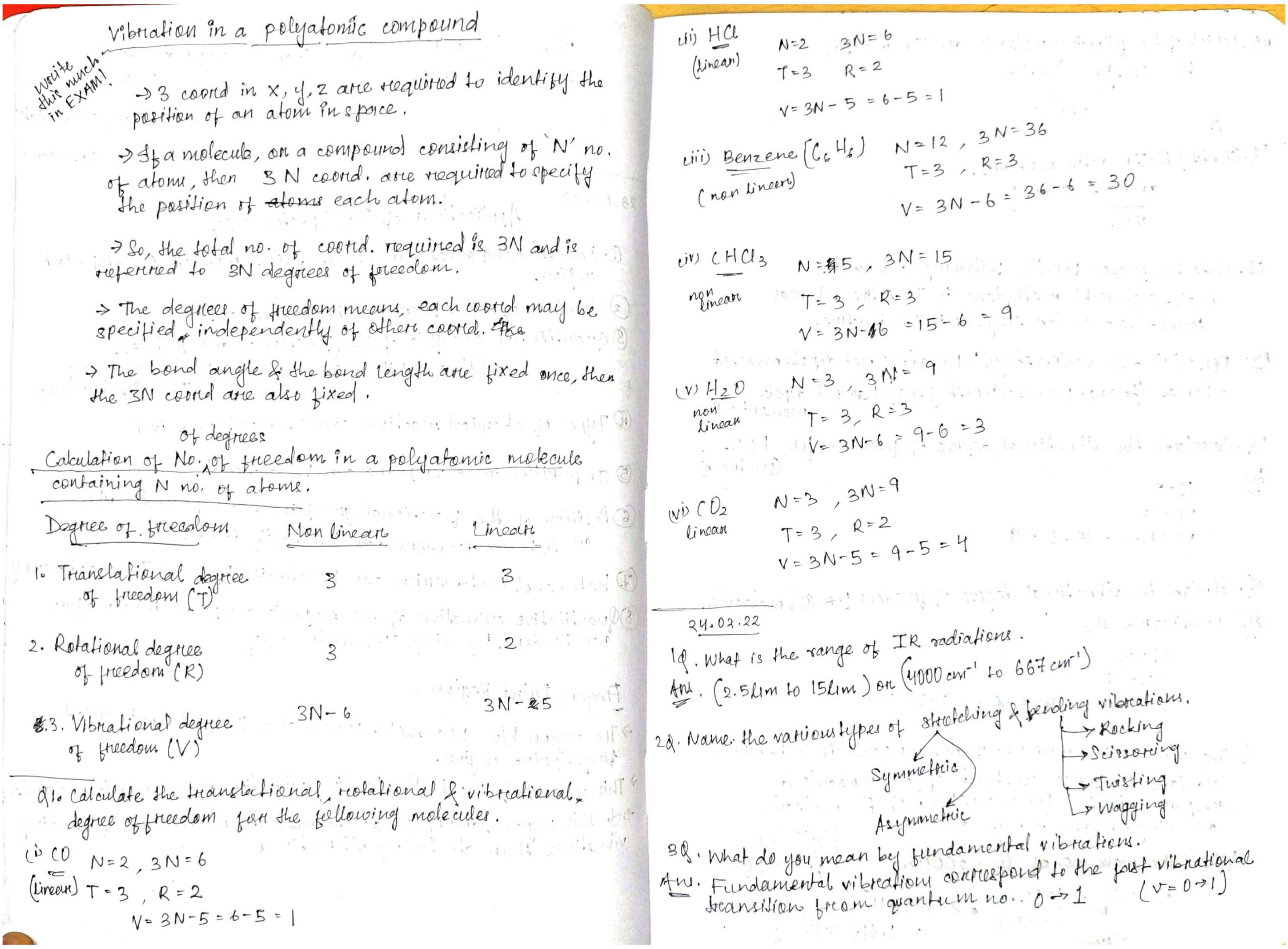
⑧ Quantitative estimation of the organic compound in a mixture can be done. by using IR spectroscopy.

Finger Print Region -

→ The region b/w 500 cm⁻¹ & 1500 cm⁻¹ in IR spectrum is called fingerprint region.

→ This is caused due to the bending vibration of the organic molecules.

→ In this region, absorption occurs due to more amount of bending vibrations than stretching vibrations.



Vibration in a polyatomic compound

Write this much in EXAM!

→ 3 coord in x, y, z are required to identify the position of an atom in space.

→ If a molecule, or a compound consisting of 'N' no. of atoms, then 3N coord. are required to specify the position of ~~atoms~~ each atom.

→ So, the total no. of coord. required is 3N and is referred to 3N degrees of freedom.

→ The degrees of freedom means, each coord may be specified independently of other coord. ~~the~~

→ The bond angle & the bond length are fixed once, then the 3N coord are also fixed.

Calculation of No. of degrees of freedom in a polyatomic molecule containing N no. of atoms.

Degree of freedom	Non linear	Linear
1. Translational degree of freedom (T)	3	3
2. Rotational degree of freedom (R)	3	2
3. Vibrational degree of freedom (V)	3N − 6	3N − ~~2~~5

Q1. Calculate the translational, rotational & vibrational degree of freedom for the following molecules.

(i) CO (linear)
$N = 2$, $3N = 6$
$T = 3$, $R = 2$
$V = 3N - 5 = 6 - 5 = 1$

(ii) HCl (linear)
$N = 2$ $3N = 6$
$T = 3$ $R = 2$
$V = 3N - 5 = 6 - 5 = 1$

(iii) Benzene (C_6H_6) (non linear)
$N = 12$, $3N = 36$
$T = 3$, $R = 3$
$V = 3N - 6 = 36 - 6 = 30$

(iv) $CHCl_3$ non linear
$N = 5$, $3N = 15$
$T = 3$, $R = 3$
$V = 3N - 6 = 15 - 6 = 9$

(v) H_2O non linear
$N = 3$, $3N = 9$
$T = 3$, $R = 3$
$V = 3N - 6 = 9 - 6 = 3$

(vi) CO_2 linear
$N = 3$, $3N = 9$
$T = 3$, $R = 2$
$V = 3N - 5 = 9 - 5 = 4$

24.02.22

1Q. What is the range of IR radiations.

Ans. (2.5μm to 15μm) or (4000 cm⁻¹ to 667 cm⁻¹)

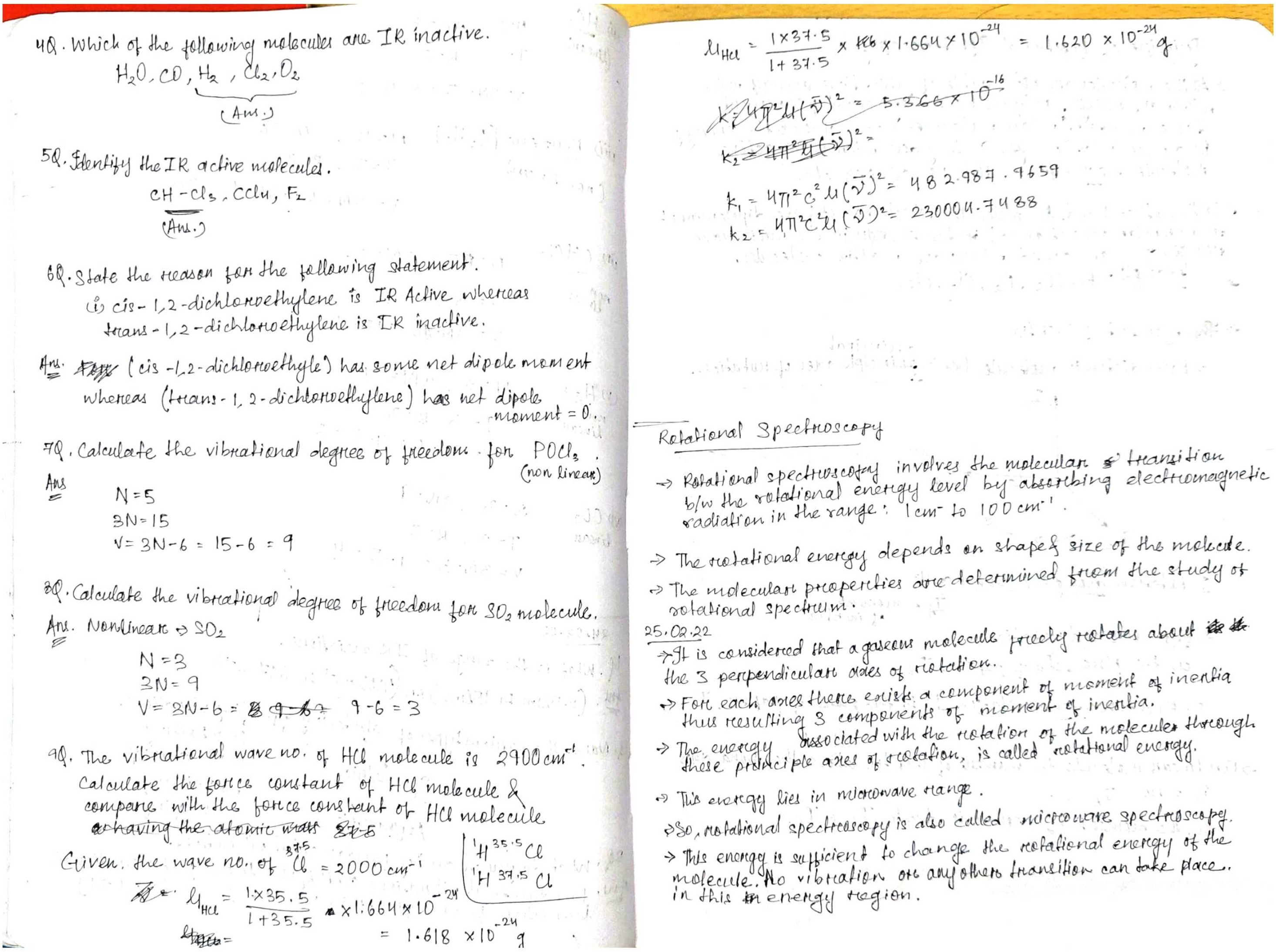
2Q. Name the various types of stretching & bending vibrations.

stretching → Symmetric, Asymmetric

bending → Rocking, Scissoring, Twisting, Wagging

3Q. What do you mean by fundamental vibrations.

Ans. Fundamental vibrations correspond to the first vibrational transition from quantum no. 0 → 1 ($v = 0 \rightarrow 1$)



4Q. Which of the following molecules are IR inactive.

$\underbrace{H_2O, CO, H_2, Cl_2, O_2}_{}$

(Ans.)

5Q. Identify the IR active molecules.

$\underline{CH-Cl_3}$, CCl_4, F_2

(Ans.)

6Q. State the reason for the following statement.

(i) cis-1,2-dichloroethylene is IR Active whereas trans-1,2-dichloroethylene is IR inactive.

Ans. ~~Fass~~ (cis-1,2-dichloroethyle) has some net dipole moment whereas (trans-1,2-dichloroethylene) has net dipole moment = 0.

7Q. Calculate the vibrational degree of freedom for $POCl_3$. (non linear)

Ans

$N = 5$

$3N = 15$

$V = 3N - 6 = 15 - 6 = 9$

8Q. Calculate the vibrational degree of freedom for SO_2 molecule.

Ans. Nonlinear → SO_2

$N = 3$

$3N = 9$

$V = 3N - 6 = \cancel{8\ 9-6} = 9 - 6 = 3$

9Q. The vibrational wave no. of HCl molecule is 2900 cm^{-1}. Calculate the force constant of HCl molecule & compare with the force constant of HCl molecule ~~having the atomic mass 37.5~~

Given, the wave no. of $^{37.5}Cl = 2000\ cm^{-1}$

$^1H\,^{35.5}Cl$

$^1H\,^{37.5}Cl$

$\mu_{HCl} = \frac{1 \times 35.5}{1 + 35.5} \times 1.664 \times 10^{-24}$

$= 1.618 \times 10^{-24}$ g

$\mu_{HCl} = \frac{1 \times 37.5}{1 + 37.5} \times 1.664 \times 10^{-24} = 1.620 \times 10^{-24}$ g

~~$k_1 = 4\pi^2\mu(\bar{\nu})^2 = 5.366 \times 10^{-16}$~~

~~$k_2 = 4\pi^2\mu(\bar{\nu})^2 =$~~

$k_1 = 4\pi^2c^2\mu(\bar{\nu})^2 = 482987.9659$

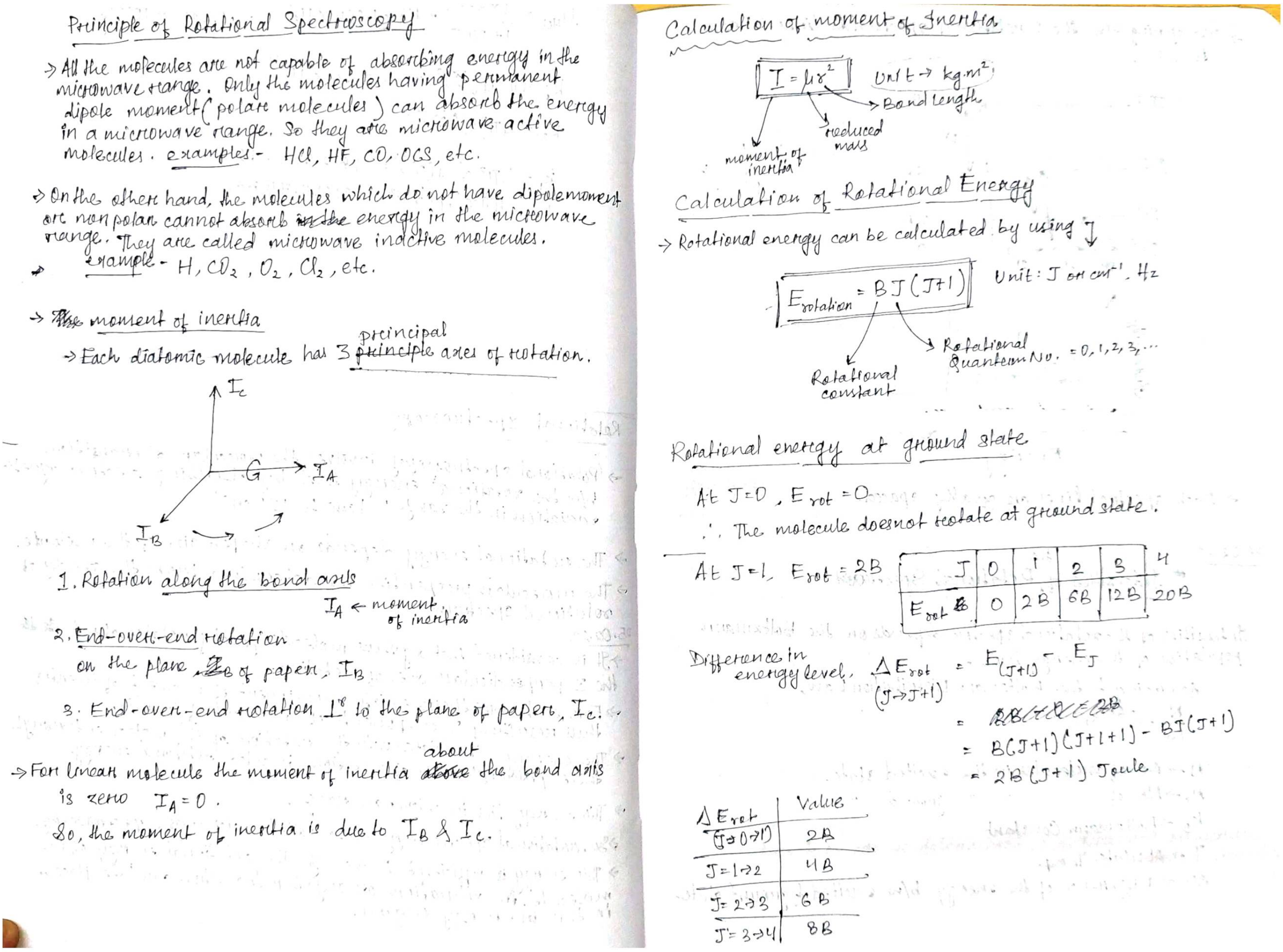
$k_2 = 4\pi^2c^2\mu(\bar{\nu})^2 = 230004.7488$

Rotational Spectroscopy

- → Rotational spectroscopy involves the molecular transition b/w the rotational energy level by absorbing electromagnetic radiation in the range: 1 cm^{-1} to 100 cm^{-1}.
- → The rotational energy depends on shape & size of the molecule.
- → The molecular properties are determined from the study of rotational spectrum.

25.02.22

- → It is considered that a gaseous molecule freely rotates about the 3 perpendicular axes of rotation.
- → For each axes there exists a component of moment of inertia thus resulting 3 components of moment of inertia.
- → The energy associated with the rotation of the molecules through these principle axes of rotation, is called rotational energy.
- → This energy lies in microwave range.
- → So, rotational spectroscopy is also called microwave spectroscopy.
- → This energy is sufficient to change the rotational energy of the molecule. No vibration or any other transition can take place in this ~~en~~ energy region.



Principle of Rotational Spectroscopy

→ All the molecules are not capable of absorbing energy in the microwave range. Only the molecules having permanent dipole moment (polare molecules) can absorb the energy in a microwave range. So they are microwave active molecules. examples:- HCl, HF, CO, OCS, etc.

→ On the other hand, the molecules which do not have dipolemoment are non polar cannot absorb ~~in the~~ energy in the microwave range. They are called microwave indctive molecules.

example - H, CO_2, O_2, Cl_2, etc.

→ ~~The~~ moment of inertia

→ Each diatomic molecule has 3 ~~principle~~ principal axes of rotation.

1. Rotation along the bond axis
   I_A ← moment of inertia
2. End-over-end rotation on the plane ~~I_B~~ of paper, I_B
3. End-over-end rotation ⊥r to the plane of paper, I_c.

→ For linear molecule the moment of inertia ~~above~~ about the bond axis is zero $I_A = 0$.

So, the moment of inertia is due to I_B & I_c.

Calculation of moment of Inertia

$$\boxed{I = \mu r^2}$$ Unit → kg·m²

I → moment of inertia
μ → reduced mass
r → Bond length

Calculation of Rotational Energy

→ Rotational energy can be calculated by using ↓

$$\boxed{E_{rotation} = BJ(J+1)}$$ Unit: J or cm⁻¹, Hz

B → Rotational constant
J → Rotational Quantum No. = 0, 1, 2, 3, …

Rotational energy at ground state

At $J=0$, $E_{rot} = 0$

∴ The molecule doesnot rotate at ground state.

At $J=1$, $E_{rot} = 2B$

J	0	1	2	3	4
E_{rot} ~~B~~	0	2B	6B	12B	20B

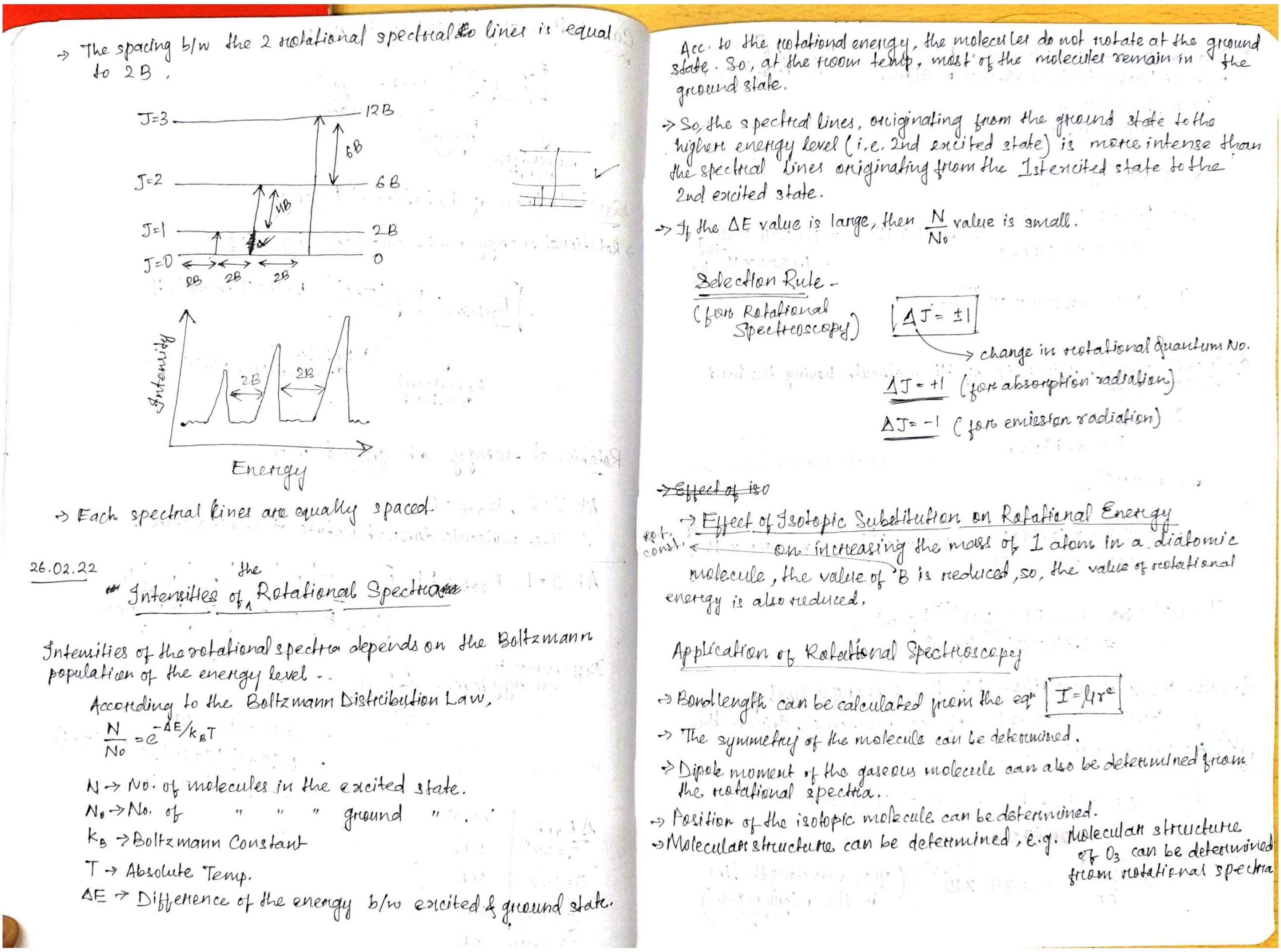
Difference in energy level, $\Delta E_{rot\,(J \to J+1)} = E_{(J+1)} - E_J$

$= $ ~~[illegible]~~

$= B(J+1)(J+1+1) - BJ(J+1)$

$= 2B(J+1)$ Joule

ΔE_{rot}	Value
$(J = 0 \to 1)$	2B
$J = 1 \to 2$	4B
$J = 2 \to 3$	6B
$J = 3 \to 4$	8B



→ The spacing b/w the 2 rotational spectral lines is equal to 2B.

→ Each spectral lines are equally spaced.

26.02.22

Intensities of the Rotational Spectra

Intensities of the rotational spectra depends on the Boltzmann population of the energy level.

According to the Boltzmann Distribution Law,

$$\frac{N}{N_0} = e^{-\Delta E/k_B T}$$

N → No. of molecules in the excited state.
N_0 → No. of " " " ground ".
k_B → Boltzmann Constant
T → Absolute Temp.
ΔE → Difference of the energy b/w excited & ground state.

Acc. to the rotational energy, the molecules do not rotate at the ground state. So, at the room temp, most of the molecules remain in the ground state.

→ So, the spectral lines, originating from the ground state to the higher energy level (i.e. 2nd excited state) is more intense than the spectral lines originating from the 1st excited state to the 2nd excited state.

→ If the ΔE value is large, then $\frac{N}{N_0}$ value is small.

Selection Rule -
(for Rotational Spectroscopy)

$\boxed{\Delta J = \pm 1}$ → change in rotational Quantum No.

$\Delta J = +1$ (for absorption radiation)

$\Delta J = -1$ (for emission radiation)

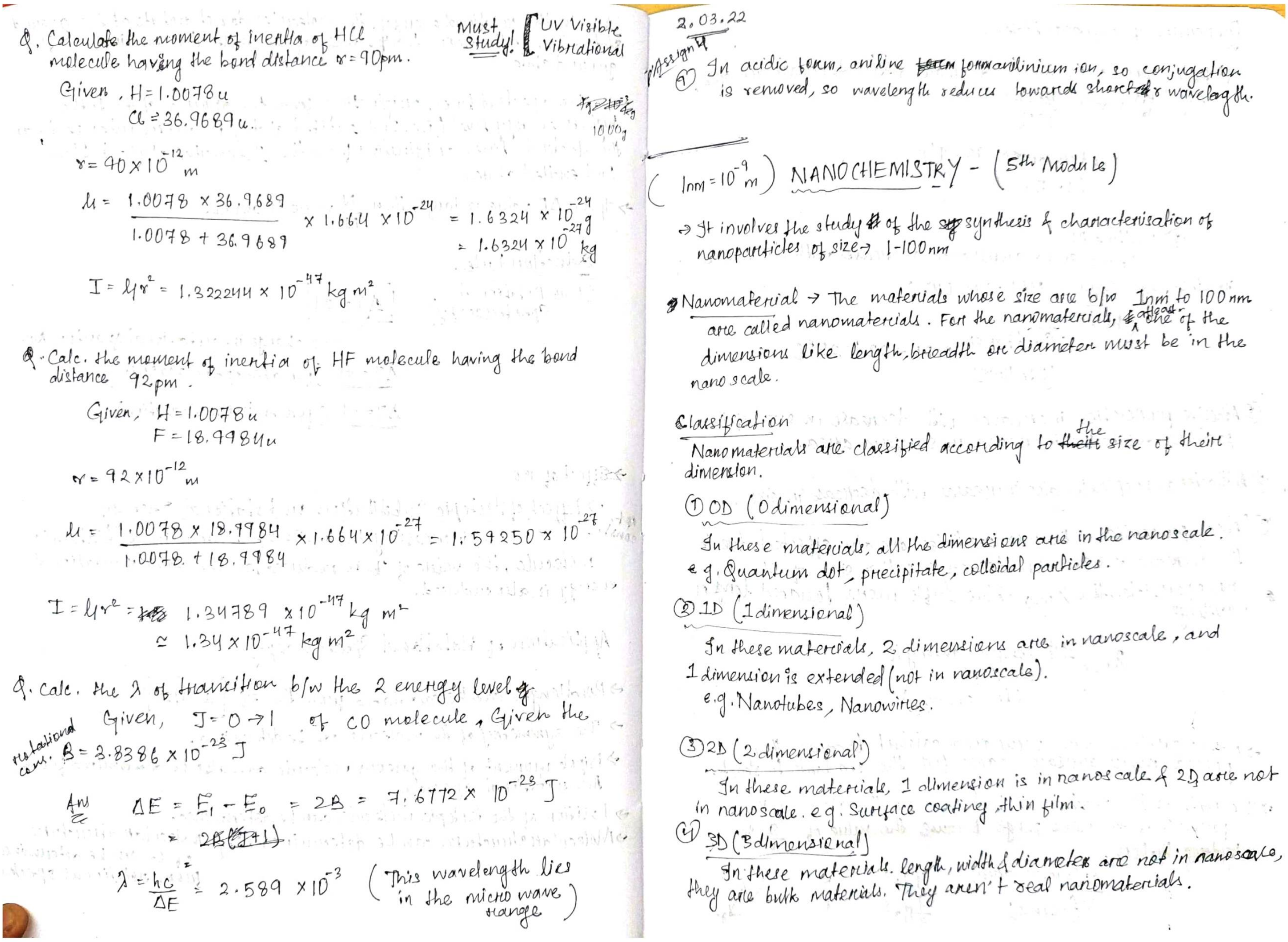
~~→ Effect of iso~~

→ Effect of Isotopic Substitution on Rotational Energy

Rot. const. ← On increasing the mass of 1 atom in a diatomic molecule, the value of B is reduced, so, the value of rotational energy is also reduced.

Application of Rotational Spectroscopy

→ Bond length can be calculated from the eqn $\boxed{I = \mu r^2}$
→ The symmetry of the molecule can be determined.
→ Dipole moment of the gaseous molecule can also be determined from the rotational spectra.
→ Position of the isotopic molecule can be determined.
→ Molecular structure can be determined, e.g. Molecular structure of O_3 can be determined from rotational spectra



Q. Calculate the moment of inertia of HCl molecule having the bond distance r = 90pm.

Must Study! [UV Visible, Vibrational

Given, $H = 1.0078u$

$Cl = 36.9689u.$

$1g = 10^{-3} kg$

$1000g$

$r = 90 \times 10^{-12} m$

$$\mu = \frac{1.0078 \times 36.9689}{1.0078 + 36.9689} \times 1.664 \times 10^{-24} = 1.6324 \times 10^{-24} g$$

$$= 1.6324 \times 10^{-27} kg$$

$$I = \mu r^2 = 1.322244 \times 10^{-47} kg\,m^2$$

Q. Calc. the moment of inertia of HF molecule having the bond distance 92pm.

Given, $H = 1.0078u$

$F = 18.9984u$

$r = 92 \times 10^{-12} m$

$$\mu = \frac{1.0078 \times 18.9984}{1.0078 + 18.9984} \times 1.664 \times 10^{-27} = 1.59250 \times 10^{-27}$$

$$I = \mu r^2 = 1.34789 \times 10^{-47} kg\,m^2$$

$$\simeq 1.34 \times 10^{-47} kg\,m^2$$

Q. Calc. the λ of transition b/w the 2 energy level of Given, $J = 0 \rightarrow 1$ of CO molecule, Given the rotational cons. $B = 3.8386 \times 10^{-23} J$

Ans

$$\Delta E = E_1 - E_0 = 2B = 7.6772 \times 10^{-23} J$$

$$= \cancel{2B(J+1)}$$

$$\lambda = \frac{hc}{\Delta E} = 2.589 \times 10^{-3}$$

(This wavelength lies in the micro wave range)

2.03.22

Assign

⑨ In acidic form, aniline ~~form~~ form anilinium ion, so conjugation is removed, so wavelength reduces towards shorter wavelength.

($1nm = 10^{-9} m$) NANOCHEMISTRY - (5th Module)

→ It involves the study of the synthesis & characterisation of nanoparticles of size → 1-100nm

Nanomaterial → The materials whose size are b/w 1nm to 100nm are called nanomaterials. For the nanomaterials, atleast one of the dimensions like length, breadth or diameter must be in the nano scale.

Classification

Nanomaterials are classified according to ~~their~~ the size of their dimension.

① 0D (0 dimensional)

In these materials, all the dimensions are in the nanoscale. e.g. Quantum dot, precipitate, colloidal particles.

② 1D (1 dimensional)

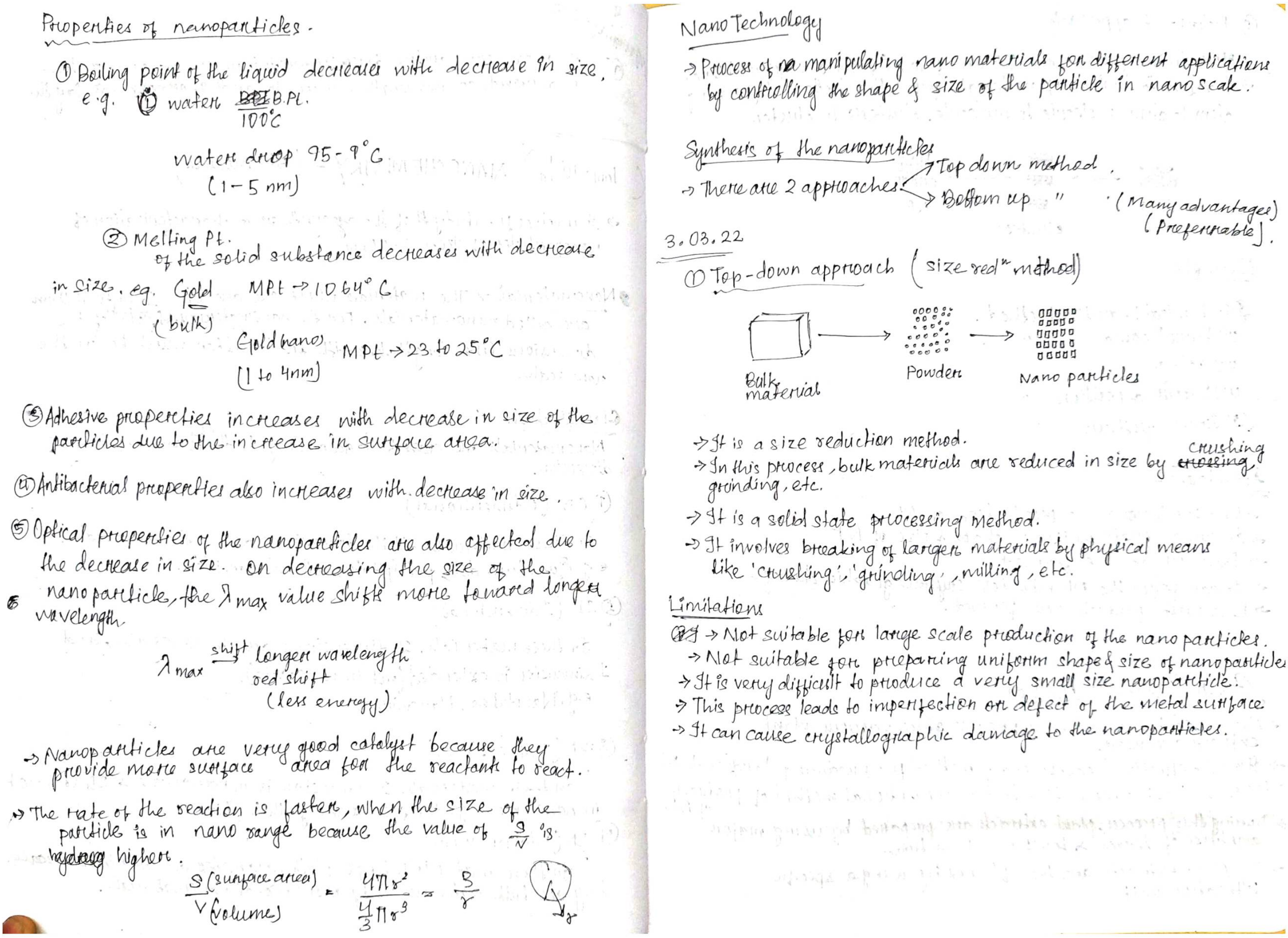
In these materials, 2 dimensions are in nanoscale, and 1 dimension is extended (not in nanoscale). e.g. Nanotubes, Nanowires.

③ 2D (2 dimensional)

In these materials, 1 dimension is in nanoscale & 2D are not in nanoscale. e.g. Surface coating, thin film.

④ 3D (3 dimensional)

In these materials. length, width & diameter are not in nanoscale, they are bulk materials. They aren't real nanomaterials.



Properties of nanoparticles.

① Boiling point of the liquid decreases with decrease in size, e.g. ① water B.Pt. 100°C

water drop 95-9°C
(1-5 nm)

② Melting Pt. of the solid substance decreases with decrease in size. eg. Gold (bulk) MPt → 1064° C

Gold nanos (1 to 4nm) MPt → 23 to 25°C

③ Adhesive properties increases with decrease in size of the particles due to the increase in surface area.

④ Antibacterial properties also increases with decrease in size.

⑤ Optical properties of the nanoparticles are also affected due to the decrease in size. On decreasing the size of the nanoparticle, the λ_{max} value shifts more toward longer wavelength.

$$\lambda_{max} \xrightarrow{\text{shift}} \text{longer wavelength}$$
red shift
(less energy)

→ Nanoparticles are very good catalyst because they provide more surface area for the reactants to react.

→ The rate of the reaction is faster, when the size of the particle is in nano range because the value of $\frac{S}{V}$ is higher.

$$\frac{S\,\text{(surface area)}}{V\,\text{(Volume)}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

r

Nano Technology

→ Process of ~~na~~ manipulating nano materials for different applications by controlling the shape & size of the particle in nano scale.

Synthesis of the nanoparticles

→ There are 2 approaches: → Top down method.
→ Bottom up " (Many advantages) (Preferrable).

3.03.22

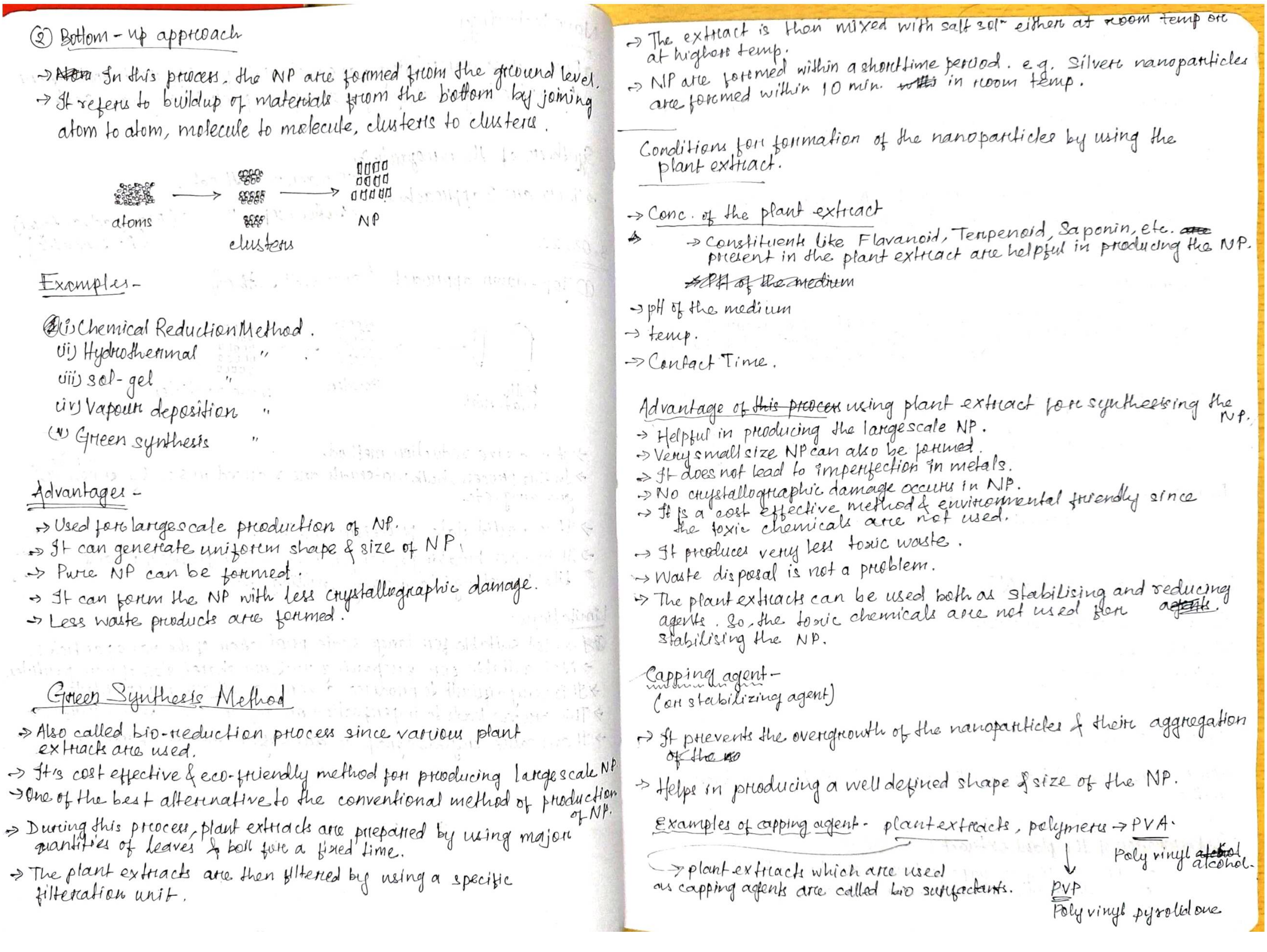
① Top-down approach (size red^n method)

Bulk material → Powder → Nano particles

→ It is a size reduction method.
→ In this process, bulk materials are reduced in size by ~~crossing~~ crushing, grinding, etc.
→ It is a solid state processing method.
→ It involves breaking of larger materials by physical means like 'crushing', 'grinding', milling, etc.

Limitations

→ Not suitable for large scale production of the nano particles.
→ Not suitable for preparing uniform shape & size of nanoparticles
→ It is very difficult to produce a very small size nanoparticle.
→ This process leads to imperfection or defect of the metal surface
→ It can cause crystallographic damage to the nanoparticles.



② Bottom - up approach

- → ~~Atom~~ In this process, the NP are formed from the ground level.
- → It refers to buildup of materials from the bottom by joining atom to atom, molecule to molecule, clusters to clusters.

atoms → clusters → NP

Examples -

(i) Chemical Reduction Method.
(ii) Hydrothermal "
(iii) sol- gel "
(iv) Vapour deposition "
(v) Green synthesis "

Advantages -

- → Used for largescale production of NP.
- → It can generate uniform shape & size of NP.
- → Pure NP can be formed.
- → It can form the NP with less crystallographic damage.
- → Less waste products are formed.

Green Synthesis Method

- → Also called bio-reduction process since various plant extracts are used.
- → It's cost effective & eco-friendly method for producing largescale NP.
- → One of the best alternative to the conventional method of production of NP.
- → During this process, plant extracts are prepared by using major quantities of leaves & boil for a fixed time.
- → The plant extracts are then filtered by using a specific filteration unit.
- → The extract is then mixed with salt sol^n either at room temp or at higher temp.
- → NP are formed within a short time period. e.g. Silver nanoparticles are formed within 10 min. ~~with~~ in room temp.

Conditions for formation of the nanoparticles by using the plant extract.

- → Conc. of the plant extract
  - → Constituents like Flavanoid, Terpenoid, Saponin, etc. ~~are~~ present in the plant extract are helpful in producing the NP.
  - ~~→ PH of the medium~~
- → pH of the medium
- → temp.
- → Contact Time.

Advantage of ~~this process~~ using plant extract for synthesising the NP.

- → Helpful in producing the largescale NP.
- → Very small size NP can also be formed.
- → It does not lead to imperfection in metals.
- → No crystallographic damage occurs in NP.
- → It is a cost effective method & environmental friendly since the toxic chemicals are not used.
- → It produces very less toxic waste.
- → Waste disposal is not a problem.
- → The plant extracts can be used both as stabilising and reducing agents. So, the toxic chemicals are not used for ~~agents~~ stabilising the NP.

Capping agent -
(or stabilizing agent)

- → It prevents the overgrowth of the nanoparticles & their aggregation ~~of the NP~~
- → Helps in producing a well defined shape & size of the NP.

Examples of capping agent - plant extracts, polymers → PVA · Poly vinyl ~~alcohol~~ alcohol.
↓
PVP
Poly vinyl pyrolidone

→ plant extracts which are used as capping agents are called bio surfactants.

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Preparation of the Nanoparticles -

→ Nanoparticles are prepared in following ways & the steps involved for the preparation of the NP are as follows -

① Use of Precursor salt -

→ Various salts are used to produce the NP. e.g. of salts used to prepare NP are - $AgNO_3$, $CuSO_4$, $Cu(NO_3)_2$, $ZnSO_4$, $Zn(NO_3)_2$, $AuCl_3$, etc.

② Reducing Agent -

→ These are used to produce the NP. examples of the reducing agents → Plant extracts, hydrazine (N_2H_4), hydrogenperoxide (H_2O_2), Na_2BH_4, etc

③ Use of stabilising Agent -

→ These are used to make the NP more stable by preventing their overgrowth & aggregation e.g. Biosurfactants, polymers.

Example -

$$\underset{\text{(plant extract)}}{Au^{3+} + 3e^-} \longrightarrow \underset{\text{(NP)}}{Au}$$

Characterisation of the NPs -

① UV-Visible Spectral analysis.

② XRD - analysis. (X-ray diffraction)

Synthesis of Au NPs -

→ Au NPs are prepared by using the plant extract by bio-reduction method.

→ It involves the following steps -

① Preparation of the plant extract

→ approx. 10g of papaya leaves are boiled in 100ml of double distilled water taken in a beaker for 30min.

→ The solⁿ is cooled down to RT (Room temp) & filtered through 0.45 µm membrane filter.

→ The filtrate is collected & used as reducing & stabilising agents

② Preparation of the precursor salt -

→ for preparing Au NP, $AuCl_3$ or $HAuCl_4$ is used as precursor salt.

→ Au solⁿ is prepared by measuring 20mg of the salt in 5ml of double distilled water.

→ This solⁿ is kept for preparing the NPs.

③ Preparation of Au NPs -

→ Approx. 20ml of the plant extract is taken in a beaker & heated slowly in a magnetic stirrer at 40°C.

→ After 30min, 1ml of cold solⁿ is added dropwise ~~immediately~~

→ Immediately, the solⁿ turns pink indicating the formation of Au NPs.

→ This sample is collected for following characterisation.

Reacⁿ

$$Au^{3+} + 3e^- \left(\begin{array}{c}\text{released from}\\ \text{plant extract}\end{array}\right) \longrightarrow Au$$

Characterisation -

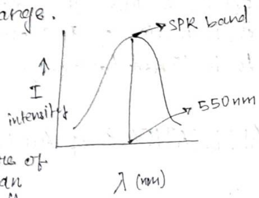
(i) UV-Visible spectral analysis

→ Au NPs are characterised by UV visible spectrum which is observed in the visible range.

→ The SPR band occurs at 550nm.

$\downarrow$

(Surface Plasmon Resonance)

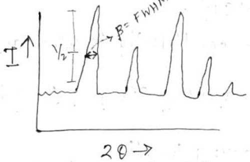


→ It is a prominent feature of metal NPs which produces an intense absorption band in the visible range. It originates due to the resonant oscillation of the free e⁻ in the conduction band of the metal induced by a resonating electric field.

→ It is the characteristics of a coherent oscillation of conduction band e⁻.

(ii) XRD Analysis

→ This analysis shows the appearance of an intense peak at the angle of diffraction when a graph is plotted taking intensity vs. angle of diffraction.



→ It indicates the size of the NPs.

→ The size of the NPs can be calculated by using Debye- Scherrer equation

$$\boxed{d = \frac{0.94\lambda}{\beta \cdot \cos\theta}}$$

λ → wavelength of absorption

θ → angle of diffraction

β → Full ~~wave~~ width at half maximum of an intense peak (F W H M)

d → diameter of the crystal or crystalline size

$\because$ $d \propto \frac{1}{\beta}$

$\therefore$ Size of the particle increases with decrease in β value.

→ For the Au NPs, the peak is observed at $2\theta = 38°$. It indicates the formation of FCC structure & size of the Au NP is found to be 15nm. ($d = 15$nm) & value of β is in range (0.001 to 0.2).

APPLICATIONS of Au NPs

- → It is used as a good sensing agent.
- → As a biomarker for detecting cancer, heart disease, etc.
- → As a good catalyst in solar cell.
- → Used in water treatment plant or in cosmetic industry.
- → Used in fuel cell.
- → It's a good antibiotic and antifungal agent.

Synthesis of Ag NPs

Following steps are used -

① Preparation of the plant extract -

→ neem leaves are used (20g) → boiled in 100ml of double distilled water, boiled for 30min in a beaker.

→ The solution is then filtered using 0.45 µm membrane filter.

→ The filterate is then collected & kept as stabilising agen & reducing agent.

② Preparation of precursor salt -

→ $AgNO_3$ is used.as.

→ Suitable amount of $AgNO_3$ is added to double distilled water 10ml of 1mM solⁿ.

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③ Synthesis of Ag NPs

→ 5mL of the plant extract is taken in a 50mL beaker & placed in a magnetic stirrer.

→ Then, it is heated at 40°C. In this condition, 1mL of the precursor salt solⁿ ($AgNO_3$ solⁿ) is added dropwise using a micropipette. Within 10min ~~of~~ of addition of $AgNO_3$ solⁿ, Ag NPs are formed.

→ Color of the Ag NP is yellowish-brown.

Reaction $Ag^{+} + e^{-}$ (from neem leave extract) $\xrightarrow{\text{at } 40°C}$ Ag NPs.

→ The constituents like flavanoids, terpenoids, polyol present in the neem leaves helps in reducing & stabilising the Ag NPs.

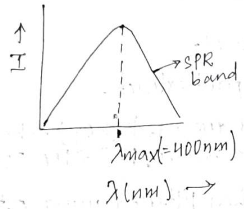
→ The NPs are collected & kept for the following characterisation -

(i) UV-Visible Spectral Analysis.

→ formation of Ag NPs are confirmed

by observing SPR

-> The SPR band occurs at 400nm for Ag.

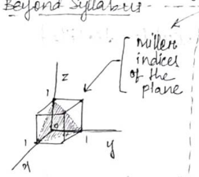


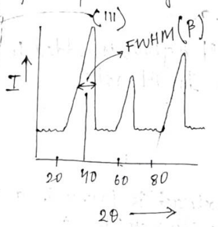
(ii) XRD Analysis

-> This analysis helps in determining the crystallite size & structure of the NPs.

-> The graph is plotted by taking I vs 2θ

-- Beyond Syllabus --





-> In the XRD pattern, the intense peak is observed at 2θ = 38° indicating the formation of FCC structure

-> The size of the NPs can be calculated by using Debye-Scherrer equation.

$$\boxed{d = \frac{0.94\lambda}{\beta \cdot \cos\theta}} = 13nm$$

-> value varries from [0.001 to 0.02]

-> The size of the Ag NP is found to be 13nm.

-> Colour : Yellowish Brown.

[If size changes, then color changes]

Application

-> Used as a bio sensor.

-> In cosmetic industries.

-> For food packaging.

-> Used As a good catalyst

-> Used in textile industry.

-> Used as a good surface coating.

-> It is used as a good antibacterial agent.

-> Au & Ag are noble ~~Ag~~ NPs.

Synthesis of metal oxide NPs -

Synthesis of Cu_2O (cuprous oxide) NPs -

-> Cu_2O NPs are ~~synthestde~~ synthesised by using 'Arka plant' - (botanical name : Calotriopis, procera).

-> The method is a bio reduction method.

-> It involves the following steps -

① Preparation of the plant extract.

-> Approx 10g of Arka leaves are added in 100mL of double distilled water & boiled for 30min.

-> The solⁿ is cooled to RT & filtered through 0.45 μm membrane filter.

-> The filtrate is ~~salt~~ collected & used as reducing ~~&~~ and stabilising agent.

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② Preparation of salt solution

-> For preparing Cu_2O NPs, $CuSO_4 \cdot 5H_2O$ is used as precursor salt.

-> The required amount of salt is measured & dissolved in 250mL double distilled water to prepare 0.1 M solⁿ.

③ Preparation of the NPs.

- → equal volume of plant extract & the salt solⁿ are mixed properly and heated at 70°C using magnetic stirrer.
- → The heating is done for 30min.
- → Hydrazine solⁿ is added dropwise from a burette.
- → The colour of the solⁿ changes from blue → reddish brown indicating the formation of Cu_2O NPs.
- → The sample is then collected and kept for characterisation.

Reaction -

step (i) $N_2H_4 + H_2O \longrightarrow N_2H_5^+ + OH^-$

step (ii) $CuSO_4 + 5H_2O + OH^- \longrightarrow Cu(OH)_2 + SO_4^{2-} + H_2O$

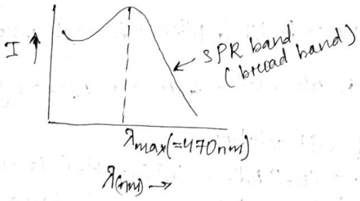
step (iii) $Cu(OH)_2 + N_2H_5^+ \longrightarrow \underset{(NPs)}{Cu_2O^*} + N_2 + 2H_2 + H_3O^+$

Characterisation

- → Cu_2O NPs are characterised by using U-V Visible spectrophotometer & X-ray ~~defractometere~~ diffractometer.

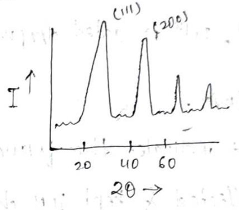
① UV-Visible Spectral analysis

- → The SPR band occurs at 470nm indicating the formation of Cu_2O NPs



② XRD Analysis

- → The appearance of intense peak at 2θ = 36.8 (or 37°) and 42.3° indicate the formation of $(111)_{plane}$ & $(200)_{plane}$ of crystalline structure.



- → The structure is FCC [Face-centred cubic]
- → Size of Cu_2O → 17

Application -

- → It is used as a gas sensing agent. It is a good photocatalyst.
- → Used for water treatment.
- → Used as a catalyst in solar cell.
- → It is used in magnetic storage device.
- → Super conductivity increases with decrease in size of the NP.
- → It is a good anti bacterial agent.

Synthesis of ZnO NPs -

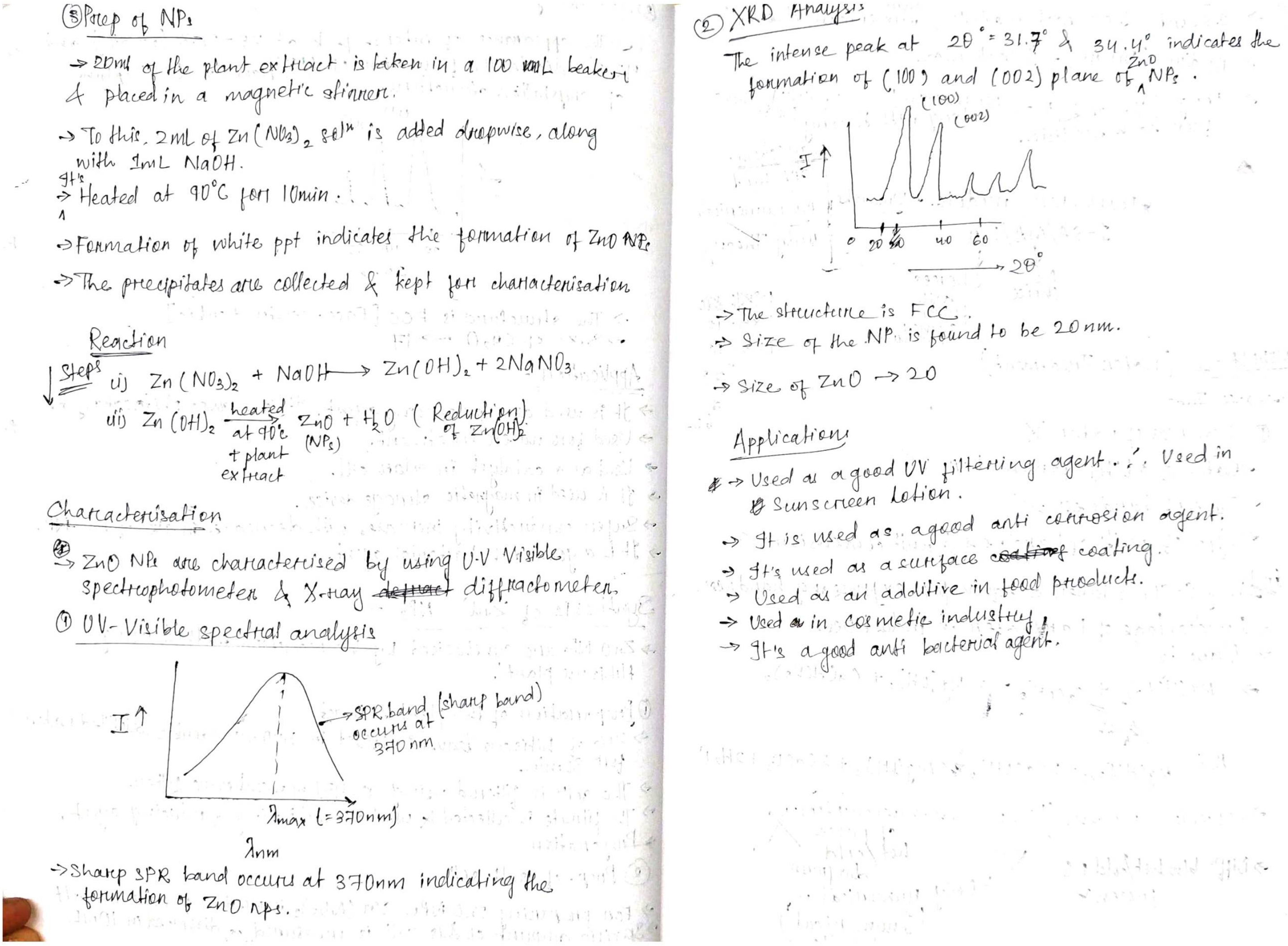
- → ZnO NPs are synthesised by bio reduction method using Hibiscus plant.

① Preparation of the plant extract.

- → 20g of hibiscus leaves is boiled in 500mL double distilled water for 30min.
- → The solⁿ is filtered using 0.45μm membrane filter.
- → The fitrate is collected & used as stabilising & reducing agent.
- ~~→ Preparation~~

② Prep. of salt solⁿ

- → For preparing ZnO NPs. $Zn(NO_3)_2$ is used as precursor salt
- → Specific amount of this salt is measured & dissolved in 10mL double distilled water to prepare 0.05M solⁿ



③ Prep of NPs

→ 20ml of the plant extract is taken in a 100 mL beaker & placed in a magnetic stirrer.

→ To this, 2mL of $Zn(NO_3)_2$ soln is added dropwise, along with 1mL NaOH.

→ It's Heated at 90°C for 10min.

→ Formation of white ppt indicates the formation of ZnO NPs

→ The precipitates are collected & kept for characterisation

Reaction

Steps

(i) $Zn(NO_3)_2 + NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$

(ii) $Zn(OH)_2 \xrightarrow[\text{at } 90^\circ C \text{ + plant extract}]{\text{heated}} \underset{(NPs)}{ZnO} + H_2O$ (Reduction of $Zn(OH)_2$)

Characterisation

→ ZnO NPs are characterised by using U.V Visible spectrophotometer & X-ray ~~defract~~ diffractometer.

① UV-Visible spectral analysis

→ Sharp SPR band occurs at 370nm indicating the formation of ZnO nps.

② XRD Analysis

The intense peak at 2θ° = 31.7° & 34.4° indicates the formation of (100) and (002) plane of ZnO NPs.

→ The structure is FCC.

→ Size of the NP is found to be 20nm.

→ Size of ZnO → 20

Applications

→ Used as a good UV filtering agent ∴ Used in Sunscreen lotion.

→ It is used as a good anti corrosion agent.

→ It's used as a surface ~~coatinf~~ coating.

→ Used as an additive in food products.

→ Used ~~as~~ in cosmetic industry.

→ It's a good anti bacterial agent.