17/20..

Nuclear Magnetic Resonance

Active
Nuclear spin → $\frac{1}{2}$

Boltzman Distribution law

H — β $-\frac{1}{2}$

H — α $+\frac{1}{2}$

100% population not possible

ext EM. ?

Resonance

Flipping of nucleus

magnetic field

nucleus

spinning like lattoo

should be changed

^1H nuclear spin → $\frac{1}{2}$

CH_4

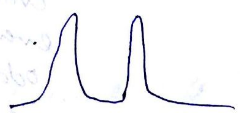
H — C(H)(H) — H

MHz

200

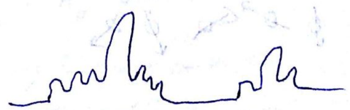
400

$CH_3 - CH_2 - CH_3$



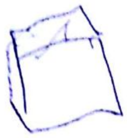
2 signals

difference between the 2 splitting is called coupling constant.



- Coupling constant remains same

Nucleus opposes app. mag field



Resistive Shielding

Shielding effect

~~Resistive shielding~~

20.3.17

NMR Spectroscopy

No. of orientations $\rightarrow 2I+1$

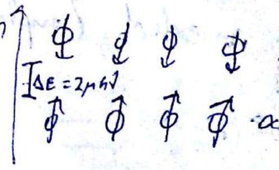
$I = 0, \frac{1}{2}, \frac{3}{2}, 2, \frac{5}{2}, \ldots$

Atomic No.	Atomic Mass	I
even	even	0
odd	even	$\frac{1}{2}, \frac{3}{2}, 1$
even	odd	$1, \frac{3}{2}$

Magnet

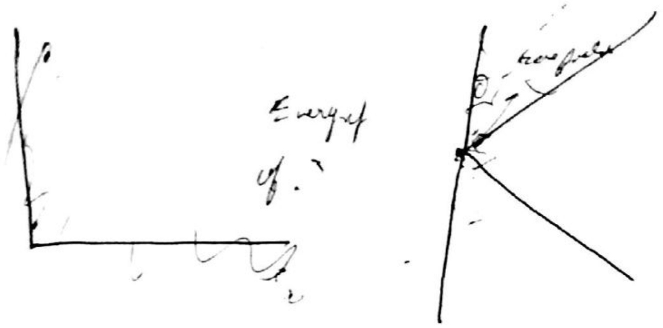
orientation

Apply mag. field



$\mu \rightarrow$ mag. moment

$\Delta E \propto$ applied mag ~~field~~ field.



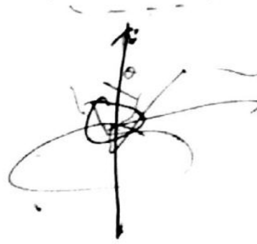
~~Do~~ ~~[illegible]~~ Strength of H_0

~~Strength of H_0~~

- Precissional

~~[illegible]~~ frequency

↑ E_{γ} ↑ ↑ ↑

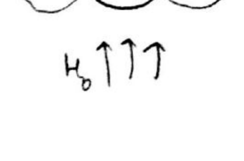


applied mag. field is having the same ν as that of visible light.

~~Rotation~~

Till saturation

Shielding, Distortion, Chemical Shift



$H_{eff} = H_0 - \sigma H_0$

σ → Shielding constant

~~diamagnetic structure~~

dimagnetic shielding

Neighbouring nuclei's induced mag. field

	Applied mag. field is	Signal
Shielding	reinforced	downfield
Deshielding	opposed	upfield

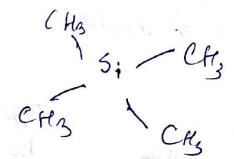
more e.n.

CH_3F	CH_3Cl	CH_3Br	CH_3I
4	3	2	1

downfield

Reference used in NMR → TMS

Tetra methyl silane



(Signal = 0)

upfield $\xrightarrow{\text{Towards}}$ TMS $\xrightarrow{\text{away}}$ downfield

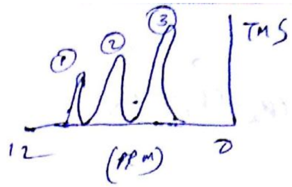
0

Factors affecting chemical shift

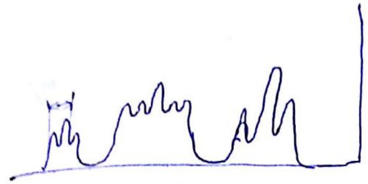
- Electronegativity
- H bonding

H-bonding ↑ Signal ↓

$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{OH}$



NMR spectra



Splitting of signal

↓

(n+1)

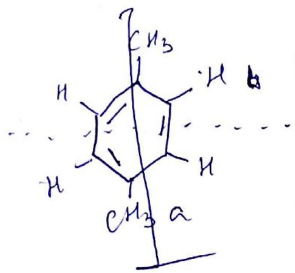
governed by Pascal's Δ^{le}

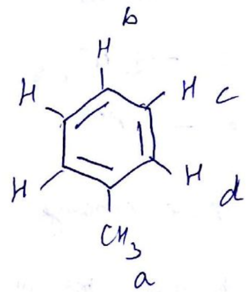
Coupling constant

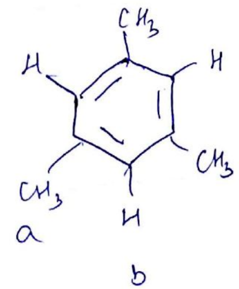
Difference between chemical shift of 2 splitting

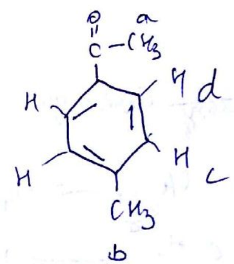
J = Hz

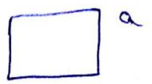
Unit → Hz











$CH_3-CH_2-CH_2-CH_3$

22.3.17

Mass Spectrometry

Ionization methods :

- Electron impact $\dot{x}$a

700 V e^- beam

$M + e \longrightarrow M^+ + 2e$

Parent ion / Molecular ion

$M + e^- \longrightarrow M^-$

$M + e^- \longrightarrow M^{n+}$

Only +ve charge

- Chemical ion method

~~Carrier~~ Carrier gas.

eg $CH_4 + e \longrightarrow CH_4^+$

$CH_4^+ \longrightarrow {}^+CH_3 + H$

$CH_3^+ + CH_4^+ \longrightarrow CH_5^+$

$CH_3^+ + CH_3^+ \longrightarrow C_2H_5$

$RH + \overset{+}{CH_5} \longrightarrow RH_2 - H$

~~M+1~~ (M-1). peak

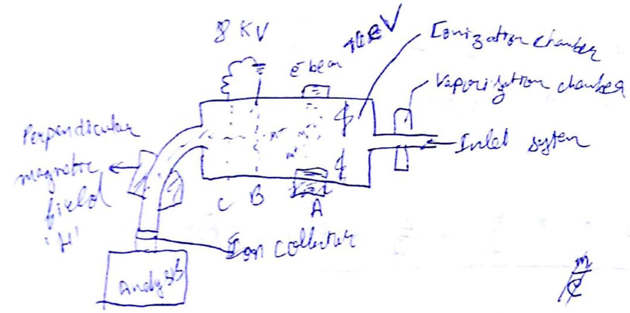
~~Mechan~~ & fragmentation

$M + e \longrightarrow M^-$

$M^+ \longrightarrow A^+ + B$ Fragmented ions

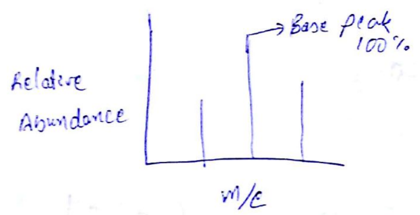
$M^+ \longrightarrow C^+ + D$

daughter ions.



$\frac{1}{2} mv^2 = eV$

$\frac{m}{e}$



$CH_4 \rightarrow 16$

1
2
3
.
.
16 — 100%
17

$$\boxed{\frac{m}{e} = \frac{H^2 r^2}{2V}}$$

27.3.17.

Ring Rule, Index of hydrogen or deficiency, or degree of double bond

- Mol. ion → odd e^- ion

- C_nH_{2n+2} alkane like structure

odd → Z → 1, 2, 3, 4, 5 . .

even → 3.5, 5.5, . . .

$$\underline{I_m H.D = x - \frac{y}{2} + \frac{z}{2} + 1}$$ for $C_xH_yN_zO_n$

eg: C_xH_y CH_3COCH_3

$C_3H_6O_1$

$I_m H.D = 3 - \frac{6}{2} + 0 + 1$

$= 1$

need 1 pair of H

$I = 4 - \frac{5}{2} + 1$

$= \frac{5}{2}$

... sum of double bond + ring + thrice the triple bond

Beynon's rule

According this rule of a compound has odd no. of N ...

Valency

Given - Even

odd - odd

N is exception

Atomic #

3/4
100
17.2
1.83

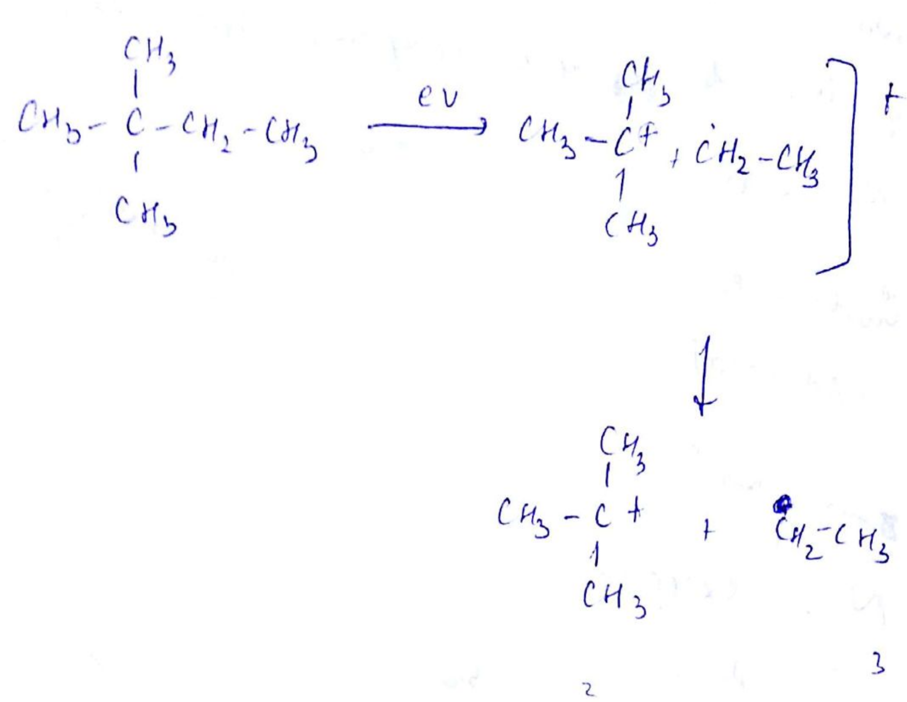
m ≠ 0

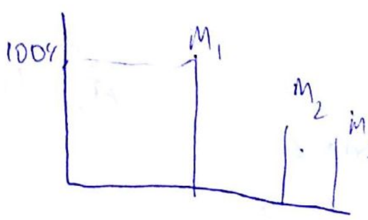
M+1 M+2

	M+1	M+2
$C_7H_{10}N_4$	9.25	0.38
$C_8H_8NO_2$	9.25	~~0.78~~ 7.23
$C_8H_8N_2O$	9.25	9.61
$C_8H_{10}N_2O$		9. 9.6
~~C_2H_{10}~~		1.34
		1.71

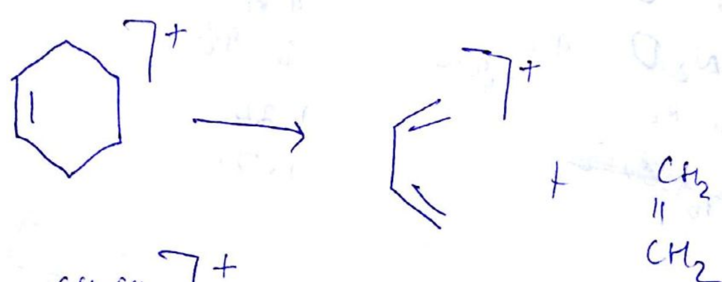
29.3.17.

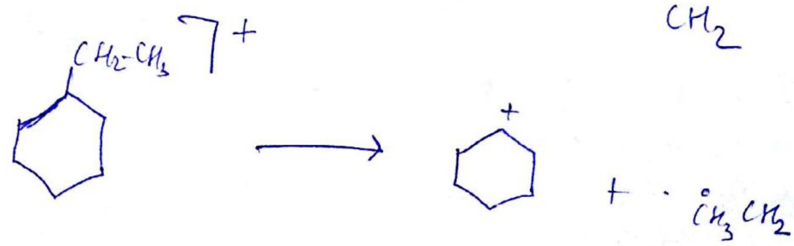
Molecular ion fragmentation

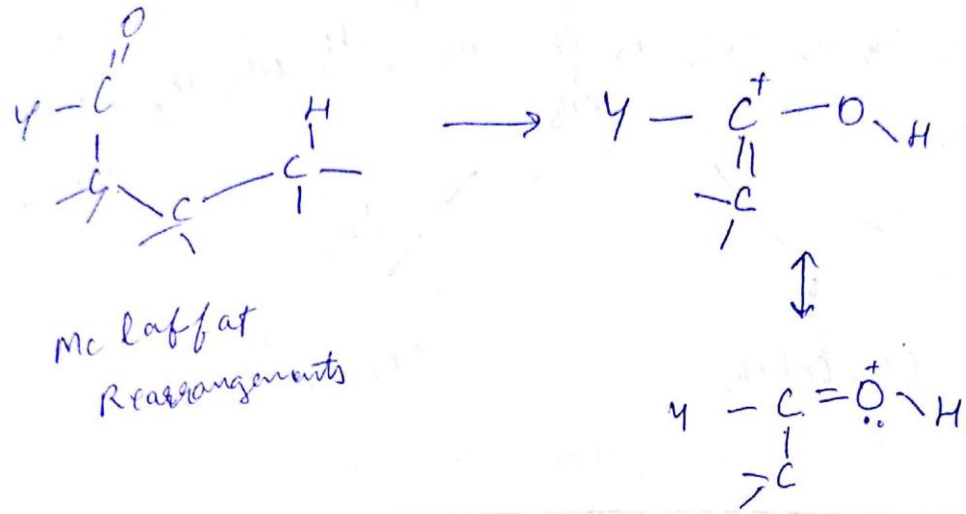




* Mass spectrum only detects +ve ions *

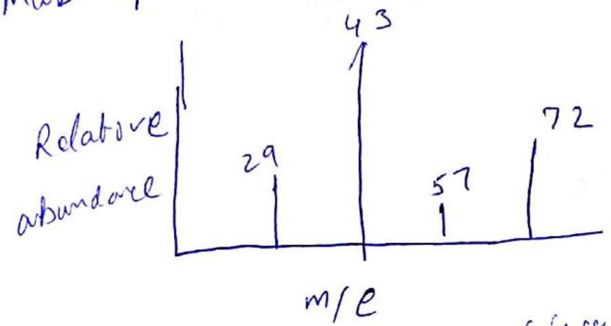






Mc laffat Rearrangements

Mass spectrum of n-pentane

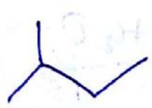


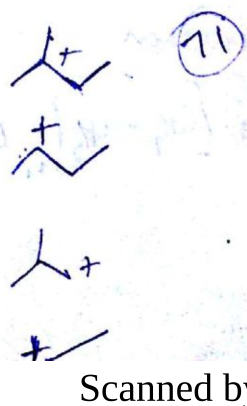
$$CH_3-CH_2-CH_2-CH_2-CH_3\ ]^{+}$$

- $\xrightarrow{CH_2CH_3}$ $CH_3CH_2\overset{+}{C}H_2 \xrightarrow{\text{rearr}} CH_3-\overset{+}{C}H-CH_3$ $\quad \frac{m}{e}=43$
- $\xrightarrow{CH_3CH_2CH_3}$ $CH_3\overset{+}{C}H_2$ $\quad \frac{m}{e}=29$
- $\xrightarrow{CH_3}$ $CH_3CH_2\overset{+}{C}H_2$ $\quad \frac{m}{e}=57$
- $\overset{+}{C}H_3$ $\quad \frac{m}{e}=15$

C_5H_{12}

$\frac{m}{e}$ = 72, 71, 57, 35, 43, 41

2 methyl butane 



5.3.17

POLYMER

Ionic Mechanism

Anionic	Cationic

Anions]

R - Mg - X

R - O - R

eg:- n- butyl ether

Anionic

Initialization

$$CH_2 = CH_2 \xrightarrow{n\,BuLi^+} n\text{-}Bu\text{-}CH_2\text{-}\bar{C}H_2$$

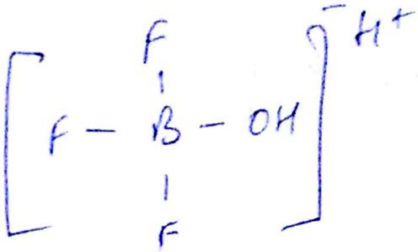
Propagation

$$n\,Bu\text{-}CH_2\text{-}\bar{C}H_2\,Li^+ + n\,CH_2 = CH_2 \longrightarrow n\,Bu\text{-}[CH_2\text{-}CH_2]_n\,CH_2\text{-}\bar{C}H_2$$

Termination

$$n\text{-}Bu\text{-}[CH_2 - CH_2]_n\,CH_2\text{-}\bar{C}H_2\,Li^+ \xrightarrow{H_2O} n\text{-}Bu\text{-}[CH_2\text{-}CH_2]_n\,CH_2\,CH_3 + LiOH$$

Cationic H^+ or ~~ionic~~ Lewis Acid

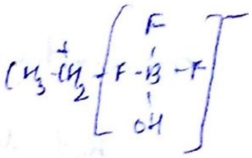


Initialisation

$$CH_2=CH_2 + H^+[BF_3-OH] \longrightarrow [BF_3]^{\delta-}\, CH_2-\overset{+}{C}H_2$$

Propagation

$$R^-[CH_3-CH_2^+] \xrightarrow{CH_2=CH_2} CH_3\{CH_2-CH_2\}\, CH_2-\overset{+}{C}H_2\, (BF_3)OH^-$$



Termination

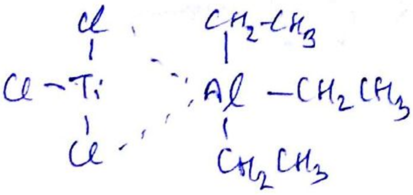
① $CH_3\{CH_2-CH_2\}_n CH_2-\overset{+}{C}H_2 \longrightarrow CH_3-[CH_2-CH_2]_n CH=CH_2$

② $CH_3\{CH_2-CH_2\}_n CH_2-\overset{+}{C}H_2 \xrightarrow{H^-} CH_3-[CH_2-CH_2]_n CH_2-CH_3$

Coordination polymerisation

Ziegler Natta catalyst

$TiCl_3 + \cancel{AlCl_3}\ Al(Et)_3$



Initialisation $\qquad$ $d\pi - p\pi$ interaction

$CH_2=CH_2$

$$-Ti- \; + \; Al- \longrightarrow M-C$$

$CH_2=CH_2$

$$M - \underbrace{CH_2-CH_3}_{R} \longrightarrow M-CH_2-CH_2-R$$

Propagation

$$M-CH_2-CH_2-R \xrightarrow{CH_2=CH_2} M-[CH_2-CH_2]_n-CH_2-CH_3$$

Termination

Hydride Transfer

$$M\{CH_2-CH_2\}_n CH_2-CH_3 + R'H \longrightarrow MR' + CH_3-[CH_2-CH_2]_n CH_2CH_3$$

We can also have ~~mon~~ monomer? ~~to~~ Transfer

Advantage

- Achieve stereo regular polymer
- Synthesize high density polythene

using

Designed on the basis of functional

Classification of stereo polymers

1) Attactic
2) Isotectic
3) Stereotactic / Syndiotactic

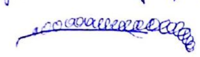
1) No defined rule,
Position of func. gp is irregular

2) functional gps are arranged in a regular manner

3) Alternative arrangement

This phenomenon is called tacticity (arrangement of funct. gp in chain)

Higher density polythene



Low density polythene
obtd by cationic / anionic mechanism

10.4.17

Condensation Polymerisation

Nylon, 6-6 — No. of 'C' atoms

Adipic acid + Hexamethylenediamine

$HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \xrightarrow{-H_2O}$

Kevlar

Nomex

- Polythene

$n\ CH_2=CH_2 \longrightarrow -\!\!\left[CH_2-CH_2\right]_n\!-$

	LDPE	HDPE
Syn.	free radical polymerisation	coordination polymerisation
	1000-5000	60-700 °C
	750 °C	6-7 atm
		Ziegler-Natta catalyst
		Linear

Crystalline

- Polypropylene

$n\ \overset{CH_3}{\overset{|}{CH}}=CH_2 \xrightarrow{Z.N.\ catalyst}$

Highly crystalline

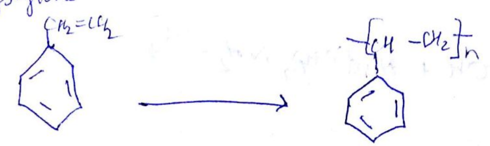
mpt 160-170°C

moisture resistant

electrically insulated

Baby bottles, flasks, ropes

- Polystyrene



Highly transparent

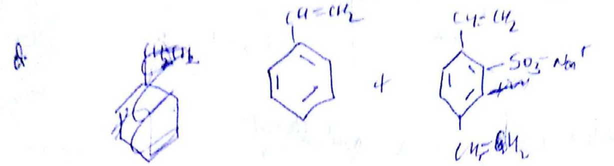
$\mu \sim 1.6$

Very low distortion temp. (~85°C)

Resistance to low alkaline reducing agents

Used in bulbs, jars,

&



Ion exchanger

- Poly vinyl chloride (PVC)

$CH_2=CH-Cl \longrightarrow [CH_2-CH(Cl)]_n$

Colourless
Odourless
Non inflammable
Partial ~~BPK~~ synthetic (silent?)
Low

PVC $\xrightarrow{\Delta}$ $-HCl$

Poly vinylacetate

$CH=CH-COOCH_3 \xrightarrow{FR} [CH_2-CH(COOCH_3)]_n$

Chewing gum
Surgical dressing
Lacquers, Paints, Resins
Bonding
Textile

Upon hydrolyzing (water insoluble) we get poly vinyl alcohol (water soluble)

- Polymethyl methacrylate (PMMA)

$$n\left[CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_3\right] \xrightarrow[F.R]{} \left[CH_2-\overset{CH_3}{\overset{|}{\underset{CO_2CH_3}{\underset{|}{C}}}}-\right]_n$$

Excellent outdoor life period & good strength

Amorphous in nature (because of side groups)

~~Rubber like at 85°~~

Rubber like at 85°C

~~[illegible]~~

Glass transition

* Plexi Glass

Bath tubs

Wind Screen, TV Screen

- Teflon (PTFA)

Polytetra fluoro ethylene

~~[illegible]~~ ~~$CH_2=CH$~~

$$n\ CF_2=CF_2 \xrightarrow{F.R} [CF_2-CF_2]_n$$

Regular st. → Isotactic

Crystalline → Hard

Softening pt → 327°C

Decomposed without changing into vapour

Resistant to chemicals

Only hot alkali metals can react with PTFE

Density = 2.1 — 3.0

Excellent mechanical properties

Can be machined

Very slippery and waxy

Used in chemical carrying pipes

~~[illegible]~~ Gasket

Non lubricating Bearing

Non stick coating

Fibres - Belts,

Industrial Polymers

Polyesters
Nylons 6
Plastic

Polyamides

Polyamides are a group of polymers
[illegible] linkage (strength)

It is a type of linear aliphatic polyamide
capable for fibres

Nylon 66

$HOOC-(CH_2)_4-COOH + H_2N-(CH_2)_6-NH_2$

Adipic acid   hexa methylene diamine

$\downarrow$

$\left[\overset{O}{\overset{\|}{C}} -(CH_2)_4- \overset{O}{\overset{\|}{C}} - NH -(CH_2)_6- NH_2 \right]_n$

Nylon 6 10

$HOOC-(CH_2)_8-COOH$

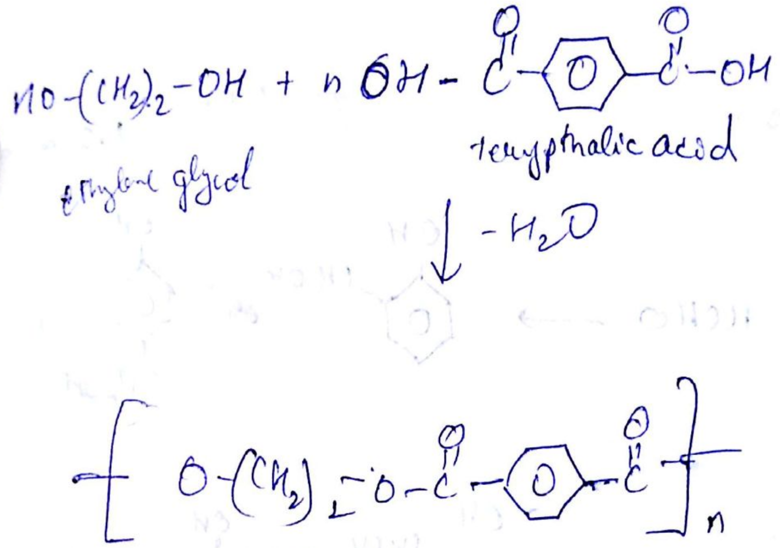
sebacic acid

Properties of Nylon

- high strength
- high elasticity
- insoluble in common solvents
- very good moisture resistance

- a wear abrasion & fire resistance
- Nylon 6 6 used as plastic as well as fibre
- It is used as fire & waterproof jackets, helmets, tyres ; gears , springs, sockets , rollers ; slide doors

Polyesters



Polyester

They are condensation product of dicarboxylic acid with dihydroxy alcohol

The industrially more important polymer is polyethylene terephthalic acid

Weak acid & bases

at room temperature

PET fibres are abrasion & ...

It has good elastic properties

Resistant to insect attacks

Used in making

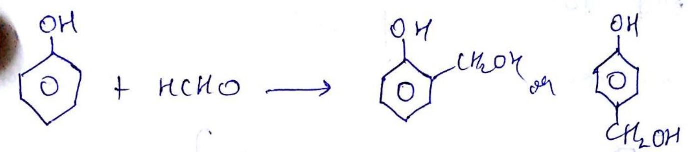
Synthetic fibres

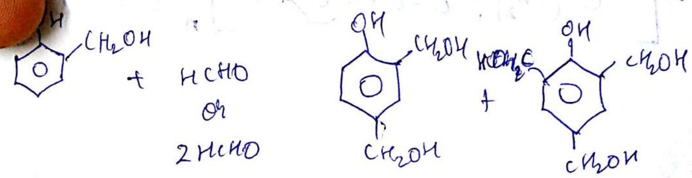
terylon, decaron

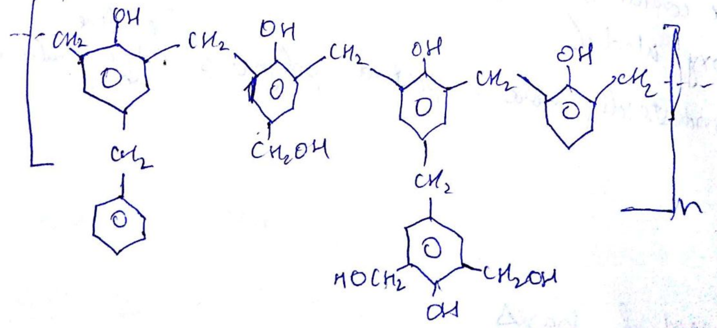
Used in making electrical insulators, plastic bottles

Phenol Resin

1:2 mole ratio







Most important synthetic plastic

Phenol formaldehyde resins etc.

High Dimensional stability

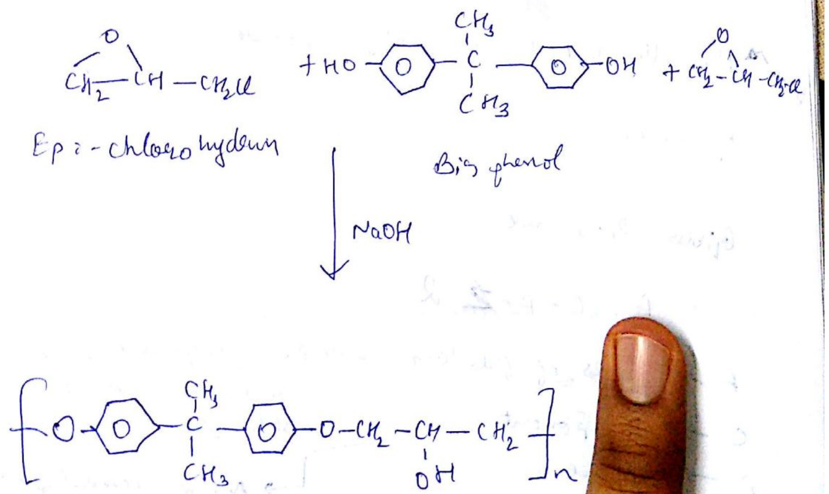
Dielectric properties

Hard Stretch

Telephone parts, laminates, radio-television, automobile parts

Water softening

Epoxy Resin



Chemical Resistance

Tough

Chemical & ~~dynamic~~ dimensional stability

Stretch Excellent structural

High surface

Electrical insulator

Rubber & elastomers

↓

Polymers capable of decompressive strength 150% of original without breaking

Natural rubber 7 isoprene

26.4.17.

Phase Equilibria

Phase → Physically distinct, mechanically seperable

eg water

Gibbs Phase Rule

$$F = C - P + \cancel{1}\ 2$$

F → degrees of freedom → No. of independent variables which are arbitrarily fixed to define the state of system in equilibrium

C → component → No of chemical species which can define whole system

P → phase

$2\ \cancel{1}$ → variables (T, P, x_i)

$[CaCO_3, CaO, CO_2] \rightarrow$ 2 component system

$CaCO_3 \rightleftharpoons CaO + CO_2$.

N → total no. of chemical species

E → No. of chemical equations to define equilibrium

I → ~~Electronegativity~~ Electroneutrality

Non ionic
$C = N - E$

Ionic eq^n
$C = N - E - 1$

$N = 3$, $C = N - E$
$= 3 - 1 = 2$

$KCl, NaCl, H_2O$

No eq^n

~~$KCl + H_2O \rightarrow KOH + HCl$?~~

~~$NaCl + H_2O \rightarrow NaOH + HCl$?~~

~~$H^+ + OH^- \rightleftharpoons H_2O$~~

$C = N - E \cancel{- 1}$

$3 - 0 \cancel{- 1}$

$= 3$

$KCl, NaBr, H_2O$

~~$K^+ + Cl^- \rightarrow KCl$~~

~~$Na^+ + Br^- \rightarrow NaBr$~~

$KCl + NaBr \rightleftharpoons NaCl + KBr$

$C = N - E$

$3 - 0 1$

$= 5 - 1 = \underline{4}$

$KCl, NaCl, K^+, Cl^-, H_2O, Na^+$

$K^+ + Cl^- \rightleftharpoons KCl$

$Na^+ + Cl^- \rightleftharpoons NaCl$

$C = N - E - 1$

$= 6 - 2 - 1$

$= 3$

$KCl, NaBr, H_2O, K^+, Br^-, Cl^-, Na^+$

$K^+ + Cl^- \rightleftharpoons KCl$

$Na^+ + Br^- \rightleftharpoons NaBr$

$K^+ + Br^- \rightleftharpoons KBr$

$Na^+ + Cl^- \rightleftharpoons NaCl$

$C = N - E - 1$

$9 - 4 - 1$

$= \underline{4}$

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2 component system

H_2O ?
One component

B- $CaCl_2 \cdot 6H_2O$, Ca^{2+}, Cl^-, H_2O (l), H_2O (g)

$CaCl_2 \cdot 6H_2O \xrightarrow{\Delta} CaCl_2 \cdot H_2O + 5H_2O \xrightarrow{\Delta} CaCl_2 + H_2O$

→ $Ca^{2+} + 2Cl^- \rightleftharpoons CaCl_2$, $H_2O_{(l)} \rightleftharpoons H_2O$ (g)

$CaCl_2 \cdot 6H_2O \rightleftharpoons CaCl_2 + 6H_2O$

$C = N - E - 1$

$= \cancel{5 - 3 - 1}$

$= \cancel{2}$

$CaCl_2 \cdot 6H_2O \rightleftharpoons Ca^{2+} + 6H_2O + 2Cl^-$

$C = 4 - 1 - 1$
$= 2$

$C = 5 - 2 - 1$
$= 2$

$F = C - P + 2$

One Component

$F = 3 - P$

eg:- H_2O, Sulphur

Two Component

$F = 4 - P$

eg:- Cu-Ni , Pb-Ag

P	F	System	Representation
1	2	Bivariant	Area
2	1	Monovariant	Line
3	0	Invariant	Point

T, P

H_2O

A-B Solid vapour

Any chang

B-C Solid Liquid

→ Triple

2 component system

H_2O ? One component

B. $CaCl_2 \cdot 6H_2O$, Ca^{2+}, Cl^-, $H_2O\,(l)$, $H_2O\,(g)$

$CaCl_2 \cdot 6H_2O \xrightarrow{\Delta} CaCl_2 \cdot H_2O + 5H_2O \xrightarrow{\Delta} CaCl_2 + H_2O$

→ $Ca^{2+} + 2Cl^- \rightleftharpoons CaCl_2$, $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$CaCl_2 \cdot 6H_2O \rightleftharpoons CaCl_2 + 6H_2O$

$C = N - E - 1$

$= \cancel{5 - 3 - 1}$

$= \cancel{2}$

$CaCl_2 \cdot 6H_2O \rightleftharpoons Ca^{2+} + 6H_2O + 2Cl^-$

$C = 4 - 1 - 1$

$= \underline{\underline{2}}$

$C = 5 - 2 - 1$

$= \underline{\underline{2}}$

$F = C - P + 2$

One Component — Two Component

$F = 3 - P$ — $F = 4 - P$

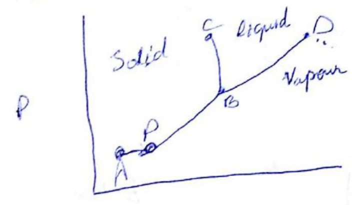
eg:- H_2O, sulphur — eg:- Cu-Ni, Pb-Ag

Phase	F	System	Representation
1	2	Bivariant	Are[a]
2	1	Monovariant	Lin[e]
3	0	Invariant	Poi[nt]

T, P   1 component

~~Sulphur~~ ~~Cu-Ni~~ ~~Pb-Ag~~.

H_2O



A-B Solid vapour equilibrium   Solid $\overset{AB}{\rightleftharpoons}$ Vapour

Any change in P or T ~~point~~

B-C Solid liquid equilibrium   Solid $\overset{BC}{\rightleftharpoons}$ Liquid

BD

Liquid $\rightleftharpoons$ Vapour

B → Triple point of water

$f = 0$

Solid ⇌ Liquid ⇌ Vapour

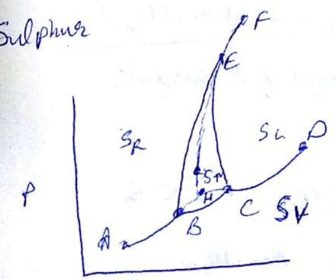
Area → 2 degree of freedom

→ 0

Phase + Lattice change

24.4.17

Sulphur



4 triple pts → B, C, E, H

H → Metastable point

S_R S_m S_L S_V

Two component system

$F = C - P + 2$

$= 4 - P$

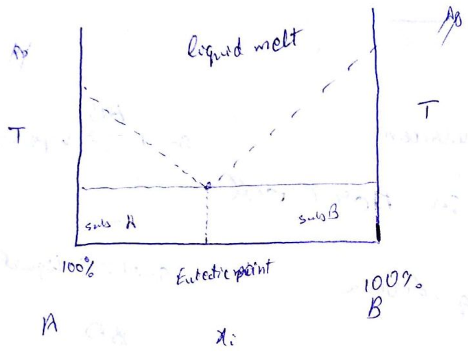
Isobaric

$F = C - P + 1$

$\boxed{F = 3 - P}$

Isomeric ~~...~~ (Cu-Ni)

Isobaric (continuous) (Pb-Ag)



3 phase equilibria

$F = 0$

Composition of A & B @ Eutectic pt → Eutectic mixture

Atom Economy

Atom-y :

$$\% = \frac{\text{Formula weight of atom utilized}}{\text{Formula weight of all reagents}}$$

$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$

Reagent	Formula mass	Atom utilized	
C_2H_5Br	109	C_2H_5	29
$NaOH$	40	OH	17
	149		

$\% = \frac{46}{149} \times 100$