WATER CHEMISTRY

Hardness of Water :

Water which does not produce lather with Soap is terme as hard water. The hardness is usually expressed in terms of Ca & Mg Salts like bicarbonate, Carbonate, Sulphate, Chloride etc.

Cause of Hardness → Hardness are due to the two types of impurities.

① Metalic Impurity – Ca^{++}, Mg^{++}, He^{++} etc.

(ii) Ionic Impurity – CO_3^{--}, HCO_3^{-}, SO_4^{--}, Cl^{-}, NO_3^{-} et

Q. Why hard water consumes a lot of soap ?

Ans. This is due to presence in water of certain salt of Ca, Mg & other heavy metal ions like Al^{3+}, Fe^{3+} & Mn^{2+} dissolved in it.

Formation of Hard water :

Hard water is formed due to presence of minerals like Ca & Mg. they are not removed or separated by sedimentation or filteration. When hard water reacts with Soap (Sodium Salt of Stearic acid or pametic acid) gives Curdy precipitate.

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} + \underset{\text{Hardness}}{CaCl_2} \longrightarrow \underset{\text{Calcium Stearate (Insoluble)}}{Ca(C_{17}H_{35}COO)_2} \downarrow + NaCl$$

&

$$C_{17}H_{35}COONa + MgSO_4 \longrightarrow \underset{\text{Magnesium Stearate (Insoluble)}}{C_{17}H_{35}(COO)_2Mg} \downarrow + Na_2SO_4$$

Difference between Hard Water & Soft Water :-

Hard Water	Soft Water
) Water which does not produce lather with Soap Solution readily, out forms a white Curd, is Called hard water.	Water which ~~laters~~ lathers easily on Shaking with Soap Solution, is Called 'Soft Water'.
) Hard Water Contains dissolved Calcium & Magnesium Salts in it.	Soft Water does not Contain dissolved Calcium & Magnesium Salts in it.
) In hard Water, Cleansing Quality of Soap is depressed & a lot of t is wasted during washing & bathing.	In Soft Water, Cleansing quality of Soap is not depressed & So Soap is not wasted during washing & bathing.
Due to the presence of dissolved hardness producing Salts, the boiling point of water is elevated. Consiquently More fuel & time are required for Cooking.	less fuel & time are required for Cooking in Soft Water.

3

Types of Hardness.

Temporary Hardness.

Temporary hardness of Water is Caused by Ca & Mg bicarbonate. Which Can be easily removed by boiling of Water - Due to boiling biCarbonate is Converted into Carbonate.

→ use Hydrated lime to remove hardness.

→ also Know as Carbonate hardness or Alkaline harness

→ Determine by titration with HCl using methyl orange indicator.

Permanent hardness

Permanent hardness is Caused by the presence of Soluble Salt of Ca & Mg other than bicarbonat Such as Chloride & Sulphate.

. Permanent hardness Cannot be removed by boiling of Water or hydrated lime - It Can be eliminate by Water Softening Techniques.

→ Also Known as non-Carbonate or non-Alkaline hardness.

$$\left.\begin{array}{l} Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow \\ Mg(HCO_3)_2 \rightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow \end{array}\right\} \text{Boiling}$$

$$Ca(HCO_3)_2 + \overset{\text{lime}}{\overline{Ca(OH)_2}} \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

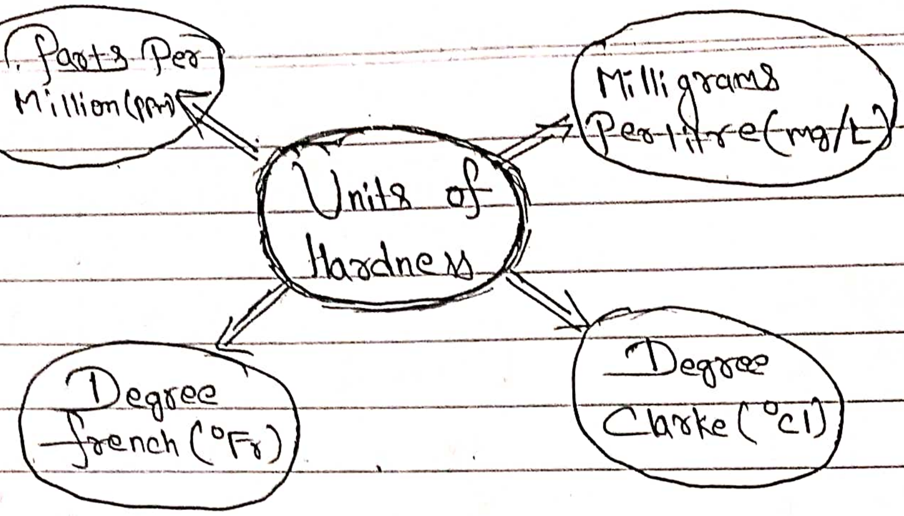
$$Mg(HCO_3)_2 + \underset{\text{lime}}{\underline{Ca(OH)_2}} \longrightarrow \cancel{Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow} + 2H_2O$$

$$MgCO_3 + CaCO_3 + 2H_2O$$

Degree of Hardness :

1. ~~Degree French~~ Although hardness of Water is never presen in the form of Calcium Carbonate because it is insoluble in Water, hardness of Water expressed in terms of equivalent amount (Equivalents) of $CaCO_3$.

Reason → Molecular Weight is exactly 100.



1. Degree French (°Fr) : The impurities which is prensent 10^5 parts by weight of water are detected by °Fr unit.

2. Degree Clarke (°Cl) : The impurities which is present 70000 parts by weigh of water are detected by °Cl unit
$1°Cl = 1$ Part of $CaCO_3$ Per 70,000 Parts of water.

3. Milligrams Per litre (mg/L) : It is the no. of milligrams of Calcium Carbonate equivalent of hardness present per litre of water.
$1 \text{ mg/L} = 1 \text{ PPM} = 10^6$

4. Parts per Million (PPM) ; It is also known as parts per Million (PPM) is the parts of Calcium Carbonate equivalent weight of present in 1 Million water or 10^6 parts of water.

Boiler Feed Water
(Water for Steam Generation)

Water is mainly used in boilers for the generation of steam (for industries & power houses). For such water all the impurities are not necessarily eliminated, & only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.

① Its hardness should be below 0.2 PPM.

⑪ Its Caustic alkalinity (due to OH^-) should lie in between 0.15 & 0.45 PPM.

⑪ Its Soda alkalinity (due to Na_2CO_3) should be 0.45 – 1 PPM.

* Excess of impurities, if present, in boiler feed water generally cause the following problems:

① Scale & Sludge formation.

⑪ Corrosion.

⑪ Priming & foaming.

ⓘⓥ Caustic embrittlement.

Priming & foaming :- When the boiler is steaming, some particles of the liquid waters are carried along with the stear

The process of the wet – steam formation is called Priming.

Caused by :-

① ~~The presence of~~ Due to high steam velocities i.e improper boiler design.

⑪ The sudden increase in the steam production rate.

⑪ The presence of the large amount of dissolve solids.

Foaming is the production of the persistent {foam or bubbles} in the boiler which do not break easily. Foaming is due t the presence of substances (like oils) which greatly reduce th surface tension of water sometimes.

→ Priming & foaming generally occurs together. they are objectionable because –

i) The dissolve Salt in water (boiler) are Carried out by the wet Steam to the Super heater and turbine the blades.
ii) Where they get deposit as the water evaporation,

i) Dissolve Salts may enter the parts of other machinery where the Steam is being used their by the decreasing the life of the machinery.

i) The actual heigh of the water Column Cannot be judge properly their by making the maintainance of boiler becomes difficult.

Priming Can be avoided by –
ⓐ Fitting the mechanical Steams purifier,
ⓑ Avoiding the rapid Change in Steaming rate.
ⓒ Maintaining the low water lebelling in boilers.

Scale and Sludge

In the boilers water evaporates Continuously & the Concentration of dissolve Salts increased progressively, When their Concentration reach the Solution point. they are thrown out of water in the form of the precipitates on the inner. wall of the boiler, If, the precipitation ~~on~~ takes place in the form of loose & the Slimy precipitates it is Called the Sludge. On the other hand if the precipitate forms a hard. and Crust Casting on the inner wall of the boiler is Called the Scale.

Boiler Corrosion :

Boiler Corrosion is "decay" or ~~distt~~ disintegration" of boiler body material either due to Chemical or electrochemical reaction with its environment having O_2, CO_2 & Mineral acids

The disadvantages of Corrosion are :-

① Shortening of boiler life,
(II) leakages of the joints & rivets ;
(III) increased Cost of repairs & Maintanance .

Caustic Embrittlement :

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to accumulation of Caustic Substances. This type of boiler Corrosion is Caused by the use of highly alkaline water in the high pressure boiler.

Water Softening techniques

(I) Soda-lime method
(II) Zeolite Method
(III) Ion-exchange method
(IV) Calgon method or (Permuted Method)

1. Soda-lime Method : The basic principle of this proces is to chemically Convert all the Soluble hardness Causing impuritie into insoluble precipitates, which may be removed by Settlin & filteration.

Lime → Temporary hardness (HCO_3^- of Ca^{++} & Mg^{++}
$Ca(OH)_2$ CO_3^{--} of Ca^{++} & Mg^{++}

$Ca(HCO_3)_2 + Ca(OH)_2 \xrightarrow{\Delta} 2CaCO_3 + H_2O$

Soluble. Insoluble.

$CaCO_3 + Ca(OH)_2 \xrightarrow{\Delta} \underset{\text{Soluble}}{CaCO_3} + H_2O + CO_2 + H_2$

Soluble impurity. Which is present in Water Sample.

$Mg(HCO_3)_2 + Ca(OH)_2 \xrightarrow{\Delta} Mg(OH)_2 + CaCO_3 + H_2O.$

$MgCO_3 + Ca(OH)_2 \xrightarrow{\Delta} Mg(OH)_2 + CaCO_3 + H_2O.$

Permanent hardness : $\{CaCl_2, MgCl_2, CaSO_4, MgSO_4, Fe_2O_3\}$

Soda + lime

$Na_2CO_3 + Ca(OH)_2 + CaCl_2 \xrightarrow{\Delta} CaCO_3 + CaO + H_2O + 2NaCl.$

$CaSO_4 + Ca(OH)_2 + Na_2CO_3 \xrightarrow{\Delta}$ ~~Mo~~ $Na_2SO_4 + CaCO_3 + CaO + H_2O$

$MgSO_4 + Ca(OH)_2 + Na_2CO_3 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + CaCO_3$

$MgCl_2 + Ca(OH)_2 + Na_2CO_3 \xrightarrow{\Delta} Mg(OH)_2 + CaCO_3 + 2NaCl$

Q. Calculate the amount of Soda for purification the 50,000 litre of hard water Containing the Calcium Carbonate 25 PPM & Magnesium Carbonate 144 PPM, Calcium chloride 111 PPM & Magnesium Chloride 95 PPM.

Sol^{n} : Given : $CaCO_3 = 25$ PPM, ✓

$MgCO_3 = 144$ PPM,

$CaCl_2 = 111$ PPM

$MgCl_2 = 95$ PPM

Required amount of Soda lime

$$= \frac{\text{Eq. wt of Soda or lime}}{\text{Part Eq. wt. of } CaCO_3} \times \left(\begin{array}{c}\text{Eq. wt of all hardness} \\ \text{Present in the form of} \\ CaCO_3\end{array}\right) \times \begin{array}{c}\text{Volume of} \\ \text{Hard water}\end{array}$$

$$\underset{100}{CaCO_3} + Ca(OH)_2 \xrightarrow{\Delta} \underset{100.}{CaCO_3} + CaO + H_2O$$

100 Part of insoluble $CaCO_3$ = 100 Parts of $CaCO_3$

1 Part of insoluble $CaCO_3$ = $\frac{\cancel{100}}{\cancel{100}} = 1.$

25 Parts of insoluble $CaCO_3$ = $1 \times 25 \boxed{= 25}$

$$MgCO_3 + Ca(OH)_2 \xrightarrow{\Delta} Mg(OH)_2 + CaCO_3 + H_2O$$

84 Part of insoluble $MgCO_3$ = 100 Parts of $CaCO_3$

1 Part of insoluble $MgCO_3$ = $\frac{100}{84}$ Parts of $CaCO_3$

144 Parts of insoluble $MgCO_3$ = $\frac{100}{\underset{21}{\cancel{84}}} \times \overset{36}{\cancel{144}}$ Parts of $CaCO_3$

$= \frac{3600}{21} = \boxed{171.42}$

$$CaCl_2 + Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 +$$

111 Parts of insoluble $CaCl_2$ = 100 Parts of $CaCO_3$

1 Part of insoluble $CaCl_2$ = $\frac{100}{111}$ Part of $CaCO_3$

111 Part of insoluble $CaCl_2$ = $\frac{100}{\cancel{111}} \times \cancel{111}$ Part of $CaCO_3$

$= \boxed{100}$

$MgCl_2 + Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3$

95 Parts of insoluble $MgCl_2$ = 100 Parts of $CaCO_3$

1 Part of insoluble $MgCl_2$ = $\frac{100}{95}$ Parts of $CaCO_3$

95 Parts of insoluble $MgCl_2$ = $\frac{100}{\cancel{95}} \times \cancel{95}$ Part of $CaCO_3$

$= \boxed{100}$

Calculations for Soda requirements :

Soda requirement $= \frac{106}{100}\left[MgCl_2 + CaCl_2\right] \times 50,000$ (mg)

$= \frac{106}{100}(100 + 100) \times 50,000$

$= \frac{106}{1\cancel{00}} \times 2\cancel{00} \times 50,000$ (mg)

$= 10600000$ mg

$= 10.6$ kg

Q. Calculate the amount of lime required for Softening the 50,000 litres of hard water Containing the Calcium bicarbonate 8.1 mg, Magnessium bicarbonate 7.5 mg, Calcium Sulphate 13.6 mg, Magnessium Sulphate 12 mg & Magnessium Carbonate 20 mg & Sodium Chloride 4.7 mg Calculate the Calcium Carbonates equivalent also.

Sol^n :- Given :

$Ca(HCO_3)_2$ = 8.1 mg

$Mg(HCO_3)_2$ = 7.5 mg

$CaSO_4$ = 13.6 mg

$MgSO_4$ = 12 mg

$MgCO_3$ = 20 mg

$NaCl$ = 4.7 mg

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O + CaO$.

162 mg $Ca(HCO_3)_2$ are soft $= 100$ mg of $CaCO_3$

1 mg $Ca(HCO_3)_2$ are soft $= \frac{100}{162}$ mg of $CaCO_3$

8.1 mg $Ca(HCO_3)_2$ are soft $= \frac{100}{162} \times 8.1$

$\simeq \boxed{5 \text{ mg}}$

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

146 mg $Mg(HCO_3)_2$ are soft $= 100$ mg of $CaCO_3$

1 mg $Mg(HCO_3)_2$ is soft $= \frac{100}{146}$ mg of $CaCO_3$

7.5 mg $Mg(HCO_3)_2$ are soft $= \frac{100}{146} \times 7.5$

$\simeq \boxed{5.13 \text{ mg}}$.

$CaSO_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow 2CaCO_3 + Na_2SO_4 + CaO$

136 mg $CaSO_4$ $= 100$ mg of $CaCO_3$

1 mg $CaSO_4$ $= \frac{100}{136}$

13.6 mg of $CaSO_4$ $= \frac{10\cancel{0}}{\cancel{136}} \times \frac{\cancel{136}}{10} = \boxed{10 \text{ mg}}$

$MgSO_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 + Mg(OH)_2$

120 mg of $MgSO_4$ $= 100$ mg of $CaCO_3$

1 mg of $MgSO_4$ $= \frac{100}{120}$ mg of $CaCO_3$

12 mg of $MgSO_4$ $= \frac{10\cancel{0}}{\cancel{120}} \times \cancel{12}$ mg of $CaCO_3$

$= \boxed{10 \text{ mg}}$

$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + \cancel{CaO} + Mg(OH)_2 +$

84 mg of $MgCO_3$ $= 100$ mg of $CaCO_3$

1 mg of $MgCO_3$ $= \frac{100}{84}$

20 mg of $MgCO_3$ $= \frac{100}{84} \times 20 = \frac{\overset{1000}{\cancel{2000}}}{\underset{42}{\cancel{84}}} = \boxed{23.8 \text{ mg}}$

Equivalent Carbonates $= \frac{\text{Eq. wt. of lime}}{\text{Eq. wt. of } CaCO_3} \{ \text{Amount of } Ca(HCO_3)_2 +$

$Mg(HCO_3)_2 + CaSO_4 + MgSO_4 + MgCO_3 \} \times 50,000$

$= \frac{74}{100} \{ 5 + 5.13 + 10 + 10 + 23.8) \times 50,000$

$= \frac{74}{100} \{ 53.93) \times 50,000$

$= \cancel{\frac{74}{100}}$ ✓ 1.99 kg.

II Amount of Soda,

$\frac{106}{100} (\ldots\ldots\ldots\ldots) \times 50,000.$

3. Explain with the Chemical equation & Calculate the amount of lime & Soda needed for softening the 100000 litre of hard water containing the following.

$CaCO_3 = 25$ ppm, $MgCO_3 = 144$ ppm, $CaCl_2 = 11$ ppm
$HCL = 7.3$ ppm, $Al_2(SO_4)_3 = 34.2$ ppm, $Mg(HCO_3) = 24$ ppm
$Ca(HCO_3) = 103$ ppm.

$= CaCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + CaO + H_2O$

100 Parts of insoluble $CaCO_3$ = 100 Parts of $CaCO_3$

1 Parts of insoluble $CaCO_3$ = $\frac{100}{100}$ Part of $CaCO_3$

25 parts of insoluble = $1 \times 25 = \boxed{25 \text{ ppm}}$

$MgCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + Mg(OH)_2$

~~to~~ 84 Parts of insoluble $MgCO_3$ = 100 Parts of $CaCO_3$

1 " " " $= \frac{100}{84}$

144 " " " $= \frac{100}{84} \times 144$

$= \boxed{171.42}$

$CaCl_2 + Ca(OH)_2 + Na_2CO_3 \longrightarrow CaCO_3 +$

111 Parts of insoluble $CaCl_2$ = 100 Parts of $CaCO_3$

1 " " " " $= \frac{100}{111}$

11 " " " " $= \frac{100}{111} \times 11 = \frac{1100}{111}$

$= \boxed{9.90}$

$Al_2(SO_4)_3 + Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + Na_2SO_4$

342 Parts of insoluble $Al_2(SO_4)_3$ = 100 Parts of $CaCO_3$

1 " " " $= \frac{100}{342}$

34.2 " " " " " $= \frac{\cancel{100}}{\cancel{342}} \times \frac{\cancel{342}}{\cancel{10}}$

$= \boxed{10}$

$Mg(HCO_3) + Ca(OH)_2 \longrightarrow CaCO_3 + Mg(OH)_2$

85 Parts of insoluble $Mg(HCO_3)$ = 100 Parts of $CaCO_3$

1 " " " " $= \frac{100}{85}$

24 " " " " $= \frac{100}{85} \times 24$

$= \frac{2400}{85} = \boxed{28.23}$

$Ca(HCO_3) + Ca(OH)_2 \longrightarrow CaCO_3$

101 = 100

1 $= \frac{100}{101}$

103 $\frac{100}{101} \times 103 = \boxed{101.98}$

lime requirement $= \frac{74}{100}\left(25 + 171.42 + 28.23 + 107.98\right) \times 100000$

$= \frac{74}{100} \times 326.63 \times 100000$

$= 24,170,620$ ppm

$= 24.17$ kg

Soda requirement $= \frac{106}{100}\left(9.90 + 10\right) \times 100000$

$= \frac{106}{1\cancel{0}\cancel{0}} \times \frac{19.9}{1\cancel{0}} \times 100\cancel{0}\cancel{0}\cancel{0}$

$= 2109400$ ppm

$= 2.10$ kg

2. Zeolite or Permutit Process :

Zeolites are naturally occuring hydrated Sodium alumino silicate Minerals Capable of exchanging reversibly its Sodium ions for hardness - Producing ions in water.

Zeolites are also Known as Permutits & in Greek it means 'Boiling ~~water~~ Stone'

The Chemical formula of Zeolite.

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

//

Na_2Z

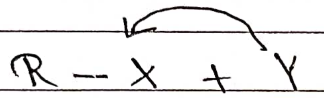
The Zeolite Softening process is used for removing both the temperory & permanent hardness of the water by precipitating the Calcium and magnesium present in water as insoluble Zeolites.

$\boxed{Na_2O\ Al_2O_3 \cdot xSiO_2 \cdot yH_2O}$

Reaction Mechanism :

Electron Displacement Effect :

The behaviour of Inorganic Compound influenced by to a large extent of by the electron displacement taking place in its Convalent bonds, these displacement may be the Permanent nature or may be the temporary nature ~~talking~~ taking place on demand in the presence of another molecule, Which is Called the



Reagent.

Reagent, the electron displacement effect are of following type :-

(I) Inductive effect
(II) Electromaric effect

① Inductive effect :- Inductive effect is the permanent effect operating in polar Co-Valent bonds, It Comes into the existance, When electron withdrawing (the attacking reager group is attacked to a chain of the singly bonded Carbon atom. So the displacement of the a electron along a Saturated Carbon due to the presence of in electron Withdrawing or the electron repling group at one end of the Carbon chain resulting in the development of partial positive or partial negative Charges in the decreasing order of the magnitude is Called Inductive effect.

② Electromaric effect :- It is the temporary effect due to the operating in the ~~undess~~ Unsaturated Compounds only

It the demand of the only nearby reagent. It involves the Complete transfer Complete transfer of π electrons so, the Complete transfer of the Shared-paired of the π electrons of the multiple bonds to the more electronegative items of in attacking reagent is Called electromaric effect ~~or E-effect~~.

When the transfer of the π electrons takes place toward the attacking reagent effect (electrofiles) is Called the electro maric effect or E-effect.

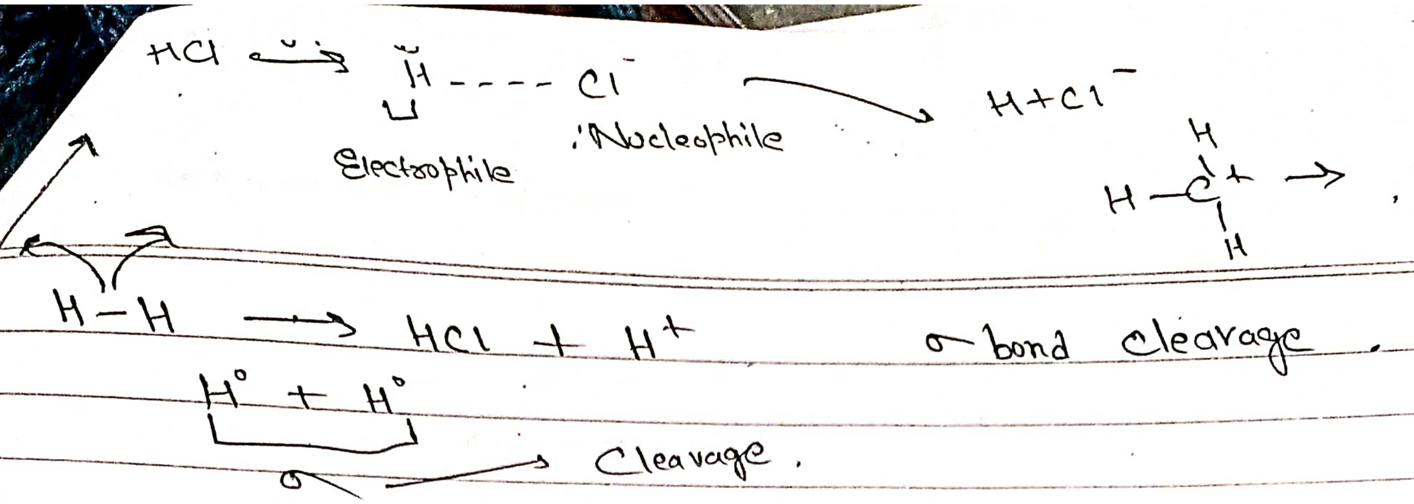
Bond Fission

Organic Compounds are the Covalent Compound having the single, double or the tripple bond between the Carbon & other atoms. Most of the organic reaction involves the fission of Covalent bonds. Generally the bond fission are of two types.

Two types

1) Homolytic fission ② Heterolytic fission.

1. Homolytic fission : In homolytic fission a Covalent bond breaks up in such a way that each atom forming the Covalent bond takes away. the one electron of the shared paired. In homolytics bonds free radicals are developed.



2. Heterolytic fission : In heterolytic fission when the Covalent bond is breakup in such a way, ~~when the both~~ then the both belongs shared paired are taken away only by the one atom forming the Covalent bond. the cleavage of the bond is Called a Symmetrical fission.

Ex

Reaction Intermediate :

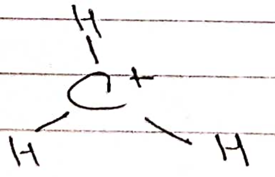
On the basis of the cleavage of the bond there are the four types of the reaction Intermediate.

Intermediate

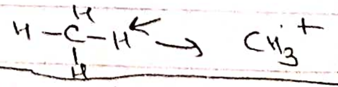
- Carbonium ion
- Carbon ion
- Free radical
- Electrophile Nucleo

1. Carbonium ion

A chemical species bearing a positive charge on Carbon & Carrying six electrons in its Valence in its Valence shell are Called Carbonium ions or Carbocations. Carbocations have a planar structure.



★ Front attack of a Carbon developed as a Carbonium ion



$H-\overset{H}{\underset{H}{C}}-H \rightarrow CH_3^+$

① Carbocations are formed by heterolytic cleavage of Covalent bonds in which the leaving group takes away the shared pair of electrons of Covalent bond with it

$$(CH_3)_3C-Cl \rightarrow (CH_3)_3\overset{+}{C} + Cl^-$$

tert-butyl Chloride — Tert-butyl Carbonium ion

② By the dehydration of alcohol at 430 - 440 K.

$$CH_3CH_2-\ddot{O}H + H^+ \xrightarrow[430-440K]{Conc.\ H_2SO_4} [CH_3CH_2-\overset{+}{O}H_2]$$

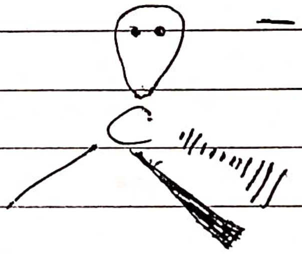
$$\downarrow$$

$$CH_3\overset{+}{C}H_2 + H_2O$$

Ethyl Carbocation

2. Carbanions

A Chemical Species bearing a negative Charge on Carbon & possesing eigth electrons in its Valence Shell is Called Carbanion.



* Back attack of a Carbon developed as a Carbon ion

→ Carbanions are formed when Covalent bonds are cleaved heterolytically, leaving the Shared pair of electrons with the Carbon atom.

$$HO^- + H-CH_2-CHO \rightarrow H_2O + :\bar{C}H_2-CHO$$

Hydroxide ion — Acetaldehyde — Acetaldehyde Carbanion.

3. Free radicals

Atom or group of atoms having an odd or unpaired Electron is Known as free radicals.

$H_3C\cdot$

* Same nature Same ions free radicals

Ex

$\dot{C}l$	$\dot{C}H_3$	$\dot{C}_2H_5$	$\dot{C}_6H_5$	$C_6H_5\dot{C}H_2$
Chlorine free radical	Methyl free radical	Ethyl free radical	Phenyl free radical	Benzyl free radical

$$Cl-Cl \longrightarrow \dot{Cl} + \dot{Cl}$$

Chlorine free radicals

4. Electrophile

(i) Chemical Species that has a positive charge (Cations)
(ii) Chemical Species that have an overall neutral charge but one or more of its atom have empty Valence Shells.
(iii) Accepts electron.
(iv) lovers of electrons
(v) Represented by E^+
(vi) They are electron deficient
(vii) They are of the Lewis ~~Acd~~ Acid Category.

5. Nucleophile

(i) Chemical Species that has a negative charge (anion)
(ii) Chemical Species that have an overall neutral charge but have one or more lone pairs (s) or free pair (s) of electrons
(iii) Donates electrons
(iv) Nucleophiles are lovers of the nucleus where protons reside
(v) Represented by Nu^-
(vi) They are electron rich
(vii) They are of the Lewis base Category

Types of Reaction Mechanism

(i) Substitutional Reaction
(ii) Additional Reaction.
(iii) Elimination Reaction.
(iv) Rearrangement Reaction.

1. **Substitution Reaction :** The reaction Which involve the direct displacement of an atom or a group by Some other atom ~~or a group by~~ group of atom are referred to as in the Substitution reaction.

Two types

① Nucleophillic Substitution Reaction (SN Reaction)

Ⅱ Electrophillic Substitution Reaction, (SE Reaction)

① **Nucleophillic Substitution Reaction (SN Reaction) :**

The Substitution reaction Where the nucleophile attack on Substrate and replaced the ion or group by other ion or groups are Known as nucleophilic Substitution reaction.

→ It is represent as $R-X + \underbrace{[OH^-]}_{\text{Attacking reagent (Strong nucleophile)}} \rightarrow R-OH + X^+$

In a reaction a weaker nucleophile is usualy replaced by the Strong nucleophile,

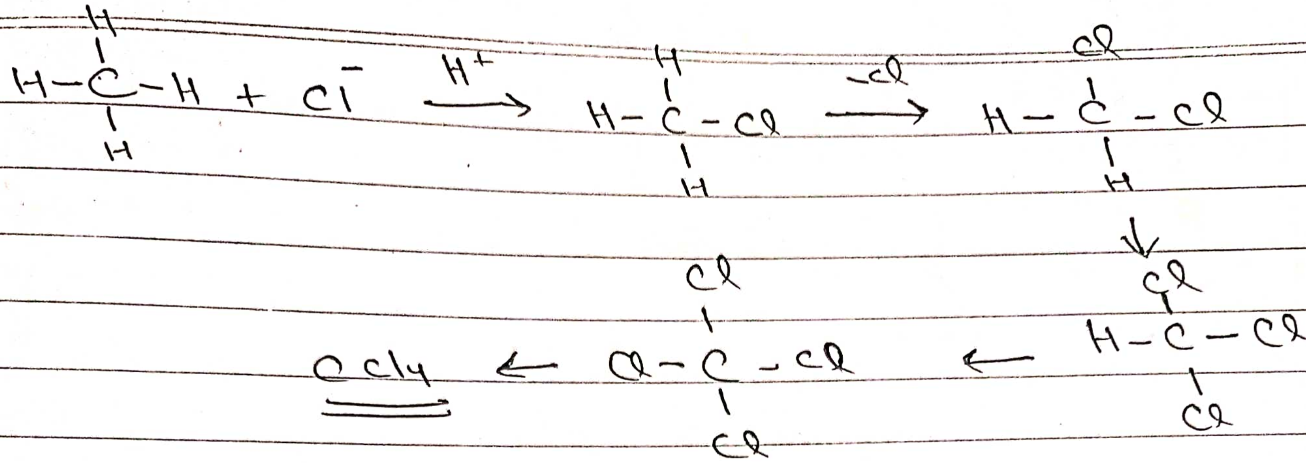
Types of Nucleophillic Substitution reaction

ⓐ Sn^1 (uni molecular nucleophilic Substitution reaction).

ⓑ Sn^2 (Bimolecular nucleophilic Substitution reaction).

ⓐ **Sn^1 :** It is the unimolecular Substitution reaction Where the nucleophillic Substitution reaction are depend on the rate of the Concentration upon the Concentration of Substrate not upon the Concentration of attacking reagents.

Rate $\propto$ Conc. of Substrate.



It is the first order reaction & rate law involve only the Concentration of the Substrate.

Reaction Mechanism

- Substitution. Reaction
  - SN
    - SN1 → 2 step
    - SN2 → 1 step.
  - SE
  - Free radicals reaction
- Elimination Reaction
  - EN
  - EE
- Addition reaction
  - Step Process
    - ① Initiation.
    - ② Propagation
    - ③ Termination
- Rearrangement reaction.
  - Isomerism

$C_2H_5OH \rightarrow C_2H_5^+ + OH^-$ — ①

$C_2H_5^+ + Br^- \rightarrow C_2H_5Br$,

eg

$CH \equiv CH + HBr \rightarrow CH_2 = CHBr$.

Acetylene

$CH \equiv CH$ open the bonds

$\downarrow$ $2H^+ \cdot Br^-$

$-\dot{C}H = \dot{C}H-$.

$\downarrow$

$H - CH = CH - Br$

$\downarrow$

$H - CH = \overset{\delta+}{CH} - - - - - \overset{\delta-}{Br}$

$\downarrow H^+ Br^-$

Propagation Process

Termination Process.

$CH_2 - CH_2Br_2 \rightarrow CH_2 - CH - - - Br_2 \rightarrow CH_2 - CHBr$.

$\rightarrow CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-Pentane

$\rightarrow CH_3 - CH_2 - \overset{CH_3}{\overset{|}{CH_3}} - CH_3$

Iso butane or

1 methyl butane .

$_2$-CHBr

Substitution Reaction

The Mechanism of Sn^1 reactions

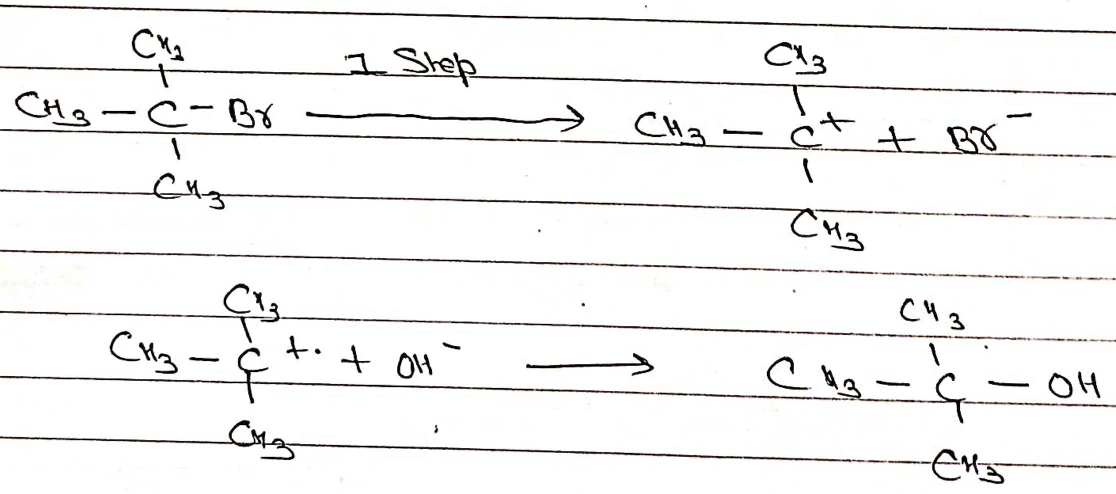
Sn^1 reaction is the unimolecular nucleophilic Substitution reaction.

Sn^1 reaction are Completed in two Steps & it is depend on the Concentration of the Substrate.

Step 1 : It is a Very Slow Step where the old bond brea

$C_2H_5OH \rightarrow C_2H_5^+ + OH^-$ (Slow reaction)

Step 2 : It is Very fast Where new bonds are formed. The rate determine Step is the first Step as the first Step does not involve the attacking nucleophile & Molar Concentration of one reactant is only Changed So the over all reaction is the 1^{st} order reaction.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow{1\ Step} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + Br^-$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}^{+} + OH^- \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

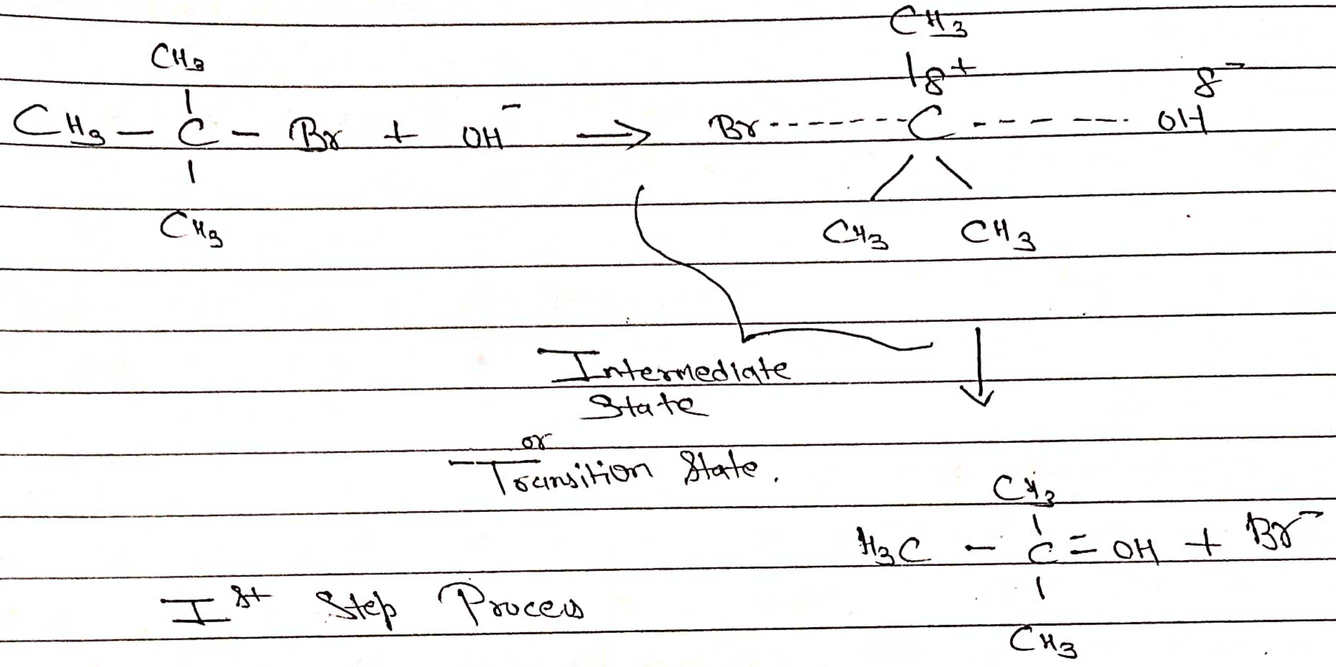
Tertiary Butyl alcohol.

The Mechanism of Sn^2 reactions

(i) Bimolecular nucleophilic Substitution reaction.

(ii) It is 1^{st} step process

Where the both nucleophile are attack on same time & Stronger nucleophile replace the whether nucleophile.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + OH^- \longrightarrow Br\cdots\overset{CH_3}{\overset{|\delta+}{C}}\cdots\overset{\delta-}{OH} \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}=OH + Br^-$$

Intermediate State or Transition State.

I^st Step Process

Sn² reaction Involves Simultaneous bond breaking & the bond. making in this reaction attacking nucleophile (OH) attack at the Carbon in the Substrate forming a high energy transition State and nucleophile Carbon is in the process forming a Compound & the weaker nucleophile Carbon is in the process of breaking with the Simultaneous Sesion of the leaving group.

Addition Reaction

The reaction where they ready to adopt the any Kind of the double or tripple bond presence in the Substrate Molecule referred as in the addition reaction.

$$CH_2=CH_2 \xrightarrow{H_2} CH_3-CH_3$$

The σ bond or the π bond are also weak the Consituent of the addition reaction So, The reaction which is reffered to as in the addition reaction when a reagent Site of double or tripple bond add any molecule A double bond is Composed of 1σ & 1π bond where as a tripple bond is made up of 1σ & 2π bonds. A π bond is weaker than 2σ bonds & need the less energy for its clearage.

* 1π bond is weaker than the 2σ bond.

$C \overset{\sigma}{\underset{2\pi}{\equiv}} C$

$C \overset{\sigma}{\underset{2\pi}{\equiv}} C$

σ → 2σ → $\boxed{\text{more energy}}$

2π → 1π + 1π → $\boxed{\text{less}}$

When a attacking reagent attack on the Substrate double or tripple bond, the π bond gets broken & reagent gets added at the Site of the Clearage of π bond.

$$\underbrace{CH_2 = CH_2}_{\text{Substrate}} + \underbrace{Cl_2}_{\text{reagent}} \longrightarrow Cl-CH_2-CH_2-Cl$$

(i) Depending upon the nature of the attacking reagents.

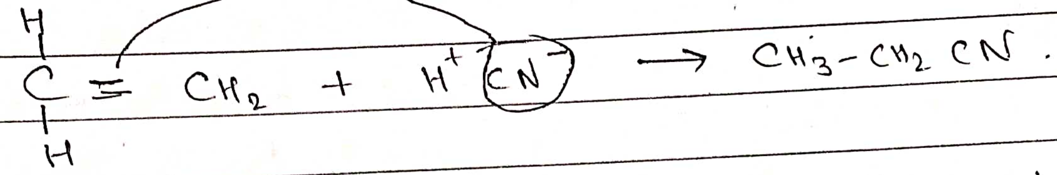
(ii) Attacking reaction are of three types

(a) Nucleophilic addition reaction.

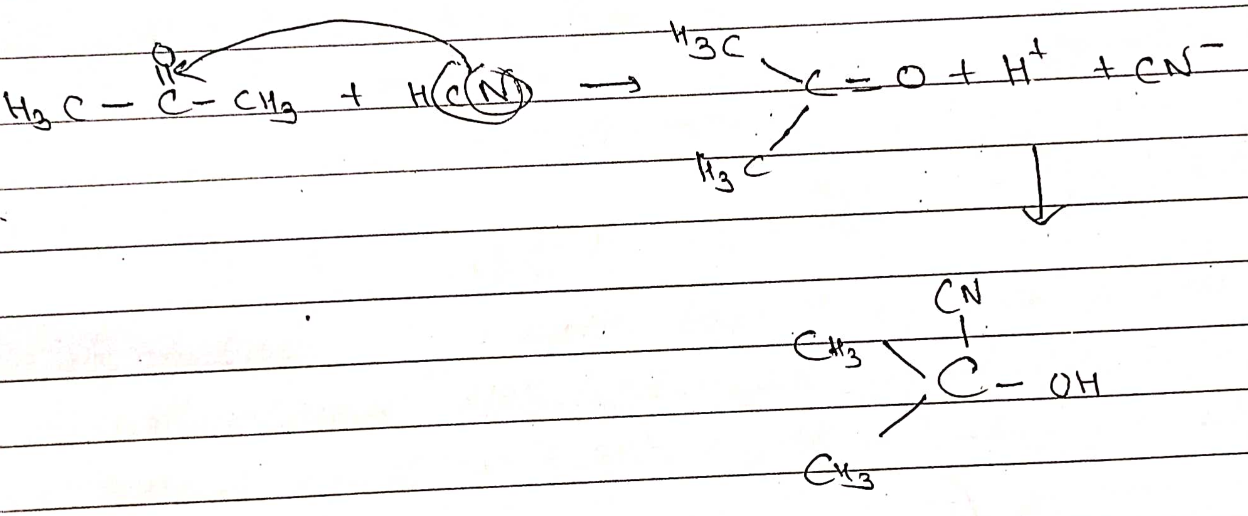
(b) Electrophilic addition reaction.

(c) free radicals Addition reaction.

a) Nucleophilic addition reaction → When the nucleophiles are play the role of the reagent.

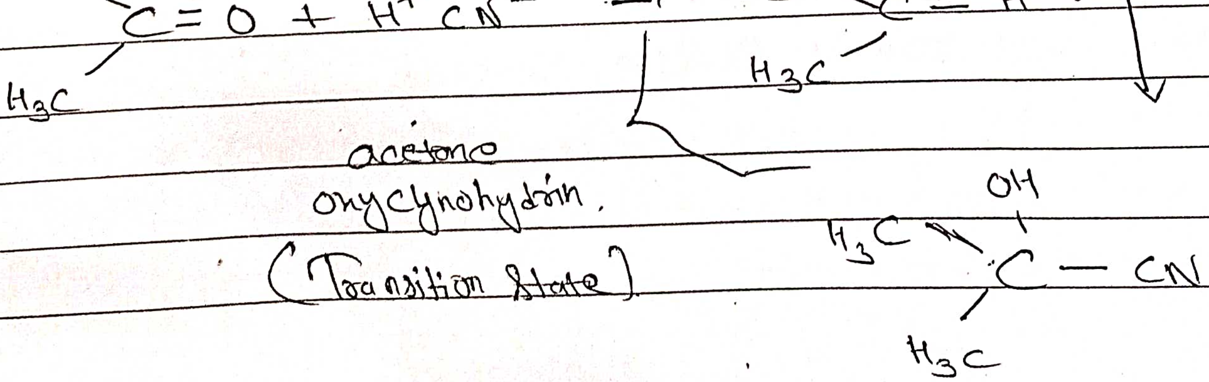


When a reaction is intiated by, the attack of the nucleophile, the reaction is termed as nucleophilic addition reaction.



Acetone Cynohydrine.

b) Electrophilic addition reaction → The addition reaction intiated by the attack of electrophile are called the electrophilic addition reactions. These reactions are usually shown by the alkenes & alkynes.



acetone oxycynohydrin.
(Transition State)

(c) Free radicails addition reaction → When the free radicals reagent are attack on the double bond of the Substrate for cleavaging the bond & Make the product is Called the free radicals addition reaction.

$\boxed{Cl_2}$

$\dot{Cl} + \dot{Cl}$

$CH_2 = CH_2 + \dot{Cl} \longrightarrow \underbrace{Cl \cdot CH_2 - CH_2\,\dot{Cl}}$

Dichloro ethane.

Elimination Reaction → Reverse process

$CH_3 - CH_3 \xrightarrow{-H_2} H - - \big) - - CH_2 - CH_2 \big| H \xrightarrow{-H_2} \dot{C}H = CH$

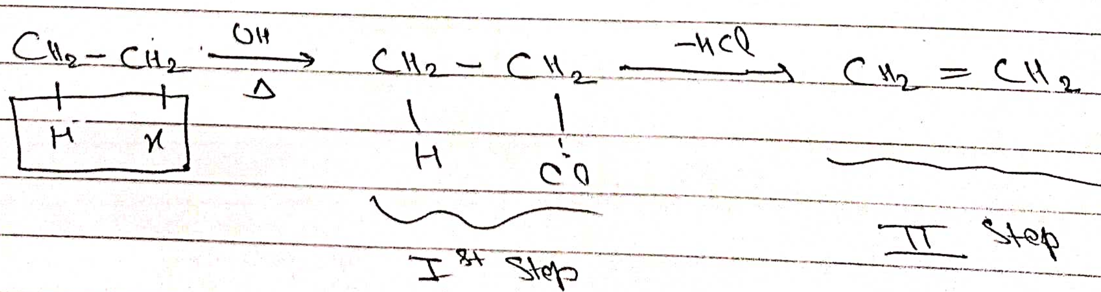
$\downarrow -H_2$

$H^+ + CH \equiv CH$

It is the reverse process of Addition reaction in an elimination reaction, Saturated Substrate Compound are Convert into the unsaturated products.

The Mechanism of Elimination Reaction :

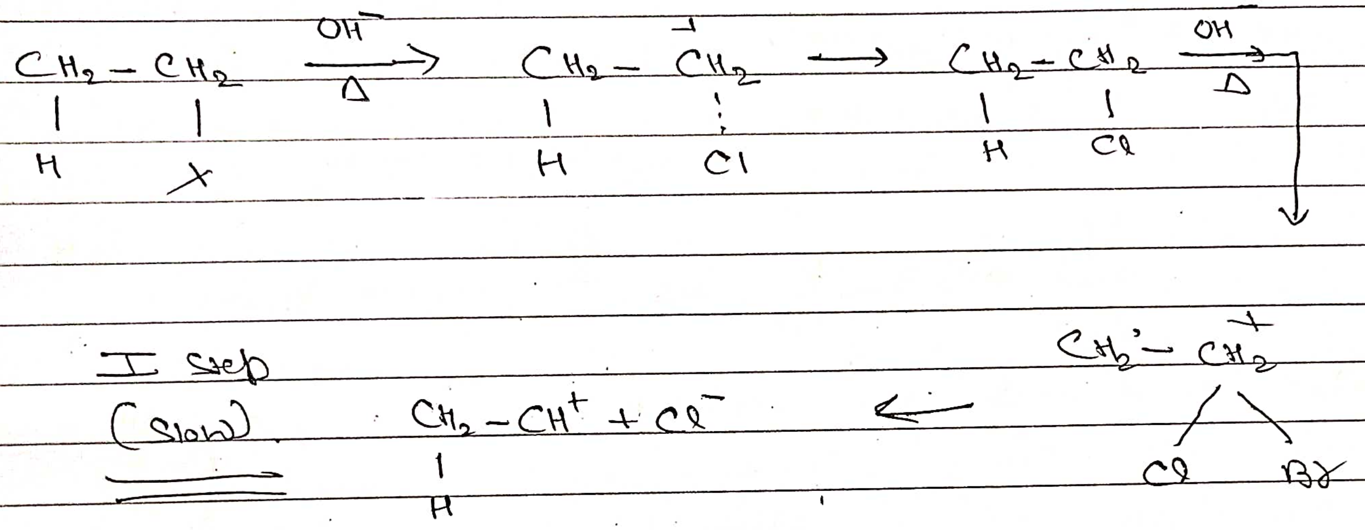
Dehydro halogenation of alkyl halide in presence of alcohol.

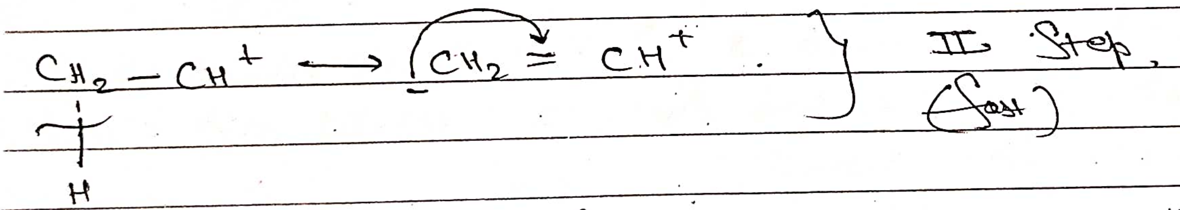


$$\underset{\boxed{H \quad X}}{CH_2 - CH_2} \xrightarrow[\Delta]{OH} \underbrace{\underset{H \qquad \dot{C}l}{CH_2 - CH_2}} \xrightarrow{-HCl} CH_2 = CH_2$$

Depending upon the nature of alkyl halide and other Condition the elemination reaction may be proceed by the two Steps :-

In the first Step heterolytic fission and to found a Carbocation.





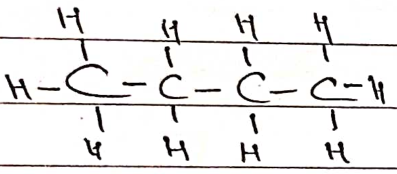
In the 2nd Step is fast reaction between the fission, to get the Carbenion which is further form a double bond between the alkyl group.

ISOMERISM

When the same molecular formula have the different Structural formula is termed as Isomerism.

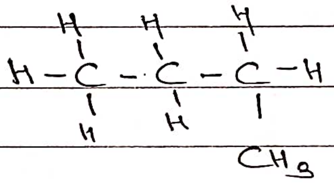
C_nH_{2n+2}

C_4H_{10} C_5H_{12}

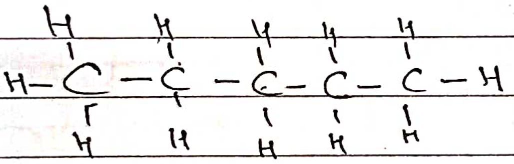


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

n-butane

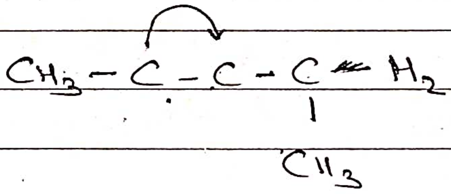


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-H$



$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

↔

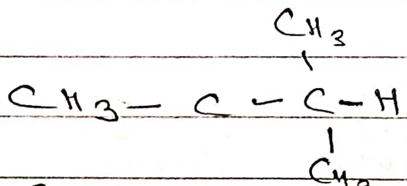


$CH_3-C-C-\underset{CH_3}{C}-H_2$

n - Pentane

Iso Pentane

↕



$CH_3-C-\underset{CH_3}{\overset{CH_3}{C}}-H$

(Neo Pentane)

Isomerism → Isomerism is the phenominal that make two or more than two organic compounds with the same molecular formula & due to the different structural formula compounds having the different physical & chemical properties. That kind of the compounds are known as the isomers & this phenomenon is known as the isomerism.

Isomerism

Structural isomerism

- Chain Isomerism
- Position Isomerism
- Functional Isomerism
  - CH_3-O-CH_3
  - CH_3-CH_2-OH
- Tautomerism
- Metamerism

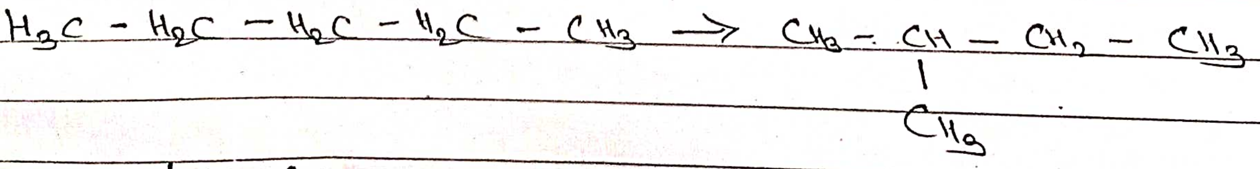
Stereo Isomerism

- ① Geometrical Isomerism
- ② Optical Isomerism

Structural Isomerism.

1. Chain isomerism :- The change in the structure of ~~atom~~ compound due to the change in the carbon chain isomers belong to same close of compound.

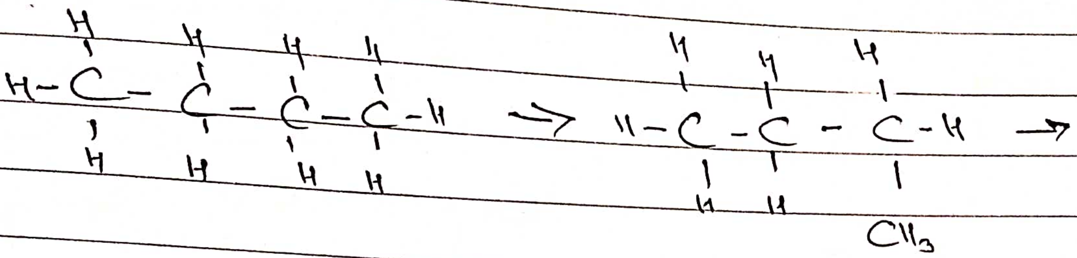
for ex → Physical change, temperature differaction, Taste change - Basisity, Colour change.



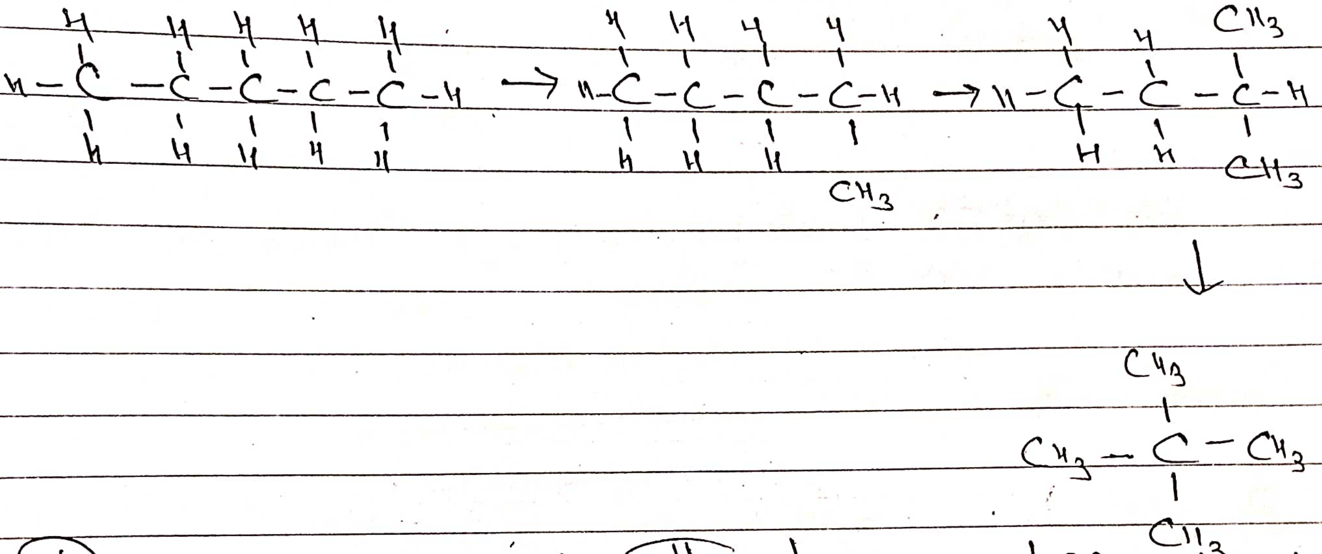
$$H_3C-H_2C-H_2C-H_2C-CH_3 \rightarrow CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_3$$

light Colour → Darken Colour. due to ~~Br~~ chain Creating.

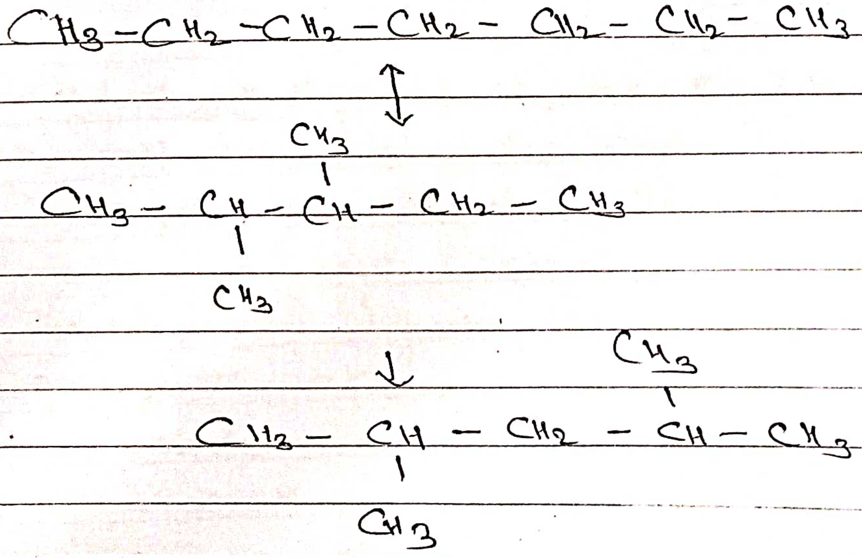
C_4H_{10}



C_5H_{12}



2. Position isomerism → They have a differente in the position occupied by the particular fonctional group or Atoms double bond & triple bond also be Considered as in the fonctional group.

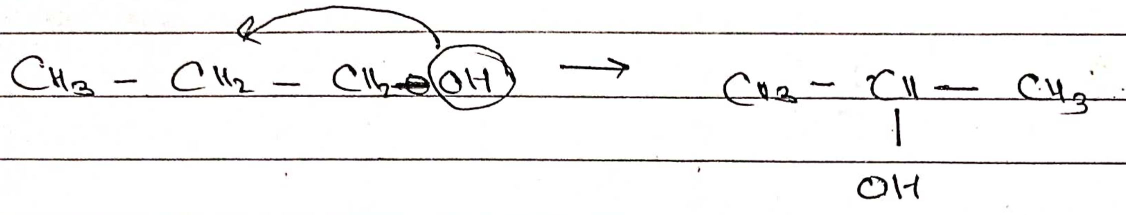


$H_3C-CH=CH-CH_2-CH_3 \longrightarrow CH_2=CH-CH_2CH_3$

$\downarrow$

$H_3C-CH=CH-CH_2$

C_3H_8O.



$CH_3-CH_2-CH_2-\boxed{OH} \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

.Functional isomerism:→ Functional isomerism having the Same molecular formula with the different functional groups.

Eg. Alcohol & Ether.

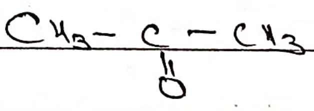
$H_3C-O-CH_3 \longrightarrow CH_3-CH_2-OH$.

~~Acids & esters~~

Aldehyde & Ketone.

$R-CHO$ & $R-\overset{\displaystyle O}{\overset{\|}{C}}-R$.

Eg

Aldehyde	Ketone
CHO	C=O.
CH_3-CH_2-CHO	 $CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$
Propanal dehyde.	Propanone,
M.F = C_3H_6O	M.F = $C_3H_6.O$.
Carbonyllic acid	esters
$R-COOH$	$R-COR$
CH_3-CH_2-COOH	$CH_3-COO-CH_3$
Propanoic acid	Methyl ethanoate

Aldehydes easily Oxidize to acids of the Same number of Carbon but in the Ketone undergoes Oxidation number Extreme Condition only.

4. Metamarism → The type of the isomerism is due to the Unequal distribution of Carbon atom or either Side of the functional group belongs to the Same homologous Series.

$C_4H_{10}O$

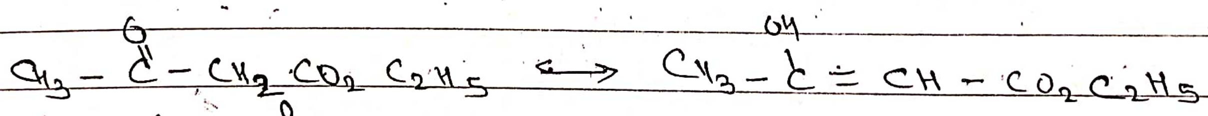
$H_3C - CH_2 - O - CH_2 CH_3 \longrightarrow H_3C - O - CH_2 - CH_2 - CH_3$

Diethyl amine

$CH_3CH - NH - CH_2CH_3 \longrightarrow CH_3 NH CH_2 CH_2 CH_3$

Unequal distribution of Carbon.

5. Tautomerism → This is Very Special type of Structura isomerism in which the isomers are present in the dynamic equalibrium with each other.



$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_2\,CO_2\,C_2H_5 \rightleftharpoons CH_3 - \overset{OH}{\overset{|}{C}} = CH - CO_2C_2H_5$$

Keto form — enol form.

In ethyl aceto acetate is the equilibrium mixture of the two forms i.e. Keto & enol form.
Where as the 93 % of Keto form & remaining 6 % of enol form are obtained, remaining 7 % are due to the different dynamic Structure are not be Converted in any form.

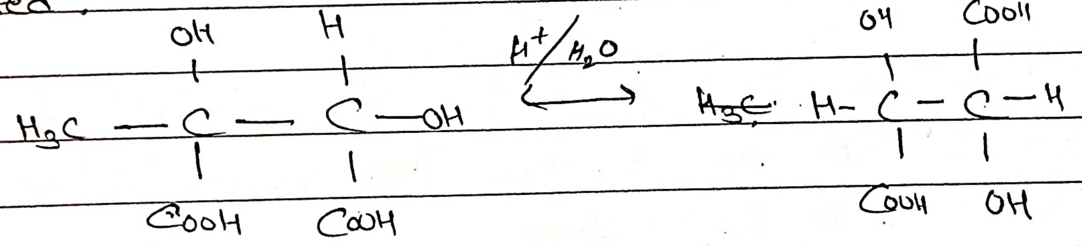
Sterio Isomerism →

Sterio Isomerism are those molecules that are ~~same interm of~~ Seen in molecular formula but the ~~qoitens~~ arrianlation of the atoms are different the ~~othe~~ only possible way of Converting Sterio Isomers to the other in Chemical treatment.

① Optical Isomers
② Geographical Isomers.

1. Optical Isomerisms:

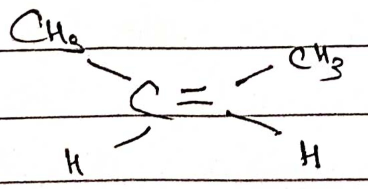
On passing a plane polarized light through an of the iron Substance. The plane of the polarization is rotated.



A Substrains that has the Capability to rotate a plane of polarized light is Called to be optically active.

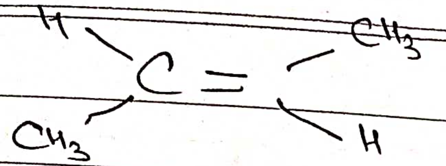
2. Zeometrical Isomerism:

It is also Called the Cisterance isomerism, this isomerism results from the restriction in the rotation about the double bond or about Single bond in Cyclic Compound.

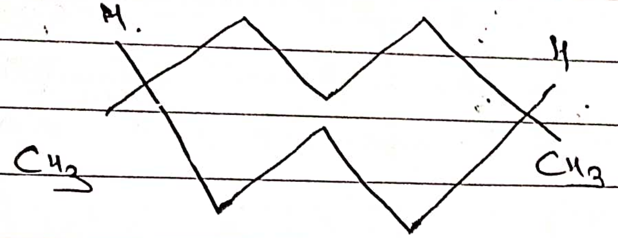


2 - butene Cis form

$\rightleftharpoons$

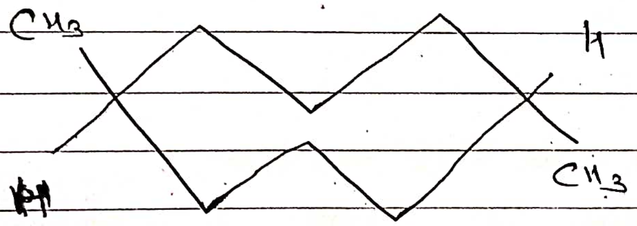


2 butene trans form.



1,4 Diethyl Cyclohexane
Cis

$\rightleftharpoons$



1,4 Diethyl Cyclohexane
trans

In both structure, C–C Single bond second position of C = C double bond 1st position.

C = C are sp^2 hybridised is Consist one σ, 1 π bond the σ bond is formed by the overlap of sp^2 hybridize orbital.

The two Carbon atom of and four atoms that are attach & lie in one plane & their positions so that are fixed rotated in along the Carbon Carbon double bond is not possible to π bond. because rotation would break the π bond.

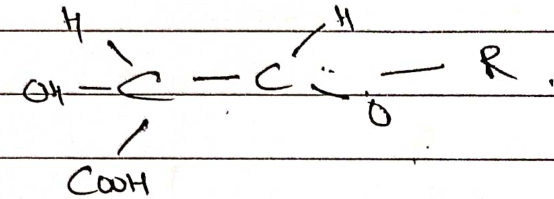
The Geometrical Isomerism ~~distinguage by form~~ each distributing by from each other by the terms. Cis & trans forms. this Cis isomer is one in ~~they are~~ there are two similar group is one is same state of the double bond of the trans isomers is that in which to ~~group or~~ similar group are opposite side of double bond

(i) Di-asteriomers
(ii) Enent antinomus.
(iii) Resnic mix.

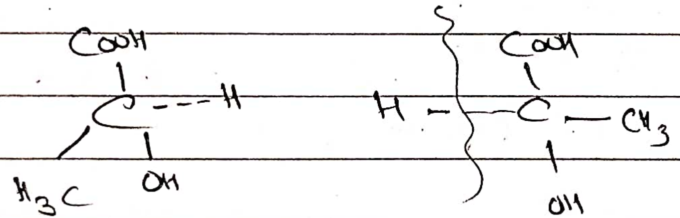
I) Di-asteriomers:- A pair of the Sterio isomers having a no. mirror image relationship.

Ex

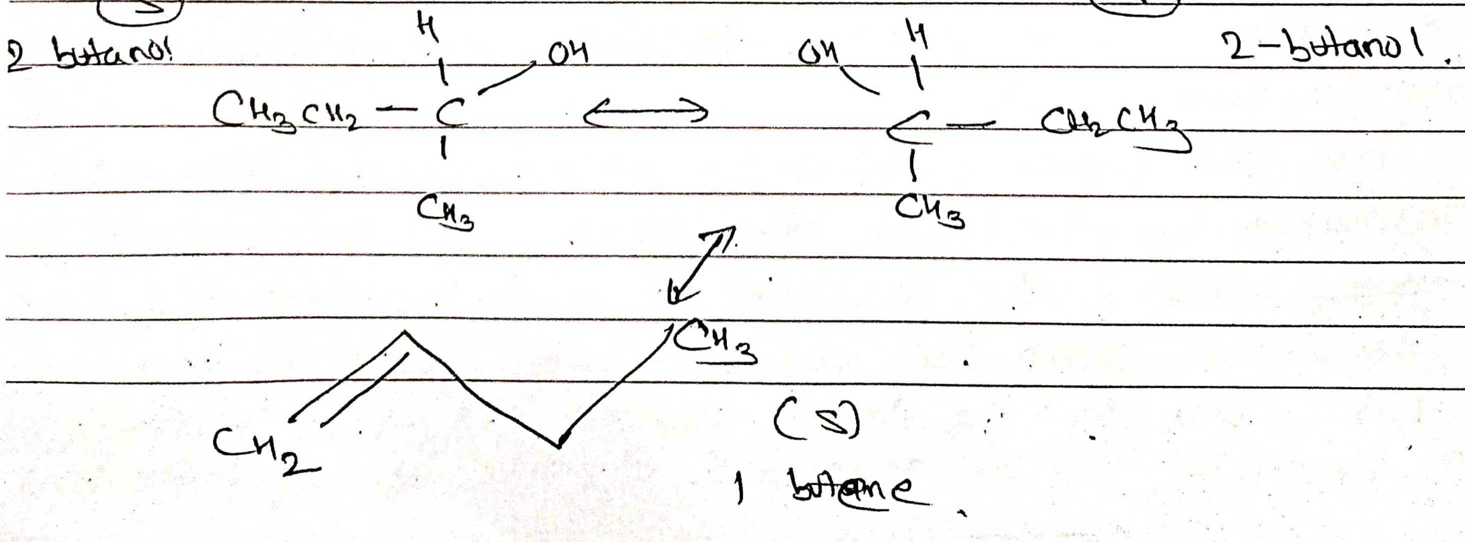
Miso-titric. acic (+) & (-).



II) En-antinomers :- If the two molecules are non Super Imposible mirror image are Called Eneantinius.



II) Resenic mixture :- Resenic mixture is that one of the optically enactive due to the equal & opposite Specific rotation & Contain the Enantinomus in Equal amount of the 50-80 ratio.



Unit → 4.

Wave Mechanical Modals of the Quantum Kinetics

Quantum theory :

Quantum mechanics is the Special branch of Science that deals with the properties associated with the microscopic particles. Classical mechanics does not Consider the dual behaviour of matter & only explain its particles like behaviour. Quantum mechanics was developed by Edwin Schrodinger but has Significant Contribution from the heisenberg.

The functional Equation of the quantum mechanics is based on the wave particles duality of matter which was proposed by de-broglie.

$$E = K + P \quad — ①$$

$$E = Mc^2 \quad — ① \quad \text{Einstein eq}^{-n}.$$

$$E = h\nu \quad — ② \quad \text{Plank's Equation}$$

Because of dual nature,

de broglie →

from eq^{-n} ① & ②

$$E = Mc^2 = h\nu$$

Where, $\nu = \frac{c}{\lambda}$.

$$Mc^{\cancel{2}} = \frac{h\cancel{c}}{\lambda}$$

$$\lambda mc = h$$

$$\lambda = mc$$

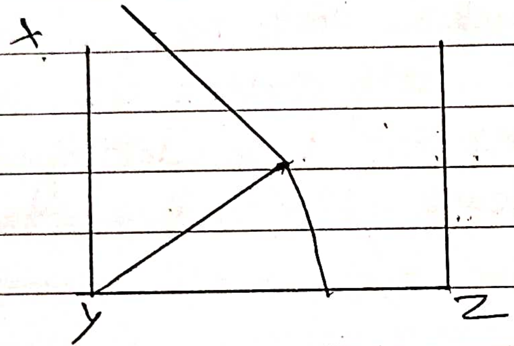
$$\boxed{\lambda = \frac{h}{p = mv}}$$

Ware theorem :

Quantum Mechanics State that the Electrons occupy in three dimentional Space Which are termed as Orbitals.

In atomic orbitals is Characterised by a wave function Which Specifies in electron in an atom. Wave function is denoted by Ψ (Sie) many wave functions are possible for in electrons.

Eg



Schrodinger Ware Equation :

Heisenberg States the Uncertainity of the electrons in the particle So the enact motion Cannot be determine. it is impossible to determine the enact Structure of an atom. Schrodinger follow debroglie Concept & treated the electrons as the wave & developed in equation which Could explain the wave properties of an electrons in three dimensions. Which is Called the Schrodinger wave equation for a Standing wave of the wavelength λ. If the f(x) is the amplitude at. the point then, for the x axis

$$H\phi = E\Psi$$

$$\frac{\delta^2 f(x)}{dx^2} = \frac{-4\pi^2}{\lambda^2} f(x)$$

The movement of in electron is one dimentional movement Just like a wave So,

$$\frac{\delta^2 \psi}{dx^2} = \frac{-4\pi^2}{\lambda^2} \psi$$

If the movement along three dimentional

$$\frac{\delta^2 \psi}{dx^2} + \frac{\delta^2 \psi}{dy^2} + \frac{\delta^2 \psi}{dz^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

If the three partical differential like.

$$\delta^2 \psi = \frac{-4\pi^2}{\lambda^2} \psi,$$

According to de broglie.

$$\lambda = \frac{h}{mv}.$$

$$\delta^2 \psi = \frac{-4\pi^2 m^2 v^2}{h^2} \psi$$

or $$\delta^2 \psi + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \quad — ①$$

But, $$E = K + V.$$

$$K = E - V$$

But, $$K = \frac{1}{2} mv^2$$

$$\frac{1}{2} mv^2 = (E - V).$$

$$v^2 = \frac{2(E-V)}{m}$$

Putting the Value v from -

Put v in ⓘ eq^{-n}.

$$\delta^2 \psi + \frac{8\pi^2 m}{h^2 (E-V) \psi} = 0$$

The main properties of ψ (Sie) have the properties :-

① ψ must have the single value.
② ψ should be continous in the nature.
③ ψ must have the finite value.

Corrosion

Corrosion occurs everywhere and represents are huse economic loss. It can be reduced, the substantially by the proper understanding of the corrosion process and taking appropriate control measure.

Corrosion of a bridge is the measure problem & its replacement involves that use cost generally corrosion occurs in the Suphuric acid plants, Petroleum industry, Paper industry & automobile.

Corrosion and its protection involve the Surface Science, Chemistry, Metullurgy & Engineering.
The cost of the corrosion can be considerally reduced by

① Paper selection of the material
② Modification of metals.
③ Change in design.
④ Change in the corroesive environment.
⑤ Surface ~~Putting~~ Coating
⑥ Electrochemical corrosion protection.

for examples of the Corrosion may be deffined as the reaction of Solids with it's environment

(i) Rusting of Iron.
(ii) Dissolution of Marble.
(iii) Dissolution of the Stone by the acid rain.

ex

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

acid rain is Caused due to the presence of pollutants Such as Sulphur dioxide (SO_2), NO_2, HCl etc in the atmosphere. The most favorable en. ~~diddoction of~~

Generally we use the Corrosion in metullurgy, the overall reaction for the extraction of iron from th hematite ore are

$$3C + 2Fe_2O_3 \rightarrow 4Fe^{++} + 3CO_2$$

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

Commision of mild Steel.

$$Fe \rightleftharpoons Fe^{++} + 2e^-$$

$$O_2 + 2H_2O + 2e^- \rightleftharpoons 4OH^-$$

$$Fe^{+2} + 4(OH)^- \rightleftharpoons 2Fe(OH)_2$$

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

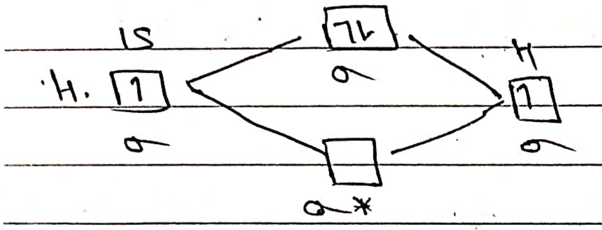
$$2Fe(OH)_2 \rightleftharpoons Fe_2O_3 + 3H_2O$$

Rust

Molecular Orbitals diagram of Diatomic Molecules

$H_2 \rightarrow$ 2 atoms of H

↳ H → $1s^1$ → 1s



$$BO = \frac{\text{Total no of BMO} - \text{no of ABMO}}{2}$$

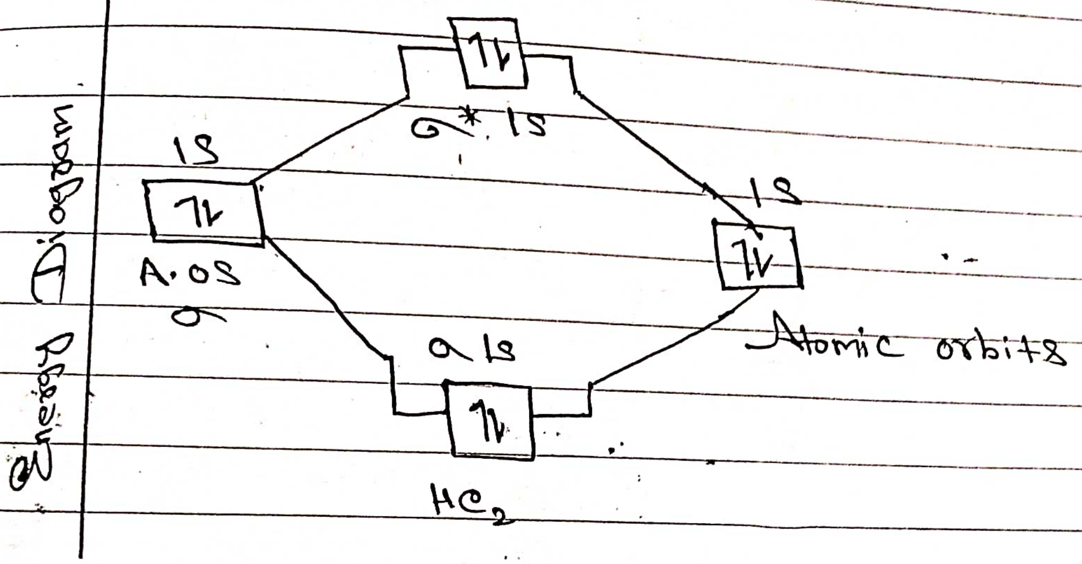
$$= \frac{2-0}{2} = 1$$

Paramagnetic

If the atomic orbitals are degenerate their interaction of proportional to their overlap integral S. The extent of the overlaping may be large or small depending on the nature of the atomic orbitals.
Greater overlap results in stronger bonding or antibonding. on the Basis of MO (Molecular orbitals) or ABMO (Anti Bonding Molecular orbitals'). Bond order is ~~defined~~ determined from the half of the difference between the number of bonding & antibonding electrons in a molecule and can be obtained from the MO configuration of the molecules

$$\boxed{B.O = \frac{1}{2}(N_B - N_A)}$$

MOD of He_2 Molecules



$BO = \frac{2-2}{2} = 0$. There is no magnetic Str.

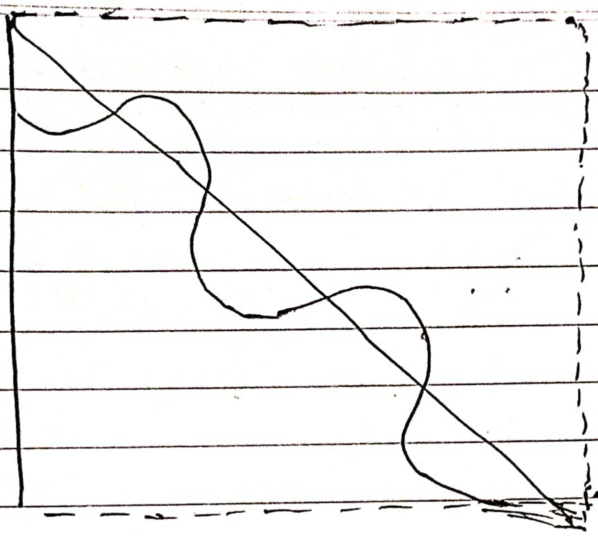
No Structure exists

Helium molecules also Contained 1s atomic orbital ~~each & make the~~ on two helium atoms Which Combine to form bonding and antibonding molecular orbitals. The molecular orbital Configuration of helium molecule is $\sigma^* 1s$ & $\sigma 1s$.

Spactoscopic techniques :

Visible light is a form of Energy & it travels in a wave motion all the properties of light Can be explained by the two Complementary theories the Corpuscular theory and the wave theory, as per the wave theory light travels in the form of wave. It was believed that radient energy is emmitted by the fluctuati of electric charge and magnetic field.

UV & fluoroscenes



In the Case UV (Ultraviolet) & flouroscenes Spratoscopic the electric field Vector has the great significance & from electron paramagnetic & nuclear magnetic resonance (NMR) Spratoscopic. the magnetic field Vector is important. light exhibits in dual nature that of both wave as well as the particle while acting as a particle, light wave interact with the metal & its energy will be exchange

$$E = \frac{hc}{\lambda} = h\nu$$

Where as,

E = Energy

h = Plank's Constant = 6.6×10^{-37} J

ν = the frequency of the light radiation