

Unit 2

Phase → A phase is a homogenous, physically distinct and mechanically separable part of a system which is separated from other part of the system by definite boundaries.

Example

1) One phase system

A gaseous mixture, being thoroughly miscible in all proportion constitutes one phase only.

Example → A mixture of N_2 & H_2 forms one phase only.

Two miscible liquids (eg water & alcohol) constitute one phase only.

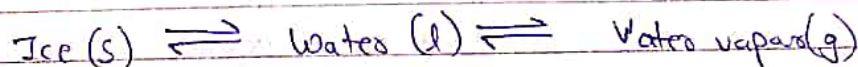
A solute completely dissolved in a solvent constitutes a single phase.
like salt in water (Mohr's salt)

2) Two phase system

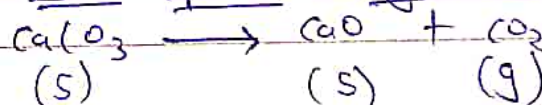
If two liquid are immiscible eg (oil & water) they will constitute two separate phases.
ex) benzene & water.

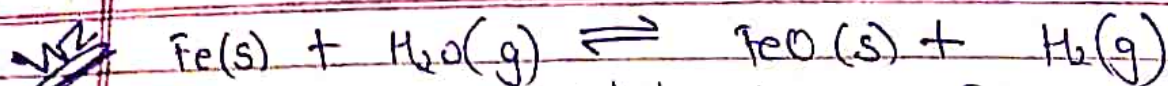
3) Three phase system

At freezing point water consist of three phases



WZ When CaO_3 is heated in closed vessel, it decompose into CaO and CO_2 at equilibrium there are two solid and one gaseous phase so it is three phase system





There are two solid phases Fe and FeO and one gaseous phase consisting of $\text{H}_2\text{O(g)}$ and $\text{H}_2\text{(g)}$. Thus they are three phase exist in equilibrium.

Q3 Identify No. of phase

1) A bottle containing aqueous solⁿ of ammonium hydroxide

Ans) 1

2) Ether and water contained in stoppered flask

Ans) 2

3) A mixture containing powdered sulphur, sugar and urea

Ans) (Three) 3

4) Sulphur system $S_R = S_H = S_L = S_V$

Ans) 4

5) An aqueous solution of glucose

Ans) 1

6) Mixture of N_2 & O_2

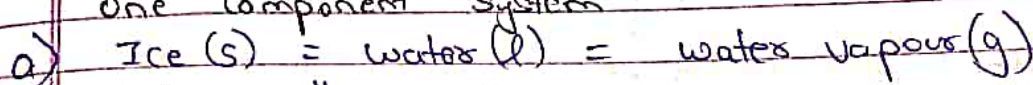
Ans) 1

Component

It is defined as the smallest number of independently variable constituent at equilibrium by means of which the composition of each phase present can be expressed either directly or in the form of a chemical reaction.

Ex →

One component System

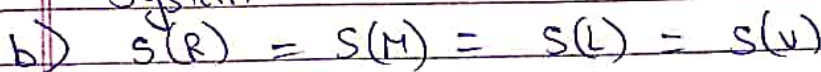


It is a three phase

but the all has a same chemical component

H_2O so they are one component

System

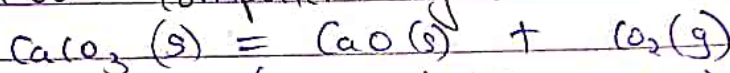


phase 4

same Sulphur composition so it is one

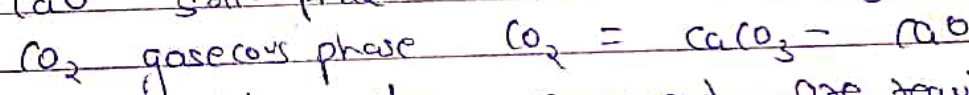
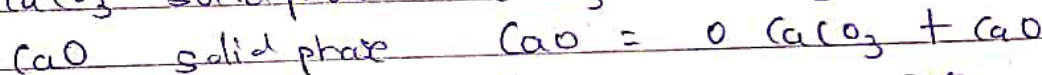
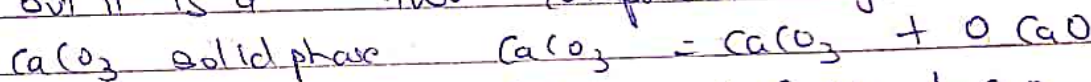
component System

Two component System



3 Phase (two solid + 1 gases)

but it is a two component System

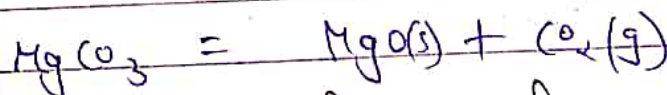


Here only two component are required

to express the composition of each

phase it is a two component System

or binary System



Calculation of No. of components

a) $C = S - R$

when No ions present

Component
of System

Substances
or
No. of
Constituent

is the relation (No of equations
relating to those
constituent in an
equilibrium state

$C = 5 - [R+I]$

When ions are also present in the system then the condition of electroneutrality (no of the +ve charges should be equal)

Q1) Predict the no. of component for dissociation of $KClO_3$ in a closed vessel (Same for $CaCO_3$)

Sol) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$ $n(CO_2)$
 $R=1$ (1 eqn only), $S=3$
 $C = 5 - R$
 $= 3 - 1 = 2$

Q2) Predict no. of component for dissociation of NH_4Cl on being heated alone in a closed system

Sol) $NH_4Cl \rightleftharpoons NH_3 + HCl$ — (1)
 $[NH_3] = [HCl]$ — (2)
 $R=2$, $S=3$
 $C = 5 - R = 3 - 2 = 1$ It is true Phase

Q3) Predict the no. of component when NH_3 and NH_4Cl is heated in a closed vessel along with HCl

Sol) $NH_4Cl \rightarrow NH_3 + HCl$ — (1)
 $[NH_3] \neq [HCl]$ — (2)
 $R=1$, $S=3$
 $C = 3 - 1 = 2$

Q4) $CaCO_3(s), CaO(s), CO_2(g)$ when CaO and CO_2 in the system are formed exclusively by decomposition of $CaCO_3$

Sol) $CaCO_3 = CaO + CO_2$
 $R=1$, $S=3$
 $C = 3 - 1$
 $(C=2)$ Ans

Q5) Explain why $KCl - NaCl - H_2O$ should be regarded as a three component system whereas $KCl - NaBr - H_2O$ should be regarded as two component system.

Sol) $KCl - NaCl - H_2O$
 $[KCl, NaCl, H_2O, K^+, Na^+, Cl^-]$ $S=6$
 $R=2$ $NaCl \rightarrow Na^+ + Cl^-$
 $KCl \rightarrow K^+ + Cl^-$
 $C = 5 - [R+I]$
 $= 6 - [2+1] = 3$

$KCl - NaBr - H_2O$
 $[KCl, NaBr, H_2O, K^+, Na^+, Cl^-, Br^-, KBr, NaCl]$
 $S=9$
 $NaCl \rightarrow Na^+ + Cl^-$
 $KCl \rightarrow K^+ + Cl^-$
 $K^+ + Br^- \rightarrow KBr$
 $Na^+ + Cl^- \rightarrow NaCl$
 $R=4$
 $C = 9 - (5) = 4$

Revised

Degree of freedom (Variance)

The minimum no. of independent variable (Such as temperature, pressure and composition of the phase) which must be specified in order to define the system completely is called degree of freedom $F=0$

- Ex) Ice \rightleftharpoons water \rightleftharpoons vapour $F=0$
- If $F=0$ system is invariant or Non variant
 - If $F=1$ system is univariant or Monovariant
 - If $F=2$ system is bivariant, $F=3$ system trivariant

Phase Rule: Phase rule enables us to predict the condition that must be specified for a system to exist in equilibrium.

Gibbs Phase Rule

No. of degree of freedom

No. of component

No. of phases

$P + F = C + 2$

$F = C - P + 2$

In Reduced Phase Rule If one component fixed

$P + F = C + 2 - 1$

if two fixed

$P + F = C + 2 - 2$

1) Calculate F

a) Solid Iodine in equilibrium with its vapour



$F = C - P + 2$
 $= 1 - 2 + 2$
 $= 1$

b) NH_3 at $42^\circ C$

$F + P = C + 2 - 1$ (because one $42^\circ C$ given)

$F + P = C + 1$
 $F + 1 = 1 + 1$

$F = 1$

Phase diagram for water system (one component system)

Minimum $F = 0$

$F = C - P + 2$

$C = 1$

$P = 1$ (Minimum phase)

$F = C - P + 2$

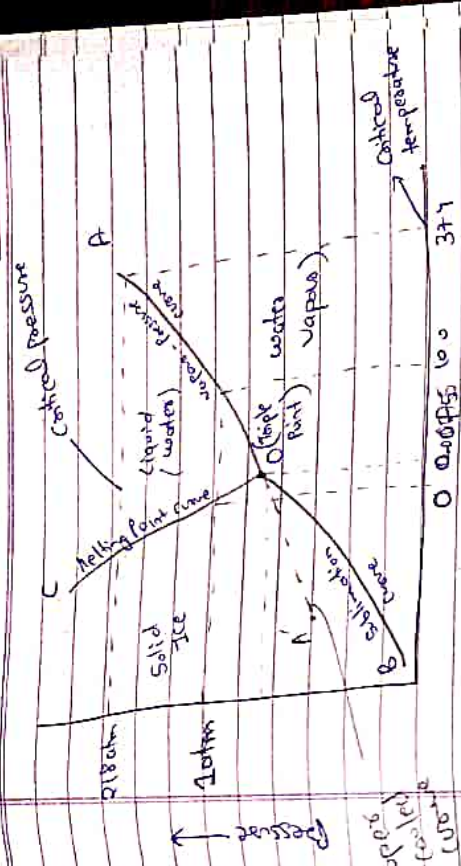
$= 1 - 1 + 2$

$= 2$

$0 = C - P + 2$

$0 = 1 - P + 2$

$P = 3$



Temperature ($^\circ C$)

Three equilibrium

Solid \rightleftharpoons liquid Sublimation \rightarrow Solid to gas directly

Solid \rightleftharpoons gas

Liquid \rightleftharpoons gas

Critical temperature \rightarrow a temp. temperature above which

Critical pressure a pressure above which change of state

Triple point \rightarrow is a point where all three phases can co-exist in equilibrium

OA curve $F = C - P + 2$
 $F = 1 - 2 + 2 = 1$
 at $0^\circ C$ water

OB curve $F = C - P + 2$
 $= 1 - 2 + 2 = 1$
 change its state and become liquid

OC curve $F = C - P + 2 = 1$
 at $374^\circ C$ and 218 atm called critical point

at Triple point $0 = F = C - P + 2$
 $= 1 - 3 + 2 = 0$

above $374^\circ C$ and 218 atm called supercritical fluid

Phase Rule
Water system
Sulphur system

Date: / /

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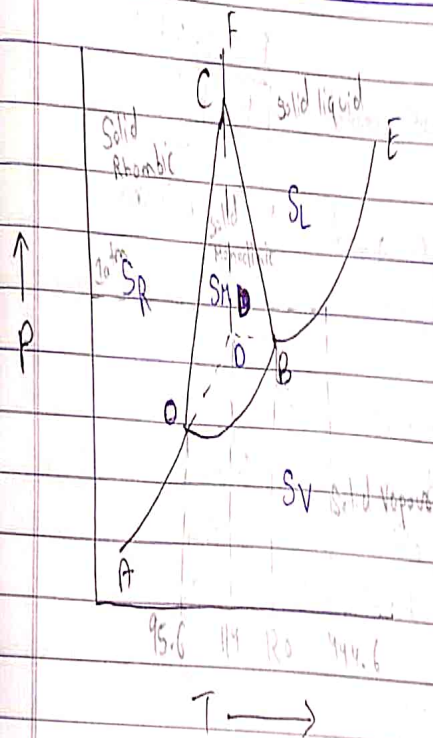
One component system
water system

Sulphur system

$$S_R \geq S_M \geq S_L \geq S_V$$

$$S \quad S \quad S \quad S$$

$C=1$ because one component system



Area (A)	Curve	Point
AOCF, COBC	OA, OB, BE	O, B, C
FCBE, ADBE	OC, BC, CF	O

$C=1, P=1$ (at one point)

$F = C - P + 1$

$F = 1 - 1 + 1 = 1$

$F=1$

Isobars

OB \Rightarrow $S_R \rightleftharpoons S_V$ } equilibrium separates

OC \Rightarrow $S_R \rightleftharpoons S_H$

OB \Rightarrow $S_H \rightleftharpoons S_V$

BE \Rightarrow $S_L \rightleftharpoons S_V$

BC \Rightarrow $S_H \rightleftharpoons S_L$

these are separately the equilibrium b/w the two phases.

CF \Rightarrow $S_R \rightleftharpoons S_L$

C=1 P=2 (Two deg. Integ.)

$F = C - P + 2$

$F = 1 - 2 + 2$

$F = 1$

OH = Sublimation curve of S_R

S_R

OC = Transition curve of S_R to S_H if D univariant

S_R to S_H

OB = Sublimation curve of S_H

BC = Vapor pressure curve

BC = Melting curve of S_H

CF = Melting curve of S_R

for points

O, B, C, D

C=1

P=3

$F = 1 - 3 + 2 = 0$

for O, B, C

triple point

O $S_R \rightleftharpoons S_H \rightleftharpoons S_V$

B $S_H \rightleftharpoons S_L \rightleftharpoons S_V$

C $S_R \rightleftharpoons S_H \rightleftharpoons S_L$

95.6°C

120°C

151°C

6.06 mm

0.01 mm

1288 atm

Point D

S_R

S_L

S_V

Metastable point Triple

Point

11°C & 0.03 mmHg

Three component system

$F = C - P + 2$

at C=2

$F = C - P + 2 = 2 - P + 2 = 4 - P$

if P=1

$F = 3$

P, T, C

$F = C - P + 2$

for one phase component system

$F = C - P + 1$

for two component system

this is called

Condensed phase rule

Solid \rightleftharpoons Liquid \rightleftharpoons

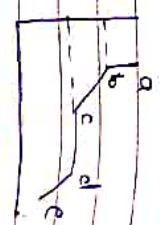
Reduce of system condensed system

Cooling Curve

i) Pure Substance

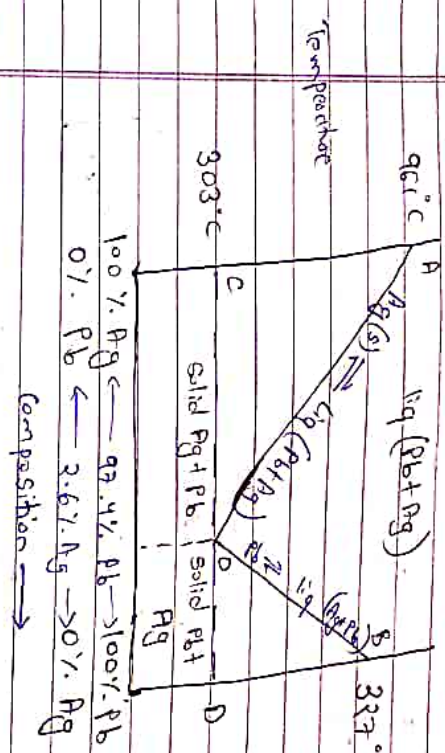


ii) Mixture of Substance



Two Component System

Lead-Silver System (Pb-Ag system)



Areas	Curves	Points
Above BOB	OA	A
Below line BOB	OB	B
Below line COB		O

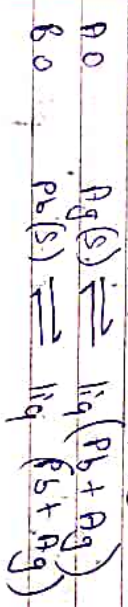
A point is Melting point of silver (Ag) at 961°C

B point is Melting point of lead (Pb) at 327°C

O point is Eutectic point (below O all component solidify)

Area BOB $P=1$ $C=2$

Area below line BOB



$F = C - P + 1 = 2 - 1 + 1 = 2$



$$F = C - P + 1$$

$$= 2 - 2 + 1$$

$$[F = 1]$$

Area below COD

$$P = 2 \quad [Pb(S) + Pb(S)]$$

$$C = 2 \quad Ag, Pb$$

$$F = C - P + 1$$

$$F = 2 - 2 + 1 = 1$$



Point O (has lowest Melting point)
Eutectic Point

Temp = $303^\circ C$

$$C = 2 \quad P = 3$$



$$F = C - P + 1$$

$$F = 2 - 3 + 1 = 0$$

Composition (97.4% Pb, 2.6% Ag)

Eutectic point is two curve AO & BO intersect at point O at

Temp $303^\circ C$ This point is

known as eutectic point.

Desilverization of anti ferrous lead
(Pattinson's Process)

Eutectic

Eutectic system A binary system consisting of two substances which are miscible in all proportion in the liquid phase & do not react chemically.

Eutectic mixture The two substance involved have the property of lowering each other freezing point. Solid soln of two or more substance having the lowest freezing point of all the possible mixture of the component is known as Eutectic mixture.

The process of heating argentiferous lead containing a very small quantity of Ag (0.1%) and cooling it to get pure lead and liquid rich in silver is called Pattinson's Process

Two component chemical reaction

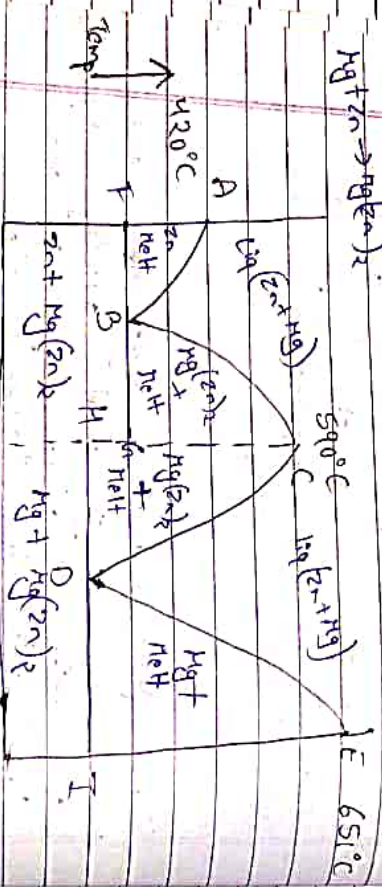
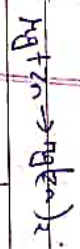
No Eutectic system

(miscible in all proportion)

(Zn-Hg)

(Na-K)

Zn-Hg system



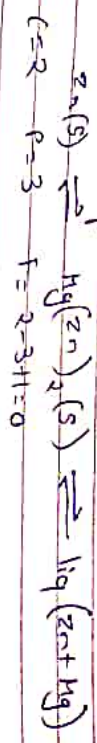
Zn = 100%
Hg = 0%
Zn = 0%
Hg = 100%

Composition

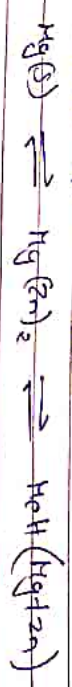
Points

A \rightarrow MP of Zn 420°C
C MP of $Hg(Zn)_2$ 590°C
E MP of Hg \rightarrow 651°C

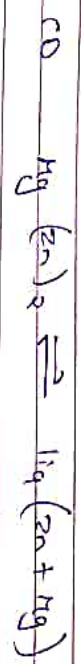
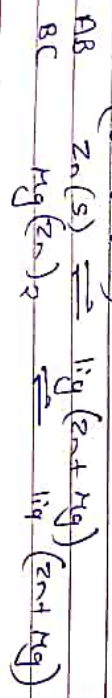
B Eutectic point 342°C



O \rightarrow Eutectic point 342°C



Curve (Univariant)



$C=2 \quad P=2$
 $F=C-P+1=2-2+1=1$

Area
ABFA
BCCB
CHDC
EODC
 $P=2 \quad C=2 \quad F=2-2+1=1$

Area above ABCDE $P=1 \quad C=2 \quad F=2-1+1=2$

Area below FBG & HDI

$C=2 \quad P=2$
 $F=2-2+1=1$

freedom

PolymerPolymer

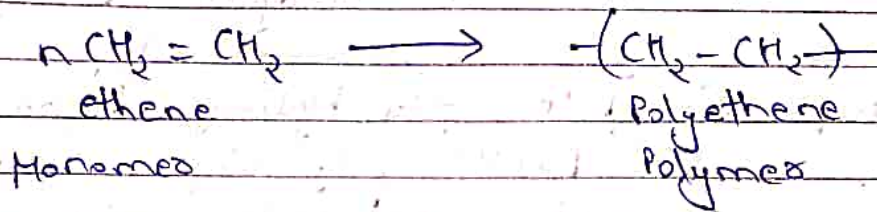
Many Parts/unit

Monomers

Single Part/unit

It is composed a large no. of repeating unit of identical structure called Monomers (combination or large chain of Monomers forms polymer)

(e.g.)

Polymer

Natural

Cellulose, Protein, Silk

Synthetic

Nylon, plastics

Degree of Polymerization The no. of repeating units in a chain formed in a polymer is called degree of Polymerization.

Degradation of Polymer (Breakdown of Polymer)

Breakdown of Polymer by heat called

Thermal degradation if by water

it is called Hydrolytic degradation

if by Microorganism it is called Biodegradation

if by light it is called photodegradation

if by oxygen is called Oxidative degradation

Environmentally Biodegradable Polymer
A polymer based on the C-C backbone tends to be Non biodegradable whereas hetero atom containing polymers backbones confer biodegradability.

Biodegradable Polymers Degradation Caused by Biological activity (Microorganism)

- Example a) (PHB) poly hydroxy butyrate
b) (PVOH) poly vinyl alcohol
c) PLA Poly Lactic acid

Classification of Polymer

1) On the Basis of origin

Natural
starch
Protein
Cellulose

Semisynthetic
ex) Rayon

Synthetic
PVC, Nylon
Polyethylene
etc

2) On the basis of chemical structure

Homopolymer

Consist same Monomer
ex) Vinyl chloride \rightarrow PVC
ethylene \rightarrow Polyethylene

Copolymer

or
Heteropolymer
Consist More than one type of Monomer

3) On the Basis of polymeric structure

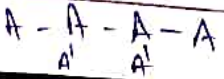
Linear polymer

High density



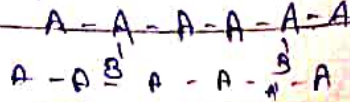
Branched Polymer

low density



Cross linked polymer

Network



4) On the Basis of Thermal Behaviour

Thermoplastic

Thermosetting

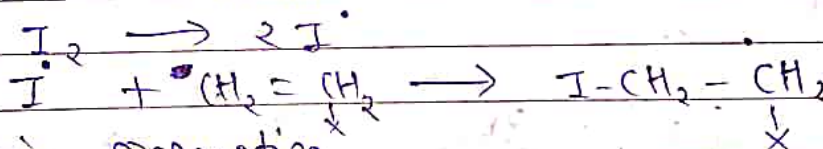
Mechanism of Polymerization

① Additive Polymerization

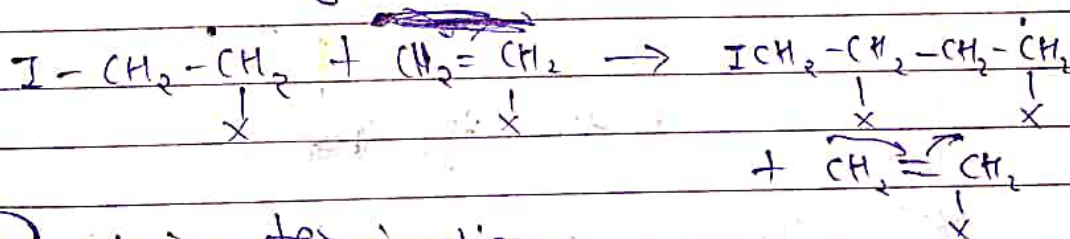
② Condensation Polymerization

1) Free radical addition polymerization

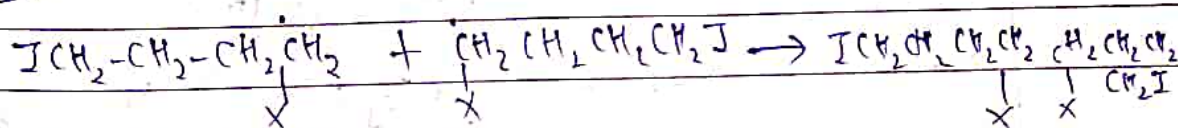
(Step 1) chain initiation



(Step 2) chain propagation



(Step 3) chain termination

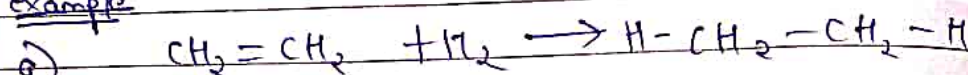


- 2) Ionic Mechanism (cationic or anionic)
3) Coordination Mechanism
(In the presence of organometallic compound)
(as Ziegler Natta catalyst)

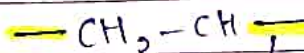
Polymer Functionality

The No of reactive sites in a molecule is termed as functionality
for molecule to act as monomers it must have at least two reactive sites
then its functionality should be two

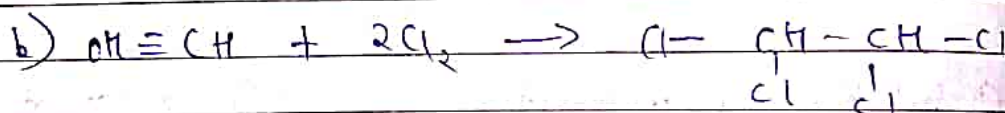
Example



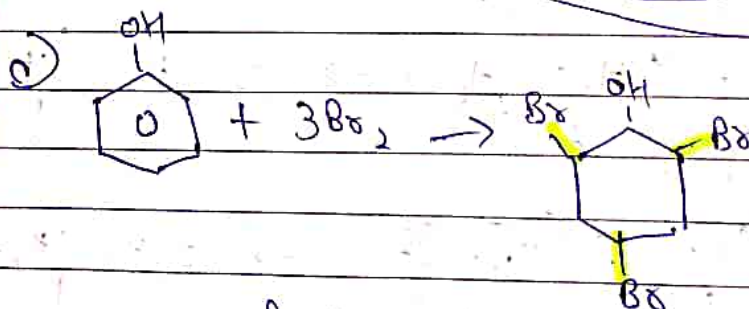
Here



functionality = 2



functionality = 4



functionality = ~~2~~ 3

Note

Monomer has functionality = 2 it is linear polymer

Monomer has functionality = 3 it is cross linked polymer

Molecular weight of polymer

Two ways

- ① Number average Molecular weight (M_n)
 n_1, n_2, n_3 - are No of Molecules & Molecular Mass M_1, M_2, M_3 - - -

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3}$$

$$= \frac{\text{Total Mass of Polymer}}{\text{Total No. of Molecules}}$$

- ② weight average Molecular weight
 If m_1, m_2, m_3 are weight of ~~the~~ species
 M_1, M_2, M_3 - ~~weight~~ Molecular Mass

$$M_{w0} = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3}{m_1 + m_2 + m_3}$$

Polyethylene (Addition Polymers)

Polyethylene also known as polyethene, it is important thermoplastic resin ~~propa~~ prepared by the addition polymerization of ethylene.

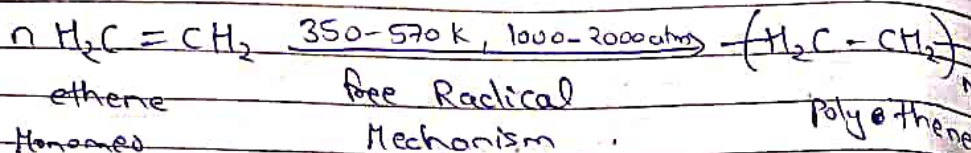
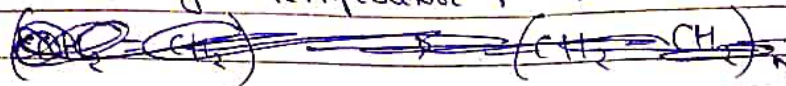
Types

- a) Low density polyethene (LDPE)
- b) High density polyethene (HDPE)
- c) Linear low density polyethene (LLDPE)
- d) Ultra high molecular weight polyethene (UHMWPE)

1) Low density poly-ethene (LDPE)

Preparation

High Temperature & Low Pressure



Property

- a) Low density
- b) weak intermolecular force
- c) chemically inert
- d) Branched
- e) Soft

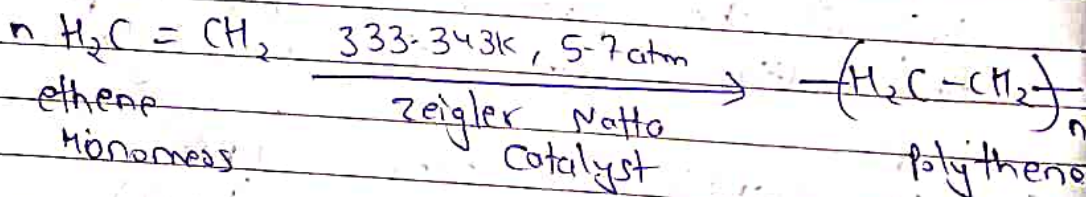
uses

- a) soft Toys
- b) Squeeze bottles

2) High density polythene (HDPE)

Preparation

It can be obtained from ethene Monomers by using Ziegler Natta catalyst ($\text{TiCl}_4 + \text{AlR}_3$) low temperature & pressure



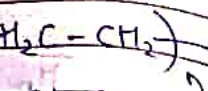
Property

- a) Hard
- b) High density
- c) Unbranched

uses

- ① Bucket
- ② Dustbins
- ③ Bottles, pipes

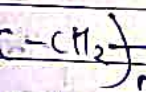
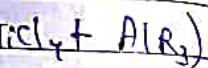
Pressure



Polyethylene

bottles

Monomers



Polythene

c) LLDPE (Linear low density polyethylene)

It is actually a copolymer of ethylene and 1-butene
Manufactured with Ziegler type catalyst

- LLDPE is attractive because it requires less energy to produce than LDPE

Uses

- a) Golf ball covers Making
- b) Bottle

d) UHMWPE (Ultra-high Molecular-weight polyethylene)

UHMWPE sheet is cut into small blocks to be used as a bone

UHMWPE is a successful bio material for use in hip knee

UHMWPE is used for Manufacturing of Hydraulic seals

It is used in Making surgical Machine parts.

Polymer Synthesis

① Condensation polymerization

② Addition Polymerization

① Condensation polymerization

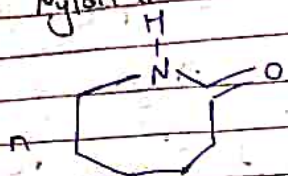
→ For condensation polymerization Monomers should have at least two functional groups
Both functional group may be same or not

→ Monomers having two functional groups always give linear polymer

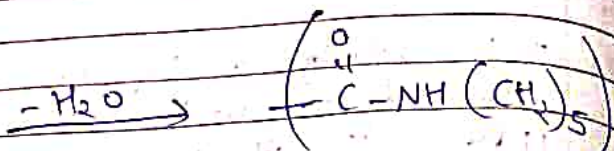
→ Monomer having three functional group always give cross linked polymer

★ All resins are cross linked polymer & all cross linked polymer are condensation polymers.

2) Nylon 6



Caprolactam

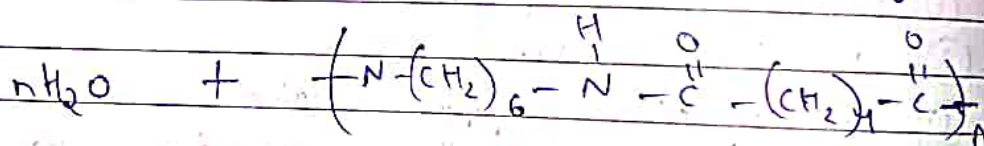
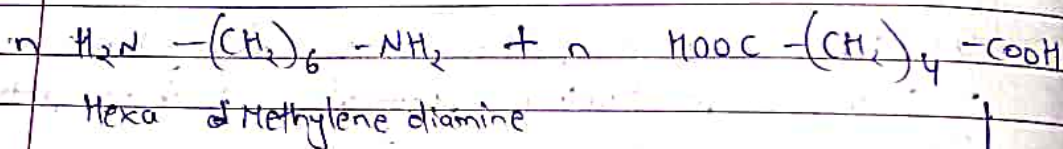


(Nylon 6) polyamide

Same type of Monomers combined together called homo polymerization (Self polymerization)

- Removal of water molecule
- Six Carbon atom present in the Monomer
- So this polymer is called Nylon-6
- It is used for Manufacture of tyre cords and ropes

3) Nylon 66



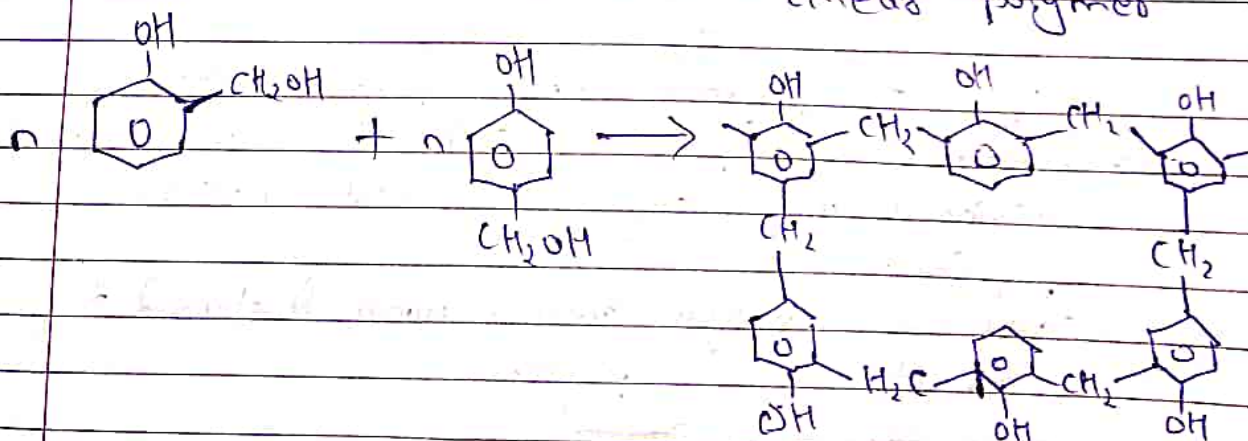
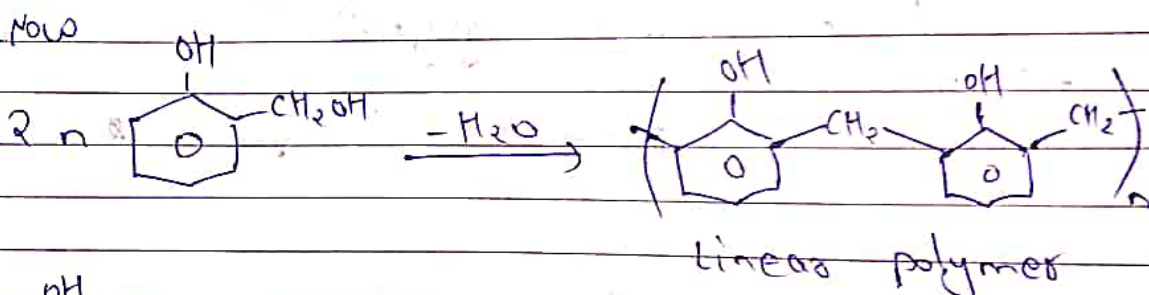
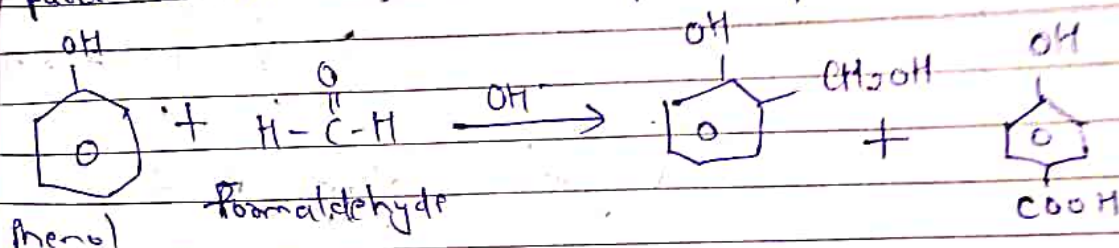
Polyamide (Nylon 66)

If different types of Monomers combined together called copolymerization with the elimination of H_2O . Both Monomers have 6 Carbon atom so it is Nylon 66.

Uses → Sheets, brushes, textiles

c) Phenol-formaldehyde resin (Bakelite)
 → starting material is phenol and formaldehyde
 in the presence of basic catalyst
 two combine & give either ortho & para
 hydroxy methyl phenol.

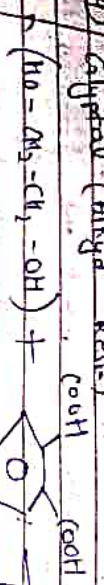
→ This ortho para hydroxy methyl phenol on
 condensation to produce cross linked polymer
 bakelite involving methylene bridges in either
 para or both ortho para position.



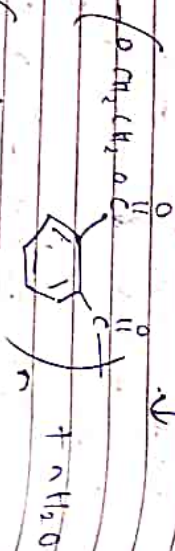
Phenol formaldehyde
 resin (Bakelite)

Cross linked polymer

2) Glyptal (Alkyd resin)



(Glycol) glyptol resin



→ Copolymerization condensation with elimination of H_2O form glyptal
→ uses

① Manufacture of paints

Specialty Polymers

② ~~Engineering~~ polymers are polymers having designed for engineering and medical purposes.

They are ranged from mono functional to multifunctional polymers.

① It is used in automobile industry for making

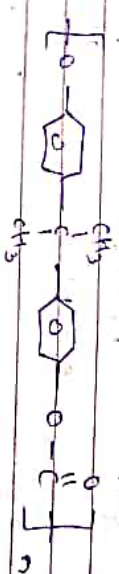
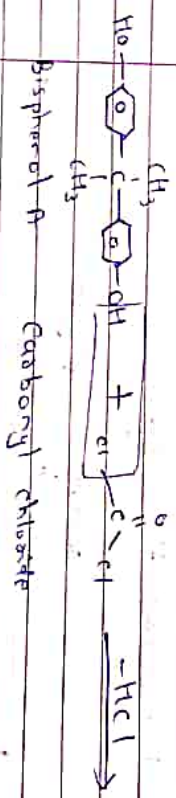
② It is used for making helmets etc.

③ Due to its temperature resistance, stability

and chemical inertness it finds use in manufacturing of baby bottles etc.
It is used for making for computers, CDs, DVD, hair driers etc.

① polycarbonate or engineering thermoplastics

commonly known as lexan or melon. obtained by reacting bisphenol A with diphenyl carbonate or carbonyl chloride



Poly carbonates

Properties

- ① High impact strength
- ② Highly transparent (about 88%)
- ③ Good heat resistant
- ④ Low combustibility
- ⑤ High melting point
- ⑥ Good thermal stability

Application

- ① Data storage
- ② Electrical and electronic components.
- ③ Construction material

3) Conducting polymers
Some polymers have been synthesised which have high planarity and conjugation of π e⁻ so these polymers are known as conducting polymers.

Application

- i) Zn rechargeable light weight batteries
- ii) Zn transistors, photodiodes & LEDs
- iii) Used in photovoltaic devices
- iv) use in solar cells
- v) Telecommunication systems

Conducting polymer

Aromatic cycle Double bond

ex) POC

Aromatic cycle and double bonds

ex) PPV

Aromatic Heteroatom

ex) Poly fluorines

Sulpha containing

ex) PT

PEDOT

ex) Polyacetylene



conductivity 10⁵

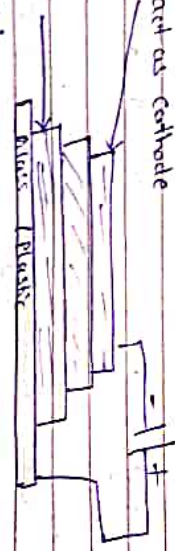
3) Electroluminescent Polymers

Electroluminescence is a phenomena in which a material emit light in response to the passage of an electric current or strong electric field

ex) PPV (Poly p-phenylene vinylene)
These polymers are used in LED

Polymer light emitting diode (PLED)

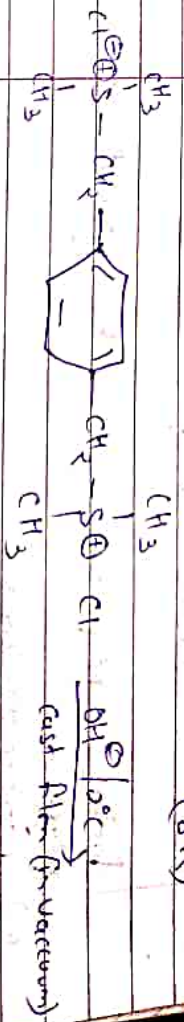
Cathode (act as cathode)



Triplet state (it is not as a ground)

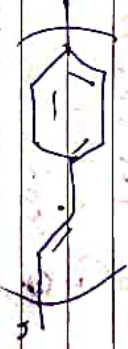
blue cathode & anode a electroluminescent polymer layer has been pulled when current pass it emit light. The energy gap of a e⁻ transfer E_{HOMO} & electroluminescence and conductivity occurs and light emits

PPV Preparation



Precaution

Elimination $T=200^\circ C$



Uses & application

1) PLED

Liquid crystalline polymers

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase.

It has high mechanical strength at high temperature.

High heat stability & flexibility.

A very common known liquid crystalline polymer is Kevlar. It is an aromatic polyamide. It is prepared by the polycondensation of aromatic dihalide and aromatic diamines.

Uses

1) It is used in aerospace and aircraft industries.

2) It is used in the fabrication of protective wear including bullet proof vests.

Biodegradable Polymers (Same as starting value)

Factors Responsible for biodegradation of polymers:

a) Microorganisms

b) Environment

c) Nature of Polymer

Features of Biodegradable polymers depend on functional group
eg: ester, ether, amide

3) Hydrophilic has more degradable than hydrophobic

3) Amorphous are more degradable than crystalline

Classification

<p>Natural Biopolymers obtain from plant & animals eg: cellulose</p>	<p>Biosynthesis Biopolymers obtained from microorganisms eg: PHB, PHV</p>	<p>Synthetic Biopolymers Produced synthetically</p>
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Application

1) Used as food Packaging

2) Used in agriculture

Example PHB (polyhydroxy butyrate) produced by fermentation of glucose by bacteria

2) PHV

3) PHBV