BTech CSE
1st Year Sem1
Full notes PDF

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ENGINEERING CHEMISTRY

Syllabus Engineering chemistry (BAS 102)

Unit 1

Atomic & Molecular Structure :-

- Molecular orbital's of diatomic molecules
- Bond order.
- Magnetic characters
- Numerical problems.

Chemistry of Advanced materials.

- Liquid crystals:- Introduction, Types, Application, Imp industrial materials used as liquid crystals.
- Graphite & fullerene:- Introduction, Structure, Applications.
- Nanomaterials. (New)
  - Introduction, Preparations
  - characteristics of nanomaterials
  - Applications of nanomaterials
  - carbon nano tubes (CNT)
- Green chemistry (New)
  - introduction
  - 12 principles and importance of green synthesis
  - Green chemicals
  - Synthesis of typical organic compounds by conventional and green route (Adipic Acid) & (paracetamol),
  - Environmental impact of green chemistry in society

(Engineering Chemistry) 23-Nov-2022

(Module-1)

Valence Bond theory (VBT)

1) It deals with electronic configuration of elements.
2) its the no of unpaired e^- present in the valence shell of atom. that takes part in bonding.
3) Covalent bond is formed by overlapping of appropriate orbitals.

(Defects of Valence Bond theory)

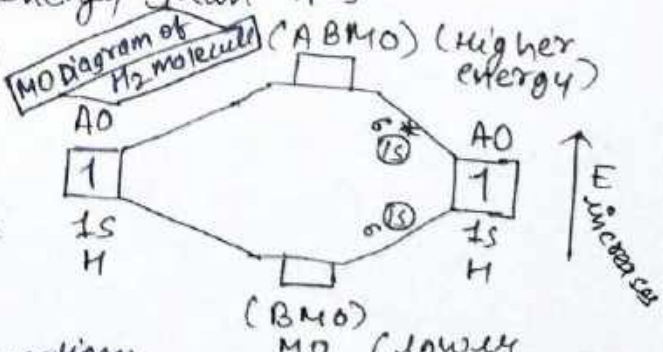
1) it fails to explain the paramagnetic behaviour of O_2 & some other molecules.
2) VBT is unable to explain the formation of $\boxed{\text{coordinate bond}}$ ↓ $\boxed{\text{Eg: } A: \rightarrow B}$
3) It fails to explain Bonding in H_2^+, He_2^+, B_2H_6 etc. (Diboron)
4) it is unable to explain the colour of compounds

(Molecular orbital theory) (MOT)

* MOT was proposed by Hundt & Mulliken and later on developed by Lennards and coulson.

1) According to this theory $\boxed{\text{Atomic orbitals (AOs)}}$ having similar energy & symetry combines to form molecular orbitals by linear combination Atomic orbitals Principle (LCAO).
2) The no of molecular orbitals formed will be same as the AOs overlaps
3) Two AOs after overlapping gives 2 molecular orbitals out of which one is bonding $\boxed{\text{MO (Molecular orbital)}}$ with lower energy and other one is ABMO with higher energy than AOs.

* ABMO = Anti Bonding Molecular orbital
* BMO = Bonding Molecular orbital



• The decrease in the energy of Bonding of MO is approx same as the increase in the energy of ABMO.

4) Two atomic orbitals having wave functions side 1 & side 2 (ψ_1 & ψ_2) are overlapping, its called LCAO. As per this method.

$$\boxed{\psi_{(molecule)} = c_1\psi_1 + c_1\psi_2}$$

(ψ = Si)

⑤ where C_1 & C_2 are constants showing extent of overlap.
Depending upon the type of overlapping MOs are designated as

$\boxed{\delta, \delta^*}$ for D block elements. (Not in syllabus)

$\boxed{\sigma, \sigma^*, \pi, \pi^*}$ (In syllabus)

⑥ Each molecular orbital accomodate $2e^-$ with opposite spin like AOs.

⑦ The filling of e^- in various MOs obeys afbau's rule, hund's rule, Pauli's exclusion principle.

⑧ Energy levels of molecular orbitals as per spectroscopic studies are of (2 types) :- (Need to be learnt, no pattern)

① Upto $14e^-$ System

σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}, $(\pi_{2p_y} = \pi_{2p_z})$ σ_{2p_x}

$(\pi^*_{2p_y} = \pi^*_{2p_z})$ $\sigma^*_{2p_x}$.

② Beyond $14e^-$ System

σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}, σ_{2p_x} $(\pi_{2p_y} = \pi_{2p_z})$, $(\pi^*_{2p_y} = \pi^*_{2p_z})$ $\sigma^*_{2p_x}$

⑨ Bond order :- its the no of Bonds b/w 2 bonding atoms and we can also determine it by formula.

$$\boxed{\text{Bond order} = \frac{\text{no of } e^- \text{ in BMO} - \text{no of } e^- \text{ in ABMO}}{2}}$$

Eg = for H_2 molecule.

$\boxed{\sigma_{1s} = 2}$ $\frac{2-0}{2} = 1$ → shows molecule exists.

• Bond order maybe exist in whole no's as well as in fraction

* $\boxed{\text{Bond order} \propto \text{strength of Bond (Stability)}}$

* $\boxed{\text{Bond order} \propto \frac{1}{\text{Bond distance}}}$

⑩ Magnetic Properties depends on the no of paired & unpaired e^- present in the molecule.

$\boxed{\text{Unpaired } e^- = \text{Paramagnetic}}$ & $\boxed{\text{Paired } e^- = \text{Dimagnetic}}$

Extras :- Afbau's Rule :- The orbital having low energy will get filled first by e^-.

Hund's Rule :- A/c to this, orbitals having same energy will get themselves fill up (1) then if any electron remains it will come as (↓) Eg $4e^-$: $\boxed{\uparrow\downarrow|\uparrow|\uparrow}$ found in $\boxed{\text{P-orbitals}}$.

Pauli's Exclusion :- atom have $2e^-$ they occupy outmost shell with opp spins

(Chemistry) (24/Nov/2022)

Significance of MOT

- MO configuration came into knowledge.
- With the help of Bondorder we can determine existence of molecule.
- Bond order $\propto \frac{1}{\text{Bond length}}$ (This decides stability level)
- Higher bond order higher the energy need to break.

Why we see colours?

As electrons emits waves (visible) of range 400nm–800nm (10^{-9}) our eyes can see them as they're sensitive to it.

* He_2 (EC)

	2	$1s^2$
He =	2	$1s^2$
	$4e^-$	

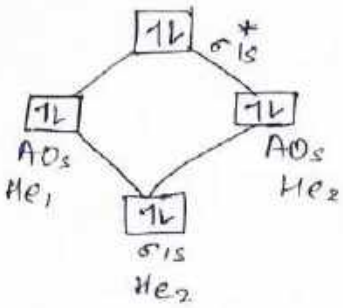
MO configuration :- σ_{1s}, σ^*_{1s}
BMO ABMO

Bond order = $\frac{2-2}{2} = \frac{0}{2} = 0$

molecule doesn't exist.

This is a case of upto 14e⁻ system

* 1 MO have 2e⁻ at max.



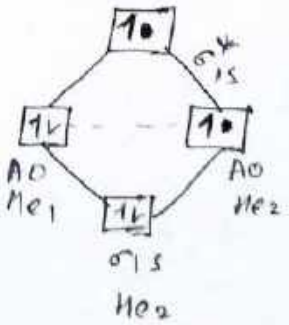
energy increases.

Magnetic behaviour.
= Dimagnetic (Paired)

* He_2^+ (EC)

He_1 =	2	$1s^2$
He_2	1	$1s^2$
	$3e^-$	

Mo config:- $(\sigma_{1s})^2 (\sigma^*_{1s})^1$



energy increases.

σ_{1s} is filled 1st cause its on lower energy and A/c to the rule of Aufbau.

Bond order :- $\frac{2-1}{2} = 1/2$

molecule exists

Magnetic behaviour.
= Paramagnetic (unpaired)

Be_2 = Atomic no = 4
EC = $1s^2 2s^2$

$Be_1 = 4$ – $1s^2 2s^2$
$Be_2 = 4$ $1s^2 2s^2$
8

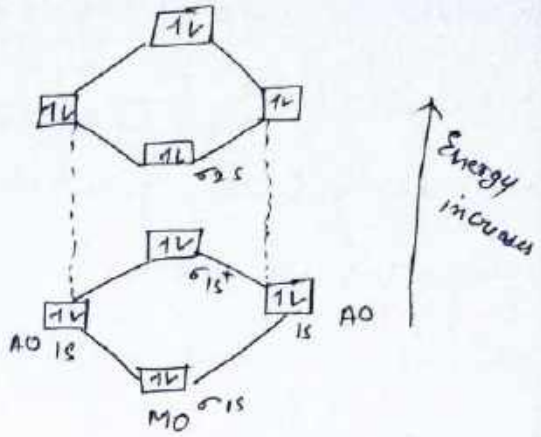
MO configⁿ

$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2$

Bond order = $\frac{\overset{BMO}{4} - \overset{ABMO}{4}}{2} = 0$

molecule doesn't exist.

Magnetic Behaviour = Dimagnetic (Paired e⁻)

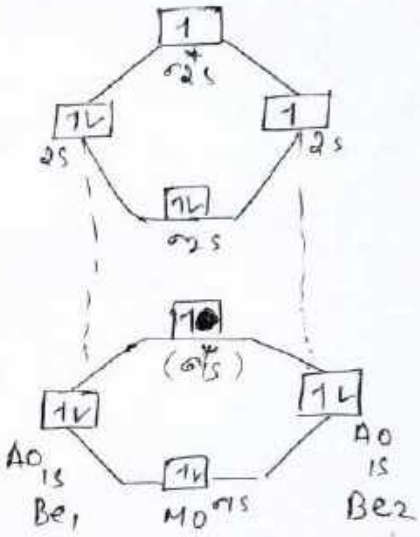


Be_2^+
$Be_1 = 4$ $1s^2 2s^2$
$Be_2 = 3$ $1s^2 2s^1$

$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2$

Bond order = $\frac{4-3}{2} = 1/2$ (exists)

Magnetic Behaviour = Paramagnetic (unpaired)



B2 $B_1 = 5$ – $1s^2 2s^2 2p^1$
$B_2 = 5$ $1s^2 2s^2 2p^1$
$10e^-$ } $10e^-$ System

MO configuration = $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_2 p_y^1 = \pi_2 p_z^1)$ $\sigma_{2px} (\pi_2^* p_y = \pi_2^* p_z)$ $\sigma_2^* p_z$

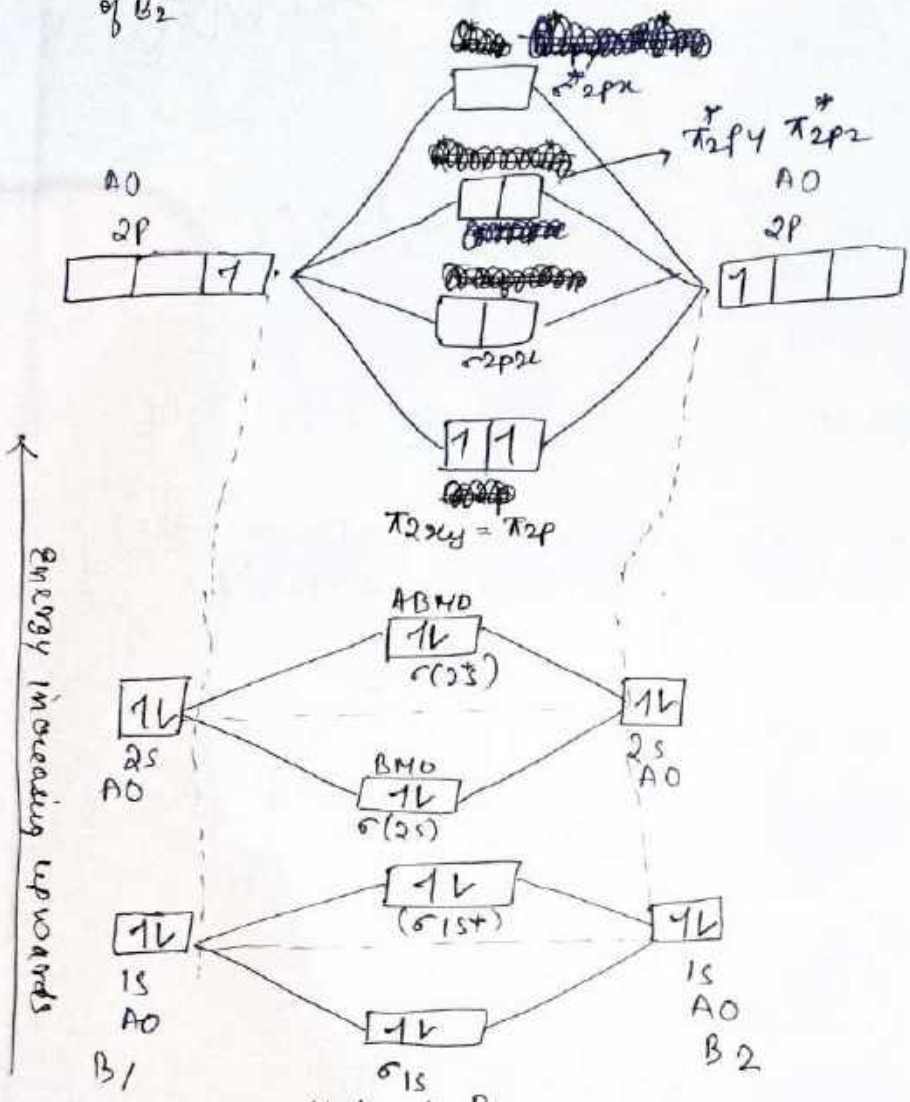
Bond order = $\frac{\overset{BMO}{6} - \overset{ABMO}{4}}{2} = 1$ (exists)

Magnetic behaviour = $\boxed{\text{Paramagnetic.}}$

This molecule can be ~~shown~~ written & shown as B–B by Single Bond.

MO diagram of B_2

25/NOV/2022



Molecule B_2
(MO diagram of B_2 molecule)

* lines should be straight use scale.

σ_{1s}^* is less stable than σ_{1s}

(N₂) Atomic No = 7

$N_1 = 7$ $\quad 1s^2\ 2s^2\ 2p^3$

$N_2 = 7$ $\quad 1s^2\ 2s^2\ 2p^3$

$14\ e^-$

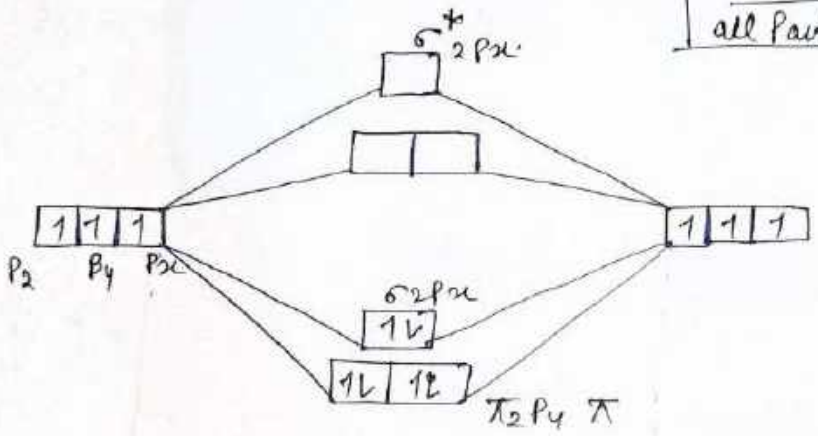
MO configⁿ :-

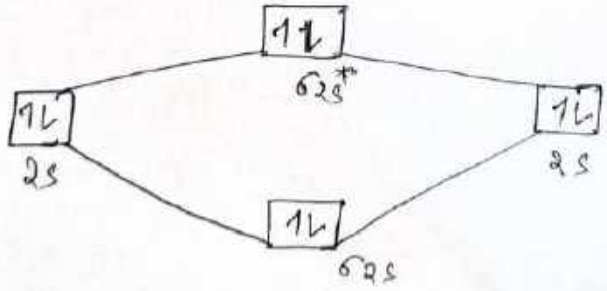
$$(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi^2_{2p_y} = \pi^2_{2p_z})(\sigma^2_{2p_x})$$

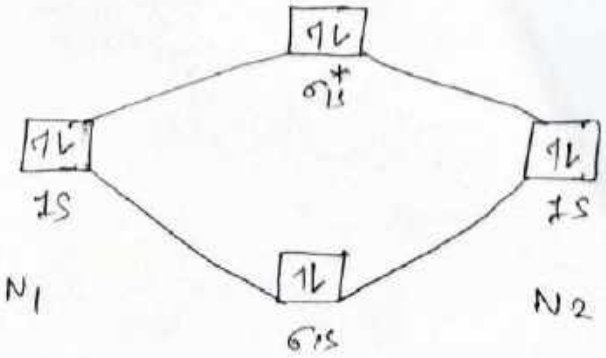
$$(\pi^*_{2p_y} = \pi^*_{2p_z})\ (\sigma^*_{2p_x})$$

Bond order = $\frac{10-4}{2} = \frac{6}{2} = 3$ exists $N \equiv N$

Diamagnetic
all Paired e^-







Li Be B C N O F Ne
1s 2s 2p

N_2^+

$N_1 = 6$ $\quad 1s^2\, 2s^2\, 2p^2$

$N_1 = 6$ $\quad 1s^2\, 2s^2\, 2p^2$

Bondorder $= \frac{9-4}{2} = 5/2$

2.5

MO <u>config</u>

$$(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi^2_{2py} = \pi^2_{2pz})(\sigma_{2px})^1$$
$$(\pi^*_{2py} = \pi^*_{2pz})\ (\sigma^*_{2px})$$

N_2^-

$N_1 = 6$

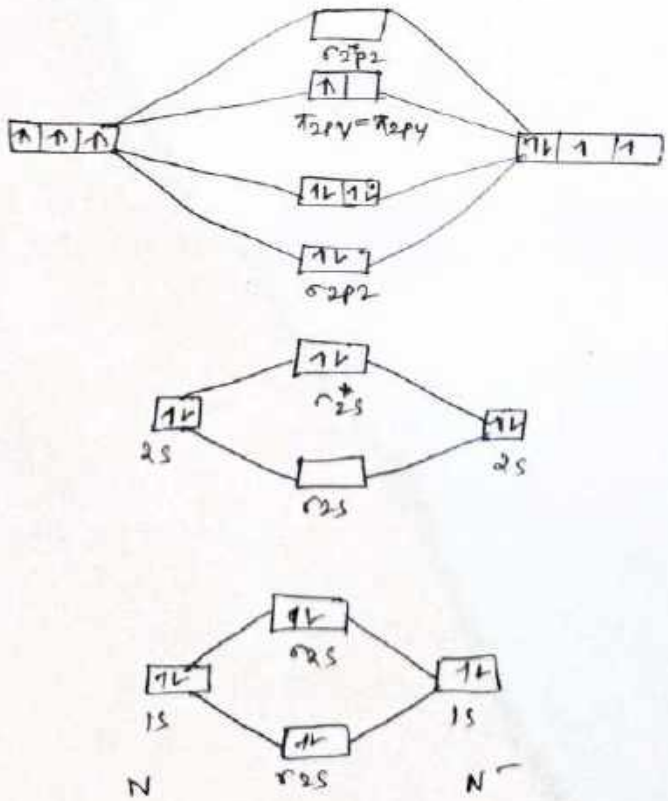
$N_1 = 7$

Bond order $= \frac{10-4}{2} = \frac{6}{2} = 3$

exists

MO <u>config.</u>

$$(\sigma_{1s})^2\ (\sigma^*_{1s})^2\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi^2_{2py} = \pi^2_{2pz})(\sigma_{2px})^2$$
$$(\pi^*_{2py} = \pi^*_{2pz})\ (\sigma^*_{2px})$$



(Imp) Note

- Pair of molecular orbitals σ_{1s}^*, σ_{1s}^* have lower energies than pair of MOs σ_{2s} & σ_{2s}^* due to the fact former are obtained from 1s (low energy atomic orbital), Then the later are formed from 2s AOs (Higher energy) AOs.
- Degenerate orbitals have same energy ($\pi_{2p_y} = \pi_{2p_z}$) ($\pi_{2p_y}^* = \pi_{2p_z}^*$)

Note:- • The extent of Stabalisation & destabalziation during formation of BMOs & ABMOs is equal.

- σ MOs are more stable so it has lower energy in comparn of π MOs. So from O_2 to Ne_2 the energy order of MOs is $(\sigma_{2p_x}) < (\pi_{2p_y} = \pi_{2p_z}) < (\pi_{2p_y}^* = \pi_{2p_z}^*) < \sigma_{2p_x}^*$.
- The elements of lower effective nuclear charge from H_2 to N_2 the energy difference b/w S & P orbitals is least & their are interactions b/w pair of orbitals of the same energy. These interactions are repulsive like b/w σ_{2s} & σ_{2p_x} orbitals and similarly b/w σ_{2s}^* & $\sigma_{2p_x}^*$ orbitals.
- This leads to stabalisation of σ_{2s} & σ_{2s}^* orbitals and destabalization of σ_{2p} & σ_{2p}^* orbitals & that's why for molecules B_2 to N_2 order of molecular orbitals is:- (Same as upto 14 system)

29/Nov/2022 Engineering chemistry BAS-102

Unit-1 : Atomic & Molecular structure, chemistry of Advanced materials., Green chemistry. (1)

unit2 :- Spectroscopic Technique & stereochemistry (5)

unit3 :- Electrochemistry, chemistry of Engg. Materials (4)

unity :- Water technology, fuel & combustion. (3)

unit5 :- Materials chemistry. (2)

BY Dr. Archna Srivastava. Maam

(Chemistry of Advanced Materials)

* liquid crystals

• Distinct phase of a matter observed between the crystaline (Anisotropic) solid and simple liquid state is known as liquid crystals. (Isotropic)

Solid state $\xrightarrow[84^\circ C]{\Delta}$ liquid crystal $\xrightarrow[150^\circ C]{\Delta}$ liquid state

• Anisotropic :- All physical properties in different directions.

• Isotropic = All physical properties in same directions.

PROPERTIES # IMP POINTS #

• liquid crystals has broad light molecular structure & the molecules points along a common axis known as director.

The liquid crystal shows some properties of solid state and some properties of liquid state.

The liquid crystals have important character of solid state as anisotropy and shows double refraction of light, interference pattern in polarised light

the liquid crystal shows the flow, surface tension, viscosity etc. properties like liquid. Eg: Screens, LCDTV.

The solid state of the substance has longer range of ordered arrangement of Molecule and definite orientation and when it changes to liquid crystal, it retains the orientation but shorter ordered arrangement result.

The important property in some liquid crystal for the practical application is the arrangement of molecule can be upset by very slight change in their temperature or electric field. Eg = • para-azoxyanisole
• ethyl para-azoxy benzoate

(Types of liquid Crystals) # 30/Nov/2022

1. Smectic liquid crystal (Soap like) (SLC)
2. Nematic liquid crystal (Thread like) (NLC)
3. cholestroic liquid crystal () (CLC)

(Smectic liquid crystal) # (SLC)

structure.

- In which molecule maintains the general orientational order. These retain long range order.
- In liquid crystal the parameter which is described are Positional order, orientational & Bond orientational order.
- The tendency of smectic (LC) are alligned themselves in layer or plain. ie: positional order. ∴ it flows in layer. The layers are held together by weak inter layer force and hence they flow past each other.

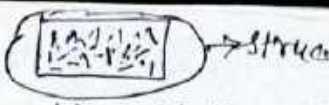
Examples = Cholesteryl Oleyl carbonate

formula = $C_{27}H_{40}O-COO(CH_2)_6CH=CH(CH_2)_7\cdot CH_3$.

structure.

(Nematic liquid crystal) # (NLC)

- It contains thread like structures/textures with no positional order but tendancy to point along the director.
- Nematic phase is less ordered than Smectic phase
Eg = premethoxy cinamic Acid.
- This (NLC) can't conduct (I) in pure form.

• In this Now: # (Cholestrolic LC) # 

• In this type of molecules are arranged in same as nematic type. but its molecules are optically active. It has high optical rotation.

• These are named cholestrolic (LC) Because the skeleton of the substance passing through this state is similar to that of cholestrol.

• Also known as Chiral nematic (LC)

Examples - • cholestery benzoate
• cholesteryl esters

(Applications of liquid crystal) # 30/Nov/2022

① In LCD - (liquid crystal Display), LCD TV, Projector,
② In Lubricant, isotropic liquid have been used in gas liquid chromatography
③ Thermography for detecting tumor.
④ In liquid crystal thermometer for measuring skin temp.

(Learn only for safety) (Since 2017 Not Asked) 01/Dec/2022

Q#1 Discuss the principle & working, Appl^n of liq crystal in LCD? (5marks)

Ans:-

* Principle of Display *

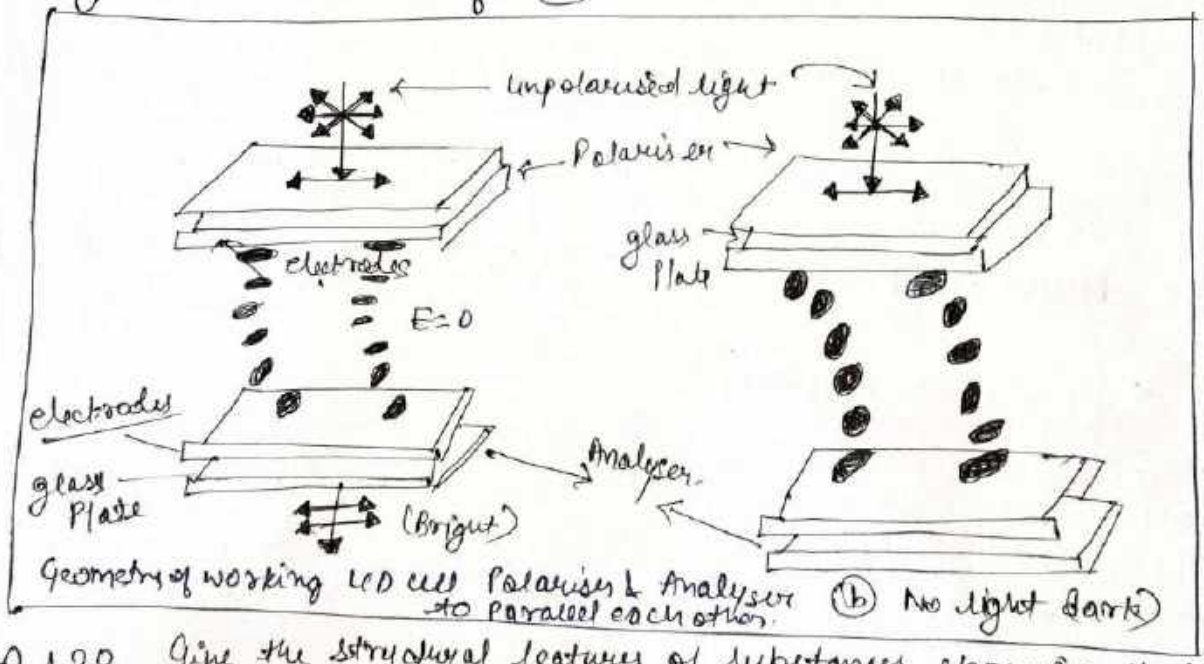
• The molecules in LDC is fluidy liquid crystal phase are mobile and their movement, allignment in thin film can be controlled by application of small electric field. due to this nature the molecule in different directions have different optical properties.

• A LCD consists of an array, of tiny segment called as pixel, that can be manipulated to present the information
• Each one of the pixels effectively seperates red, blue, green that can be switched on or off very rapidly. Electronically to rotate light to make coloured picture. by using (LC).

#(Working) of LCD

Polariser · Pass light · Pass no

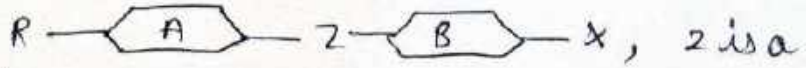
- The (LC) have rod like molecule and can be rotated the direction of polarised light based upon alignment.
- The alignment of molecules can be controlled by application of electric field.
- A twisted nematic liquid crystal display cell consists of 2 glass plates with conductive transparent [Indium Tin Oxide] coating and nematic crystal liquid material sealed like passing through one polariser b/w them. There is a Polariser.
- There is a special tool to control cell gap.
- Light passing through polariser has its polarisation with the alignment direction of (LC).



Geometry of working LCD cell Polariser & Analyser to parallel each other (b) No light (Dark)

Q.1.20 Give the structural features of substances showing liquid crystal behaviour?

Ans:- Molecular Structures play an important role in determining the phase, transition, temperature optical & electro-optical properties of liquid crystal. Many liquid crystal have chemical structure represented as R is the side chain group.



, Z is a linking group & X is terminal grp.

Chemistry 01 Dec 2002

R :- The side chains are in the form of alkyl, alkoxy or alkenyl groups, The length & flexibility of side chain effect the phase transition temperature & the type of liquid crystal depends upon it.

eg :- if no of carbon atoms in R is 1 or 2 then the substance doesn't show (LC) behaviour. if no of carbon atom in the side group are 3 to 7 nematic phase occur. if carbon atom are 8 or higher in R. then smectic phase appears.

A & B :- Aromatic ring A & B may be same or different. The substitution over the rings by -CN, -F, -Cl polar group which changes the dielectric property of (LC)

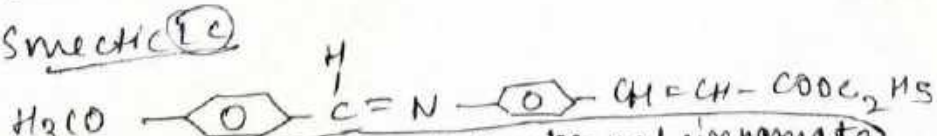
(Z :- linking group Z makes contribution to phase transition temp & other physical

Properties

The linking group can be like :-
Ester (-CO -O-) , ethylene ($-CH_2-CH_2-$), azo -N=N- etc.
The linking group like -N=N-, -CH=CH- help for delocalization or resonance at longer length and the electronic transition takes place at longer wavelength.

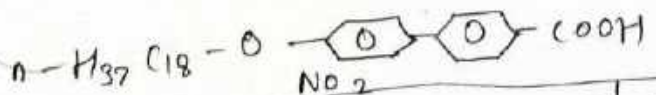
- Terminal group X contributes to dielectric anisotropy. The X may be like -CN, -OR, -R, -CNO, $-CF_3$, -Cl etc. The stronger e^- attracting (-I effect) groups increases the dielectric property to larger extent. some examples of liquid crystalline compounds are:-

① Smectic (LC)



(77 - 118°C)

Ethyl P - ethoxy benzal cinnamate



(159 - 195°C)

P' - N - octadecyloxy 3' - Nitro diphenyl Carboxylic Acid.

02/Dec/2022 | Ans-2 (1.20.1).

# R. above 8 C (smectic)
# Z = linking group Ex:- Ester, ethylene.
# R - alkyl (1,2c) does not shows LC behaviour.
# R → 3,7 carbon atom (Nematic)
X = Terminal grp. (-N≡N-Cl) etc.

[Important Materials used as liquid Crystals]

- (LC) material plays an important role in various industries:-

1) Cholestryl benzoate :- In making hair color (Dyes), makeup & cosmetics. prep^n. and In LCD.

2) p-azoxy anisole (PAA) = having high cost, applications electrical & electronic components, aerospace application.

3) liquid crystal Polymer = Ex = fibers (Polyamide) heat resistant fibres for making aerospace & military applications. such as bullet proof jacket, marine hull, polyester, rope & cord application, creep elongation of it for fire clothes.

- fire resistance coating of fibre optical cable, used for moduling with improved elastic module.

4) Ammonium Oleate = used for making commercial lubricants which can be applied in various machines at industrial level.

[Graphite]

It's an allotropes of Carbon in which carbon atom are of SP_2 hybridisation.

$C_6 = 1s^2, 2s^2, 2p^2$

1s	2s	2p
↑↓	↑	↑ ↑

Ground State.

C : excited state

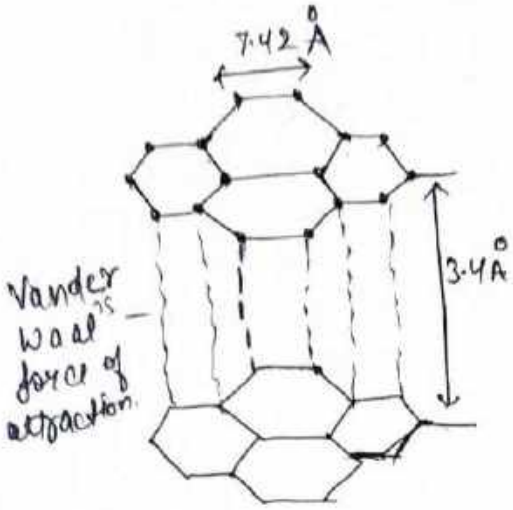
1s	2s	2px	2py	2pz
↑↓	↑	↑	↑	↑

[02/Dec/2022] chemistry.

- SP_2 carbon has 3 hybrid orbital at 120° angle in ⊥ plane and 1 unhybrid orbital having $1e^-$ at right angle to the plane.

[5/Dec/2022]

Graphite structure



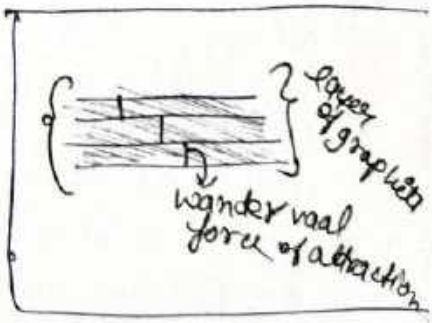
C-C → 1.42 Å

Properties

① Conduction Properties:- Attachment of every carbon with another 3 carbon atom.

- 1/4 πe^- is free; free e^- can move throughout graphite sheet.
- it makes graphite a good conductor.

② lubrication Properties:-



- graphite has hexagon structure or it has in the form of layer.
- sliding nature (easily rapture)
- it has higher chemical reactivity than diamond. because C=C double bond
- graphite sheet on folding from carbon nanotubes

(Applications of Graphite):-

- It can be used to be good conductor,
- its used to form electrode, rocket nozzle, nuclear vessel, lead pencil.
- its a good lubricant, graphite is good lubricant > than MoS_2 because its stable at high temp.

(fullerene)

- its an allotropic form of carbon (hollow), spherical cluster.
- smallest fullerene is carbon 20 but its extended carbon 600

Structure

Carbon 60:- Buckminster's fullerene

carbon 120 : Pentagons
carbon 20 : Hexagons

- Two pentagon cannot share a common side.

Synthesis:-

Graphite Rod $\xrightarrow[\text{Electric of Phyl}]{\text{Vapours}}$ Mix of fullerene. (separated by solvent extraction Method)

16/Dec/2022.

(Properties of fullerenes)

- it has conduction properties.
- pure fullerenes acts as a semi-conductor.
- if fullerene doped with alkali metal, it behaves as super conductors.
- Mustard colour changes to dark brown.
- it gives magenta colour solution when dissolved in Toulene.

(Application of fullerenes)

- its used as superconductor.
- C60 used as a catalyst antioxidant.
- Various derivatives of fullerenes acts as inhibitor of HIV.
- its used as a sensors, used in formation of carbon nano tube, nano wire

06/Dec/2022 Chemistry

$(1nm = 10^{-9} m)$ # (Nanomaterials) # (Nanotechnology) #

nanotechnology is the science of designing, producing & using structures & device having one of more dimension of about few nanometer to 100 nm.

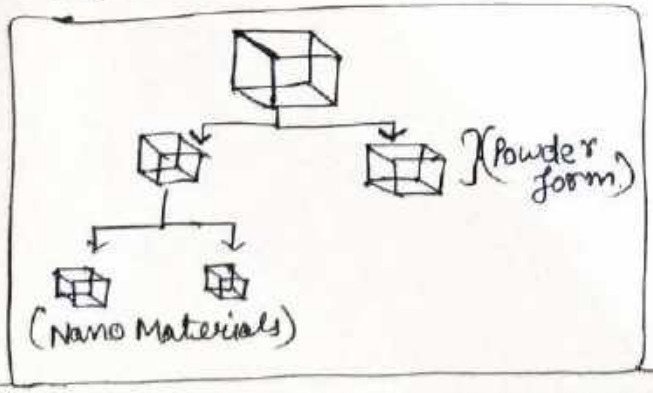
Simple materials (natural property) $\xrightarrow{\text{converts to}}$ Nano material (1nm - 100 nm) (will show different properties of simple materials)

	Material	Simple Properties	Properties of Nanomaterial
1	Silicon	insulator.	Conductor / Semi
2	Platinum	As an inter material	catalytic Properties
3	Aluminium	Stable	combustible

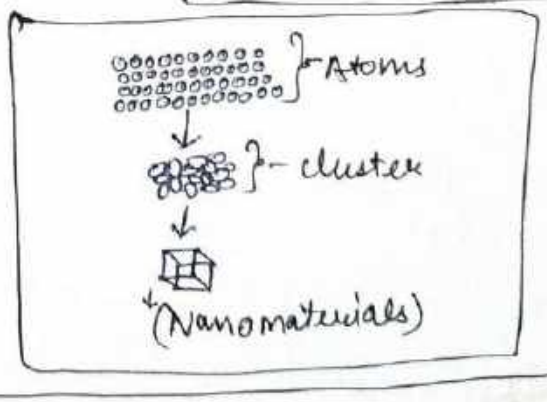
07/Dec/2022

{Preparation of Nanomaterials}

1 * Top to bottom Approch *



2 * Bottom to up approch *



Properties of Nanomaterials

1) optical properties :- Metallic nanoparticles & semiconductors

① Metallic nanoparticles :- The glasses of windows are made up of dissolving small amount of metal particles like gold, silver, cobalt, iron, nickel.

7. Dec 2022 (chemistry)

- Gold metal nanoparticles produces intense red colour against yellow appearance of bulk gold metal

(a) Semiconductor Nanoparticles : (NP)

- They have valence band and conduction have minute or finite energy gap. where as simple metallic (NP) behaves like insulator.

(B) Electrical Properties :-

- high current density/area cross section
- Variable electrical conductivity.
- high heat conductivity.
- Anisotropic thermal conductivity
- super conductor under cond^n.
- field emission props.

(C) Magnetic Properties :-

- used in electronic circuit, transformers, motors, sensors.
- reducing magnetic components from nano materials data capacity is improved.
- Magnetic materials are converted into nanomagnetic as they are reduced at least in one of the dimensions

(D) Structural Properties of nanoparticals

- lattice parameters may not be same as in bulk.
- that is a little lattice contraction of 1% for 1.4nm ZnS nanop.
- on applying pressures structural transformations may occurs.

(e) Mechanical properties of nanoparticles (NP)

- Depends on building materials,
- may be weak / strong by presence of impurities
- Jab clay nanoparticles ko cluster krke polymer create hoga toh voh ek strong plastic hoga.
- Different nanostructures have various mechanical properties.
- High tensile & compressive strength, flexible, high young's modulus.

07/Dec/2022 Chemistry

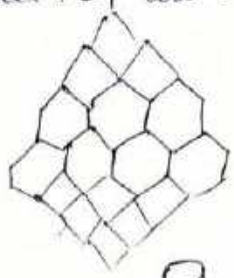
(Application of Nanomaterials)

1) in Diagonis :- DNA segment, Genetic sequencing
2) specific Drugs delivery :- Medicines delivered.
3) Reduction in energy consumption. increases the efficiency and energy produce.
4) Info & communication :- Making of memory card, TV screens, monitor etc
5) food science :- food safety & food packaging
6) In medical :- Detection of HIV, & repairing of diabetes.

8/Dec →

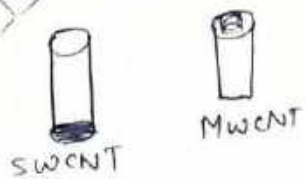
(Carbon Nano tubes) # (CNT) (100% sure for short Note).

- A graphene sheet which has been rolled up into cylindrical shape is called (CNT).



- Graphene :- A single sheet of graphite

Types :- (1) single walled CNT
(2) Multi walled CNT



- Many properties of SWCNT depends on (NM) type.
- CNT is the strongest & stiffest material.
- unlike graphene which is 2D semimetal, CNT are metallic, semiconducting along with tubular axis
- CNT have extraordinary electrical conductivity, heat conductivity.
- Best e^- field emitter.
- Polymers made of pure carbon & can be reacted and manipulated using the well known rich chemistry of carbon.
- CNT can exhibit remarkable electrical conductivity which others are semiconductors.

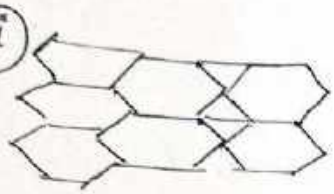
(Classification of CNT)

09/Dec/2022

① According to No of layers
ⓐ Single walled CNT
ⓑ Multiwalled CNT.

(Structure of CNT)

(i)



Armchair

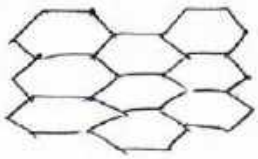
- Its electrically conductive.
- Tube axis is parallel C-C Bond.

(ii)

Zigzag (Semiconductor)

- Tube axis is ⊥r to C-C Bond

(iii)



Chiral (Helical)

C-C bond are inclined to tube axis

(Properties)

(i) electrical property • they are mettallic, semiconducting depending on the diameter & chirality.

- energy gap $\propto \frac{1}{\text{diameter}}$ in conducting chiral CNT.
- Band gap of CNT varies from 0.2 to 1.2 ev.
- In SWCNT's conduction occurs by discrete electric states.

∴ So it can be treated as quantum wires at very low temp.

(ii) Mechanical Property :- ① The mechanical strength of CNT is high (C-C Bond is strong).

② Young's Modulus of CNT = 18T Pascals.

③ CNT have high stability to withstand extreme strain

④ CNT can recover from severe structural distortions

(iii) Physical properties:-

- strength to weight ratio is high (around 100X of steel)
- Density of SWCNT = $0.8 g/cm^3$
  MWCNT = $1.8 g/cm^3$.

(iv) chemical property:- CNT's are highly resistant to chemical reactions.

(v) Thermal Property:- Thermal conductivity of CNT is high. its value increase with decreasing diameter.

(Application of CNT)

- used in flat panel display.
- used in vaccum tube lamps., Good brightness.
- Plastic composets is a good light weight shield from electromagnetic radiation.
- used to make field effect transistor.
- High thermal conductivity, low resistance: used as interconnect in chips.
- used as gas sensors
- used in battery technology.

(Green Chemistry)

- Use of chemistry for pollution prevention by means of proper design of chemical products and process that reduce or eliminate the use of/generation of hazardous substances.

(Principles of Green chemistry)

- Prevention of waste
- Maximize atom economy
- less hazardous chemical syntheses.

(4) Design safe chemicals
(5) safer solvent & Auxiliaries
(6) Design for energy efficiency
(7) use of Renewable feedstock (Raw materials)
(8) Reduce derivatives
(9) use of catalyst
(10) Design for degradation
(11) Real time analysis for pollution prevention
(12) safer chemistry for accident prevention

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(Prevention of waste)

- tonnes of Hazzard waste are released into air, water & land by industry every day.
- its better to prevent waste than to treat or clean up waste after its been created.
- Ability of chemist to redesign chemical transportation to minimize generation of hazard waste is an important step.

Example:- Chemical process should be designed in such a way that less Biproduct are formed (HCl, O_2, Cl_2 or H_2)

VVIMP # (Atom Economy) #

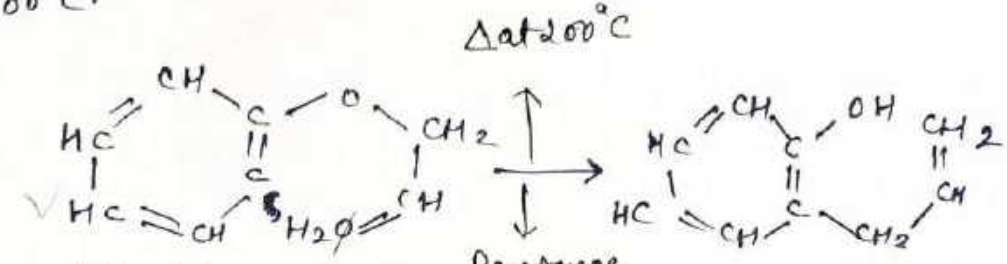
- its a method of expressing the efficiency of a particular reaction in which reactant atom incorporated into the final product.
- The main objective of this concept is to develop a new synthesis in which most of the reactant atom become incorporated into final desired product.
- The % of yield of any reⁿ is calculated by

$$\% \text{ atom economy} = \frac{\text{Mass of atom in desired Product}}{\text{Mass of atom in reactants}} \times 100$$

12/Dec/2022 Chemistry

eg :1) Rearrangement reⁿ :-

Allyl Phenyl ether give o-allyl Phenyl by heating at 200°C.



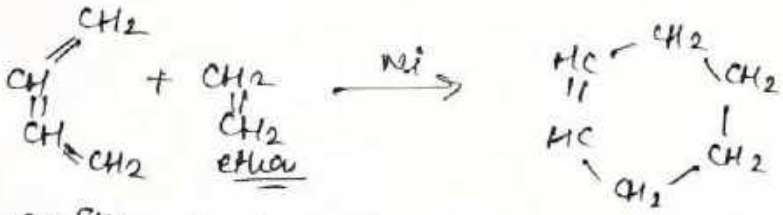
Allyl Phenyl ether (MW = 134.175gm)

o-allyl Phenol (MW = 134.175g) (Desired Product)

% of atom economy = $\frac{134.175}{134.175} \times 100$ = 100%

2) Addition Reaction :-

Butadiene.



MW = 54g MW = 28g.

Cyclohexene

* % of Atom Economy = $\frac{82}{54+28} \times 100$

= 100%

Ans 13/12/22

14/Dec/2022 chemistry

(2) Addition catalytic Reⁿ

$$H_3C-CH=CH_2 + H_2 \xrightarrow{Ni} CH_3-CH_2-CH_3$$

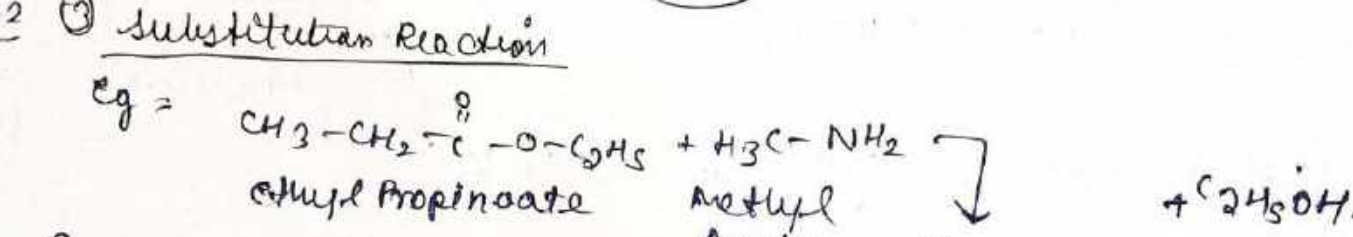
Propene (MW = 42g) | MW = 2g | Propane MW = 44.5

Atom economy = $\frac{44}{42+4} \times 100 = \frac{\cancel{44}^{1}}{\cancel{44}} \times 100$

= 100 %

(3) Substitution Reaction

eg =

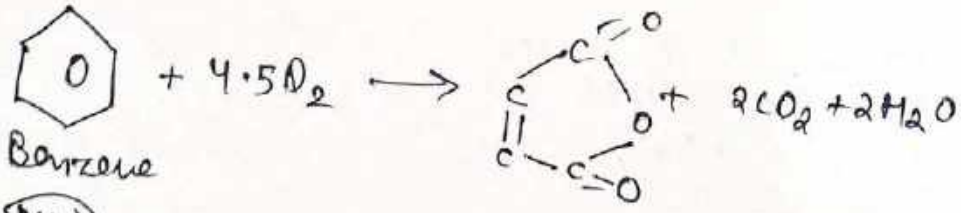


Ethyl Propinoate (MW = 102.132g m) | Methyl Amine (MW = 31.056gm) | (Desired product) (87.70g)

% atom economy = $\frac{87.706}{133.189} \times 100$.

$\boxed{65.40\ \%}$

(4) Oxidation Reaction:-



Benzene (MW) (78 gm)

Maleic anhydride desired product MW = 98 gm

% atom economy = $\frac{96}{78+144} \times 100$

$\boxed{= 43.243}$ %

Date / /

GREEN CHEMISTRY

Introduction of Green chemistry:

An ideal chemical reaction shoul have a no. of attributes such as:

- Safety.
- Simplicity.
- high yield.
- Use of renewable or recycleable reagents or raw materials.
- Absence of hazardous by products.

It is a challenge for chemist and engineers to find enviro-nmentally preferable reactions to balance all the points mentioned above.

- The solⁿ is green path way.
- Green chemistry is the design of chemical products and process that reduce or eliminate the use and generation of hazardous substances.

Marks (8) Names

12 principles of Green chemistry –

1. Prevention :– Avoiding or reducing waste regeneration is the first step in pollution prevention bcz the disposal of waste becomes so expensive and associated with many problems.

Example – Disinfection of water by chlorination generates harmful chlorinate compounds which can be prevented by using green oxidents like O_3 & $KMnO_4$.

2. Atom Economy :– The principle of green chemistry emphasize (include) maximum product formation by reactant. Atom economy is a major of the %age of reactant atom leading to product form.

②

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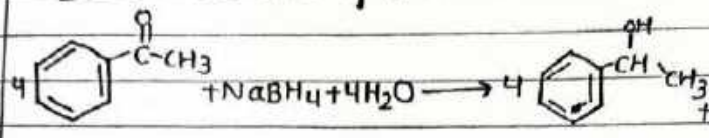
$$\% \text{ Atom Economy} = \frac{\text{Formula wt. of utilised product}}{\text{Formula wt of all reactant}} \times 100$$

Ex:- reduction of ketone into secondary alcohol.

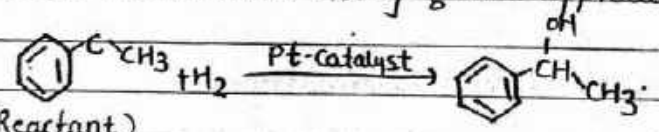


Reactants	form of reactant	utilised product	form. wt of products
$4C_8H_8O$	$4 \times 120 = 480$	$4C_8H_{10}O$	$4 \times 122 = 488$
$NaBH_4$	$1 \times 38 = 38$		
$4H_2O$	$4 \times 18 = 72$		
	590		488

$$\% \text{ Atom Economy} = \frac{\text{Fw of product}}{\text{Fw of Reactant}} \times 100$$

$$= \frac{488}{590} \times 100 = 82.7\%$$

Some conversion using green approach is as follows:



(Reactant)

C_8H_8O	120	$C_8H_{10}O$
H_2	2	
	122	

$$\% A.E = \frac{122}{122} \times 100 = 100\%$$

Q:- Calculate the % AE and waste % for given reaction.

Ans: $CH_4 + H_2O \longrightarrow CO + 3H_2$.

Reactant	Fw of reactant	Utilised product	F.w of product
CH_4	16	CO	28
H_2O	18		
	34		

$$\% A.E = \frac{\text{F.w of product}}{\text{F.w of reactant}} \times 100 = \frac{28}{34} \times 100 = 82.35\%$$

VISTA

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3. Minimization of Hazardous chemical synthesis :—
Green chemistry aims at adopting those synthetic process ure which use on produce non-toxic products which do not harm the living organism and environment.

4. Design safer chemicals:—The reaction product should be designed in such a way that they should be fully effected without having any toxic effects.
Example:— CFC causes ozone depletion due to release of chlorine free radical which can be prevented by hydrofluoro carbons in which chlorine group is replaced by hydrogen.

5. Use of safer solvents and Auxiliaries (helping reagent):—
The use of Auxiliary substance in purification and seperation generally produce carcinagetic and volatile products which should be minimized.
Example:- In dry cleaning liquid CO_2 is used in place of per chloro ethylene for cleaning of grease.

6. Design for Increase in Energy efficiency :— Chemical reactions generally require a lot of energy which comes from the use of fossil fuels, green chemistry includes the development of process carried out at room temp. or the energy can be supplied by photochemical or microwave process.

7. Selection of renewable feed stocks at starting material:—
Green chemistry includes the need to use raw materials that are renewable.
for ex:- In electricity generation instead of coal, biomass or bagasse should be used as a fuel.

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8. Reduce or avoid chemical Derivatives:- Green chemistry avoids adding extra steps and modification of chemical process as they require addition reagents and can generate extra waste. (Synthesis of adipic acid).

9. Use of catalyst:- Use of selective catalyst increases the speciality of the reaction and reduce the formation of by-products.
Example:- Hydrogeneation of Alkyne ~~to~~ into alkene in presence of a stereo selective catalyst.
propyne $\xrightarrow{H_2(Pd-BaSO_4)}$ propene.

10. Products Design should be Biodegrable after use:- Chemical substances are design in such a way that they degrade in the enviroment to give harmless and products.
Example:- In place of DDT, Diarylhydrine should be used as pesticides or insecticide.

11. Analysis in real time to present pollution:- Analytical methods should be adopted to allow process monitering and control which minimize the formation of toxic substances

12. Use of safer chemicals for accident prevention:- Chemicals should be design in such a way that they do not cause severe accident like fire explosion in case of accident or in that way they convert into non-toxic products.

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Importance / Significance of Green Chemistry / Green Synthesis:-

The chemical Industry releases about 5 Billions tons of chemical waste for year and 3 hundred Billion dollars have been spend for the treatment of waste.

Green synthesis helps in following ways -

- To avoid the production of harmful by products.
- It is an ecofriendly method, which is based on using ecological solvents, reduce energy consumption, reduction of toxid products e.t.c.
- To reduce adverse environmental impact, try appropriate material and their chemical transformation.
- To improve energy efficiency by developing low temprature and low pressure process using new catalyst.
- To develop the process that are less chemical release fire and explosion.
- To develop the process which is based on renewable raw materials rather than non-renewable materials.
- It is responsible for clean air, clean water, increase safety for worker in various industries.

Adipic Acid

Mark (5)

- Adipic acid is used for the production of naylon as a monomers.
- Around 60% adipic acid is used for synthesis of naylon.
- It is also used in many drugs.

Synthesis by conventional Method / Route:-

Step 1:- Reduction of Benzene to cyclohexane using Roney Nickel and hydrogen.

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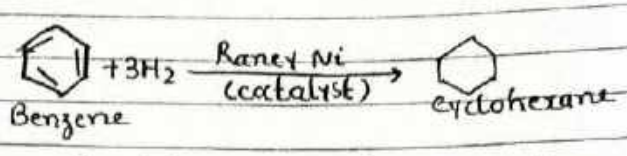
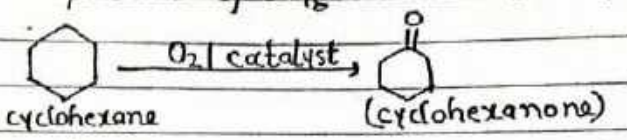
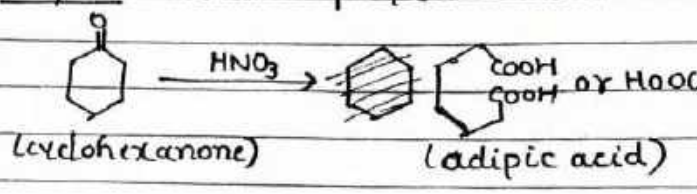


Step2:- Oxidation of cyclohexane into cyclohexanone in presence of oxygen and catalyst.

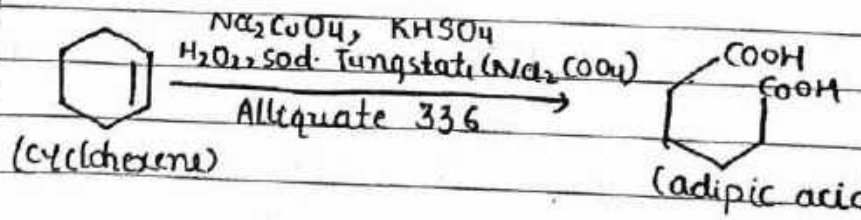


Step3:- Oxidation of cyclohexanone into adipic acid.



* Green route of Synthesis:- With the help of green route adipic acid can be synthesis in a single step.

For synthesis of adipic acid we use cyclohexene which convert into adipic acid using various catalyst such as H_2O_2, sodium Tungstate, Alliquat 336 which is an organic solvent.



* Second Green Route of Synthesis of Adipic Acid:-

This route is based on enzyme catalysis and the reacⁿ takes place in 3 steps.

Step1:- Reduction of glucose by E-coli (Escherichia coli)-

In this step glucose converts into 3-hydroxyshikimate.

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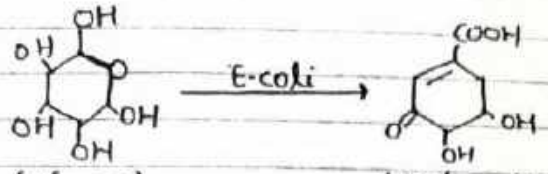
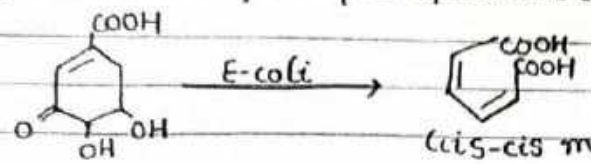
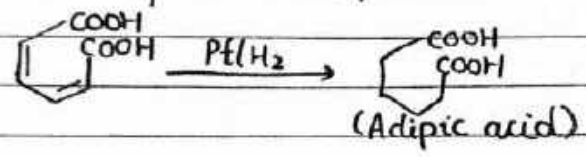


Step 2:- Reduction of 3 hydroxyshikimate by E-coli.



Step 3:- Reduction of cis-cis muconic acid into adipic acid in presence of a catalyst.

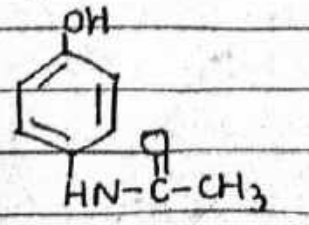


Drawback of conventional Method:-

The starting material which is used in conventional method of adipic acid is benzene which is carcinogenic and volatile in nature and pollute air so we should prefer the green route of synthesis of adipic acid.

Paracetamol

- It is also known as Acetaminophen.
- It is a medicine which is used in treatment of fever, mild to moderate pain, It is essential medicine as per WHO.
- The IUPAC name of paracetmol N(4-hydroxy phenyl) ethanamide.



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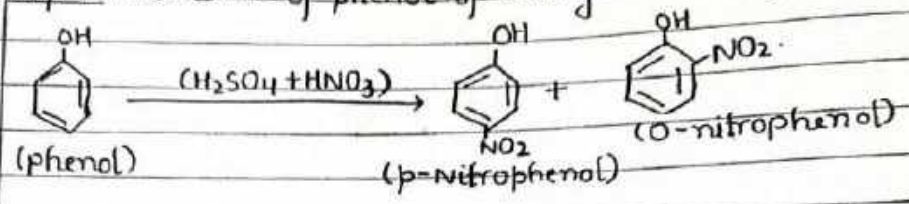
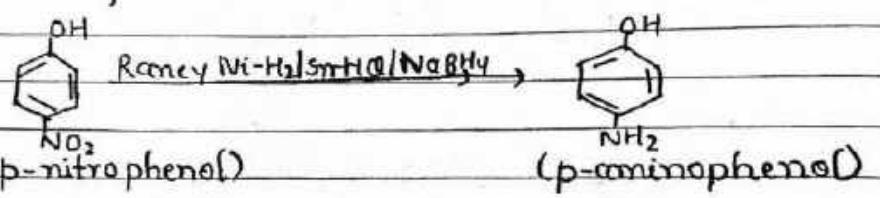
* **Synthesis of paracetmol by conventional route –**

It is a 3 step process –

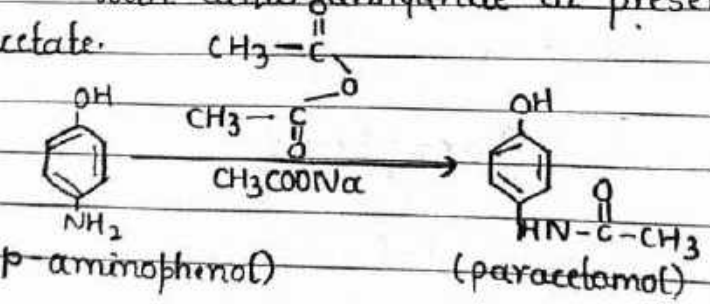
Step1:– Nitration of phenol of using Nitrating Mixture.



Step2:– Reduction of nitro group into amine group using reducing agent such as Raney Ni, Tin in the presence of acidic medium or sodium boro hydride.



Step3:– Nucleophillic addition reaction of p-aminophenol with acitic anhydride in presence of sodium acetate.



Drawback of Conventional Method –

In conventional method of synthesis the percent atom economy is calculated about 36% only and the remaining are wasted as by product.

Hence, the green route of synthesis of paracetmol should be used to increase the percentage of atom economy.

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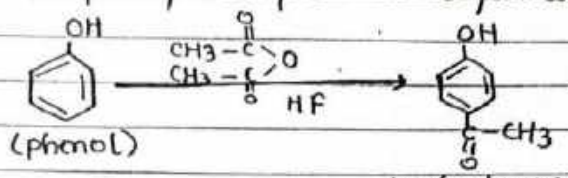
* Green Route of Synthesis—

It is direct acylation of phenol with acetic anhydride in presence of a strong catalyst.

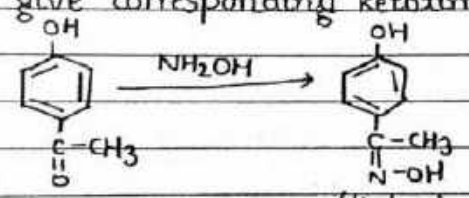
It is a 3 step process

Step 1:— Reaction of phenol with acetic anhydride by which 4-hydroxy acetophenone is formed as a product.



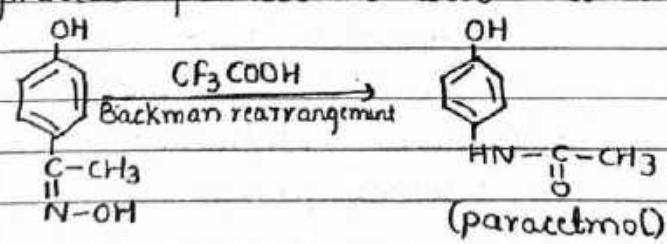
(phenol) (4-hydroxy acetophenone)

Step 2:— Reduction of 4-hydroxyacetophenone with hydroxylamine to give corresponding ketoxime.



(Ketoxime)

Step 3:— Oxime in acidic medium undergoes backman rearrangement to produce paracetmol used acid is trifluro acetic acid.



(paracetmol)

Percent Atom Economy of this route is 58%.

* Green chemicals:— A green chemical is one that provides higher performence and functionally while being more environment friendly and not harmful throughout its entire life cycle.

VISTA

Date / /

Green chemicals are ecofriendly chemicals that are used in various process without generating harmful or hazardous substances. Some of them are as follows:

[A] Green Solvents:- Solvents play an important role in most chemical reactions but there is no solvent which is considered as green solvent because the role of solvent is limited to specific reaction.

e.g;

- water and alcohol can be used as a green solvent in various chemical reactions.
- Ionic liquids are non-volatic organic compounds which can be used in manufacturing of paints.
- Super critical water (water without hydrogen bond):- It is formed at temprature 647K and pressure 210atm. It is capable to dissolve organic solvent like ~~pa~~ paraffins which are in general not soluble.
- Liquid CO_2:- It is used for dry cleaning instead of using chlorinated substances.

[B] Green fuel:- Biodiesel which is an environment friendly fuel.

[C] Green oxidants:- Ozone and $KMnO_4$ are used in disinfection of water.

[D] Supercritical fuel:- e.g; CO_2:- which is used as a blowing agent without using any hazardous chemicals.

VISTA

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(E) Green plastic:— Green plastic or bio plastic is a category of biodegrable plastic which is used for food packaging.

(F) Hydro Fluoro Carbons:— It is used in placed of CFC to reduce ozone depletion.

(G) Zeolite:— It is used as a catalystic, having by functional applications. It is used in removal of permanent of Hardness of water and also used in Hydrocarbon transformation.

Environmental Impact of Green Chemistry:—

- Low level of chemical release to the environment.
- Green chemistry reduces emission and product impact.
- Plants and animals suffers less harm from toxic chemicals in the environment.
- Green chemistry lower potential for global warming, ozone depletion and smog formation.
- It is responsible for clean air, clean water.
- It improves the safety condition for workers.
- Less use of landfills which impact the quality of food products.

13/12/22

Unit - 5.
Material Chemistry

#. Polymers

The word polymer means "Many parts" it is a compounds of High molecular weight molecule. It is formed by many smaller units (Monomer). Polymer are the long chain molecule.

$$\ldots -M-M-M-M-M- \ldots$$

polymer (long chain)

$$[M]_n$$

e.g. $nCH_2=CH_2 \xrightarrow{\text{Heat Light}} [CH_2-CH_2]_n$

ethylene → polyethylene

Monomer :- It is small unit which make long chain molecule.

Repeat Unit :-

$[A-A-A-A]_n$	$[A-B-A-B-A]_n$
monomer — A	Monomer — A & B
Repeat unit — A	Repeat unit — $[A-B]$
Homopolymer	Hetropolymer

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Polymerisation.

The process of joining large no. of simple molecule to form large polymer molecule is known as polymerisation.

Ex.

$$\underset{\substack{\text{ethylene} \\ \text{(Monomer)}}}{nCH_2 = CH_2} \longrightarrow \underset{\substack{\text{polyethylene} \\ \text{(Polymer)}}}{[CH_2 - CH_2]_n}$$

B.)

* Degree of polymerisation

Degree of polymerisation is the average no. of repeating unit in the molecule of polymer

Degree of polymerisation are found in homopolymer single type of monomer but in hetropolymer the degree of polymerisation are not defined (not calculated) c).

Classification

1.

A) On the basis of monomers.

Homopolymer	Hetropolymer.
It is made up of single type monomer unit	It is made up of different type of monomer unit.
$[A-A-A-A]_n$	$[-x-y-x-y-x]_n$
e.g. Polyethylene polystyrene Polyvinlchloride (PVC) etc.	e.g. Buna-S, Buna-N Nylon 6 Nylon 6,6 Nylon - 10, etc.

Hetropolymer.

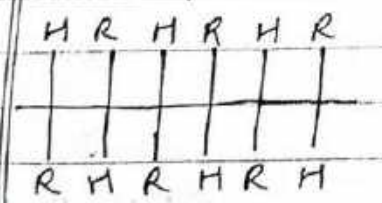
- Regular Hetropolymer $[x-y-x-y-x]_n$
- Irregular Hetropolymer $[x-x-y-y-x-y]_n$

B.) On the basis of arrangement or structure of monomer.

- Linear $[A-A-A-A]_n$ e.g. HDPE
- Branched $[M-M-M-M]_n$ (M branches off M and M) e.g. LDPE
- Cross linked $[x-x-x-x]$ (x branches off x and x) e.g. Bakalite

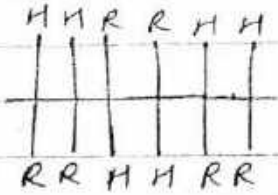
c). On the basis of Tacticity / Macromolecule / Sterespecific.

1. Isotactic



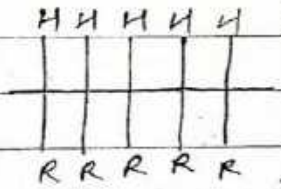
(Regular arrangement of Macromolecule) e.g. polyisoprene

Atactic



(irregular arrangement of Macromolecule) e.g. polypropylene

Syndiotactic or trans type



e.g. Gutta Percha

Polymerisation :- The process of formation of polymer.

Monomer $\xrightarrow{\text{Polymerisation}}$ Polymer

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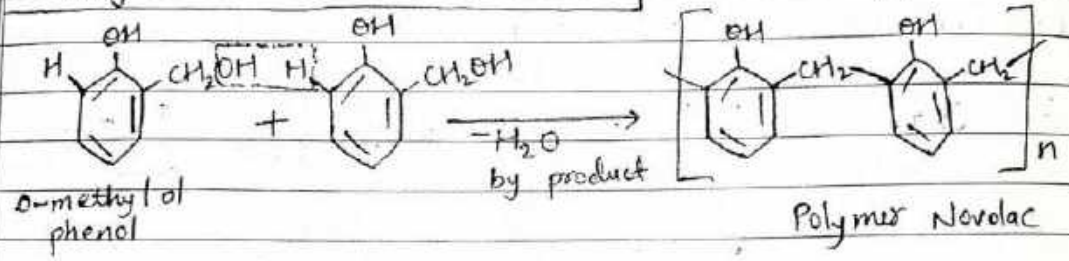
* Types of polymers

Polymer

Addition polymer	Condensation polymer
In which there is no by product formation	In which their is formation of by product
e.g. $nCH_2=CHCl \xrightarrow{\text{Polymerisation}} [CH_2-CHCl]_n$ (Vinyl chloride → PVC)	e.g. $-H_2O$, $-OH$, $-COOH$, $-NH_2$, etc.

e.g.



Mechanism of polymerisation.

Mechanism of polymerisation are catogories into three parts.

A) Free Radical polymerisation.

$$A-B \xrightarrow[\text{Fission}]{\text{Homolytic}} \dot{A} + \dot{B}$$

Free radical

(i) Chain Initiation step :-

$$I-I \xrightarrow[\text{bond fission}]{\text{Homolytic}} I^{\bullet} + I^{\bullet}$$

Free radical.

$$I^{\bullet} + CH_2=CH_2 \longrightarrow I-CH_2-CH_2^{\bullet}$$

ethylene → monomer free radical

(ii) Chain propagation :-

$$I-CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow I-CH_2-CH_2-CH_2-\dot{C}H_2$$

Monomer free radical + Monomer

$$I-[CH_2-CH_2]_{n-1}CH_2-\dot{C}H_2 + CH_2=CH_2 \longrightarrow I-[CH_2-CH_2]_n CH_2-\dot{C}H_2$$

elongated chain of polymer

(iii) Chain Termination :-

$$I-[CH_2-CH_2]_n CH_2-\dot{C}H_2 + I^{\bullet} \longrightarrow I-[CH_2-CH_2]_n CH_2-CH_2-I$$

polymer
polyethylene

B.) Anionic Polymerisation

(i) Chain Initiation – $x-y \xrightarrow[\text{bond fission}]{\text{Hetrolytic}} x^{\oplus} + y^{\ominus}$

cation anion

e.g.

$$y^{\ominus} + CH_2=CH_2 \longrightarrow y-CH_2-CH_2^{\ominus}$$

anion ethylene (monomer chain initing species)

(ii) Chain propagation

$$y-CH_2-CH_2^{\ominus} + CH_2=CH_2 \longrightarrow y-CH_2-CH_2-CH_2-CH_2^{\ominus}$$

$$y-[CH_2-CH_2]_{n-1}CH_2-CH_2^{\ominus} + CH_2=CH_2 \longrightarrow y-[CH_2-CH_2]_n CH_2-CH_2^{\ominus}$$

(iii) Chain Termination step.

$$y-[CH_2-CH_2]_n CH_2-CH_2^{\ominus} + x^{\oplus} \longrightarrow y-[CH_2-CH_2]_n CH_2-CH_2-x$$

polymer

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c.) Cationic Polymerisation

(i) Chain Initiation – $x-y \xrightarrow[\text{bond fission}]{\text{Hetrolytic}} \underset{\text{cation}}{x^{\oplus}} + \underset{\text{anion}}{y^{\ominus}}$

$$\underset{\text{cation}}{x^{\oplus}} + \underset{\text{ethylene}}{CH_2 = CH_2} \longrightarrow x - CH_2 - CH_2^{\oplus}$$

(cation chain initiation species)

(ii) Chain propagation.

$$x - CH_2 - CH_2^{\oplus} + CH_2 = CH_2 \longrightarrow x - CH_2 - CH_2 - CH_2 - CH_2^{\oplus}$$

$$x - [CH_2 - CH_2]_{n-1} CH_2 - CH_2^{\oplus} + CH_2 = CH_2$$

$$x - [CH_2 - CH_2]_n - CH_2 - CH_2^{\oplus}$$

elongation chain

(iii) Chain Termination step.

$$x - [CH_2 - CH_2]_n - CH_2 - CH_2^{\oplus} + y^{\ominus}$$

$$x - [CH_2 - CH_2]_n - CH_2 - CH_2 - y$$

polymer

D On the basis of molecular processes

① Elastomer ② Fibres ③ Thermoplastic ④ Thermosetting

1. Elastomer :- In elastomer the polymer chain are held together weakest intermolecular force. hence they can be easily stratched by applying an external force. and regain their orginal shape on removing the force.
e.g. Vulcanised Rubber

2. Fiber :- In this polymer the chain are held together by strong intermolecular force of Hydrogen bond.
e.g. Nylon6, silk, Nylon 6,6, wool, terylene, etc.

3. Thermoplastic :- It is a linear polymer made by monomer with only two functional
These are soften on heating and can be moduled to desired shape. In thermoplastic intermolecular force of Attraction are found and this force is intermediate elastomer and fiber.
e.g. Polyethylene, polypropylene, polystyrene, PVC, etc.

4. Thermosetting :- These are highly cross linked polymer they do not melt on heating and do not dissolve in any solvent.
e.g. Bakalite, urea, formaldehyde, melamine, etc.

Ques. Difference between thermoplastic & thermosetting. 3 Marks

Thermoplastic	Thermosetting.
1. They do not have cross link between the chain	1. They have cross links between the chain.
2. They soften on heating & hence can be moduled again and again.	2. They from cross-link on heating & hence become hard & infusible

3. They are soft & weak	4. They are formed by condensation polymerisation.
4. They are formed by addition polymerisation e.g. Polyethylene, PVC, Teflon, etc	3. They are hard & strong e.g. Bakalite, Melamine, formaldehyde, etc.

E. On the basis of functionality/structure :-

1) Linear or straight chain polymer :-
In these polymer monomers are joined together by covalent bonds to form long chains. Different chains are held together by vander waal's forces & form packed structure. These polymers have high M.P., high density & high tensile strength
e.g. Polytene, nylons, polyester, etc.

2) Branched chain polymer :-
In these polymers have branched or side chains in addition to main chain. due to side chain the main chains are less tightly packed. Hence these polymer have low M.P., low density, low tensile strength.
e.g. glycogen, starch, polythene, etc.

3. Cross linked Polymer :-
In these polymer, the monomers are cross linked togethers to form 3 dimensional network. To form cross linked, the monomer molecule should have at least two functional groups. These polymers are rigid hard & brittle.
e.g. Bakalite, formaldehyde, etc.

F. On the basis of type of monomers used :-

1) Homopolymer :- A polymer formed by polymerization of one type of monomer known as homopolymer.
e.g. :- Polythene, PVC, PMMA, etc.

2). Copolymers :- A polymer formed by polymerisation of more than one type of monomer is known as copolymer.
e.g. Nylon 6,6, Terylene, etc.

Ques. Difference between addition & conduction polymer.

Addition	Conduction
1. They are formed from unsaturated monomers	1. They are formed from bifunctional monomer.
2. No small molecules are eliminated during their formation.	2. Small molecules are eliminated during their formation.
3. Initiation is needed for their formation.	3. No initiation is needed for their formation.
4. Empirical formula of addition polymer is same as that of monomer used e.g. Polythene, Polystyrene, PVC, etc.	4. Empirical formula of condensation polymer is different from that of monomer used. e.g. Terylene, Bakalite, Nylon 6,6, etc.

V. Mark (5)

Polymer Blend

* If one or more polymers are mixed together to from polymer blend. There no chemical bond formation.
* Only physical crystal / mixture are formed.

$$\underset{P_1}{A} + \underset{P_2}{B} \longrightarrow AB.$$

Blend polymer

Types of Blend Polymer :-

① On the basis of Glass transition temperature (T_g) :-
At which polymer behave as a glass.
Ex. :- Rubber ball at T_g (−265°C) it behave as glass.

Homogenous / Missible

If there are two polymer blended together, but T_g is only one.

$$\underset{T_{gA}}{A} + \underset{T_{gB}}{B} \longrightarrow \underset{T_n}{\text{Blends}}$$

Ex. Mixture of PET with PBT
Polyethylene terithylete
Polybutylene terithylete

Hetrogenous / Immissible

If there are two polymer are blended together, but, T_g is observed a two different

$$\underset{T_{gA}}{A} + \underset{T_{gB}}{B} \longrightarrow \underset{T_{gA}+T_{gB}}{\text{Blend}}$$

Ex. PET with PVA.
Polyvinyl alcohol.

② On the basis of preparation of polymer blends.

(i) Mechanical Blend :- Amorphous and semicrystalline polymer mix together.

(ii) Solution cast blend :- It is used as common solvent.

(iii) Latex blends :- Dispersion of polymer in H_2O.

(iv) Chemical blend :- Cross linked polymer + monomer which get polymer.

Polymer Composites :-

1. It is 3 dimensional Combination of at least two material.
2. There is a chemical bond formation between materials.

Polymer Composites = Matrix phase + Reinforcing phase

- Matrix phase is the basic materials and it is tough material.
- Reinforcing phase is empowering material and it is strong and low density material.

The main part of composite polymer is different.

Types.

On the basis of Matrix phase Composites

- Metal Matrix Composite (MMC)
- Ceramic matrix composite (CMC)
- Polymer matrix composite (PMC)

(iii) Latex blends :- Dispersion of polymer in H_2O.

(iv) Chemical blend :- Cross linked polymer + monomer which get polymer.

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Types :

On the basis of Matrix phase

Composites

- Metal Matrix Composite (MMC)
- Ceramic matrix composite (CMC)
- Polymer matrix Composite (PMC)

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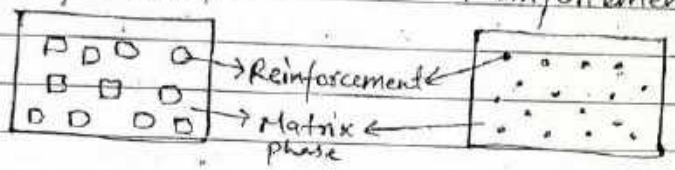
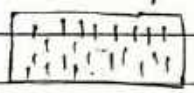
* On the basis of Reinforcement.

- Particle Reinforcement.
  - Large particle Reinforcement.
  - Small particle Reinforcement.
- Fibre Reinforcement.
  - Long fibre
  - Short fibre





Applications :-
Component of transport, Musical instrument, machinery, sporting material, Circuit board, etc.

Advantages :-
Economical, good thermal property, Corrosion resistance, low weight

Conducting polymer.

Polymer are bad conductor of electricity and hence some of them find application in electrical condition

The bad conductor of electricity cause of non availability of large no. of free e^- require for conduction.
A polymer which can conduct electricity is known as conducting polymer.

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* Conditions.

(i) They form conjugation $-[C=C-C=C]_n$

(ii) Doping

* Types

Electrically conducting polymer are classified into two parts.

① Intrinsically Conducting polymer (ICP)

② Extrinsically Conducting polymer (ECP).

1. Intrinsically Conducting polymer. (ICP)
(Compound can not change the central atom)
Doping the side chain

① Polymer having conjugation or conjugated polymer

② Dopped conducting Polymer
① → P dopping
② → N Dopping

2. Extrinsically Conducting polymer (ECP)
(change the central atom chain by the External factor).

* Types.

① Blended Conducting Polymer

② Co ordinate C.P.

③ Conductive Element filled polymer

#. Conjugated Polymer.

① These polymer have πe^-

② Polymer placed in electric field by the π electro conductivity behaviour.

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③ π e^- get change excited state. (Moving from Ground State to excited state).

④ Overlapping of Valence band & conduction band. It make the polymer a good conductor.

e.g. :- Polyacetylene, polypyrrol, polyphenylene.

① $nCH \equiv CH \xrightarrow{\text{Polimerization}}$

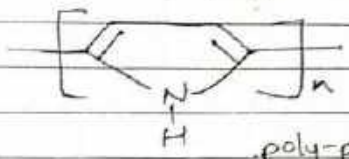
Acetylene

Trans polyacetylene

②

pyrrole

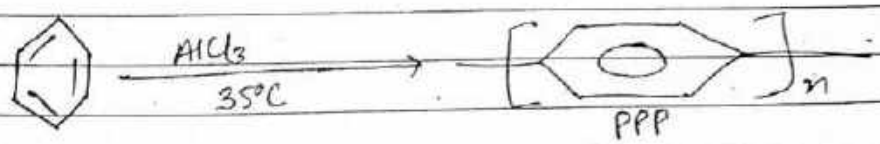
$\xrightarrow{\text{Polymerization}}$



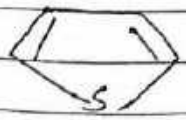
poly-pyrrole.

Polyphenylene.

③ Poly (p-phenylene) (PPP)

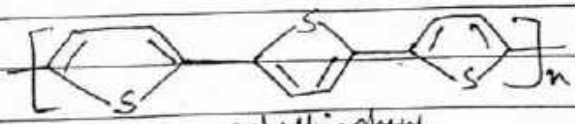


④ Poly thiophenes.



Thiophene

$\xrightarrow{\text{Polymerization}}$



polythiophene.

Doping.

P doping	N doping.
→ It form oxidation	→ It form reduction
→ With use Lewis acid	→ With use Lewis base
→ Develops +ve charge on polymer	→ Develops −ve charge on polymer.
$P + Acid \rightarrow P^{\oplus} - Acid^{\ominus}$	$P - base \rightarrow P^{\ominus} - base^{\oplus}$
e.g. $\underset{\text{Polyacetylene}}{(C_2H_2)_n} + \underset{\text{acid}}{2FeCl_2}$	$\underset{\text{Polyacetylene}}{(C_2H_2)_n} + \underset{\text{base}}{NH_2}$
$(C_2H_2)\ FeCl_4 + FeCl_2$	$C_2H_2)^{\ominus}\ NH^{\oplus} + H_2$

2.# Extrinsically Conducting polymer.

(i) Conductive element filled polymer
In this type of polymer generally posses reasonable amount of conductivity.
This polymer acts as the binder to hold the conducting element such as metallic fibres carbon black. Metal oxides together in the said entity.

These are usually low in cost, light in weight, mechanically sound & easily processable in different form shaped & size.

(ii) Blended Conducting polymer

The blending of a conventional polymer with a conductive polymer result of the formation of blended conductive polymer.
These polymer posses physical, chemical, electrical, Mechanical property

Application
i) Producing
ii) Make button type battery
(iii) Electro chemical accumulation, solar cell, transistor.

Biodegradable Polymer.

A large amount of polymeric material used as a plastic fibre & ~~Elest~~ Elastomer. These do not offer serious health problem through the main problem associated with the disposal of polymer waste these create accute environmental problem.
A biodegradable polymer is One that would be decomposed by microorganism. Biodegradable polymer degraded by

Biodegradable synthesis polymer mostly have functional group in protein, polysaccaride and lipid.
e.g.
① Polyhydroxybutrate – Co – β – hydroxy Valrete (PHBV)
② Polyglycolic acid (PGA)
③ Polylactic acid (PLA)
④ Nylon 2, Nylon 6.

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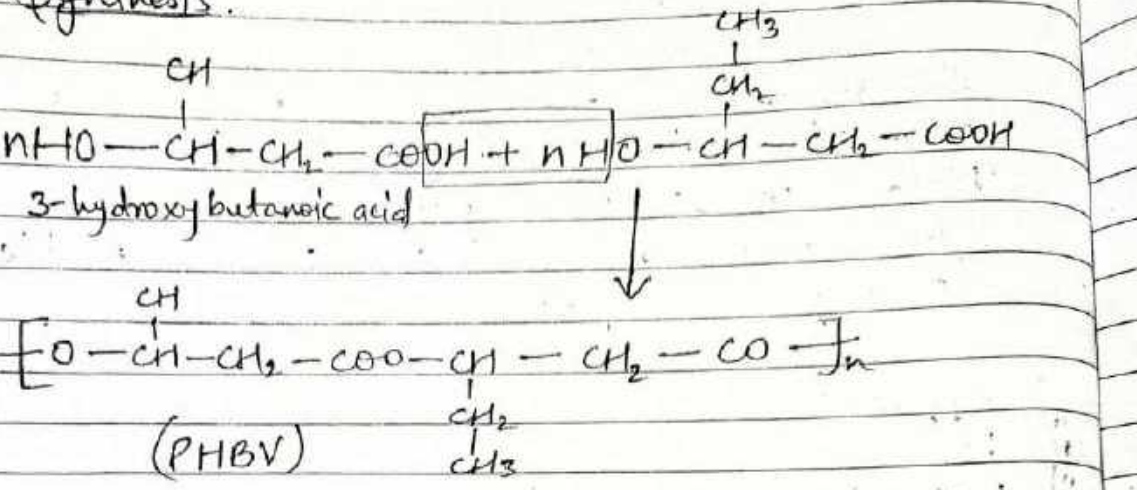
* Synthesis.



3-hydroxybutanoic acid

(PHBV)

* Application.

Pakaging, Orthopedic device to make capsules.

Elastomer

The Elastomer posses the tendency to recover their original shape after they have been greatly deformed. Elastomer are organic polymer having elastic property of upto 200 – 300%. It has coiled like structure. It has weak intermolecular force of attraction.

* Types of Elastomer

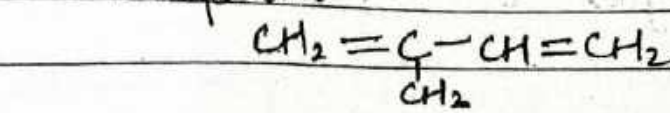
It is of two types.

① Natural Rubber.
e.g. Polyisoprene

② Synthetic Rubber
e.g. Buna S, Buna-N, Neoprene

1.* Natural Rubber :- Polyisoprene.

① Monomer Unit → Isoprene



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② Types of polymer — Homopolymer
③ Types of polymerization — Addition polymerization.
④ Synthesis —

$$nCH_2-\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2\right]_n$$

Isoprene. → polyisoprene Natural rubber

* ~~Bulk~~ Valcanization :- It consists of heating the raw rubber at 100 – 140°C with sulphur the sulphur combine chemically at the double bond of different spring and provide cross linked b/w chain. The amount of sulphur added determine the extent of stiffness of valcanized Rubber

$$\left[CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right]_n + 4S \longrightarrow \left[CH_2-\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-CH_2\right]$$

4 mole of Sulphur

$$\left[CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2\right]_n$$

(Unsaturated linear)

$$\left[CH_2-\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}-CH_2\right]_n$$

(Saturated Cross linked)

2.* Synthetic Rubber

1. Nitrile Rubber (Buna – N)

① Monomer unit — (1) 1,3, butadiene (2) Acrylonitrile

$CH_2=CH-CH=CH_2$ $CH_2=CH(CN)$

② Types of polymer — Hetropolymer or Copolymer
③ Types of polymerization — Addition polymerisation
④ Synthesis.

$$mCH_2=CH-CH=CH_2 + nCH_2=\underset{CN}{\underset{|}{CH}} \longrightarrow \left[\left(CH_2-CH=CH-CH_2\right)_m CH_2-\underset{CN}{\underset{|}{CH}}\right]_n$$

1,3, butadiene 75% Acrylonitrile 25%

C/N — Buna-N
I/N — Polyacrylonitrile butadiene

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⑤ * Property.

Due to presense of cyano group nitrile rubber is less resistance than natural rubber, good strength, low solubility, good insulating property it form After emession in gasoliene & oil.

⑥ * Application.

Fuel tank, ceramic Artical, printing roller, Automobile part, high attitude Aircraft component, paper and textile industries, decorative materials, etc

(ii) Styrene Rubber (Buna – S).

① Monomer Unit :- (i) 1, 3 butadiene (ii) Styrene

$CH_2=CH-CH=CH_2$ $CH_2=CH$

② Types of polymer :- Metro polymer or copolymer

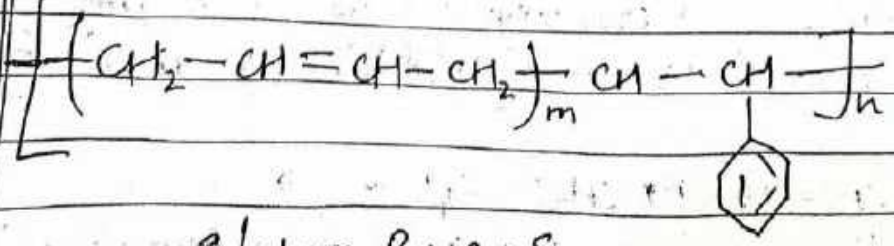
③ Types of Polimerisation :- Addition Polymerisation

④ Synthesis :-

$nm\ CH_2=CH-CH=CH_2 + n\ CH_2=CH$

1,3, butadiene 75% | styrene 25%

$\downarrow$



C/N – Buna S

I/N – Polystyrene butadiene.

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⑤ Properties
1. like natural rubber
2. High load bearing capacity
3. Low oxidation resistance.
4. It swells in oils and solvent.

⑥ Applications.
Shoe sole, motor tyres, toys, floor tiles, cables, carpet, decorative materials

(3)
(iii) Neoprene

① Monomer unit :- chloroprene
$(CH_2 = \underset{Cl}{C} - CH = CH_2)$

② Types of polymer :- Homo polymer.

③ Types of polymerization :- Addition polymerisation

④ Synthesis :-

$$n\,CH_2 = \overset{Cl}{C} - CH = CH_2 \longrightarrow \left[CH_2 - \overset{Cl}{C} = CH - CH_2 \right]_n$$

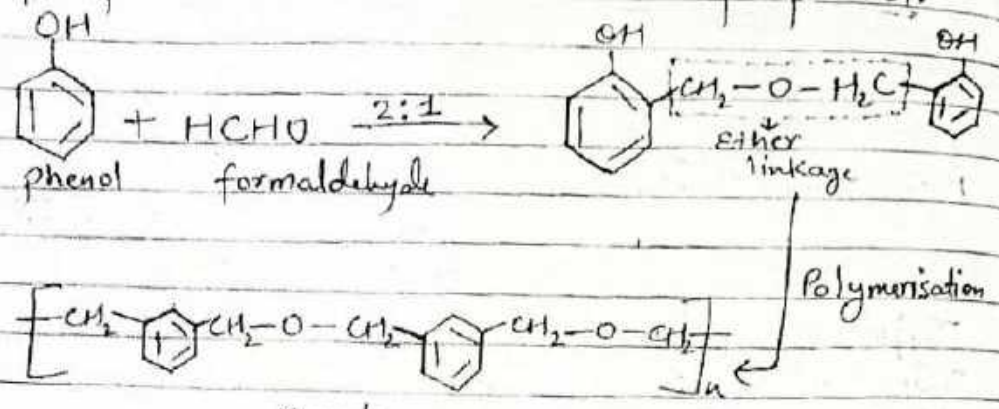
chloroprene. Neoprene Polychloroprene

⑤ Properties
Good insulating property, Good tensile strength, The presence of chlorine and trans linkage impart superior resistance to vegatable and mineral oils and high temperature

⑥ Application :- Belt, coating, corrosion resistant adhesive, mouse pad, wire and cable insulation, gloves, shoe shole.

(B) If presence in excess amount of phenol.

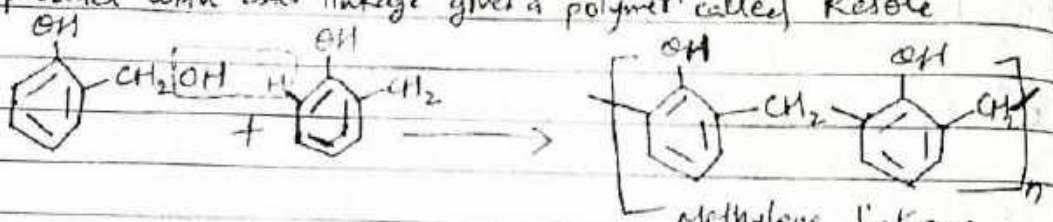
Step(i)



Resole.

The product with ester linkage gives a polymer called Resole

Step(ii)

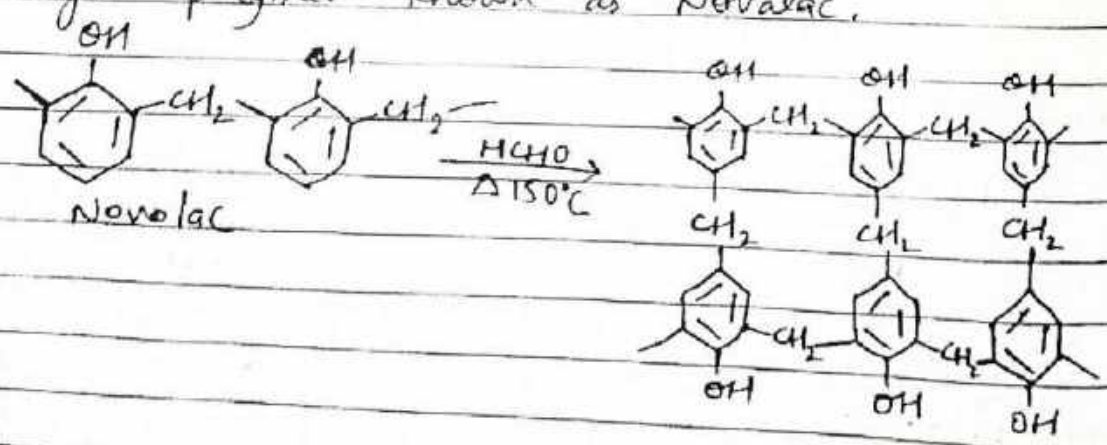


Methylene linkage

Novolac.

Mono-methylol phenol (i.e. ortho or para) can undergo polymerization to give low molecular weight polymer known as Novolac.

Step(iii)



Bakalite.

The Novolac obtained in step(ii) is simply heated at about 150°C using a catalyst whereby a highly cross linked product, bakalite is obtained.

5. Properties

1. Phenolic resins are hard, rigid and strong material
2. They have excellent heat and moisture resistance
3. They have good chemical resistance
4. They have good abrasion resistance
5. They have good electrical insulation characteristics.
6. They are usually dark coloured, pinkish brown.
7. Low molecular weight grades have excellent bonding strength and adhesive properties.

6. Application :- PF resins are generally used for :-

1. Domestic plugs and switches.
2. Handles for cooker and saucepan.
3. Distributor heads of cars.
4. Adhesives for grinding wheels and brake linings.
5. Impregnating paper, wood and other fillers, for producing decorative laminates and wall coverings and industrial laminates for electrical parts including printed circuits.
6. Varnishes, electrical insulation and protective coating.
7. The production of ion-exchange resins.

Polytetra fluroethylene (PTFE) or Teflon

Preparation :- Teflon is prepared by polymerization of tetrafluoro ethylene under pressure in the presence of benzyl peroxide as catalyst.

$$n\,CF_2 = CF_2 \xrightarrow{\text{Polimersation}} \left[CF_2 - CF_2\right]$$

Tetraflouroethylene → poly tetraflouroethylene (PTFE)

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Properties :-

1. High density
2. Chemical inertness over a wide temp. range.
3. Excellent electrical insulation properties.
4. Non adhesive character.
5. Very low coefficient of friction.
6. Excellent toughness & heat resistance.

Application :-

1. Wire & cable insulation
2. Coating of frying pans.
3. Non lubricating bearing
4. Gaskets, packing valve & pump parts.
5. Insulators for motor, generators & capacitors.

Environmental Impact of Teflon or PTFE

PTFE do not breakdown (non-biodegradable) it most likely end up in land fill & overall pollute water bodies & accumulate in soil. Its impact are follows —

Teflon fumes generated by over heating (above 300°C) can also causes polymer fumes fever in people & birds, which is much like the flu on continued exposure.

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Speciality polymers :-

Speciality polymers are specifically designed to serve a specific purpose. or.
speciality polymer are polymer having properties & characteristics specially engineered for specific purpose. They are the class of high performance polymer (HPP). including plastics, polymers, fluids membranes, smart hydro gels & elastomers that are designed to meet the critical requirement that engineers face every day in industries including plastic automobile, aeronauts, smart devices.

Main class of polymer which fall under the category of speciality polymer are as follows:-

1. Conducting Polymer. e.g. - Polyacetylene, polypyrrol, poly thiophene
2. Liquid Crystal polymer. e.g. - Kevlor, PET
3. Biodegradable polymers. e.g. - Biopol resin, PGA, PCL
4. Polymer composite.
5. Biomedical polymer. e.g. PHBV

Properties
like natural rubber
1. High load bearing capacity
2. Low oxidation resistance.
3. It swells in oils and solvent.

Applications.
Shoe sole, motor tyres, toys, floor tiles, cables, carpet, decorative materials

Neoprene

Monomer unit :- chloroprene
$(CH_2 = \underset{Cl}{C} - CH = CH_2)$

Types of polymer :- Homo polymer.

Types of polymerization :- Addition polymerisation

Synthesis :-

$$n\,CH_2 = \overset{Cl}{C} - CH = CH_2 \longrightarrow \left[CH_2 - \overset{Cl}{C} = CH - CH_2 \right]_n$$

chloroprene. Neoprene Polychloroprene

Properties
Good insulating property, Good tensile strength, The presence of chlorine and trans linkage impart superior resistance to vegatitable and mineral oils and high temperature

Application :- Belt, coating, corrosion resistante adhesive, mouse pad, wire and cable insulation, gloves, shoe sole.

* Increasing strength of Rubber on the basis of stability
Buna-S < Natural Rubber < Neoprene < Buna N
< Valcanised Rubber.

Environmental impact on Soceity

Natural Rubber contribute to deforestation, biodiversity laws, pollution & more climate change. Nitrile Rubber is not toxic. The manufacture of synthetic rubber envolve several chemical compounds which are toxic to man. Rubber manufacturing industry has a great contributer towards air pollution. Climate changes such as temp. increase↑, humidity decrease↓, rainfall, drought.

fibre

→ fibre are thin long thread like materials, which have great tensile strength in the direction of the fibre.
→ Fibres are having high interpartial force.
→ It has high length to width ratio.

Types of fibre.

Polyamide	Polyester
Amide group present $\left(-\underset{\underset{O}{\|}}{C}-NH\right)$	Ester group present $\left(-\underset{\underset{O}{\|}}{C}-O-\right)$
e.g Nylon 6,6 , Nylon 6	e.g. Terelene, Decron.

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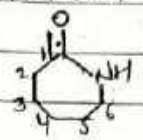
* Polyamide.

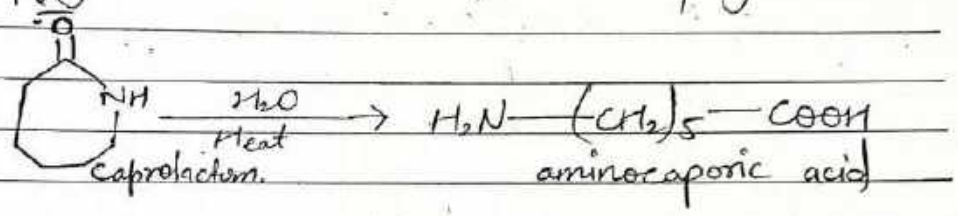
(i) Nylon – 6

1. Monomer unit :- Caprolactum (having 6 Carbon atom)

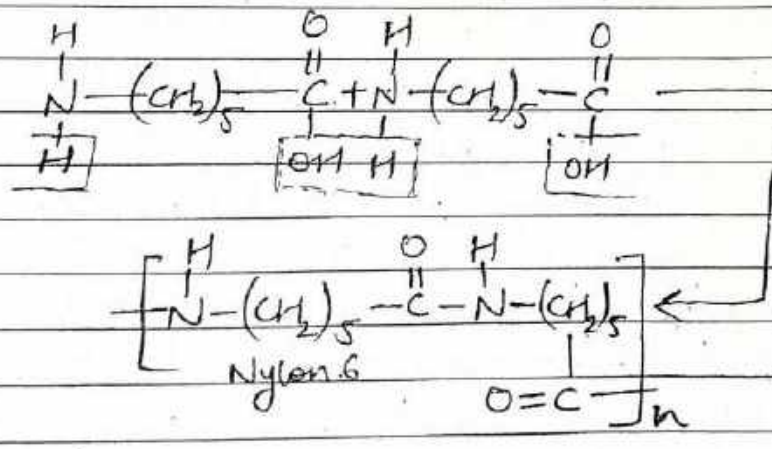


2. Type of polymer :- Homopolymer
3. Types of polymerisation :- Condensation polymerisation
4. Synthesis :-

Step1 :-



Step2 :-

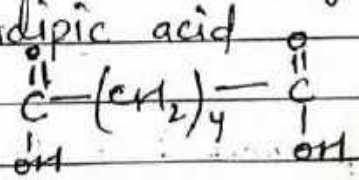


(ii) Nylon 6,6.

1. Monomer Unit :- Hexamethylene Diamine &

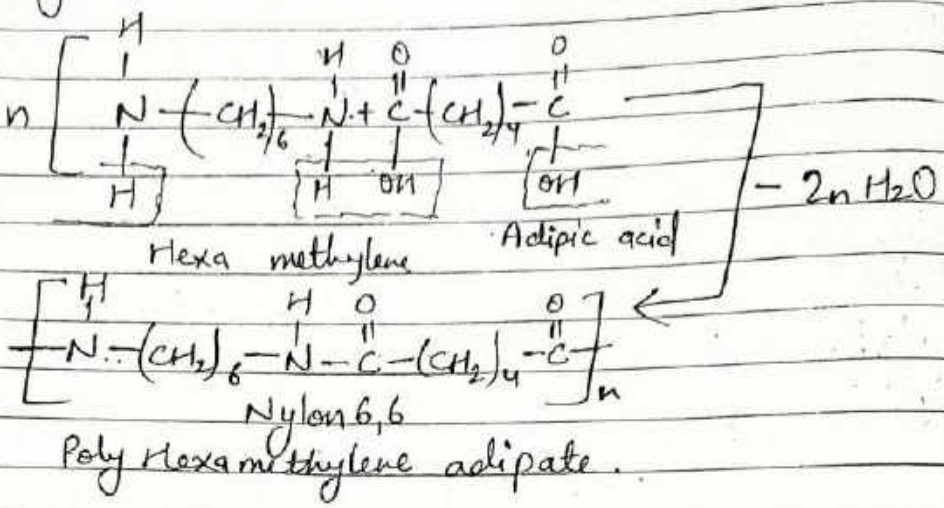
$NH_2-(CH_2)_6-NH_2$

Adipic acid



2. Types of Polymer :- Hetropolymer or Copolymer
3. Types of polymerisation :- Condensation polymerisation.

4. Synthesis :-



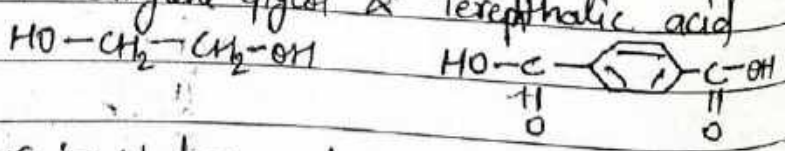
5. Properties :- Nylon 6 & Nylon 6,6

It is linear, white colour, M.P. very high, resistivity with organic solvent good physical strength, self lubricant property

6. Application :-
Synthetic fibres, rope, brushes, comb, cards of tyres, cloth, etc

* Polyester :- Terelene / Dacron (PET)

1. Monomer unit :- Ethylene Glycol & Terepthalic acid



2. Types of polymer :- Metro polymer or Co polymer.

3. Types of polymerisation :- Condensation polymerisation.

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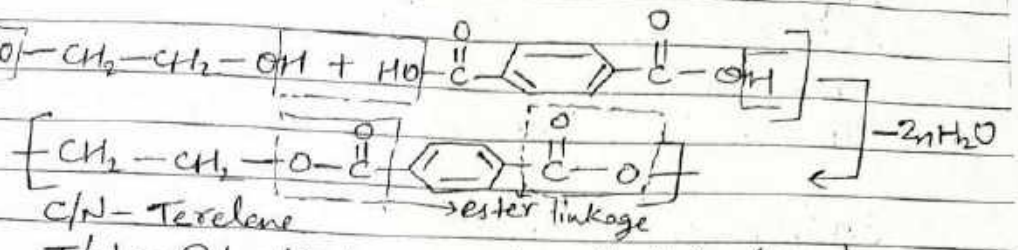
4. Synthesis.



C/N – Terelene
I/N – Polyethylene Terephthalate (PET)

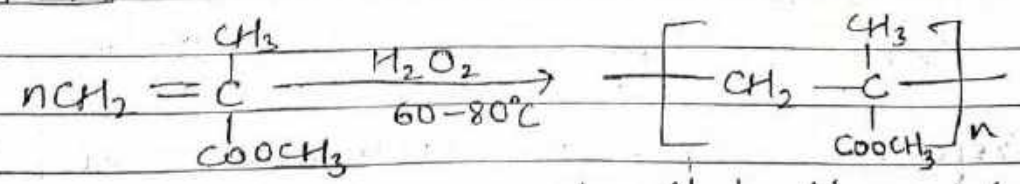
5. Properties :- Low moisture absorbing properties good insulating property
It ~~res~~ is also resist to acid, alkalies.

6. Applications :- Blend with cotton, wool, seat belts, packing insulators, artificial grass

* PMMA or Lucite or Plexiglass (Polymethylmethacrylate)

1. Monomer unit :- 1-Methyl meth acrylate
$CH_2 = C(CH_3) - COOCH_3$

2. Types of polymer – Homopolymer
3. Types of polymerisation – Addition polymerization.
4. Synthesis.



polymethyl meth acrylate (PMMA)

5. Properties :- Colour less, Transparent, amorphous, good strength, high whether resistance, chemically inert but dissolves in organic solvent, such as Ketones, esters, etc.

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6. Applications :- (i) Its optical transparency is better than glass hence excellent substitute for glass.
(ii) In contact lense, spectacles, windows, aquarium.

Environmental impact :-
Acrylics decomposition takes place approximately in 200 years, so dumped acrylics in land till remains for long time & slowly releasing green house gases & toxic chemicals into the environment.

Thiokol — (Polysulphide Rubber)

1. Monomer unit — Sodium polysulphide + Ethylene dichloride
Na_2-S_n or $Na-S-S-Na$ $(CH_2)_2Cl_2$

2. Types of polymer — Hetro polymer
3. Types of polymerisation — Condensation polymerisation
4. Synthesis

$$\underset{\text{Ethylene dichloride.}}{(CH_2)_2Cl_2} + \underset{\text{Sodium polysulphide}}{Na_2S_n} \xrightarrow{-NaCl} \underset{\text{Thiokol}}{-(CH_2)_2S_n-}$$

5. Properties :- (i) Speciality polymer is related highest having resistance to oil & gasoline.
(ii) Excellent solvent resistance
(iii) Poor mechanical property
(iv) Can not be valcanized, hence does not form hard rubber.

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6. Application :- (i) In this manufacture of oil & gasoline
(ii) It is widely used in liquid form as sealants for air craft & Marine industries.
(iii) Polysulphide is a ~~ext~~ excellent fuel material & become solid propellants for rockets when they are mixed with inorganic oxidizer (ammonium perchlorates)

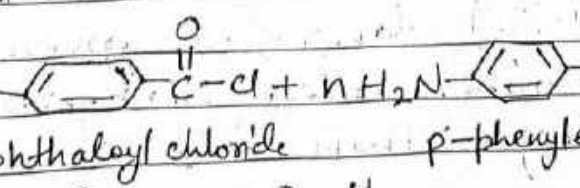
Environmental impacts :-

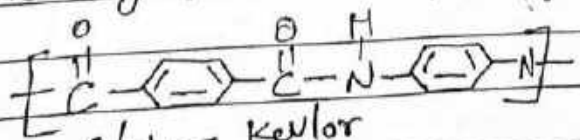
1. Non renewable non biodegradable
2. Releases harmful chemical into the environment.
3. Responsible for deforestation & climate change & Pollution

Kevlar (Polyamide) Marks (8)

1. Monomer unit :- → Poly (P-Phenylene terephthalamide (Liquid Crystal polymer) (Thermosetting Polymer)
→ Aromatic dichloride & aromatic diamine

2. Type of polymer — Hetro polymer
3. Type of polymerisation — Condensation polymerisation
4. Synthesis.





C/N — Kevlar

I/N — Poly p-phenylene terethalamide

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5. Properties :-

1. Extraordinary mechanical property
2. Kevlar's Known for its ability to be spun into fibres that have 5 times the tensile strength to steel
3. High tensile strength is due to extensive Hydrogen bonding.
4. Extreme chemical properties. (inertness).

6. Application :-

1. In the fabrication of protective wear including bullet proof vests.
2. Extensively used in aerospace & aircraft industries.

Environmental Impact.

1. Kevlar fibres are non-biodegradable polymer
2. Synthetic fibres are non biodegradable & unsustainable to the environment.
3. The production of nylon emits nitrous oxides ~~(HNO_3)~~ dangerous green house gas 300 times more dangerous to the ozone layer than CO_2.

Marks (8)

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Bakalite / PF Resin (Phenol Formaldehyde Resin)

→ Resin is network like structure

① Monomer unit :- Phenol & Formaldehyde HCHO

② Types of polymer :- Hetropolymer

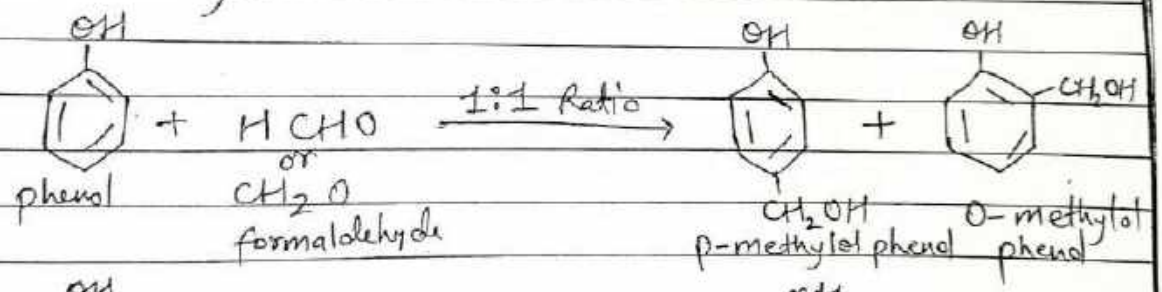
③ Types of polymerisation :- Condensation polymerisation

④ Synthesis:

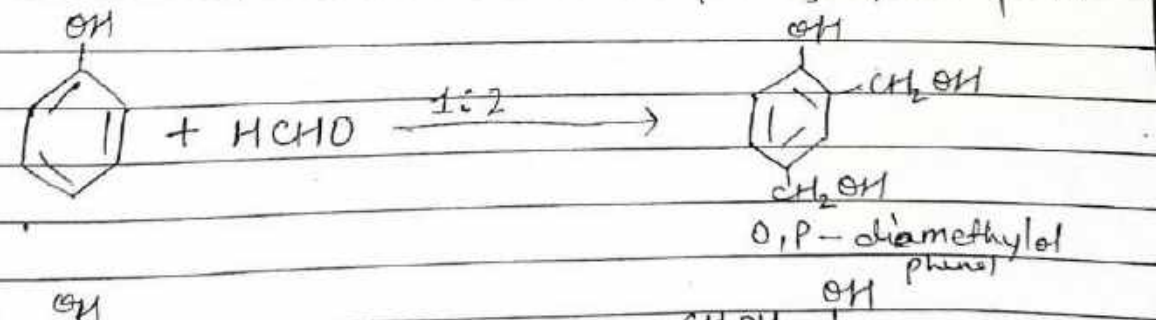
(A) Base Catalysed using excess of formaldehyde over phenol.

(B) Acid Catalysed using excess of phenol over formaldehyde.

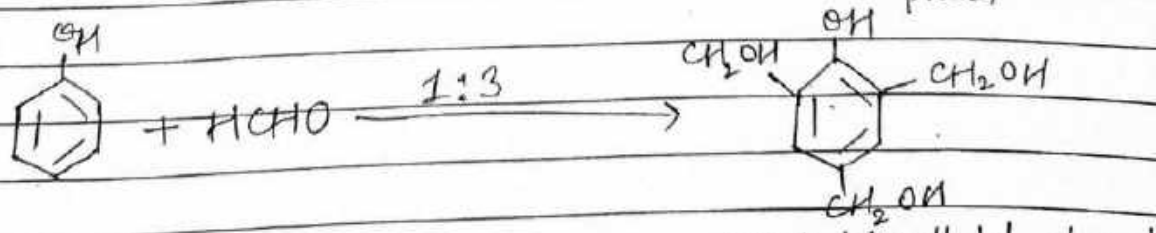
(A) (i)



(ii)



(iii)



Mark (1)

VIMP ST • 5/JAN/2023 chemistry

(Organometallic compound)

compound in which organic groups are linked directly to the metal through atleast one carbon atom.

eg:- Grignard reagent (R-Mg-x)

(Classification)

(i) (on the basis of presence functional group)

- Simple organometallic compound.
  (alkyl/aryl attached to metal)
  eg = CH_3Li, $(C_2H_5)_2Zn$. etc
- Mixed organometallic compound.
  (Group other than alkyl or aryl are also attached to metal)
  (R-Mg-x)

(ii) (on the basis of Metal)

- Main group organometallic
  • (s or P group)
  eg:- $(C_2H_5)Li$, $(C_2H_5)Si$
- d & f block organometallic compound.
  • (π Bonded compound)
  eg = Zeise salt.
  $K[PtCl_3(C_2H_4)]$

(iii) (on the basis of carbon-metal Bond)

- Ionic organometallic
  eg:- $C_{10}H_8Na^+$
  $C_6H_5Na^+$
- Bonded covalent
  C-M (covalent Bond)
  M → Non transitional
  eg = $Al(CH_3)_3$, $(C_2H_5)_3Sn$
- Non-classified organometallic
  π-organometallic
  C-M (covalent)
  M- Transitional
  eg $(C_2H_5)_2Fe$

05 Jan 2023 chemistry

(Synthesis of organometallic compound)

(i) Synthesis with organomagnesium comp :-

- $Mg + R - x \xrightarrow{\text{dry ether}} R - Mg - x$
  (grignard Reagent)
- $Mg + C_2H_5Br \longrightarrow C_2H_5 - Mg - Br$
  (ethyl Magnisium Bromide)

(ii) By Dialkyl zinc :-

- $2CH_3Br + 2Zn \longrightarrow (CH_3)_2Zn + ZnBr_2$
  (dimethyl zinc)

(iii) By Trialkyl aluminium :-

$AlCl_3 + 3CH_3 - Mg - Br \longrightarrow (CH_3)_3 - Al + 3MgBrCl$
(trimethyl aluminium)

(iv) By tetra alkyl Tin :-

$C_4H_9 - Li + Sn \longrightarrow (C_4H_9)_4Sn + 4LiCl$
(tetra butyl Tin)

(v) By Hydrocarbon Metal Complexes :-

$2C_6H_6 + Cr \longrightarrow [Cr(C_6H_6)_2]$
(vapour)
Di benzene Chromium

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe
Cs	Ba	Tl	Pb	Bi	Po	At	Rn.
fr	Ra						

05/JAN/2023 Chemistry.

Mark (f)

(Grignard reagent)

R-Mg-x.

R = alkyl/aryl ($-CH_3$ $-C_2H_5$, C_6H_5)

x = halogen (-Cl, -Br, -I)

* (Synthesis) *

1) from alkyhalide :-

$$CH_3Br + Mg \longrightarrow CH_3-Mg-Br$$

(Methyl magnisium Bromide)

(IMP)

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* (Application) (grignard's)

1) formation of alkane :-

$$R-Mg-x \xrightarrow[\text{or } H-OH]{H_2O} R-H + Mg\begin{smallmatrix}-OH\\-x\end{smallmatrix}$$

(Mag. hydroxide halide)

2) formation of alkyl halide :-

$$R-Mg-x + Cl \xrightarrow[(x_2)]{\text{Halogen}} R-x + Mg\begin{smallmatrix}-x\\-x\end{smallmatrix}$$

(alkyl halide)

3) formation of alcohol :-

(i) $R-mg-x \xrightarrow[H-\underset{\underset{O}{\|}}{C}-H]{HCHO} R-CH_2-OH$ (1° Alcohol)

(ii) $R-Mg-x \xrightarrow[R-\underset{\underset{O}{\|}}{C}-H]{} R-\overset{H}{\underset{R}{C}}-OH$ (2° Alcohol)

(iii) $R-Mg-x + R'-\overset{O}{\overset{\|}{C}}-R''$

$\hookrightarrow R-\overset{R}{\underset{R''}{\overset{|}{\overset{|}{C}}}}-OH$ (3° Alcohol)

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(iv) formation of Acids:-

$$R-Mg-x \xrightarrow[HCl]{CO_2} R-\overset{O}{\overset{\|}{C}}-OH + Mg \begin{smallmatrix} x \\ Cl \end{smallmatrix}$$

(5) formation of Aldehyde:-

$$R-Mg-x \xrightarrow[H^+/H_2O]{HCN} \underset{\text{(aldehyde)}}{R-C-H} + NH_3 + Mg \begin{smallmatrix} OH \\ x \end{smallmatrix}.$$

(6) formation of ketone:-

$$R-Mg-x \xrightarrow[H^+/H_2O]{R'CN} R-\overset{O}{\overset{\|}{C}}-R' + NH_3$$

$$\text{ketone} + Mg \begin{smallmatrix} x \\ OH \end{smallmatrix}.$$

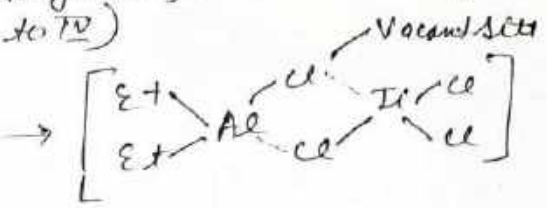
(Application of organometallic compounds)

- Application of organometallic compound in Polymerisation. eg :- Zieglar Natta Catalyst
- Application of OMC in catalysis
- Application of OMC in the synthesis of variety of comp eg :- GR.

components:- (i) Catalyst :- halides of transition metals (metal eg :- Ti, fe, Mo etc (IV or VIII grp)

(ii) organometallic comp = Hydrides of aryloralkyl. metal (I to IV)

eg = $AlCl.(C_2H_5)_2 + TiCl_3$. ⟶



(2) catalysis = Tetra ethyl lead = (TEL)

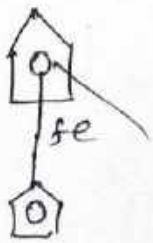
$$R-R \xrightarrow{\text{combustion}} \underbrace{R^{\bullet} + R^{\bullet}}_{\text{free Radical}} \text{ fuel}$$

Responsible for knocking

$$(C_2H_5)_4Pb \longrightarrow 4C_2H_5^{\bullet} + Pb^{\bullet}$$

$$C_2H_5 + R^{\bullet} \longrightarrow C_2H_5-R$$

(3) ferrocene:- $(C_2H_5)_2fe$.



Anti Cancer Activity.

Anti knocking Reagent.

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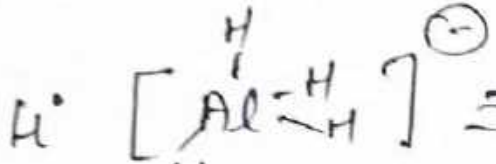
* ($Li^{+}AlH_4$) (lithium tetrahydroaluminate) (LAH).



$\equiv AlH_3 \longrightarrow Li^{+}AlH_4$

$\ominus$

Nucleophile

$\left.\begin{matrix} C=C \\ C\equiv C \end{matrix}\right\}$ Not reduce

Date 04/01/2023 Wednesday

Date
Page

MODULE :- 4

WATER TECHNOLOGY AND FUELS & COMBUSTION

Water is a universal solvent and have sp^3 hybridised.

Hard Water / Soft water:

The water which form leather with soap is known as softwater.

The water which does not produce lather with soap is known as hard water.

The soap conjuming capacity of water is known as hardness.

Sodium and potassium salts of higher fatty acid are known as soaps

Cause of hardness

Hardness of water is due to the presence of dissolved salts of calcium and magnesium and other heavy metals.

These react with soluble soduim soap to form insoluble salts of calcium and magnesium.

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Thus the precipitate form is the insoluble soap of calcium and magnesium. hence, a large quantity of soap is required to produce lather with hard water.

Types of Hardness:-

Hardness of water is of two types:-

1. Temporary hardness.
2. Parmanent hardness.

1. Temporary hardness (carbonate hardness):- It is due to the presence of dissolved salts of bi-carbonates of calcium and magnesium and other heavy metals

Removal:-

It can be removed by following two ways:-

1. By Boiling:-

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

Calcium bicarbonate → Calcium carbonate

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

Magnesium bicarbonate → Magnesium carbonate.

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② By adding slaked lime :-

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

③ PARMANENT HARDNESS (Non Carbonate hardness) :-

This hardness is due to the presence of chlorides and sulphates of calcium and magnesium and other heavy metals. like iron ; it cannot be removed by boiling. $\boxed{CaCl_2, MgCl_2, CaSO_4, MgSO_4}$

Removal :-

Parmanent hardness can be removed by following chemical method :-

① Lime soda method
② Zeolite method.
③ Reverse Osmosis method.
④ Calgon method
⑤ Ion exchange Resin method.

Disadvantages of hard water :-

① Hardwater shows soap consuming capacity as the cleaning properties of soap is depressed and lot of soap is washed. in bathing and washing

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② It causes various boiler troubles in industry like;
'Sludge' and scale formation
Boiler corrosion
③ It is not good for drinking purpose if salts are in excess

* Hardness in terms of equivalents of $CaCO_3$. (degree of hardness)

Hardness is always calculated in terms of equivalent of $CaCO_3$ although $CaCO_3$ is not responsible for any type of hardness. There are two basic reasons for choosing $CaCO_3$ as standard.

① Calculation become easy as its molecular weight is exactly 100 and equivalent weight is 50).

② It is the most insoluble salt that can be precipitated in water treatment.

$$CaCO_3 \text{ equivalent} = \frac{\text{Amount of hardness producing salt} \times \text{Eq. wt of } CaCO_3}{\text{Eq. wt. of hardness producing salt}}$$

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UNITS OF HARDNESS

Parts per Million (PPM):- 1 parts $CaCO_3$ equivalent hadness present in 1 million part of water.

mg/L – 1 parts $CaCO_3$ equivalent hadness present in 10^6 ~~million~~ parts of water.

Degree French (°Fr):- 1 part $CaCO_3$ equivalent hadness present in 10^5 parts of water.

Degree clark (°cl):- 1 part $CaCO_3$ equivalent hardness present in 70,000 parts of water.

A sample of water has hardness 304 ppm $CaCO_3$ equivalent find the hardness in term degree clark, Degree french and mg/L

	PPM	mg/L	°Fr	°cl
Hardness	304	304	$\frac{304 \times 0.1}{30.4}$	$\frac{30.4 \times 0.07}{21.28}$

A sample of water contain 248 mg calcium sulphate / Litre. Cal. the hardness in terms of $CaCO_3$ equivalent

$$CaSO_4 \text{ equivalent} = \frac{\text{Amount of hardness producing salt} \times \text{Eq. wt of } CaCO_3}{\text{Eq. wt of hardness producing salt}}$$

$40 + 32 + 4(16)$
$= 136$

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$$\text{Eq. weight} = \frac{\text{Molecular mass}}{n\,1}$$

Acid $n \rightarrow H^+$ Na
Base $n = OH^-$ No.

$$= \frac{248 \times 100/2}{136/2} = 182.35 \text{ ppm.}$$

→ Atomic mass of various elements :-

H –	1	Cl –	35.5
C –	12	Ca –	40
N –	14	Mg –	24
O –	16	Al –	27
S –	32	Fe –	56

→ Molecular weight and Equi. weight of various

Salts	Mol. mass	Eq. weight
① - Salts of calcium		
$CaCO_3$	$40+12+3\times16$	$\frac{100}{2} = 50$
$Ca(HCO_3)_2$	$40+2(1+12+3\times16)$	$\frac{162}{2} = 81$
$CaCl_2$	$40+35.5\times2$	$\frac{111}{2} = 55.5$
$CaSO_4$	$40+32+4\times16$	$\frac{136}{2} = 68$
② Salts of Mg		
$MgCO_3$	$24+12+3\times16$	$\frac{84}{2} = 42$

Salt
n = valency of cation.

Ion
n = no. of charge

$Mg(HCO_3)_2$	$24 + 2(1 + 12 + 3 \times 16)$	$\frac{146}{2} = 73$
$Mg(NO_3)_2$	$24 + 2(14 + 3 \times 16)$	$\frac{148}{2} = 74$
$MgCl_2$	$24 + 2 \times 35.5$	$\frac{95}{2} = 47.5$
$MgSO_4$	$24 + 32 + 4 \times 16$	$\frac{120}{2} = 60$
Other salts / Acids / Gases		
Na_2AlO_2	$23 + 27 + 2 \times 16$	82
$Al_2(SO_4)_3$	$2 \times 27 + 3(32 + 4 \times 16)$	$\frac{342}{6} = 57$
$FeSO_4 \cdot 7H_2O$	$56 + 32 + 4 \times 16 + 7(2 + 16)$	$\frac{278}{2} = 139$
HCl	$1 + 35.5$	$\frac{36.5}{1} = 36.5$
H_2SO_4	$2 + 32 + 4 \times 16$	$\frac{98}{2} = 49$
CO_2	$12 + 2 \times 16$	$\frac{44}{2} = 22$
Ions		
H^+	1	1
OH^-	$16 + 1$	17.
HCO_3^-	$1 + 12 + 3 \times 16$	61
Ca^{++}	40	

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Mg^{++}	24	
CO_3^{--}		

Q. A sample on analysis was found to contain following impurities

$Ca(HCO_3)_2$	4	T
$Mg(HCO_3)_2$	6	T
$CaSO_4$	8	P
Mg_2SO_4	10	P
NaCl	6	X

Calculate the temporary, ~~and~~ permanent and total hardness of water in ppm, °c, °F.

Sol

Impurities	Amount (mg/L)	$CaCO_3$ equivalent	Types of hardness
$Ca(HCO_3)_2$	4	$\frac{4 \times 100/2}{162/2} = 2.47$	T
$Mg(HCO_3)_2$	6	$\frac{6 \times 100/2}{146/2} = 4.10$	T
$CaSO_4$	8	$\frac{8 \times 100/2}{136/2} = 5.88$	P
Mg_2SO_4	10	$= \frac{10 \times 100/2}{120/2} = 8.33$	P
NaCl	6	Does not contribute to hardness.	

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Temporary hardness A + B (mg/l)

$= 2.47 + 4.10 = 6.57 mg/l$

Permanent hardness C + D (mg/l)

$= 5.88 + 8.33 = 14.21 mg/l$

Total hardness $= (A + B + C + D) mg/l$

$= 2.47 + 4.10 + 5.88 + 8.33$

$= 20.78 mg/l$

Hardness	PPM	mg/l	°Fr	°Cl
Temporary	6.57	6.57	6.57×0.1 0.657	6.57×0.07 0.4659
Permanent	14.21	14.21	14.21×0.1 1.421	14.21×0.7 0.9694
Total	20.78	20.78	20.78×0.1 2.078	20.78×0.7 0.1455

Q: Calculate the hardness of water sample containing impurity of $Ca(HCO_3)_2 = 81 mg/l$. Find the answer in °F also. [21-22 (ISAM) - 3 Mar

Ans: Given = $Ca(HCO_3)_2 = 81$ = $40 + 2(1 + 12 + 3 \times 16)$

$= \frac{81 \times 100/2}{162/2} = \frac{4000}{81} = 50$

In °F

Ten = 5.

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Q4 A water contains 10 ppm of $CaCl_2$, 3.2 mg/L of NaCl, 21.1 Fr of Al_2O_3. Calculate the hardness of water sample

Impurities	Amount/(mg/L)	Eq. wt	Types of hardness
$CaCl_2$	10 mg/L	$\frac{10 \times 100/2}{111/2}$	does not contribute
NaCl	3.2 mg/L	$\frac{3.2 \times 100/2}{58.5/2}$	does not contribute
Al_2O_3	21.1 mg/L	$\frac{21.1 \times 100/2}{102/3}$	does not contribute

$CaCl_2 \rightarrow 9.009$ mg/L

55.5

$Al_2O_3 \rightarrow$

Que 100ml of water sample has hardness equivalent to 12.5 ml of 0.08 N $MgSO_4$ solution calculate the hardness of water sample.

→ (Sem I) 2017-20

$MgSO_4 \rightarrow$ ~~12.5~~

$V_1 = 100$ ml.

$V_2 = 12.5$ ml.

$N_1V_1 = N_2V_2$

$N_1 = \frac{N_2V_2}{V_1}$

$N_1 = \frac{0.08 \times 12.5}{100} = 0.01$ eq/l

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$S = N \times E$

~~$MgSO_4 = 24 + 32 + 4 \times 16$~~
~~$= 120$~~

$S = 0.01 \times 120$

$= 0.5$ me/L
$= 500$ ppm.

Que Calculate the temporary, permanent and total hardness of a sample of water that is analysed as $Mg(HCO_3)_2$ is 7.3 mg/L $Ca(HCO_3)_2$ is 8.1 mg/m $Mg(Cl_2)$ is 9.5, $CaSO_4$ is 6.8 mg/L

Impurities	Amount (mg/L)	Eq. wt of	Type
$Mg(HCO_3)_2$	7.3	$\frac{7.3 \times 100/2}{73}$	T
$Ca(HCO_3)_2$	8.1	$\frac{8.1 \times 100/2}{81}$	T
$Mg(Cl_2)$	9.5	$\frac{9.5 \times 100/2}{95}$	P
$CaSO_4$	6.8	$\frac{6.8 \times 100/2}{68}$	P

Temporary hardness $= Mg(HCO_3)_2 + Ca(HCO_3)_2$
$= 5 + 5$
$= 10$ mg/L

Permanent $= Mg(Cl_2) + CaSO_4$
$= 10 + 5$
$= 15$ mg/L

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Total hardness = T + P
= 10 + 15
= 25 mg/L

Q. How many grams of $MgCO_3$ dissolved/L to give 84 ppm of hardness.

Sol

$MgCO_3 \rightarrow \frac{S \times 100/2}{42}$

$\frac{84 \times 42}{50} = S$

$70.56 = S$

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

$x = \frac{50}{84 \times 42}$

S = 70.56 ppm
S = 70.5

Q. What is the carbonate & non-carbonate hardness of a sample of water which has the following impurities per litre.

$Ca(HCO_3)_2 \rightarrow 40.5$ mg
$CaCl_2 \rightarrow 33.5$ mg
$Ca(NO_3)_2 \rightarrow 41$ mg
$KNO_3 \rightarrow 101$ mg
$MgCO_3 \rightarrow 33.6$ mg.

ties	amount	$CaCO_3$ equivalent	Types.
$O_3)_2$	40.5	$\frac{40.5 \times 50}{81} = 25$	T
	33.5	$\frac{33.5 \times 50}{111/2} \Rightarrow 30.18$	T
$)_2$	41	$\frac{41 \times 50}{82} = 25$	Not - participated
	101	$\frac{101 \times 50}{101} = 50$	Not - participated
	33.6	$\frac{33.6 \times 50}{42} = 40$	T.

Carbonate hardness → 25 + 40 = 65

Non-carbonate hardness → 30.18

A sample of water was found to contain

40.5 mg/L → $Ca(HCO_3)_2$
40.5 mg/L → $Mg(HCO_3)_2$
32.1 mg/L → $CaSO_4$
27.6 mg/L → $MgSO_4$
22.4 mg/L → $MgCl_2$
19 mg/L → $MgCl_2$
4.8 mg/L → NaCl.

Calculate the temporary hardness

Impurities	Amount	$CaCO_3$ equivalent	Types.
$Ca(HCO_3)_2$	40.5	$\frac{40.5 \times 50}{81} = 25$	T
$Mg(HCO_3)_2$	46.5	$\frac{46.5 \times 50}{73} = 31.8$	T

Temporary → 25 + 31.8 = 56.8

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Q. What is hardness of water? A sample on analysis was found to contain following impurities?

$Ca(HCO_3)_2 \rightarrow 40.5$ ppm.	$CaCl_2 \rightarrow 11.1$ ppm
$Mg(HCO_3)_2 \rightarrow 29.1$ ppm	$MgCl_2 \rightarrow 15.82$ ppm

Calculate carbonate & non carbonate hardness?

Impurities	Amount (ppm)	$CaCO_3$ equivalent	Types.
$Ca(HCO_3)_2$	40.5	$\frac{40.5 \times 50}{81} = 25$	T
$Mg(HCO_3)_2$	29.1	$\frac{29.1 \times 50}{73} = 19.93$	T
$CaCl_2$	11.1	$\frac{11.1 \times 50}{55.5} = 10$	P
$MgCl_2$	15.82	$\frac{15.82 \times 50}{47.5} = 16.65$	P

Carbonate $= 25 + 19.93 = 44.93$ ppm

Non-carbonate $= 10 + 16.65 = 26.65$ ppm.

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Water softening methods :-

- External method
  - Zeolite method
  - Reverse Osmosis method
  - Ions exchange method.
- Internal method
  - Calgon conditio-ning
  - Phosphate conditi-oning

* Zeolite method (Or) Permutit method :-

Zeolite is derived from 2 greek words (zein+lithos) which means boiling stone.

chemical formula:- $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$

chemical Name:- Sodium aluminum orthosilicate.

$x \longrightarrow 2-10$

$y \longrightarrow 2-6$

The artificial zeolite is called permutit. It may be obtained by fussing Na_2CO_3, Al_2O_3 and SiO_2 in a proper ratio.

Principal:-

Zeolite acts as base exchanges when brought in contact with water containing cations.

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(2) In this process, hardness is percolated at specified rate through the bed of zeolite present in cylindrical zeolite unit. zeolite holds sodium ions loosly & can be simply represented as Na_2CO_3.

(3) In hardness causing ions (Ca^{2+}, Mg^{2+} etc) are removed by zeolite as Caze & Mgze respectively which the outgoing water containing sodium salts.

Zeolite layer	+	Hardness	→	Ca/Mgze	+	Sodium salt

$Na_2ze + Ca(HCO_3)_2 \longrightarrow Caze + 2NaHCO_3$

$Na_2ze + Mg(HCO_3)_2 \longrightarrow Mgze + 2NaHCO_3$

$Na_2ze + CaCl_2 \longrightarrow Caze + 2NaCl$

$Na_2ze + CaSO_4 \longrightarrow Caze + Na_2SO_4$

$Na_2ze + MgCl_2 \longrightarrow Mgze + 2NaCl$

$Na_2ze + MgSO_4 \longrightarrow Mgze + Na_2SO_4$

Regenerations-

$Caze + NaCl \longrightarrow Na_2ze + CaCl_2$

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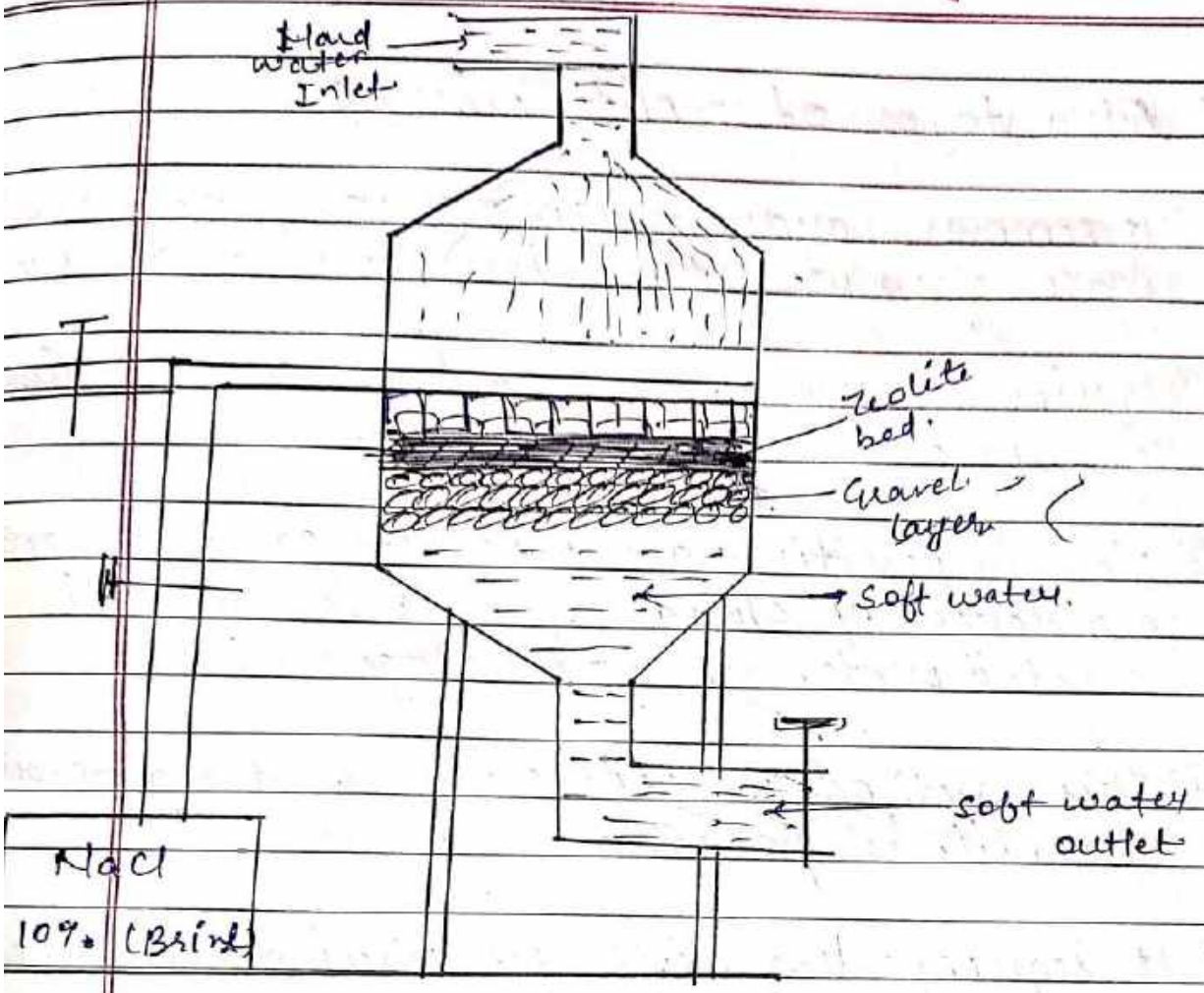

* Regeneration :-

After some time, the zeolite is completely converted into calcium and magnesium zeolite and it gets exhausted. now supply of hardwater is stop and the exhausted zeolite is treated with concentrated brine (10% NaCl) solution

$$\boxed{CaZe/MgZe} + \boxed{\text{Brine sol}^n} \longrightarrow \boxed{Na_2Ze} + \boxed{Ca/Mg\ salt}$$

(10% NaCl)

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

$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

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* Advantages of zeolite process:-

① It removes hardness almost completely and water of about 10ppm hardness is produced

② Equipment used is compact and occupies less space.

③ No impurities are precipitated therefore no danger of sludge formation in the treated water at later stage

④ This method is economic and regeneration of zeolite is possible.

⑤ It requires less skill for maintainance as well as for operations.

⑥ It requires less time for softening

⑦ The process is quiet clean.

* Disadvantages of zeolite method:-

① The concentration of sodium ion increases in soften water.

② The acidic ions such as HCO_3^-, CO_3^{--} etc remain in treated water.

③ The water containing minerals (Fe^{++}, Mn^{++})

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cannot be soften by this method as minerals distroys zeolite layer.

(4) This method is not useful for turbid water

Nomericals of zeolite method:-

Step 1 :-

Amount of NaCl required $= m \times V_2$ (gm)

$= m \times V_2 \times 10^3$ mg

Step 2 :-

$CaCO_3$ equivalent (NaCl required) $= \frac{m \times V_2 \times 10^3 \times 50}{58.5}$

(total hardness)

Step 3 :-

Hardness of water sample $= \frac{\text{Total hardness}}{\text{Vol. of water Supplied.}}$

$$H = \frac{m \times V_2 \times 10^3 \times 50}{58.5 \times V_1}$$

H = Hardness of water

m = Amount of NaCl in V_2 ml

V_1 = Volume of water supplied.

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The hardness of 1000l of sample of water was removed by passing it through a zeolite softner then the zeolite softner then required 30l of ~~na~~ NaCl solution containing 1.5gm per litre of NaCl for regeneration find the hardness of water sample.

Amount of NaCl required = $m \times V_2$ gm.

$= m \times V_2 \times 10^3$ mg

$= 1.5 \times 30 = 45.0$ gm

$= 45 \times 10^3$ mg.

$CaCO_3$ equivalent (NaCl required) = $\frac{m \times V_2 \times 10^3 \times 50}{58.5}$

(total hardness)

$= \frac{45 \times 10^3 \times 50}{58.5}$

$= 38.4615 \times 10^3$

Hardness of water sample = $\frac{\text{Total hardness}}{\text{vol. of water supplied}}$

$= \frac{38.4615 \times 10^3}{1000}$

$= 38.46$ Ans.

An exhausted zeolite softener was regenerated by passing 150 L of NaCl solution having a strength of 1.5 gm/L NaCl. Find the total vol. of water than can be soften by this zeolite softner. If hardness of water is 600 ppm

Amount of NaCl required $= m \times V_2$ gm

$= 150 \times 1.5$

$= 225$ gm.

$= 225 \times 10^3$ mg

$CaCO_3$ equivalent (NaCl required) $= \frac{m \times V_2 \times 10^3 \times 50}{58.5}$

$= \frac{225 \times 10^3 \times 50}{58.5}$

Hardness of water sample $= \frac{\text{Total hardness}}{\text{vol. of water supplied}}$

$$\text{Hardness} = \frac{225 \times 10^3 \times 50}{58.5 \times V_1}$$

$$600 = \frac{225 \times 10^3 \times 50}{58.5 \times V_1}$$

$$V_1 = \frac{225 \times 10^3 \times 50}{58.5 \times 600} = \frac{11250 \times 10^3}{35100}$$

Vol. = 320.5 litre.

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Q. A water sample have hardness having 250 ppm of zeolite process, the exhausted zeolite bed required 50 litres of 15% NaCl solution generation for regeneration. calculate the quality the water soften using zeolite bed.

100 ml NaCl = 15 gm
1000 ml NaCl = 150 gm

Amount of NaCl required = $m \times V_2 gm$

$= 50 \times 150 \times 10^3$ ml.

$= 50 \times 150 \times 10^3$ mg.

$CaCO_3$ equivalement $= \frac{50 \times 150 \times 10^3 \times 50}{58.5}$

Hardness $= \frac{50 \times 150 \times 10^3 \times 50}{58.5 \times V_1}$

$V = \frac{50 \times 150 \times 10^3 \times 50}{58.5 \times 250} = \frac{375000 \times 10^3}{14625}$

$= 25.641 \times 10^3$ ml.

$= 25641$ litre

Q. Describe zeolite process of water softning. A zeolite softner was 90% exhausted by removing a hardness completely when 10,000 litres of hard-water was pass through it. The zeolite softner then required 200 L of NaCl solution containing 150 g/L of NaCl for complete regeneration. find the hardness of water sample.

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~~100 litre → 90~~
~~100,000 Litre → 900~~
~~10,000 Litre → 9000~~

Amount of NaCl required = $m \times V_2$ gm

$= \cancel{9000} \; 150 \times 200 \times 10^3$

$= \cancel{18 \times 10^8} \; 30{,}000 \times 10^3$ mg

$CaCO_3$ equivalent $= \cancel{\frac{18 \times 10^8 \times 50}{58.5}} \; \frac{30 \times 10^6 \times 80}{58.5}$

$= 25641.025$

Hardness $= \cancel{\frac{18 \times 10^8 \times 50}{58.5 \times 150}}$

$= \cancel{\frac{6 \times 10^8}{58.5 \times 10{,}000}}$

$= 0.10256 \times 10^8$

$= 10256 \times 10^5$

$= 1025.6$ L Ans

→ Amount of hardness when 100% exhausted $= 25641.025 \times 10^3$

→ Amount of hardness when 90% exhausted $= 2564.025 \times 10^3 \times 9$

Hardness of water sample $= \frac{\text{Total hardness}}{\text{Vol. of water supplied.}}$

$= \frac{2307.6225 \times 10^3}{10{,}000}$

$= 230.76$ ppm.

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* Ion exchange Resin Method:- *

Ion exchange resins are used to remove all minerals from water. The resins used for this purpose are porous, insoluble, cross linked longchain organic polymers, capable of exchanging ions.

Example:- Styrene di-vinyl Benzene.

→ Ion exchange resins are of two types:-
① cation exchange resin
② Anion exchange resin

① Cation exchange resin:- They exchanges all cations with H^+ ions. They are represented by RCOOH / RH

② Anion exchange resin:- They exchanges all anion with OH^- ions. They are represented by ROH

Principals:-

① Cation exchange resin:- Ca^{2+} and Mg^{2+} ions present in hard water are removed by these acidic frame works and H^+ ions are added to water.

$$RCOOH + Ca^{++} \rightarrow (RCOO)_2Ca + 2H^+$$

(or)

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

Regeneration:- After the use the exhausted

cation exchange resin can be regenerated by passing it through a modiately conc-entrated solution of an acid.

$$(RCOO_2)Ca + 2HCl \longrightarrow 2RCOOH + CaCl_2$$

or

$$R_2Ca + 2HCl \longrightarrow 2RH + CaCl_2$$

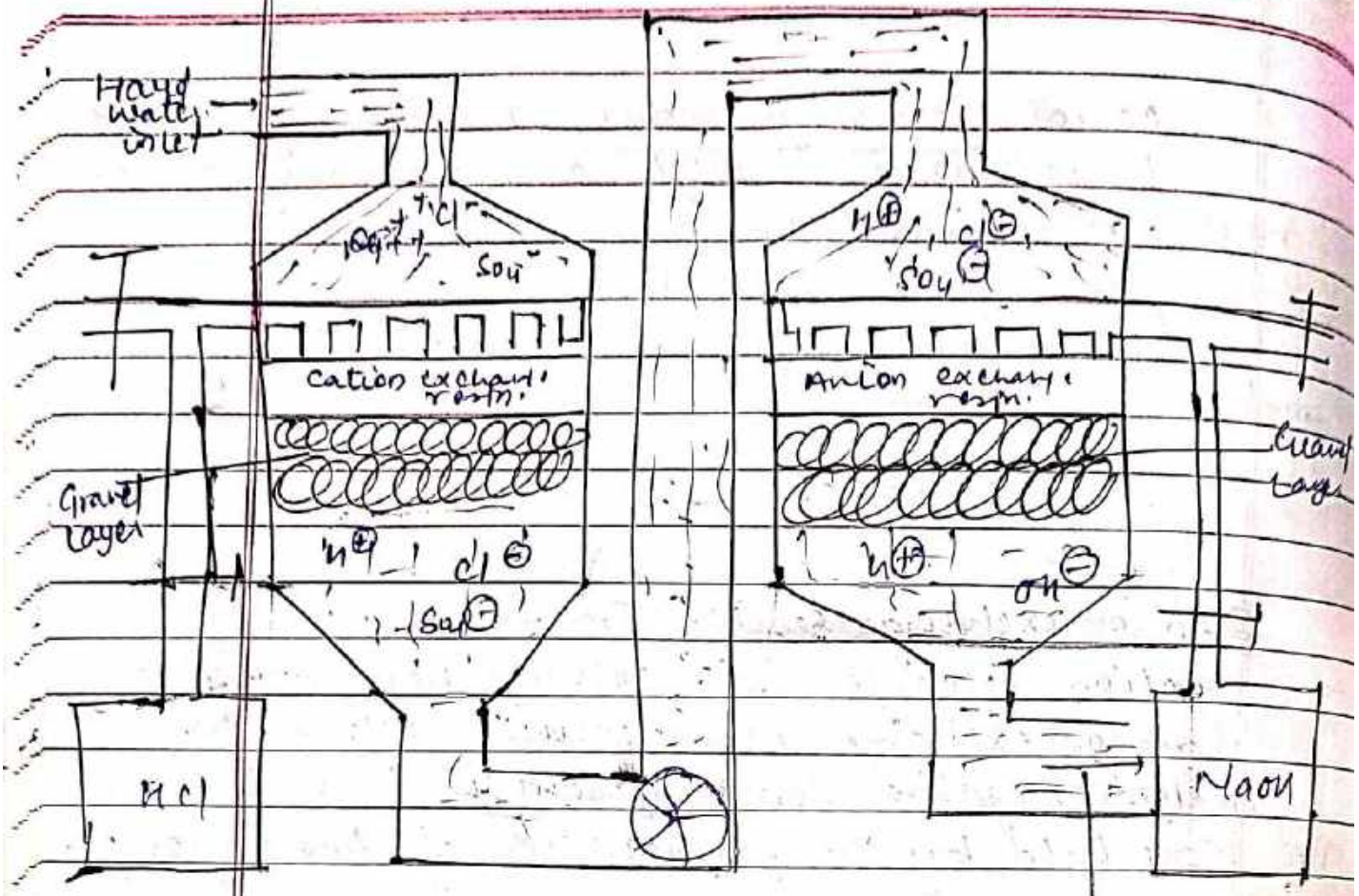
② Anion exchange resin:- The water coming from cation exchange resin column now pass through anion exchange resin column where the electronegative ions present in incoming water are held by the framework of basic groups.

$$ROH + Cl^- \rightarrow RCl + OH^-$$

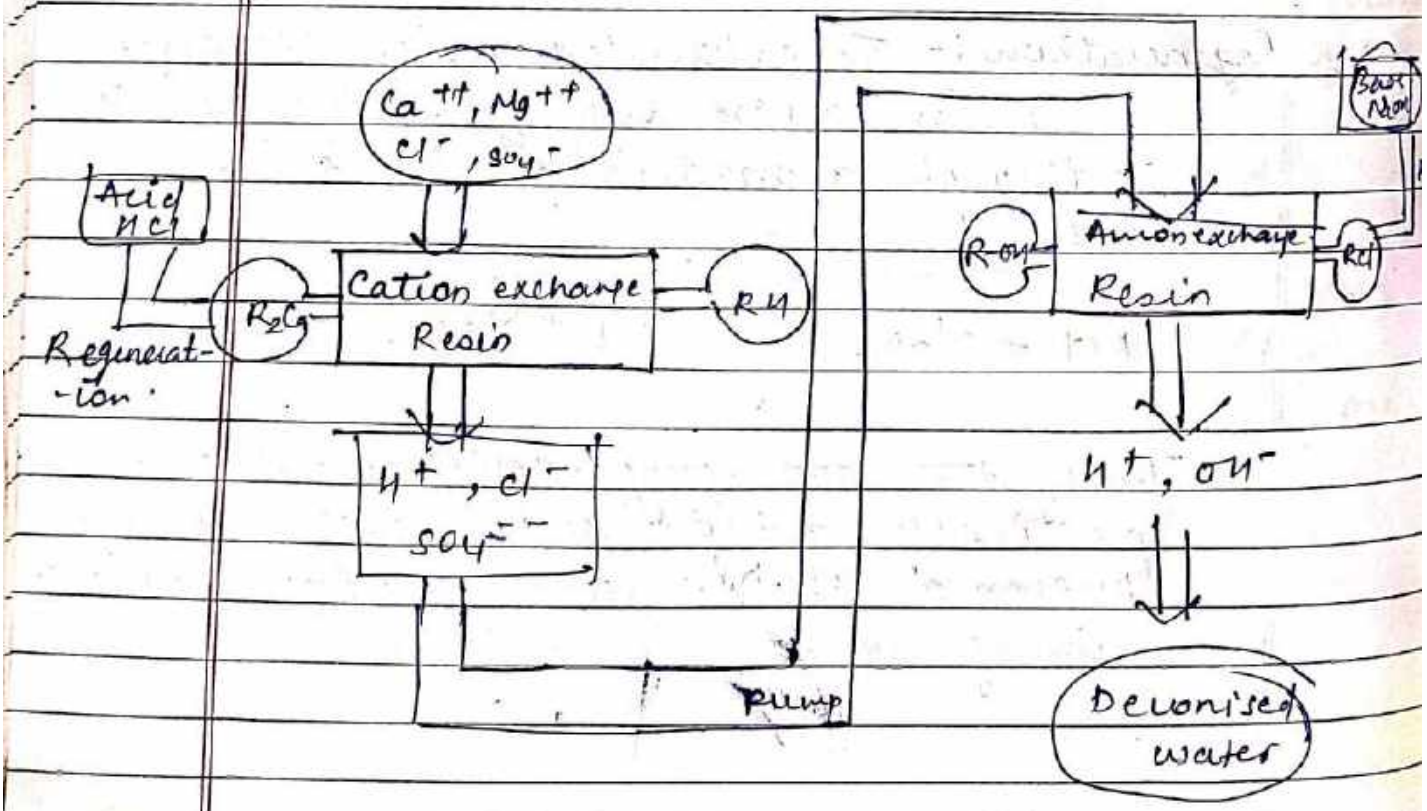
Regeneration:- The exhausted anion exchange resin can be regenerated by passing it through a moderately conc. solution of NaOH.

$$RCl + NaOH \rightarrow ROH + NaCl.$$

Thus, the out going water contains practically no ions so this process is also known as ~~the~~ Dionisation or D-miniralisat-ion of water.



* Ion exchange Resin method *



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Advantages of Ion exchange Resin :-

① This process can be used to soften highly acidic or alkaline waters.
② It produces water of very low hardness. (2 ppm) so the treated water is very good for use in high pressure boilers.

Disadvantages of Ion exchange Resin :-

① Capital cost is very high since chemical and equipment both are costly.
② If water contains turbidity then efficiency of process is reduced.

—x—

generation.

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* LIME-SODA METHOD *

In this process, soluble hardness causing impurities are chemically converted into insoluble precipitate which may be removed by settling and filteration, for this purpose hardwater is treated with lime and soda.

$Ca(OH)_2 + Na_2CO_3$
Lime Soda ash

By this method, All calcium salts are converted into $CaCO_3 \downarrow$ and All magnesium salts are converted in $Mg(OH)_2 \downarrow$ which can be filtered out

Principal :-

Salts	Reactions	Requirement
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$	L
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCO_3 + 2H_2O$	2L
Ca^{++}	$Ca^{++} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	S
$CaSO_4$	$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaOH$	
$CaCl_2$	$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$	

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Mg^{++} $MgCl_2$ $MgSO_4$	$Mg^{++} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{++}$ $MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$ $MgSO_4 + Ca(OH) \longrightarrow Mg(OH)_2 + HCaSO_4$	L+S
HCO^- / $NaHCO_3$	$2HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2H_2O + CO_3$ $2NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2H_2O + Na_2CO_3$	$\frac{L-S}{2}$
H^+ HCl H_2SO_4	$H^+ + Ca(OH)_2 \longrightarrow Ca^{++} + 2H_2O$ $2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$ $2H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O$	$\frac{L+S}{2}$

Addition of a coagulant like [$NaAlO_2$ or alum] helps in accelerating the coagulation of carbonate sludge which is removed by filteration.

TYPES OF LIME SODA METHODS :-

Lime soda method is of two types:-

1. cold lime soda process
2. Hot lime soda process

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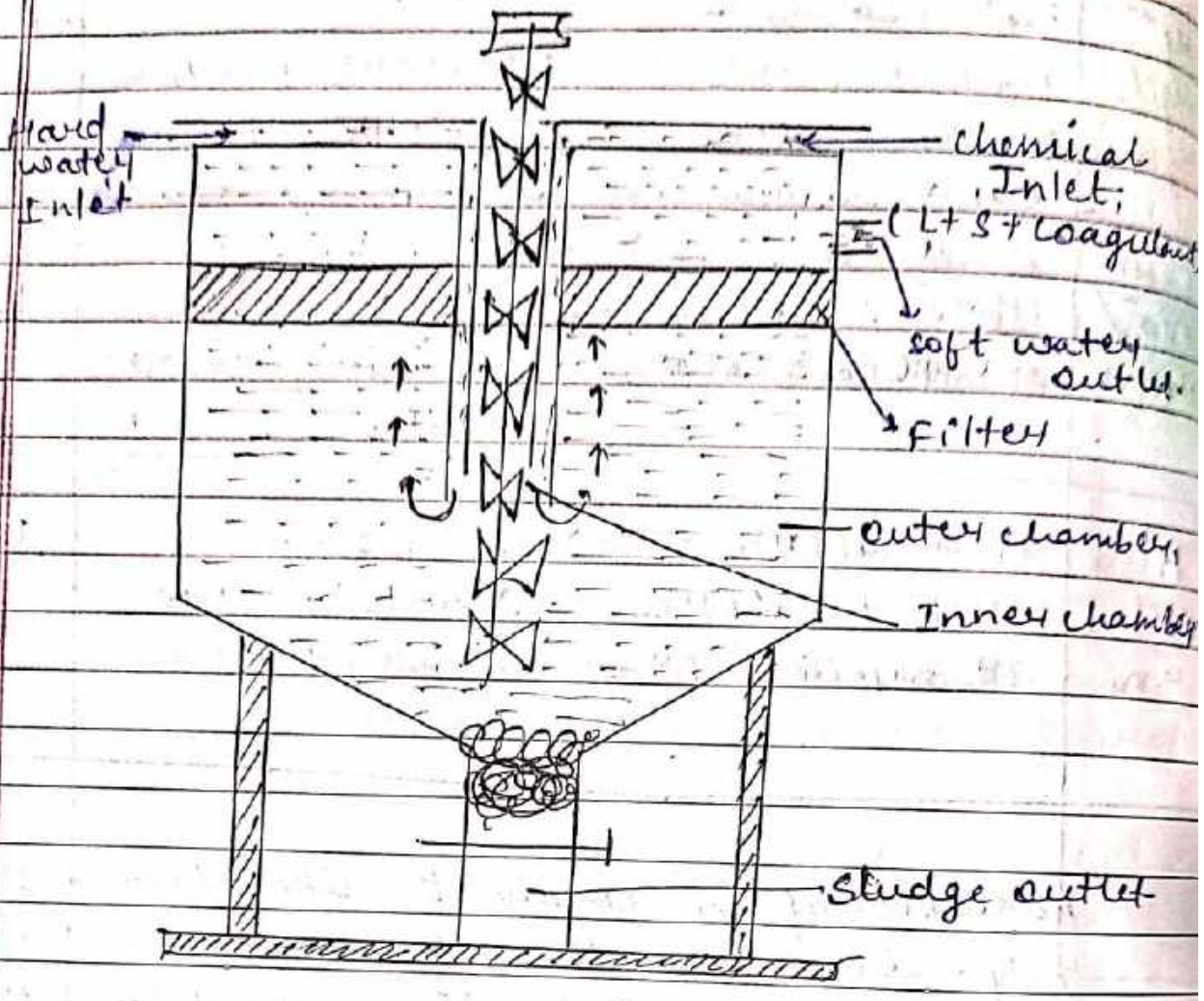
① Cold lime soda process :-



The hard water is first analysed and then fed into the inner vertical circular chamber. the apperatus contains

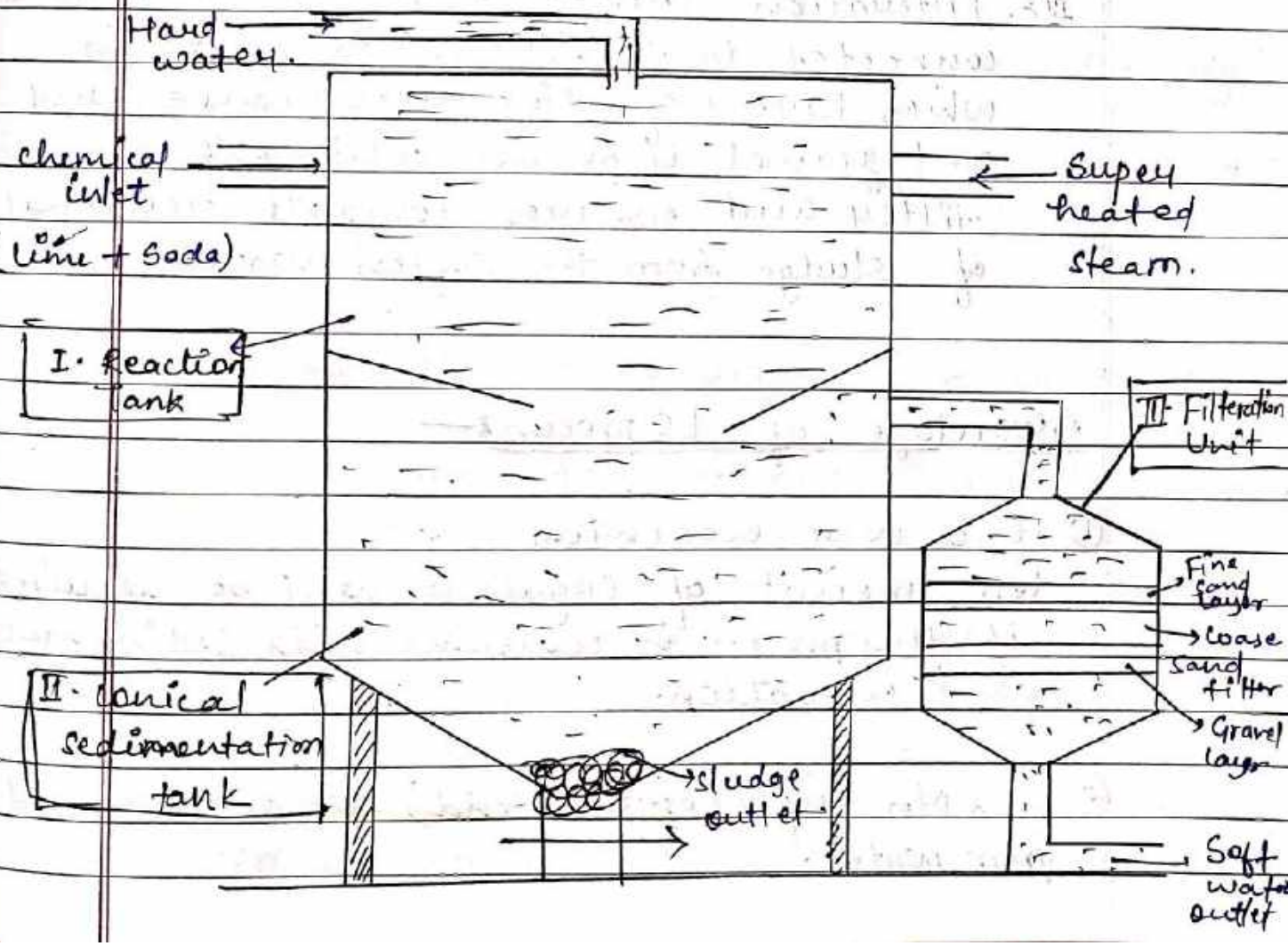
I.) Inner chamber :- In inner chamber, two inlets for hard water and chemicals [lime + soda + coagulant] are present and electrically operated stirrer is also present. Coagulant (Al_2SO_4, $NaAlO_2$) entraps the fine precipitate of $Al(OH)_3$ there by causing easy filteration. It also removes silica and oil if present in water

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

II. Outlet chamber: water become soft due to vigrous stirring, the heavy sludge settle down in the outer chamber and the soften water reaches up. The soften water then pass through filteration unit and finally filtered softwater flow out through the outlet at the top.

This process provide water containing hardness of 50-60 ppm.

III. HOT LIME SODA METHOD.



The instrument contains following three parts:-

I.) Reaction Tank:- In this process hardwater and softning chemicals are heated near about the boiling point of water. The reaction are much faster and the precipitate is almost complete.

II). conical Sedimentation Tank:- Now, the reaction content from the reaction tank comes to the conical sedimentation tank in which sludge settle down.

III). Filteration Tank:- Sedimentation Tank is connected to the filteration unit in which layers of fine ~~or~~ end course sand and gravel is present which acts as filter and ensures complete removal of sludge from the soften water.

Advantages of LS process:-

① It is very economical
less amount of coagulant will be required if this process is combined with sedimentation and coagulation.

② Fe & Mn (upto some extend) are also removed from water.

③ It helps in reducing the total minerals content of water.
④ It leads to an increase in the pH value of water. Thus reducing the corrosion of the distributing pipes

Disadvantages of LS process:—

① Careful operation and skilled supervision is required to get good results.
② Water of hardness 30ppm (Hot LS process)/ 50-60 pm (cold LS process) is obtained.
③ Formation of large amount of sludge creates its disposal problem.
④ This process cannot produce water having zero hardness.
⑤ Soften water from LS softners is not good for boilers.

Advantages of Hot LS process over cold LS process

① Hot LS Process takes about 15 minutes where as cold process takes several hours for completion.
② No coagulation is required because the precipitate and sludge formed settledown quickly in Hot LS process.
③ Residual hardness is much less than cold LS process.

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④ less chemicals are required in hot LS process.

⑤ Most of the dissolved gases like CO_2, O_2 are also removed.

⑥ Filteration becomes much easier as the viscosity of water becomes low in case of hot LS process.

Calculation of Requirement of Lime & Soda ash

$$\text{Lime Required} = \frac{74}{100}\left[\begin{array}{l}CaCO_3 \text{ equivalent of lime} \\ \text{consuming salt}\end{array}\right] \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\text{ purity}} \text{ kg.}$$

$$\text{Soda Required} = \frac{106}{100}\left[\begin{array}{l}CaCO_3 \text{ equivalent of soda} \\ \text{consuming salt}\end{array}\right] \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\text{ purity}} \text{ kg.}$$

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Table

Requirement	Salt	Requirement
L	$FeSO_4$	L+S
L	$AlCl_3$	$\frac{3}{2}$ L+3S
L	$Al_2(SO_4)_3$	3(L+S)
2L	H^+	$\frac{(L+S)}{2}$
L	HCl	$\frac{L+S}{2}$
L	H_2SO_4	L+S
S	OH^-	L+S
S	SO_4^{--}	L+S
S	HCO_3^- / $NaHCO_3$	$\frac{L-S}{2}$
S	$NaAlO_2$	-L
L+S	NaCl	
L+S	KCl	— x
L+S	Fe_2O_3	— x
L+S	Al_2O_3	
L+S	Na_2SO_4	

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Q. Calculate the amount of Lime and soda Required for requirement of 20,000 l of water whose analysis is as follows:-

$Ca(HCO_3)_2$	= 40.5	$CaCl_2$	→ 27.75
$Mg(HCO_3)_2$	→ 36.5	NaCl	→ 130
$CaSO_4$	→ 34		
$MgSO_4$	→ 30		

Salt	Amount (PPm)	$CaCO_3$ equivalent	Requirem
$Ca(HCO_3)_2$	40.5	$\frac{40.5 \times 50}{162/2} = 25 = A$	L
$Mg(HCO_3)_2$	36.5	$\frac{36.5 \times 50}{73} = 25 = B$	2L
$CaSO_4$	34	$\frac{34 \times 50}{68} = 25 = C$	S
$MgSO_4$	30	$\frac{30 \times 50}{60} = 25 = D$	L+S
$CaCl_2$	27.75	$\frac{27.75 \times 50}{55.5} = 25 = E$	S
NaCl	130	Donot consume either L & S.	X

$$\text{Lime Required} = \frac{74}{100}\left[Ca(HCO_3)_2 + 2Mg(HCO_3)_2 + MgSO_4\right] \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\text{ purity}}$$

$$= \frac{74}{100}(A + 2B + D) \times \frac{20,000}{10^6} \times \frac{100}{90}$$

$$= \frac{74}{100}(25 + 50 + 25) \times \frac{20,000}{10^6} = 1.48\ kg$$

Soda Required:- $= \frac{106}{100}\left[CaSO_4 + MgSO_4 + CaCl_2\right] \times \frac{Vol.\ of\ water}{10^6} \times \frac{100}{\%\ purity}$

$$= \frac{106}{100}\left[C + D + E\right] \times \frac{20,000}{10^6} \times \frac{100}{100}$$

$$= \frac{106 \times [75] \times 20,000}{100 \times 10^6} = 1.59\ kg$$

OH^- — P.
CO_3^{--} — P + M + M.
HCO_3^- — M

Alkalinity

Alkalinity is the measure of the ability water to neutralize the acid.

* Types of Alkalinity:-

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

Ions responsible -

$$\left.\begin{array}{l} \left.\begin{array}{l} OH^- + H^+ \longrightarrow H_2O \\ CO_3^{--} + H^+ \longrightarrow HCO_3^- \end{array}\right\} P \\ HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \end{array}\right\} M$$

Phenolphthalein , Methyl orange

P - OH^-, CO_3^{--}

M - OH^-, CO_3^{--}, HCO_3^-

Combination of Ions -

(1) OH^-
(2) CO_3^{--}
(3) HCO_3^-
(4) OH^- & CO_3^{--}
(5) CO_3^{--} & HCO_3^-

But there is no possibility with OH^- & HCO_3^- because they combine each other to form carbonate.

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

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Determination of Alkalinity

Sample (V_1) + 2 drop Phenolphthalein → Pink Colour

(V_2) + Acid (N_2) → Pink colour disappear

Red colour ← Acid (N_2) + Yellow Colour ← Methyl Orange + (V_2')

N_1 N_2
V_1 V_2 V_2'

Calculation of alkalinity -

Phenolphthalein alkalinity (P)

Alkaline Acid

$N_1 V_1 = N_2 V_2$

$N_1 \times V_1 = N_2 V_2$

$N_1 = \frac{N_2 V_2}{V_1}$

$S_P = N E$

$S_P = \frac{N_2 V_2}{V_1} \times 50 \times 10$ ppm

Methyl orange alkalinity (M)

Alkaline Acid

$N_1 V_1 = N_2 V_2''$

$N_1 \times V_1 = N_2 (V_2 + V_2')$

$N_1 = \frac{N_2 (V_2 + V_2')}{V_1}$

$S_M = N E$

$= \frac{N_2 (V_2 + V_2')}{V_1} \times 50 \times 1000$ ppm.

Alkalinity of Various Ions

S.No.	Result of Titration	Alkalinity due to		
		OH^-	CO_3^{--}	HCO_3^-
1.	$P = 0$	NIL	NIL	M
2.	$P = M$	P OR M	NIL	NIL
3.	$P = \frac{1}{2}M$ $(V_2 = V_2')$	NIL	2P	NIL
4.	$P > \frac{1}{2}M$ $(V_2 > V_2')$	2P − M	2(M − P)	NIL
5.	$P < \frac{1}{2}M$ $(V_2 < V_2')$	NIL	2P	M − 2P

Units of alkalinity -

$CaCO_3$ equivalent
PPM
mg/L

Q. 100 ml of a water sample required in 4 ml of $\frac{N}{50}$ H_2SO_4 for Neutralisation to phenophthalein end point another 16 ml of same acid was needed for further titration to methyl orange end point determine the type and amount of alkalinity in terms of $CaCO_3$ equivalent

$V_1 = 100\,ml$ $\quad V_2 = 4\,ml.$

$N_2 = \frac{1}{50}$ $\quad V_2' = 16\,ml.$

Phenophthalein alkanity ~~(N1) = 4 ml~~

$$N_1 V_1 = N_2 V_2$$

$$N_1 = \frac{N_2 V_2}{V_1}$$

$$N_1 = \frac{1 \times 4}{50 \times 100} = 0.0008\,ml.$$

$$S = N_1 E$$

$$= 0.0008 \times \cancel{50} \times \cancel{100}\,0$$

$$= \cancel{10000}$$

$$= \boxed{S = 40\,ppm}$$

Methyl orange alkalinity.

$$N_1 V_1 = N_2 V_2'$$

$$N_1 = \frac{N_2 (V_2 + V_2')}{V_1}$$

$$N_1 = \frac{1 \times (20)}{50 \times 100} = 0.004.$$

$$\boxed{N_1 = 0.004\,m}$$

$$S = N_1 \times 50 \times 100 = \frac{0.004 \times 50 \times 1000}{1000}$$

$$\boxed{S = 200\,ppm}$$

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Phenopthelein alkalinity (P) = 40 ppm

Methyl orange alkalinity (M) = 200 ppm.

$P = 0$ $\quad$ $P = M$ $\quad$ P $\quad$ $\frac{1}{2}M$.

$P(40)$ $\quad$ $\frac{1}{2}M(100)$

$$P(40) < \frac{1}{2}M(100)$$

Alkalinity of CO_3^{--} $= 2P$
$= 2 \times 40$
$= 80$ ppm

Alkalinity of HCO_3^- $= M - 2P$
$= 200 - 2 \times 40$
$= 120$ ppm.

Q. 50 ml of a sample of water required 5 ml of $\frac{N}{50}$ H_2SO_4 using methyl Orange indicator but did not give any colouration with phenopthelein what type of alkalinity is present? Express the same in ppm.

Sol $N_1 = ?$ $\quad$ $N_2 = \frac{1}{50}$ $\quad$ $V_1 = 50$ ml, V_2

phenopthelin alkalinity = 0

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Methyl Orange alkalinity.

$N_1 V_1 = N_2 V_2''$

$N_1 = \frac{N_2 (V_2 + V_2')}{V_1}$

$N_1 = \frac{1 \times (5)\,ml}{50 \times 50} = 0.002\,pml.$

$S = N_1 E = \frac{0.002 \times 50 \times 1000}{1000}$

$= 100\,ppm.$

$P = 0$

Alkalinity of $CO_3^{--} = M.$

$= 100\,ppm.$

A

A sample of water was alkaline to both phenopthalin & MO. 100 ml of water sample require 30 ml of $\frac{N}{50}$ H_2SO_4 for P. endpoint and another 20 ml for complete neutralisation determine the type and extent of alkalinity present.

$N_1 = 1$ $N_2 = \frac{1}{50}$ $V_1 = 100\,ml$ $V_2 = 30\,ml.$

$V_2'' = \frac{(100 + 20)}{50}$ $V_2' = 20\,ml$

P: $N_1 = \frac{N_2 V_2}{V_1}$

$= \frac{1 \times 1.5}{50 \times 100} = 0.006$ mol.

S: $N_1 E$

$= 0.006 \times 50 \times 1000$

$= 300$ ppm.

M: $N_1 = \frac{N_2 V_2''}{V_1} = \frac{1 \times 1.5}{50 \times 100}$

$= 0.01$

$S = N_1 E$

$= \frac{0.01}{100} \times 50 \times 1000$

$= 500$ ppm.

Methyl orange alkalinity = 500pm

P alkalinity = 300ppm

P = 0 P = M P $\frac{1}{2}$ M

$P(300) > \frac{1}{2} M (200)$

Alkalinity due to OH^- = 2P - M

= 600 - 500 = 100 ppm

Alkalinity due to CO_3^{--} = 2(M - P) = 2(500 - 300)

= 2(200) = 400 ppm

Limesode (Numerical)

Q. Calculate the amount of lime (74% pure) and Soda (90% pure) required ~~per~~ for soften 50,000 L of water containing salt

Salt	Amount	$CaCO_3$ equivalent	Required
$Ca(HCO_3)_2$	81	$\frac{81 \times 100/2}{162/2} = 50 = A$	L
$Mg(HCO_3)_2$	50	$\frac{50 \times 50}{73} = 34.24 = B$	2L
HCl	73	$\frac{73 \times 50}{36.5} = 100 = C$	$\frac{L+S}{2}$
Fe_2O_3	40	Do not contribute sode & lim	NR
$MgCl_2$	6	$\frac{6 \times 50}{47.5} = 6.31 = D$	L+S
CO_2	44	$\frac{44 \times 50}{22} = 100 = E$	2(L+S)
$Al_2(SO_4)_3$	57	$50 = F$	3(L+S)

$$\text{Lime required} = \frac{74}{100}\left[Ca(HCO_3)_2 + 2Mg(HCO_3)_2 + HCl + MgCl_2 + CO_2 + 3Al_2(SO_4)_3\right] \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\ \text{purity}}$$

$$= \frac{74}{100}\left[50 + 34.24 \times 2 + 50 + 6.31 + 100 + 3 \times 50\right] \times \frac{50000}{10^6} \times \frac{100}{74}$$

Soda Requirement :- $\frac{106}{100}\left[\frac{HCl}{2} + MgCl_2 + 3\times(Al_2)\right]$

$\times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\ \text{purity}}$

$= \frac{106}{100}\left[50 + 6.31 + 180\right] \times \frac{50,000}{10^3} \times \frac{100}{90}$

$= 106\left[206.31\right] \times \frac{5}{9\times10^3} = 12.14\ kg$

Que Calculate lime and Soda Required 30,000 l of water using 20 ppm of $NaAlO_2$ pass S congulant impurities

Ca^{2+}	160	$\frac{160\times50}{20} = 400$	S
Mg^{2+}	96	$\frac{96\times50}{12} = 400$	L+S
CO_2	34	$\frac{34\times50}{22} = 77.27$	L
HCO_3^-	403	$\frac{403\times50}{61} = 330.32$	$\frac{L-S}{2}$
$NaAlO_2$	20	$\frac{20\times50}{82} = 12.19$	-L

Lime required $= \frac{74}{100}\left[400 + 77.27 + 165.16 - 12.19\right] \times \frac{30,000}{10^6}$

$\times \frac{100}{90}$

$= \frac{630.24\times74\times30000}{100\times10^6} = 13.99\ kg$

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Soda required $= \frac{106}{100}\left[400 - 165.16\right] \times \frac{30,000}{106}$

$= \frac{106 \times 234.84 \times 30,000}{100 \times 106}$

$= 20.98$ kg.

REVERSE OSMOSIS *

Osmosis :- Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration. When two solutions of different concentration are seperated by semi-permeable membrane. The driving force responsible for the flow is known as Osmotic pressure.

Reverse Osmosis :- If a hydrolic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as its forced to move from concentrated side to dilute side across the membrane. This process is known as Reverse Osmosis.

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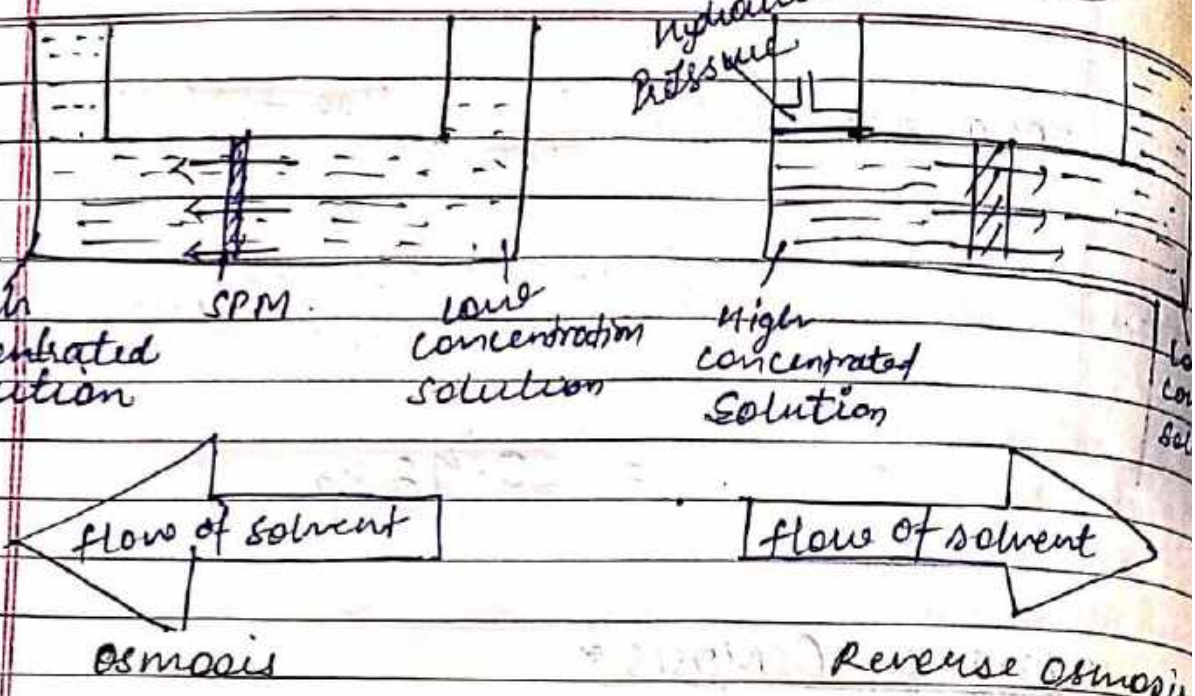
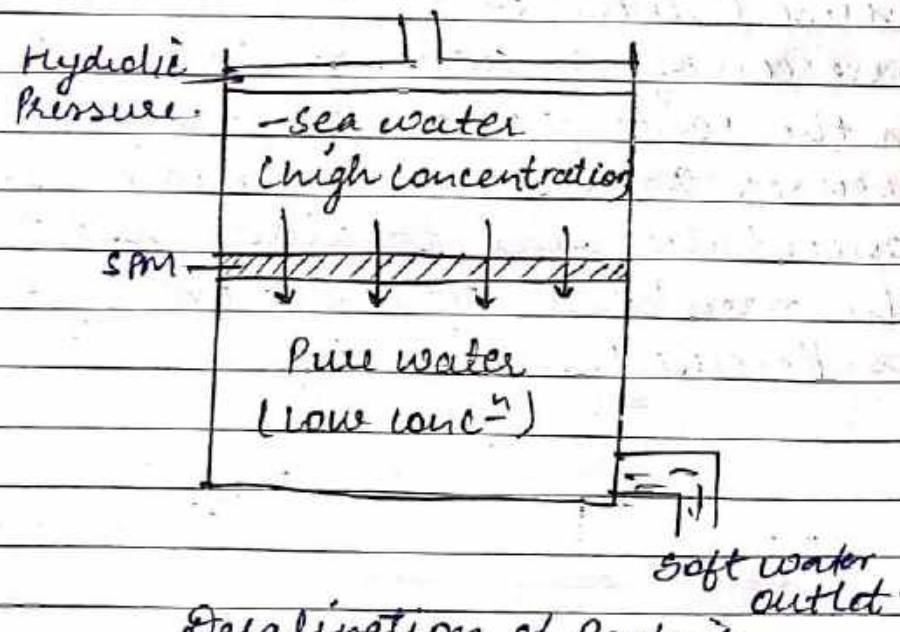


Examples of SPM :- Acrylics, polyamides, aramides.

* <u>Desalination of Brakish water</u>:- Sea water has Brakish taste, due to excess of salts. Sea water is not drinkable but by desalination (Removal of salts) method. It can be converted into pure water.



Desalination of Brakish water

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Advantages :-

It is simple and reliable process.
It operates comparatively at low temperature.
Capital and Operating cost are low.
Collidal SiO_2 can be removed by reversed Osmosis method which cannot be removed by ion exchange method.

Applications :-

In water treatment
for desalination.
for dialysis in hospitals.

CALGON CONDITIONING METHOD

Chemical Formula :- $Na_2[Na_4(PO_3)_6]$ or $Na_6P_6O_{18}$

Chemical Name :- Sodium hexa meta phosphate.

Principle :-

Ca^{2+} ion and Mg^{2+} ion present in hard water react with calgon to give complex negative ion.

$$Na_6P_6O_{18} \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$[Na_4P_6O_{18}]^{2-} + 2Ca^{++} \rightarrow [Ca_2P_6O_{18}]^{2-} + 4Na^+$$

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$$[Na_4P_6O_{18}]^{2+} + 2Mg^{2+} \rightarrow [Mg_2P_6O_{18}]^{2-} + 4Na$$

Chard water

Since the formation of complex negative ion decreases the concentration of calcium ion hence reducing ha. Calgon not only prevent the precipitation of soap as calcium salt of higher fatty acid (calcium soap) but actually dissolves such soaps. It has therefore found wide use in laundry for removing calcium soap which otherwise encrusts the washed textile.

Calgon conditioning is better than phosphate conditioning because it is workable at every pH which phosphate conditioning is workable at 9.5 pH - 10.5 pH.

* BOILER TROUBLES :-

Boilers are used for steam generation in industries and power house. If hard water is directly fed into the boilers it may lead to the following problems.

1.) Sludge and scale formation
2.) Boiler corrosion
3.) Caustic embrittlement
4.) Primming and foaming.

Sludge and Scale formation :-

Sludge :- The precipitate form in boiler is soft, loose and floats in water boilers. It is called sludges

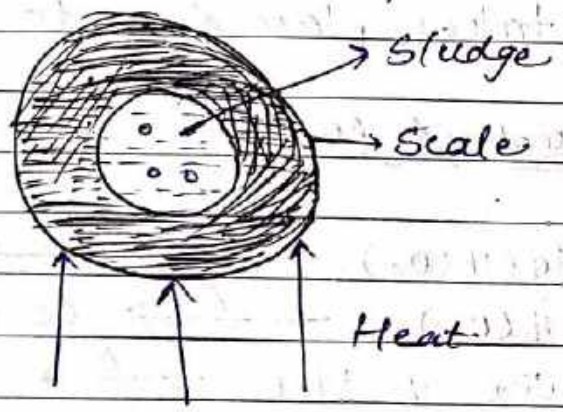
Salts responsible :- $MgCl$, $Mg(CO_3)_2$

Disadvantages :-

① Sludge are the bad conductor of electricity.
② Excessive sludge may cause choking of pipe.

Prevention :-

By frequent blow down operation.



Scale :-

Scales are the hard disposits firmly sticking on the inner wall of boiler cannot be removed easily by scraping.

Salts responsible :- $MgCl_2$, $Ca(HCO_3)_2$

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Disavantages :-

① Wastage of fuel.
② decrease in efficiency
③ Lowering of boiler Safety
④ Danger of explosion.

Removal of scales :-

① Scales can be removed by thermal chocks.
② By adding chemicals like Calgon.

2.) * BOILER CORROSION :-

Destruction of boiler body material by unwanted chemical reaction is known as boiler corrosion.

⇒ It takes place due to following Reason :-

ⓐ Dissolved CO_2 :-

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + CO_2 \uparrow$$
$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$
$$CO_2 + H_2O \xrightarrow{\Delta} H_2CO_3.$$
(Carbonic acid).

Acidic medium is always corrosive in nature.

⇒ Removal :-

By adding NH_4OH

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

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(b) Dissolved O_2 :-

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

$$\boxed{Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe(OH)_2}$$

→ Removal :-

By adding sodium sulphate :-
$$2NaSO_3 + O_2 \longrightarrow 2Na_2SO_4$$

(c) Dissolved Salts :-

$$MgCl_2 + H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
$$CaSO_4 + H_2O \longrightarrow Ca(OH)_2 + H_2SO_4.$$

Removal :-
By Neutrisation.

3.) CAUSTIC EMBRITTLEMENT :-

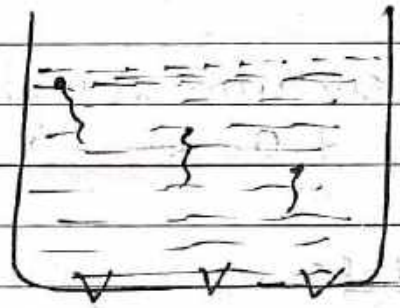
Caustic embrittlement is type of boiler corrosion due to which boiler material become brittle in presence of high concentration of caustic and static tensil stress.

When heater is softened by zeolite or calgon method, then this type of water have

excessive amount of sodium salt.

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

The caustic water flows into the hair like cracks present in inner wall of boiler by cappilary action. On progressive heating Amount of NaOH increases. Caustic embrittlement arises due to the setting up of concentration cell.



Fe at stressed part (anode)	NaOH conc	NaOH dil	Fe at unstressed part (cathode)

* Prevention :-

① By adding sodium phosphate as softening reagent.

② By adding sodium sulphate which dogges the hair like cracks

4). * PRIMMINGS AND FOAMING :-

Formation of wet steam is known as primmings.

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Reasons:-

① Faulty in design.
② Sudden rise in temperature.

Prevention:-

① By proper designing.
② By maintaining low level of water.

Formation of impersistant layer of bubbles is known as foaming.

Reasons:-

① Due to the presence of Oil and suspended impurities.

Prevention:-

By adding anti-forming reagent like castor oil.

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Que. 100 ml of a raw water sample required 25 ml of $\frac{N}{50}$ H_2SO_4 for neutrilisation to phenopthelein end point after this methyl orange indicator was added to it and further acid required is 3 ml. Calculate the alkalinity of water as $CaCO_3$ in parts per million.

Sol Phenopthelin alkalinity :-

$V_1 = 10ml$ $V_2 = 25ml$ $N_2 = \frac{1}{50}$

$V_2' = 3ml$

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{1 \times 25}{50 \times 100} = 0.5$$

0.0005 ml

$$S = NE = 0.005 \times 50$$
$$= 0.25 ml/l = 250 ppm.$$

Methyl Orange alkalinity :-

$$N_1 = \frac{N_2 (V_2''}{V_1}$$

$$N_1 = \frac{N_2 (V_2 + V_2')}{V_1} = \frac{1 \times 28}{50 \times 100}$$

$$= 5.6 \times 10^{3}$$
$$= 5.6 ppm$$

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$S = NE = 5.6 \times 50$
$= 280$ ppm.

~~Phenol~~ $= 250$
$M = 280.$

$P = 0$ $\quad P = M \quad P \quad \frac{1}{2} m.$

$250 > \frac{1}{2} m (140)$

$P > \frac{1}{2} m =$

Alkalinity due to OH^- $= 2P - M$
$= 2(250) - 280$
$= 500 - 280$
$= 220$ ppm

Alkalinity due to CO_3^{--} $= 2(M-P)$
$= 2(280 - 250)$
$= 2(30)$
$= 60$ ppm.

Q. SEM (1):- 2018-19)

Q6 (a)

Ca^{2+}	20	$\frac{20 \times 50}{20} = 50$	S
Mg^{2+}	25	$\frac{25 \times 50}{12} = 104.16$	L+S
CO_2	30	$\frac{30 \times 50}{22} = 68.18$	L
$NaCO_3^-$	150	$\frac{150 \times 50}{61} = 122.95$	$\frac{L-S}{2}$

K^+	10	$\frac{10 \times 50}{}$ it does not exist	X.

Lime required $= \frac{74}{1000}[104.16 + 68.18 + 61.47] \times \frac{10^6}{100} \times \frac{100}{87}$

$= \frac{74[233.81]}{87} = 198.87$

Q. Calculate the Quantity of lime (~~CaCO3 basis~~) and soda (~~Na2CO3 basis~~) required for cold softening of 125000 L of water with following analysis. Impurities and using 10 ppm of Na_2Al as coagulant

Analysis of water

Ca^{++}	95	$\frac{95 \times 50}{20} = 237.5$	S
Mg^{++}	36	$\frac{36 \times 50}{12} = 150$	L + S
CO_2	66	$\frac{66 \times 50}{22} = 150$	L
HCO_3^-	244	$\frac{244 \times 50}{61} = 200$	$\frac{L-S}{2}$

H^+	2ppm	$\frac{2 \times 50}{1} = 100$	$\frac{L+S}{2}$
CO_3^{--}	45ppm	$\frac{45 \times 50}{30} = 75$	S
OH^-	34ppm	$\frac{34 \times 50}{17} = 100$	L+S

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FUEL AND COMBUSTION

Fuel is a combustable substance containing carbon as main constituent which on proper burning gives large amount of heat which can be used economically for domestic and Industrial purpose.

$$\text{Fuel} + O_2 \longrightarrow \text{Product} + \text{Heat}$$

* Classification of fuel:-

- Fuel
  - Primary or Natural fuel
    - Stage of segrigation
      - Solid — Eg:- wood
      - Liquid — Eg- crude oil
      - Gaseous — Eg:- Natural gas.
  - Secondary or Derived fuel.
    - Stage of segrigation
      - Liquid — Eg:- coal, charcoal
      - Solid — Eg:- diesel, petrol
      - Gaseous — Eg:- oil gas, coal gas.

* Properties of Good Fuels:-

1. A good fuel has high calorific value.
2. It should have moderate volatile metal.
3. It should be easy to carry from one place to other.

④ It should have high amount of fixed carbon.
⑤ It should less amount of ash component
⑥ It should be ecofriendly.
⑦ It should be easily available.

* Classification of coal on the basis of percentage of carbon:-

(or)

Ranking of coal:-

Fuel	% of carbon.
Wood.	50
Peat	57
Lignite	67
Sub-Bituminous	77
Bituminous	83
Semi-Bitumineous	90
Anthracite	93

* Flash Point & Fire Point:-

Flash point is a temperature at which vapour of fuel will ignite in form of flash when ~~com~~ it come in contact with fire. (Flash may ~~will~~ last long for 5 sec).

Fire point is a temperature at which vapour of fuel will ignite

for long time when it come in contact with fire.

* Analysis of fuel :-

In order to access the quality of coal following two types of analysis of coal are made:-

1. Proximate analysis
2. Ultimate analysis

Proximate analysis:-

Proximate analysis determines the percentage of moisture, volatile metal, ash and fixed carbon. It is called proximate analysis because the data very width procedure adopted.

This analysis provides the following data.

1. % of moisture:- About 1 gram of finely powder air dryed coal sample is weighed in crussible the crussible place inside an electric hot air oven at 100-140°c for 1 hr. after it it is cooled in descicator and weighed.

$$\% \text{ of moisture} = \frac{\text{loss in weight}^{(100°c)}}{\text{weight of coal taken}} \times 100$$

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% of volatile metal :- The dried sample of coal left in the crussible (in step1) is then covered with lead placed it in electric furnace (muffle furnance) at 925 ± 20°c for 7 minutes after it, it is cooled in deciator and weighed.

$$\% \text{ of volatile Metal} = \frac{\text{Loss in weight}(925°c)}{\text{Weight of coal taken}} \times 100.$$

% of ash :- The Residual coal in crussible in (step2) is then heated by lead. in muffle furnance at 700 ± 50°c for 30 minutes and then it is colled in deciator and weighed.

$$\% \text{ of ash} = \frac{\text{Weight of Residual/Ash}(700°c)}{\text{Weight of coal taken}} \times 100.$$

% of fixed carbon :-

$$\% \text{ of fixed carbon} = 100 - (M + Vm + ash)\%.$$

Importance/ Signification of proximate analysis

Moisture :- Moisture lowers the effective calorific value of coal.

Volatile metal :- A high volatile metal containing coal burns with long flame, high smoke and low calorific value hence moderate the volatile matter better the rank of coal.

) **ash :-** It reduces the calorific value of coal.

) **Fixed carbon :-** high the % of fixed carbon, greater the

calorific value and quality of coal

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PROXIMATE ANALYSIS

Hot air oven
100 – 110°c
(1 hr)

Step 1 → **% of MOISTURE** → % of Moisture = $\frac{\text{loss of wt}}{\text{wt of coal taken}} \times 100$

Muffle furnace
covered crucible
925 ± 20°c
(7 min)

Step 2 → **% of VOLATILE MATTER** → % of VM = $\frac{\text{Loss of wt}}{\text{wt of coal taken}} \times 100$

Muffle furnace
open crucible
700 ± 50°c
(30 min)

Step 3 → **% OF ASH** → % of Ash = $\frac{\text{wt of Residue/Ash}}{\text{wt of coal taken}} \times 100$

Step 4 → **% of FIXED CARBON** → % of fixed C = 100 – % (M + VM + Ash)

Q. A sample of coal was analysed for the content of moisture, volatile metal and ash from following data. Calculate the percentage of above quantities.

1) wt of coal taken = 2.5 gm.
2) wt of coal (after heating at 100°c) = 2.365 gm.
3) wt of coal (after heating covered crucible at 950 ± 20°c) = [illegible]

4. constant weight obtained at the end of experiment = 0.460 gm

Sol:-

$\frac{x-y}{x} \times 100$

% of Moisture = $\frac{x-y}{x} \times 100$

$= \frac{2.5 - 2.365}{2.5} \times 100.$

$= 5.4\%$

$\frac{y-z}{x} \times 100$

% of VM = $\frac{2.365 - 1.165}{2.5} \times 100$

$= 48\%$

% of ash = $\frac{0.460}{2.5} \times 100.$

$= 18.4\%$

$\frac{A}{x} \times 100.$

% of fixed C = $100 - 71.8\%$

$= 28.2\%$

Q. A sample of coal was analysed as followed. Exactly 1.500g was weighed into silica crussible. after heating for an hour at 110°c the residue weight 1.415gm. The crussible was then covered with a vented lid and strongly heated for exactly 7min) at 950 ± 20°c the residue weight 0.528 gm. The crussible was heated without the cover untill a constant weight was obtained. The residue

was found to weight 0.254 g. calculate
① % result of above analysis.
② To which type of analaysis does the above discription belong? why the above analysis named so.

Sol % of Moisture $= \frac{x-y}{x} \times 100 = \frac{1.500 - 1.415}{1.500} \times$
$= 5.6\%$

% of VM $= \frac{1.415 - 0.528}{1.500} \times 100$
$= 59.13$ gm

% of ash $= \frac{0.254}{1.500} \times 100 = 16.93$ gm.

% of fixed carbon $= 100 - (5.6 + 59.13 + 16.93)\%$
$= 18.34\%$.

ULTIMATE ANALYSIS

It is also called elementary analysis. it determines following results.

① % of carbon & Hydrogen: About 1 to 2gm of accurately weighed coal sample is burned in a current of oxygen in a combustion apparatus. Carbon and Hydrogen are converted into CO_2 & H_2O respectively and absorbed by KOH and $CaCl_2$ tubes respectively. the increase in weight of these are determined

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$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{Increased wt. of KOH bulb}}{\text{wt. of coal taken}} \times 100$$

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{Increased wt. of } CaCl_2 \text{ tube}}{\text{wt. of coal taken}} \times 100$$

2) % of Sulphur:- After combustion sulphur is converted into sulphate it is treated with $BaCl_2$ then $BaSO_4$ is precipitated.

$$\% \text{ of Sulphur} = \frac{32}{233} \times \frac{\text{wt. of } BaSO_4}{\text{wt of coal taken}} \times 100.$$

% of Nitrogen :- About 1 gram of accurately weight powdered coal is heated with concen-trated H_2SO_4 along with K_2SO_4. Now it is treated with excess of KOH and librated ammonia then absorbed in known volume of standard acid solution. the unused acid then determine by back titration.

$$\% \text{ of } N = 1.4 \times \frac{\text{Normality of acid used} \times \text{Vol. of acid used}}{\text{wt. of coal taken}}$$

4) % of oxygen:-

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

% of ash will be determined by proximate analysis.

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Numerical

Que 0.2 gram of coal sample is accurately weight and is burned in a combustion apperatus. The gaseous product are absorbed in potash bulb and calcium chloride tube of known sample. The increased in weight of potash bulb and $CaCl_2$ tube are 0.66 gram and 0.08 gm respecility. calculate the % of carbon and hydrogen in coal sample.

Sol

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{\text{Increased weight of KOH bulb}}{\text{wt of coal taken}}$$

$$= \frac{12}{44} \times \frac{0.660 \times 100}{0.2}$$

$$= \frac{12 \times 660}{88} = 90 gm$$

$$\% \text{ of hydrogen} = \frac{2}{18} \times \frac{\text{Increased wt of } CaCl_2 \text{ tube} \times 100}{\text{Wt of coal taken}}$$

$$= \frac{2}{18} \times \frac{0.080}{0.2} \times 100$$

$$= \frac{80}{18} = 4.44 gm$$

Q By KZELDAHL's method 3.5 gm of coal sample was analysed. the ammonia gas was evolved was absorbed in 50 ml of 0.1 n H_2SO_4. after the absorption residual

(excess) H_2SO_4 required 15ml of 0.1n NaOH for neutrilization. Calculate the % of Nitrogen in sample of coal.

$$\% \text{ of } N. = \frac{1.4 \times \text{Normality of acid used} \times \text{Vol. of acid used}}{\text{wt. of coal taken}}$$

wt. of coal taken = 3.5gm
Normality of acid used = 0.1
Vol. of acid ~~used~~/taken = 50
Vol. of NaOH = 15
Normality of NaOH = 0.1

Acid NaOH.

$N_1 V_1 = N_2 V_2$

$\cancel{0.1} \times V_1 = \cancel{0.1} \times 15$

$\boxed{V_1 = 15}$

Vol. of acid used = 50 − 15 = 35ml.

$$\% \text{ of } N = \frac{1.4 \times N \times V}{w}$$

$$= \frac{1.4 \times 0.1 \times 35 \times 10}{3.5}$$

$$= 1.4\%$$

3gm of coal heated in Kjeldahl's flask and ~~dm~~ NH_3 gas evolved was absorbed in 40ml of 0.5m H_2SO_4. after absorbtion the excess acid required 18.5ml of 0.5n

KOH for neutrilisation. 2.3 gram of coal Sample in quantitative analysises gave 0.35 gm $BaSO_4$ calculate % of Nitrogen and Sulphur in coal sample.

acid KOH

$N_1V_1 = N_2V_2$

$0.5 \times V_1 = 0.5 \times 18.5$

$\boxed{V_1 = 18.5}$

Vol. of acid used = 40 − 18.5
= 21.5

Normality = 0.5n.

$$\% \text{ of } N = \frac{1.4 \times N \times M}{\text{wt of coal}} = \frac{1.4 \times 21.5 \times 0.5}{3}$$

$= 5.01\%$.

$$\text{wt. of Sulphur} = \frac{32}{233} \times \frac{0.35}{2.3} \times 100$$

$= 2.08\%$.

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* Calorific value *

The total quantity of heat liberated when a unit mass (volume) of fuel burnt completely.

→ ~~Ty~~ Types of Calorific value:-

(1) Higher or Gross calorific value (HCV & GCV)

The total amount of heat produced when unit mass/volume of fuel has been burnt completely and the products of combustion have to cool to room temperature

(2) Lower or Net calorific value (LCV or NCV):-

The net heat produced when unit mass/volume of fuel burnt completely and products are allowed to scape.

LCV = HCV − latent heat of steam

LCV = HCV − 9 × % of hydrogen × latent heat of fuel.

LCV = HCV − 0.09 × % of hydrogen × latent heat of steam.

latent heat of steam = 587 Kcal/kg
= 587 Cal/g

* Units of calorific value:-

(1) Calorie:- The amount of heat required to raised the temperature of 1 gram water through 1°c.

(2) K. Calorie:- The amount of heat required to raised the temperature of 1 kg water through 1°c

(3) British Thermal unit (BTHU):- The amount of heat required to raised the temperature of 1 pound water through 1°F.

(4) Centigrate heat unit (CHU):- The amount of heat required to raised the temperature of 1 pound water through 1°c

$$1\ Cal = 1000\ Cal = 3.968\ BTHU = 2.2\ CHU$$

* Calculation of calorific value:-

According to dulong's formula,

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

$$LCV = HCV - 0.09 \times \%\ of\ H \times latent\ heat\ of\ steam$$

where all element such as, carbon, oxygen, Hydrogen, Sulphur are in percent and their Calorific values are

$C = 8080$ kCal/kg
$H = 34500$ kcal/kg.
$S = 2240$ kcal/kg.

Calculate the Gross and net calorific value of coal having the following compositions.
Carbon = 85%. H → 8%. N = 2%, S = 1%.
ash 4%.

% of O = 85 + 8 + 2 + 1 + 4 = 100.

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(8 - 0\right) + 2240\right] \text{Kcal/kg}$$

$$= \frac{1}{100}\Big] = 9650.40 \text{ cal/g.}$$

9650.40 − 0.09 × 8 × 587
9650.40 − 422.64
= 9227.76 cal/g.

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* BOMB CALORIMETER *

Principle:- A known mass of fuel is burnt completely and the quantity of heat produced and is absorbed by known mass of water. for this calorific value.

Construction:-

It contains following parts:-

① **Stainless steal bomb:-** It consist of strong and cylindrical stainless steal in

which can be screwed to body of Bomb so as to make a perfect gas tite seal. the lead is provided with two stainless steel electrodes and an oxygen inlet wall. To one of the electrodes, a small ring is attached, in this ring, a nickel or stainless steal crucible can be supported.

② **copper calorimeter:-** The Bomb is placed in copper calorimeter having known mass of water, Backman therometer and electrically operated Styrer.

③ **Air Jacket / Water jacket:-** copper calorimeter is surrounded by airjacket and water jacket to prevent heat losses.

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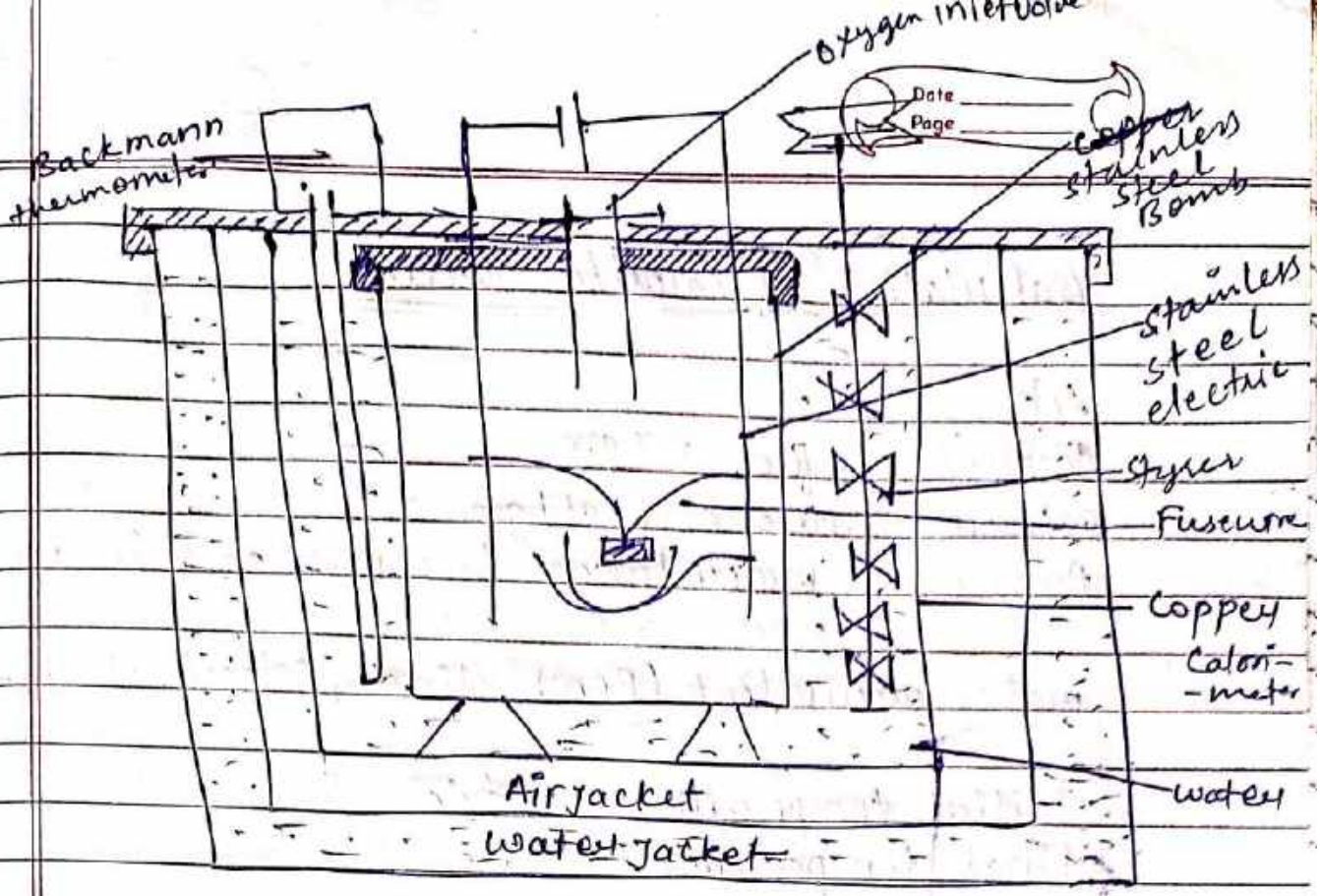

Working:-

A known mass of given fuel is taken in clean crusible ~~and~~ than crusible is supported over the ring. a fine magnisium water touching the fuel is then stretched across the ~~electrode~~ electrodes. The bomb lid is tightly screwed and bomb filled with oxygen to 25 atm ~~atm~~ pressure. The bomb is then lowered

into copper calorimeter containing a known mass of water. the styrer is work and initial of water is noted. The electrodes are then connected to 6V battery and circuit completed. The sample burns and heat is liberated. Uniform styring of water is continued and maximum temperature attain is recorded.

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Calculation of calorific value:

Let
Amount of fuel = x gm
calorific value = L cal/gm
Amount of water taken in copper calorimeter = W gm

water equivalent (Bomb, stirrer, calorimeter) = w gm

Initial temperature = t_1 °c
Final temperature = t_2 °c

Amount of heat liberated = xL

Amount of heat absorbed = $(W+w)(t_2-t_1)$

Amount of heat liberated = amount of heat absorbed

$$xL = (W+w)(t_2-t_1)$$

$$\boxed{L_{(net)} = \frac{(W+w)(t_2-t_1)}{x}}$$

Formula with correction:-

C_c → cooling correction
C_f → fuse wire correction (−)
C_A → Acid correction (−)
C_{CT} → cotton thread correction (−)

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$$HCV = \frac{(W+w)(t_2 - t_1 + c_c) - (C_F + C_A + C_D)}{x}$$

Qu On burning 0.83 gm of solid fuel in a Bomb calorimeter, a temp of 3500 gm increased from 26.5°c to 29.2°c. Water equivalent of calorometer and latent heat of heat are 385.0 gm and 587 cal/gm resp. If the fuel contain 0.7 hydrogen calculate its gross and net calorific value.

$x = 0.83$ gm $W = 3500$ $t_1 = 26.5$°.
$w = 385$ $t_2 = 29.2$°C

Latent heat = 587,
% of H = 0.7%.

$$HCV = \frac{(3500 + 385) \times (29.2 - 26.5)}{0.83}$$

$$= \frac{(3885) \times 2.7}{0.83}$$

$$= 12637.95 \text{ cal/gm}$$

LCV = HCV − 0.09 % of H + Latent heat

$$= 12637.95 - 0.09 \times 0.7 * 587$$

$$= \cancel{467364.029 \text{ cal/gm}}$$

$$= \cancel{12634}\ 12600.96 \text{ cal/gm}$$

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* BIOGAS :-

BioGas is made from organic waste matter (Biomass) by an aerobic decomposition that is in absence of air.

* Process :-

Biogas ⟶ Anaerobic decomposition (34-45°c) ⟶ Biogas

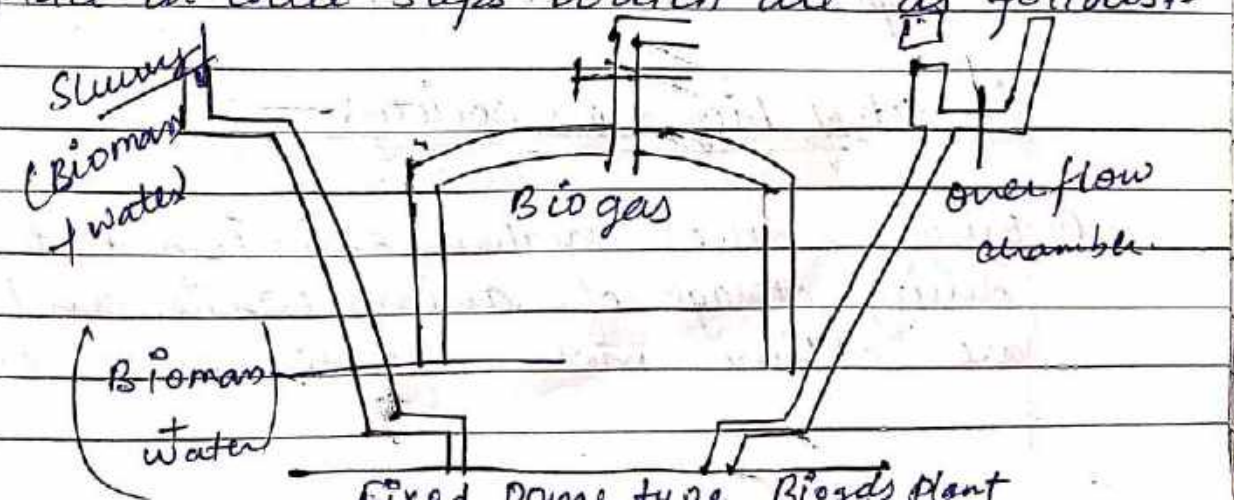
* Composition of BioGas :-

CH_4	= 55 %	N_2	= 2-3 %
CO_2	= 35 %	H_2S	= 0.3 %
H_2	= 7-8 %	O_2	= 0.2 %

calorific value 1200 cal/m³

* Process :-

An aerobic degradation of biomass takes place in three steps which are as follows:-



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Step 1:- Complex Biogas material decomposes by decomposition convert complex, butyric, propoyin and electric acid.

Step 2:- In this stage actogenic bacteria converts these acid into acedic acid, hydrogen and carbon di-oxide.

Step 3:- In this stage methanogenic bacteria reduce CO_2 to methane and consume H_2.

Construction of Biogas plant:-

* Biogas plant is of two types :-

① Fixed dome type bio-gas plant.
② floating gas holder type.

Limitation of Biogas:-

① It depends on environmental condition.

impact of biogas on society:-

① Biogas reduces methane emission that occurs during storage of animal waste and they are 21 times more effective than CO_2.

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Bio gas can replace fuel such as wood, charcoal reducing back carbon emission and deforestation.

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02/02/2023 Thursday

MODULE :- 3

ELECTROCHEMISTRY, CORROSION AND PHASE RULE

* CORROSION *

Corrosion is the deterioration of substance due to its reaction with its environment.
Example- Rusting of iron, formation of green layer of basic carbonate etc

Causes of corrosion:-

Metal exist in nature in the form of carbonates, sulphides, sulphates. These combine state of metals (Ores) has low energy and thus thermodynamically stable state of metal. a considerable amount of energy is required during metallurgy. The extracted metals has higher energy and it is thermodynamical unstable state. thus metal have a natural tendency to convert back to its natural thermodynamically stable state.

combined form (More stable) $\xrightarrow{\text{Metallurgy}}$ free state (Less stable)
$\xleftarrow{\text{corrosion}}$

Effects of corrosion:-

1. Destruction of materials.
2. Metal losses its efficiency
3. Purity of product gets affected.
4. Maintainance and cost of material increases.

Imp → **Electro chemical and Wet theory of corrosion:-**

It is also known as ~~emerged~~ immersed corrosion. it takes place under moist or wet condition through the formation of short circuited galvanic cell. In this corrosion following steps involved:-

Step 1:- Formation of two different areas:-
separate anodic and cathodic area formation takes place b/w which current flows through the conducting medium

Pure area → anode
Impure area → cathode

Step 2:- oxidation at anode:-
Accurance of oxidation at anodic areas which generates metallic ions.

$M - ne^- \rightarrow M^{n+}$ (oxidation)
(Metallic ions)

Step3:- Reduction of cathode :-
Occurance of Reduction at cathodic areas which generates non-metallic ions (OH^-)/gase).

Step4:- Formation of corrosive products:-
Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosive product some-where b/w anodic and cathodic areas takes place.
Eg:- Rusting of Iron.

→ On the basis of cathodic Reaction. corrosion is of two types:-
① Evolution of Hydrogen type Corrosion.
② Absorption of O_2-type corrosion

① Evolution of H_2 - type corrosion:-

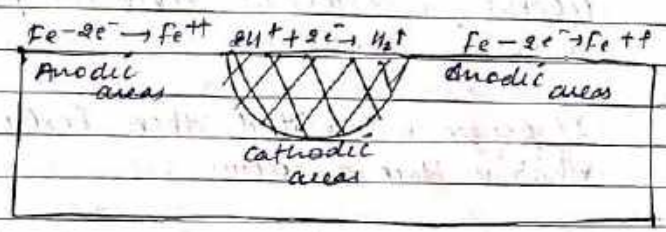
Eg:- Rusting of Iron

This type of corrosion takes place in acidic medium.

Step1:- Formation of two different areas.
Pure area — Anode
Impure area — cathode

Step2:- Oxidation of Anode:-
$Fe - 2e^- \rightarrow Fe^{+2}$
(Metallic ion)

Step3:- Reduction of cathode:-
$2H^+ + 2e^- \rightarrow H_2\uparrow$



② Absorption of O_2-type corrosion:-

It takes place in a type of Neutral and Slightly alkaline medium.
Eg:- Rusting of Iron.

Step1:- Formation of different areas
Pure area — Anode
Impure area — cathode

Step2:- Oxidation at Anode
$Fe - 2e^- \rightarrow Fe^{++}$ (Metallic ion)

Step3:- Reduction at cathode
$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
(Non-metallic ion)

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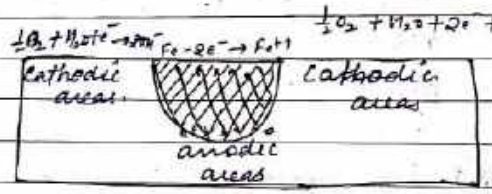
Step 4: Formation of corrosion product

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

If oxygen is present in sufficient amount $Fe_2O_3 \cdot H_2O$ is formed as corrosive product which is yellow in colour.

If oxygen is limited then Fe_3O_4 is formed which is black in colour

In this type of corrosion, cathodic areas are larger than anodic areas



* Prevention of corrosion:-

- Cathodic Protective method
- Anodic protection method
- By coating
- By proper Designing
- By corrosion Inhibitors

① ~~Sacrificial~~ Cathodic Protection Method:-

~~Cat~~ corrosion is started from anode by protecting anode, corrosion can be prevented in following methods:-

① Sacrificial anodic protection method:-
This is a cathodic protection method, in this method metal is coated or connected with metal which comes above the parent metal (which we want to protect) in electro-chemical series. so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly while the parent metal (cathode is protected). The more active so employed is called sacrificial anode. The corroded sacrificial anode block its replace by fresh one when consume completely.
Example:- Galvenization (coating of zinc on iron)

Q.1 Why an underground ~~of~~ iron pipe is connected through an insulated wire to a block of magnesium metal.?

Q-2 Why is a block of magnesium attached through an insulated metallic wire to the hull of the Ship.

Q.3 Why a iron tank is connected through a block of zinc with the help of insulated metallic wire.

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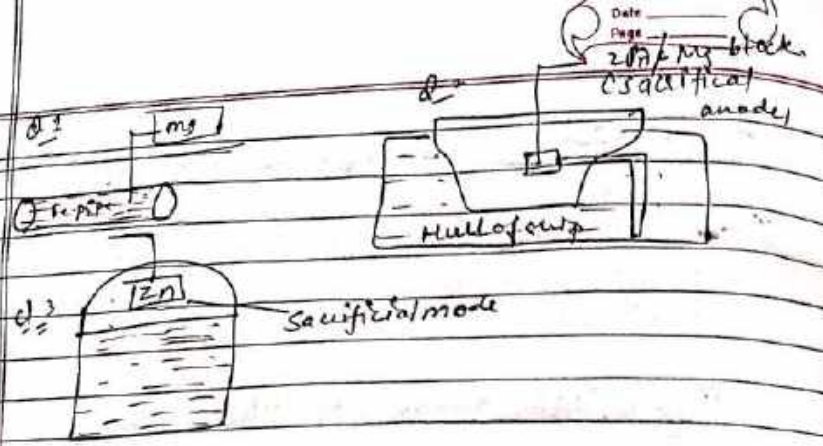


(2) Impressed current method:-

In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert corroding metal from anode to cathode.

II) By Coatings:-

There are two types of coatings:-

1. Anodic coating. Eg:- Galvanization
2. Cathodic coating Eg:- Tinning

In this method, parent metal is coated with non-reactive metal due to corrosion resistance (Non-reactive).

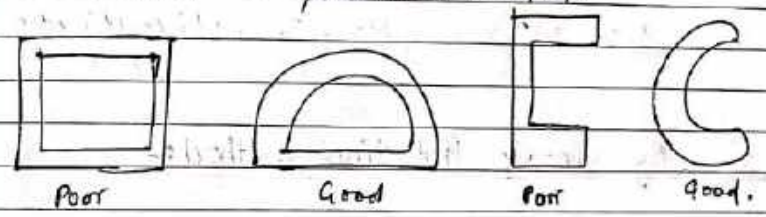
~~Properties~~:-

Metal is protected but if any crack is develop on the coating then corrosion speed up. due to the fact that the exposed metal (parents metal) acts as anode and coating become cathode.

III) By Proper Designing:-

The design of metal should be of that type that corrosion if occurs is uniform and does not result in intense and localised corrosion.

Avoid the contact of dissimilar metals if they are to be in contact the anodic material should have large area. It should not be painted or coated.



IV) By Corrosion Inhibitors:-

These are the chemical substance which reduce rate when added in small quantity to the corrosion environment.

Types:-

Corrosion inhibitors are of two types:-

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① Anodic corrosion Inhibitors:-
The substance which reduce the rate of anodic reaction are known anodic Inhibitors.
eg:- Alkalis, phosphate, cromates, molyvdates etc.

These inhibitors reacts with the ions of metal and produce insoluble precipitate which is absorbed by metal surface.

② cathodic corrosive Inhibitor:-
The substance which reduce the rate of cathodic reaction are known as cathodic inhibitors. they are used in acidic as well as neutral medium.
Eg:- Na_2SO_3, Mg, Zn, Ni (salt) etc

5). By Anodic Protection method:-

It is applicable to metals which can be passivated by deposition of oxide film (According to PBR). a protective oxide film is grown on the surface of metal to be protected.

Anodic protection is done by applying current in a direction that makes the metal more anodic.

Metal Surface is passivated at required electrode potential.
Eg:- Steel, aluminium, chromium etc

* Pilling Bedworth Ratio (oxide film growth law):

PBR rule gives idea about the nature of oxide film weather it is poras or Non-poras. The rule states that if the volume of oxide is smaller then the volume of metal consumed in metal oxide formation then the film is poras. on the other hand the film is non-poras if metal oxide form has greater volume than the metal consumed during corrosion.

$$PBR = \frac{\text{volume of metal oxide}}{\text{volume of metal consumed}}$$

If PBR is greater than 1 and smaller than 1.45 then the metal oxide film is non-poras and protective from further corrosion by any gaseous or aqueous medium.

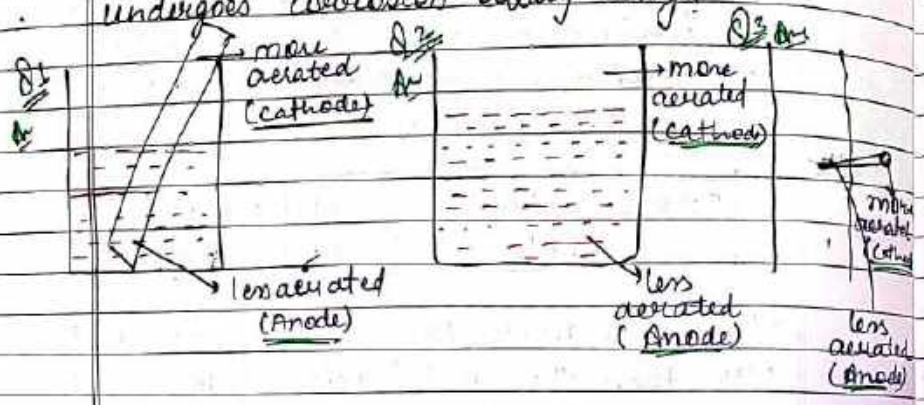
Water line corrosion

Water line corrosion takes place due to different aeration, the area which is more aerated works as cathode while the area which is less airated works as anode. and corrosion always start from anode.

Q1 A metal Rod (Or Zinc Rod) half immersed vertically. corrosion starts from bottom why?

Q2 A iron tank which is half filled with water corrosion starts just beneath the water line why?

Q3 A iron nail which is present in stem, the portion of nail which is present in the wood undergoes corrosion easily why?



Ans 1 Effect on corrosion

Reac^n	Ans (2)	Ans (3)
On Anode	At anode	At anode
$M - ne^- \rightarrow M^{n+}$	$Fe - 2e^- \rightarrow Fe^{++}$	$Fe - 2e^- \rightarrow Fe^{2+}$
On cathode	On cathode	On cathode
$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow OH^-$

Effect of corrosion in pulp and papery industry

Different type of corrosion have been identified in pulp and paper mills, including stress corrosion, tracking, uniform corrosion and crevice corrosion and pitting.

Stress tracking is caused by a combination of material, mechanical stresses and environment. these cracks can spread and lead to catastrophic failure

Effect of corrosion in oil or gas industry?

Caused by ① water ② CO_2, ③ H_2S, ④ microbial activity.

corrosion issues in power generation industries

① Hot corrosion
② Galvanic corrosion
③ oxide corrosion
④ Erosion.

Date 03/02/2023 Friday

* CEMENT *

A cement is a binding materials which sets an hardens independently and can bind other material together these have adhesive and cohasive properties.

Work of cement:-

The most important use of cement is the production of mortar and concrete, the bonding of natural or artificial agrigates to form a strong building material which is durable in the phase of normal environment effects.

Types of cement:-

Cement

Non-hydraullic cement	Hydraullic Cement
Defination: ① which cannot harden while in contact with water as a caused by hydraullic cement.	Defination: They sets or develop strength by chemical reaction with water. by formation of hydrates
① gain strength very slowly.	Eg:- Potland Cement
② Rarely utilised in modern times.	

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Pot land cement:-

Pot land cement is a type of hydraullic cement made by heating lime stone and clay mixture in a kiln and ~~pulverising~~ pulverizing material.

Raw materials of Pot land cements:-

Calcarious material	Argellacious Materials	Gypsum
Lime stone ($CaCO_3$)	Silica, Alumina, Iron oxide (SiO_2, Al_2O_3, Fe_2O_3)	$CaSO_4 \cdot 2H_2O$

Manufacture of Pot land cements:-

clinker + gypsum → Portland cement

~~$3SiO_2$~~ $2CaO\,SiO_2$

~~SiO_2~~ $3CaO \cdot SiO_2 + CaSO_4 \cdot 2H_2O$ → Portland Cement

$3CaO\,Al_2O_3$

$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

* Manufacture of Portland cement:-

Manufacture of portland cement takes place in following 5 steps:-

1) Mixing of Raw Material:-
   - → Dry method
   - → Wet Method

2) Burning → kiln
   - → Drying zone (400°c)
   - → Calcination zone (1000°c)
   - → Clinkering zone (1400-1600°c)

3) Cooling

4) Grinding

5) Packaging

1) Mixing of Raw materials – Raw materials can be mixed by two methods –

(a) Dry Method :- No water is added in grinded raw materials. It is a slow process and we get cement of inferior quality.

(b) Wet method :- In this method, water is added in grinded raw materials, it is faster, costly method and we get cement of superior quality.

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2) **Burning** :- Burning process takes place into kiln in the three different zones.

ⓐ **Drying zone (400°c)** :- In this zone moisture and slurry get evaporated. This is the upper part of kiln where the temperature is about 400°c

ⓑ **calcination zone (1000°c)** :- This is the central part of kiln, where the temp is around 1000°c. The dry material reaching this point undergo decomposition of limestone.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$
(limestone) (quicklime)

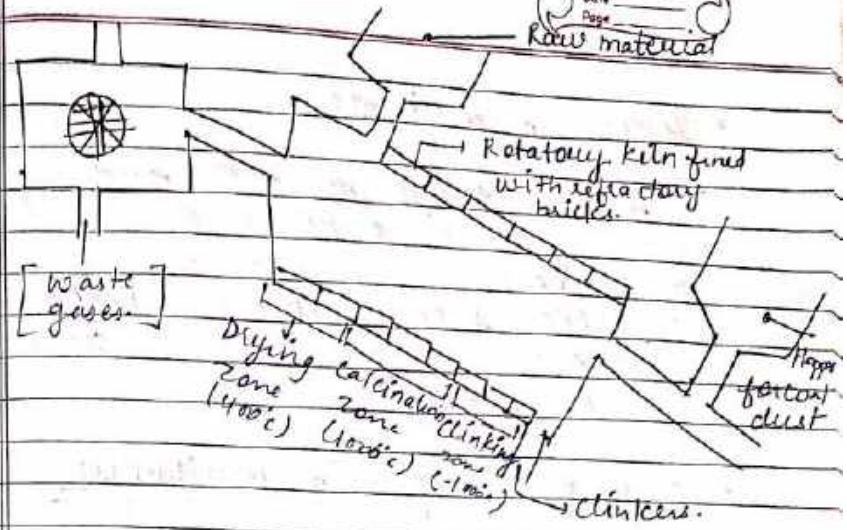
ⓒ **clinkering Zone** :- This is the hottest zone having temperature 1400-1600°c. Here the ~~material~~ main reaction between lime and clay takes place to form clinkers.

$$2CaO + SiO_2 \longrightarrow 2CaO \cdot SiO_2 \ (C_2S)$$
Di-Calcium Silicate

$$3CaO + SiO_2 \longrightarrow 3CaO \cdot SiO_2 \ (C_3S)$$
tri calcium Silicate

$$3CaO + Al_2O_3 \longrightarrow 3CaO\,Al_2O_3 \ (C_3A)$$
Calcium Aluminate

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4CaO \cdot Al_2O_3\,Fe_2O_3 \ (C_4AF)$$
Tetra calcium aluminoferrite. (clinkers)



Rotatory kiln

3) **Cooling** :- The clinkers are cooled by steam of air. The rate of cooling should not be slow if it is slow than $2CaO \cdot SiO_2$ converted into powder from which doesn't have binding property.

4) **Grinding** :- The fired clinkers is finally grinded with (2-5%) of Gypsum. gypsum retard or delay the setting of cement when it come in contact with water.

5) **Storage and Packaging** :- It requires special case. The cement retains its property untill it comes in contact with water or air.

* Composition of cement:-

clinkers + Gypsum → Portland cement

$2CaO \cdot SiO_2$
$3CaO \cdot SiO_2$ + $CaSO_4 \cdot 2H_2O$ → Portland cement
$3CaO \cdot Al_2O_3$
$4CaO \cdot Al_2O_3Fe_2O_3$

* Characteristics of main constituents:-

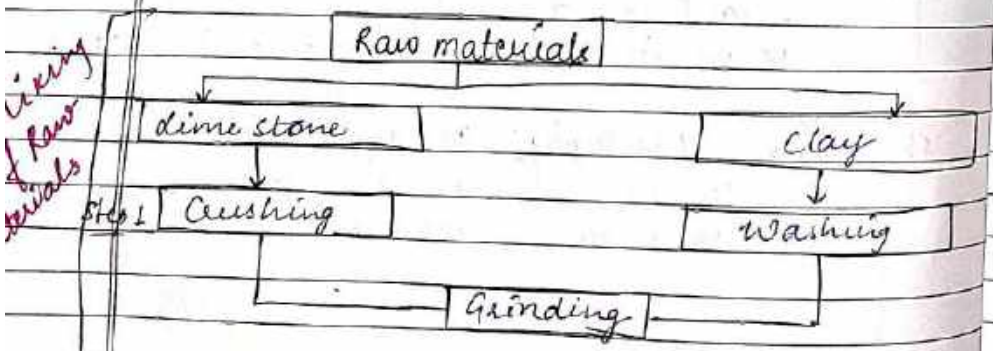
1) C_2S – Provide ultimate strength comparable to C_3S.

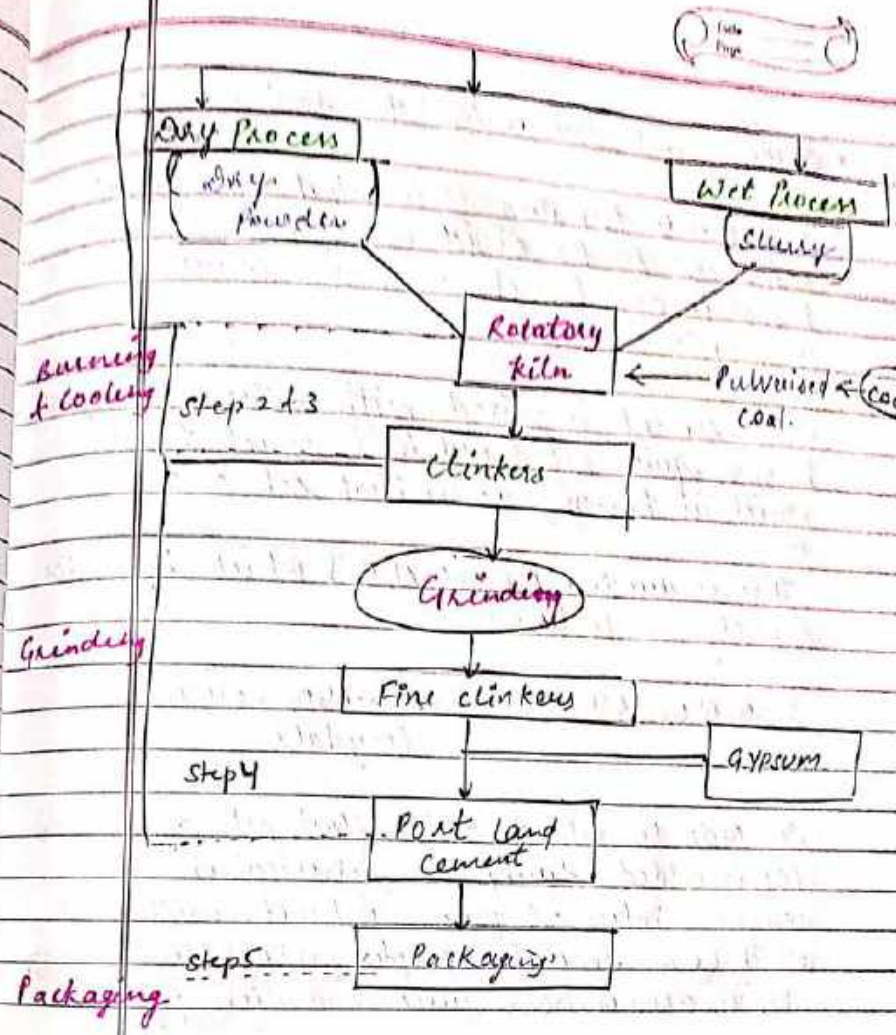
2) C_3S – Provide ultimate strength.

3) C_3A – Undergo hydration at very fast rate.

4) C_4AF – Has slow rate of hydration

5) Gypsum ← Retard the setting of cement





* Setting and Hardening of cement :-

It is due to formation of interlocking crystals reinforced by the rigid gel formed by the hydration and hydrolysis of the constitutional compounds.

When cement is mixed with water, the paste become quite rigid within a short time which is known as initial set or flash set.

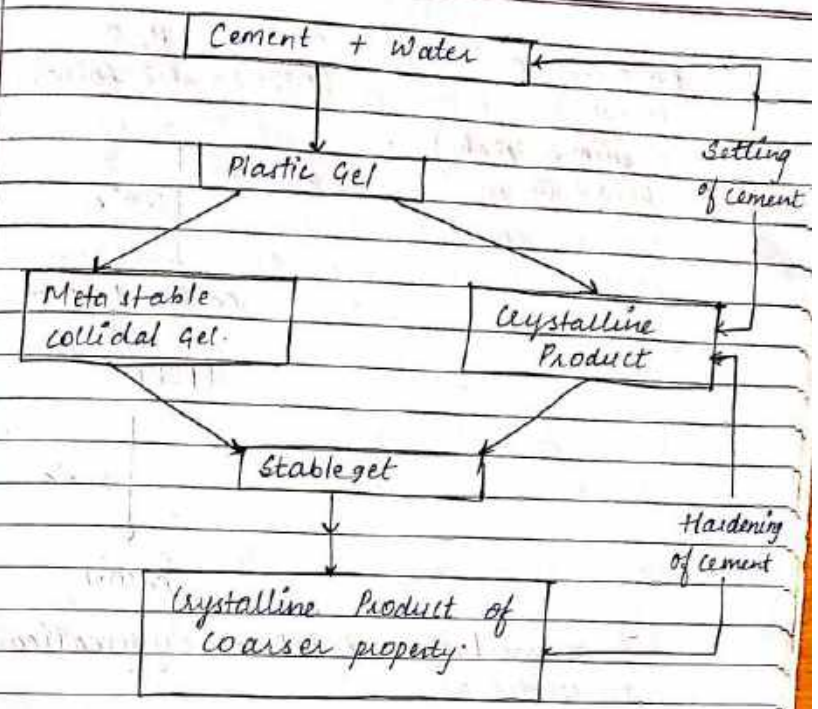
This is due to C_3A [$3CaO \cdot Al_2O_3$] which hydrates rapidly as follows:

$$3CaO \cdot Al_2O_3 + 6H_2O \longrightarrow \underset{\text{(crystal)}}{3CaO \cdot Al_2O_3 \cdot 6H_2O}$$

In order to retard this flash set gypsum or POP is added during the pulverisation of cement clinker. Gypsum interacts with C_3A which form insoluble complex sulphoaluminum which doesnot have quick hydration property

$$3CaO \cdot Al_2O_3 + xH_2O + y\,CaO \cdot SO_4 \cdot 2H_2O$$
$$\downarrow$$
$$3CaO \cdot Al_2O_3 \cdot y\,CaSO_4 \cdot z\,H_2O$$

$y = 1-3$
$z = 10-33$



* POP (Plaster of Paris) :- [$CaSO_4 \cdot \frac{1}{2} H_2O$]

* Chemical Name :- Calcium Sulphate Hemihydrate

* Manufacture :-

$CaSO_4 \cdot 2H_2O$ (gypsum) (Calcium sulphate dihydrate) $\rightleftharpoons$ $CaSO_4 \cdot 2H_2O$ (orthorombic form)

$\downarrow$ 120°c

$CaSO_4 \cdot \frac{1}{2} H_2O$ (POP)

$\downarrow$ 200°c

$CaSO_4$

The manufacture of POP is systematically represented as:-

Gypsum $\xrightarrow[\text{grinding}]{\text{crushing}}$ Powder form $\xrightarrow[100°c]{\text{Calcination}}$ Plaster of Paris

$\downarrow$

Powdered POP $\xleftarrow{\text{Pulverisation}}$ Plaster of Paris

* Properties :-

1) Setting and Hardening of POP :-

$CaSO_4 \cdot \frac{1}{2} H_2O$ (POP) $\xrightarrow{\text{Hydration}}$ $CaSO_4 \cdot 2H_2O$ (Hardening)

When water is added to POP a slurry is obtained which hardens quickly and sets easily creating the desired solid shape in a smooth finish chemically, on mixing with water POP expands to form plastic mass and regains the closely packed crystalline structure of gypsum. process of setting can be accelerated by mixing it with alkali sulphate like K_2SO_4.

Uses :-

It is used for making moulds.

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Date 13/02/2023 Monday

* ELECTROCHEMISTRY *

It is the branch of science dealing with the study of conversion of electrical energy into chemical energy and vice-versa. The device which converts chemicals energy into electrical energy or electrical energy into electrical energy into chemical energy is known as cell.

When cells are connected into series they are known as Batteries.

* Electrochemical cells:- The device which converts chemical energy into electrical energy is known as electrochemical cell.

Input — chemical reaction
output — Electricity

* Electrolytic cells:- The device which converts electrical energy into chemical energy is known as electrolytic cell.

Input — Electricity
Output — chemical reaction

→ TYPES OF CELLS:-

Cell → Primary cells, Secondary cells

(1) Primary cells:- In which the reaction occurs only in the one direction. They are known as Primary cell. that is battery become dead over a period of time and cannot be used.

Eg:- Dry cell, Mercury cell

(2) Secondary cells:- The cells in which reversible reaction takes place i.e. that can be recharges or can not be used again are known as secondary cell. They are also known as storage cell.

Ex:- Lead storage battery, Li-ion battery, Ni-cd battery.

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Decay / Deterioration of cement:-

Due of attack of salty water and other acidic solution when the surface is impermeable, then Rate of attack will be slow but structure can be weaken on long exposure.

~~except~~ Decay due to Leaching out of free lime from it due to chemical action of CO_2 in acidic water.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$
$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + 2H_2O$$

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Date
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initially insoluble $CaCO_3$ is formed which further convert into soluble calcium bicarbonate by the action of CO_2.

② Hydrolysis of sylicates and alluminates which will also be dissolved out:-

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