

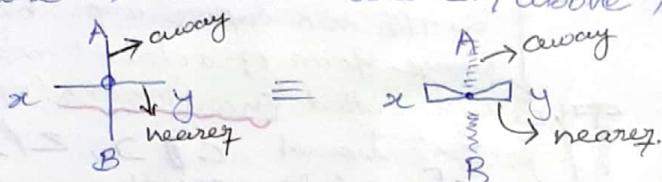
~~CYB
moderately
S14-S101~~

Stereo-chemistry: Study of properties of molecule with respective to special arrangement of g.p.s, atoms in a molecule in 3D is called stereochemistry.

Representation of 3D structure:-

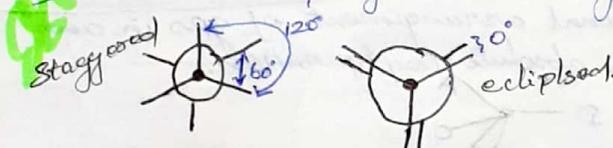
1) Fischer Representation (Flat-projection).

Rules:- 1) Project a molecule in a cross manner (+), 2) Arrange maximum no. of carbons on vertical lines. 3) keep high oxidation carbon g.p.s at top. 4) G.p.s on vertical lines \rightarrow away from observer (or) below the plane, G.p.s on horizontal line \rightarrow near to observer/above the plane



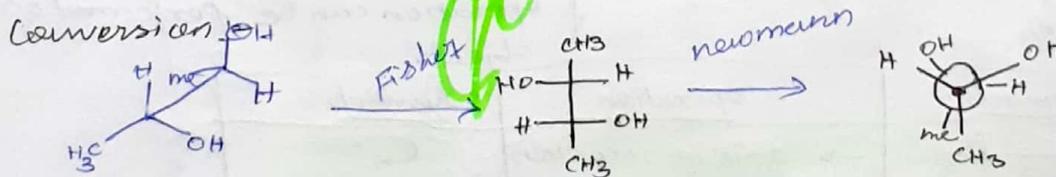
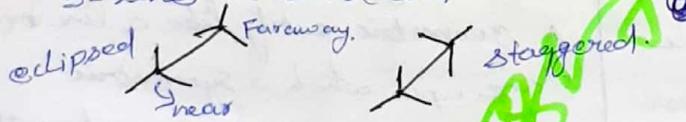
2) Newmann Projections:-

Rules:- 1) See the molecule along C-C bond axis, 2) Show front carbon as DOT and back carbon as circle. 3) keeps line on front/back carbon with 120° separation. 4) Newmann projections may be eclipsed, Gauche, Staggered



3) Saw-Horse projection:-

Rules:- 1) See the molecules in sideways 2) Show cc bonding in a diagonal manner 3) on diagonal bottom end \rightarrow near to observer and upper end \rightarrow away from observer. 4) keep 3-lines at each end with 120° separation.



S14-S102 Isomerism \rightarrow 1) Structural 2) Stereo

Structural isomerism:- 8. Isomers are compels that have the same molecular formula but diff. structural formulae.

a) Chain Isomerism:- [different in order in which carbon atoms are bonded to each other].

Ex:- $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
n-Butane

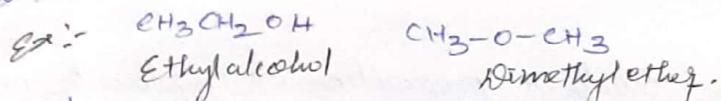
$\text{CH}_3 - \underset{\substack{\text{CH}_3 \\ |}}{\text{CH}} - \text{CH}_3 \rightarrow$ Isobutane

b) Position Isomerism:- [Diff in the position of fn gp on the chain].

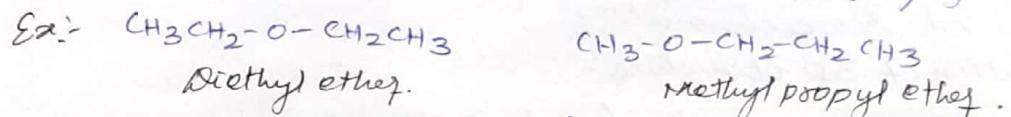
Ex:- $\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{Br}$
(α -Bromobutane)

$\text{CH}_3 \overset{\substack{\text{Br} \\ |}}{\text{CH}} \text{CH}_2 \text{CH}_3$ (β -Bromobutane).

(c) Functional isomerism:- [diff in fn grp].



d) Metamerism:- → This type of isomerism is due to unequal distribution of carbon atoms on either side of fu grp.

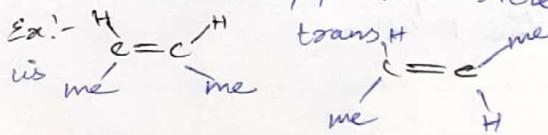


2) Stereoisomerism:- [It have same structural formula but differ in arrangement of atoms in space]

Cis-trans

optical isomerism

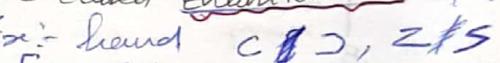
Cis isomers is one in which two similar grp are on the same side, and trans is opposite side.



[It have the ability to rotate the plane polarise light]



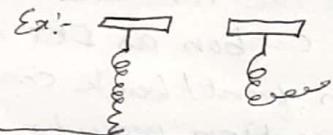
a) The non super imposable mirror images form of a chiral molecule are called Enantiomers (opposite)



[non superimposable, mirror images]

b) Diastereomers:

[non superimposable, non mirror image]



5/5 SLO-1

Configuration, Symmetry and chirality

Configurations:-

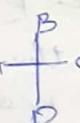
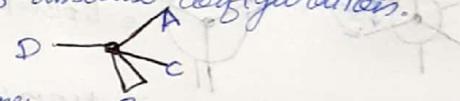
Absolute configuration:-

The actual three-dimensional arrangement of grp in an assymetric molecule is called its absolute configuration.

Relative configuration:-

For the convenient of writing

In 2D structure of the molecule is called Relative configuration.



Symmetry:-

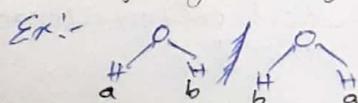
A molecule is indistinguishable from any direction from wherever we see it.

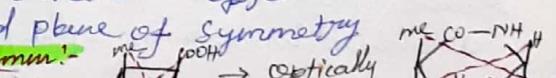
Symmetry elements

A geometric entity like a line (or) Plane upon which a symmetric operation can be performed on the object.

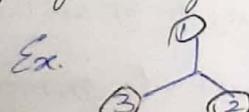
Elements	operation	Symbol.
line	→ axis of rotation	C_n
Plane	→ Reflection	$O_h \rightarrow O_h, \bar{O}_d$
Point	→ Inversion	

① Plane of symmetry:- A plane which divide an object into two halves is called plane of symmetry



/ center of symm. 

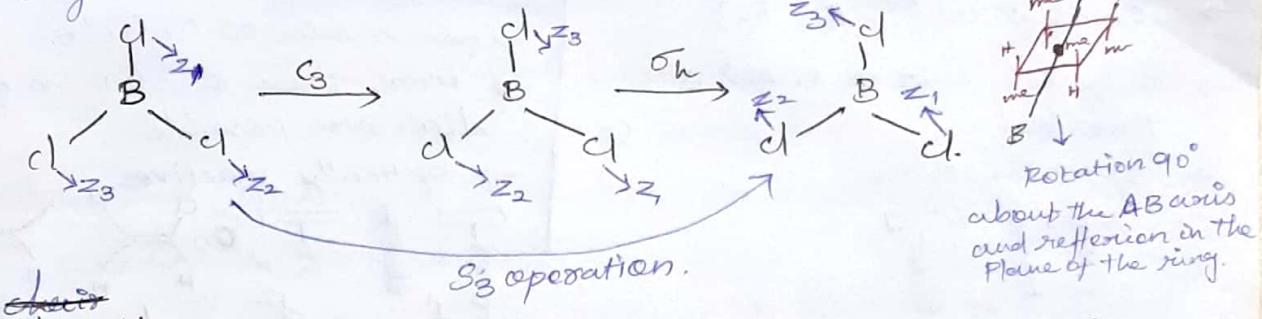
② Axis of symmetry:-



A axis which form a indistinguishable objects
C3 axis is called axis of symmetry.
A point in the object, through which any straight line also passes through two

③ Alternating axis of symmetry:-(S_n).

A operations are rotation followed by reflection in a plane is called alternating axis of symmetry. Therefore any molecule which contains C_n and S_n must also contain S_n.



~~Chiral:~~

A molecule contain different groups. (i) it gives non-superimposable mirror image is called chiral. it always optically active.



SLO-2 R and S configurations:-(Absolute nomenclature).

[Cahn, Ingold, Prelog]

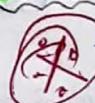
CIP-nomenclature.

Rules:-

- 1) Identify chiral centre in molecules
- 2) Give priority for groups or atoms attached to chiral centres based on Atomic number.
- 3) After giving the priority keep least priority group/atoms away from the observer.
- 4) see the priority directions of other groups. If the priority direction is clockwise → R
- 5) Anticlockwise → S

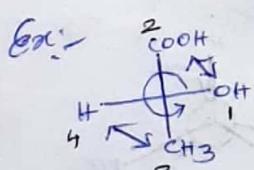
product 5
S1 S10

on Fisher projection:-

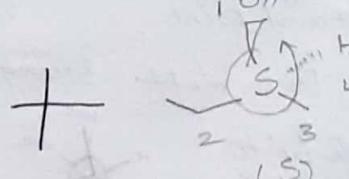
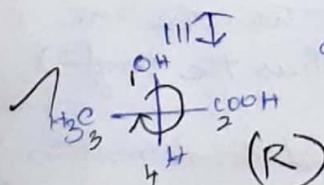


If least priority group on horizontal line (-).

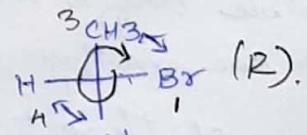
take opposite configuration.



here H atom is least
so (S) originally
but take R is correct.
(ii) Interchange the atoms
and give the name



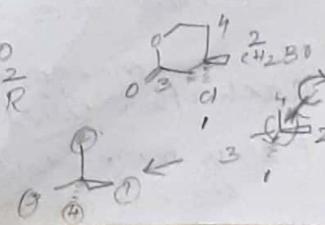
(S)



(R).

but for this

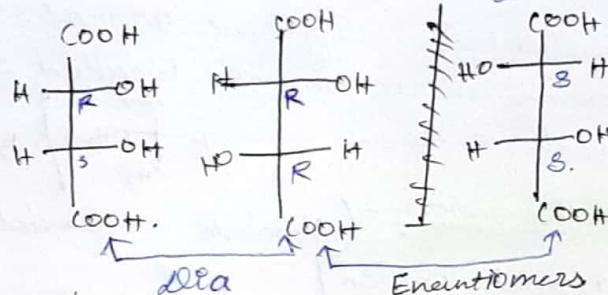
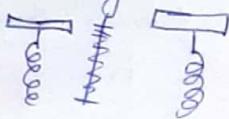
Br (S) config
is correct
bez H present
in horizontal
line.



points on the edge of the figure at the same distance
from the centre but on opposite side.

Enantiomers

- Non-superimposable mirror image isomers called enantiomers.
- Related to (S, R, S, R)
- Only one pair of enantiomers are possible.
- optically active



Racemic mixture:

Synthesis of an optically active compound produces a mixture of both (+) and (-) isomers in equal amounts is called racemic mixture.

Racemisation:-

Conversion of an optically active compds into a racemic mixture is called racemisation.



Enantiomeric excess:-

If any one of the (either + or -) isomer is in excess amount compare to other is called enantiomeric excess.

Conformations of n-Butane:-

In these molecule two distinct conformations are possible, one is methyl group is eclipsed by a methyl group other one methyl group eclipsed by hydrogen.

of these two eclipsed conformations the one, having larger me-gps eclipsing H will naturally experience more repulsive forces than the one where a me-gp is faced with hydrogen atom (2). Thus the conf(2) is favoured from stability stand point.

likewise it will be two diff staggered conformations.

one me-gps are at angle 60° to each other called Gauche conformation

(2) is more stable bcz of repulsive forces is less will lead to less energy.

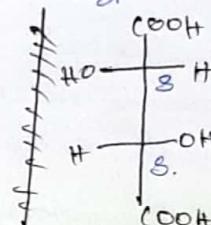
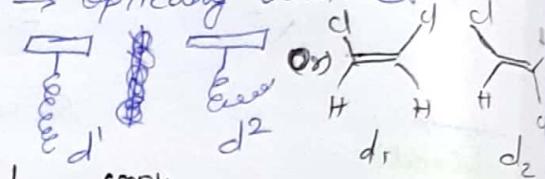
Diastereomers:-

→ non superimposable, non mirror image isomers called diastereomers.

→ non related to S, R, S, R.

→ More than one pairs of diags are possible.

→ optically inactive.



~~Enantiomers~~

Isomerism in transition metal compounds

Isomerism:- The compounds having same molecular formula but diff. structural arrangement called Isomers.

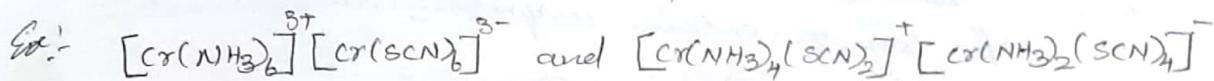
1) Structural isomerism

2) Stereo (space) isomerism.

Structural Isomerism:-

1) Coordination isomerism:-

There may be an exchange of ligands b/w the two (cation & anion) coordination spheres is called Coord. isomerism.

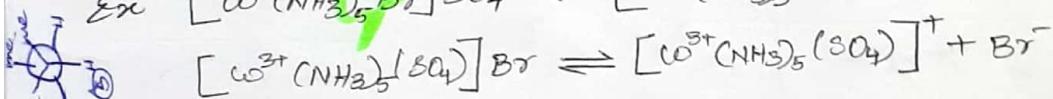
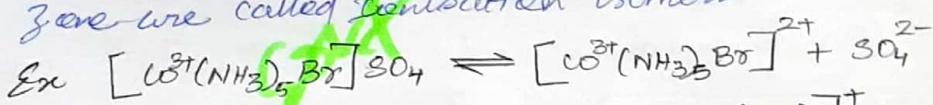


2) Ionisation isomerism:-

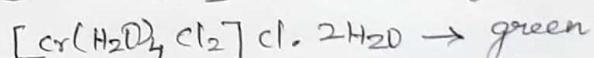
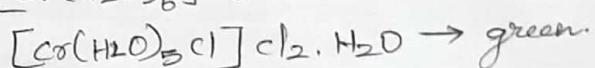
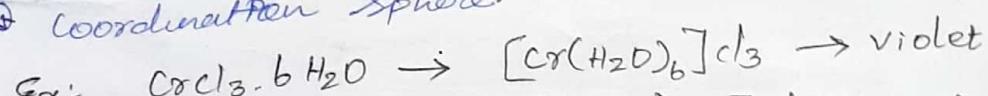
Complexes which have the same empirical formula

and produced by interchange of position of the ligand.

Inside the complex zone and anion outside the complex zone are called ionisation isomers.



3) Hydrate Isomerism:- Hydrate Isomer is different disposition of water molecules inside and outside the coordination sphere.



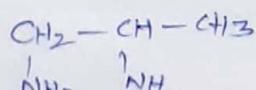
4) Linkage Isomerism:-

The tendency of ambidentate ligands due to

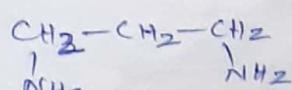
which they can be linked to the metal ion in two diff. ways to form linkage isomerism.

Ex: $\text{NO}_2 \rightarrow$ donors N & O.

5) Ligand Isomerism:-



(PN)



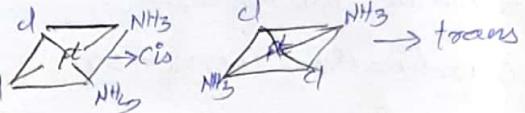
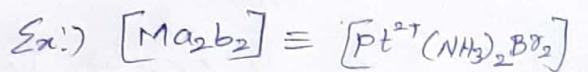
(t₂)

2) optical isomerism:-

2) Stereo (space) Isomerism:-

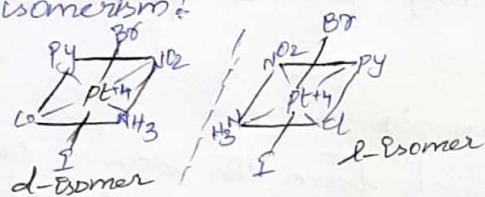
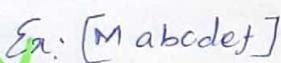
The arrangement of ligands in space is different, is called Stereo isomerism.

i) Geometrical Isomerism:- The ligands occupy different positions around the central metal atom. If it's same direction called cis, opposite direction called trans isomers.



2) optical Isomerism:-

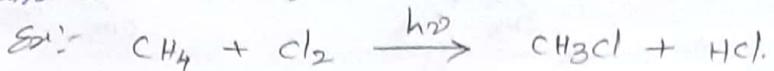
The complex contain asymmetric molecule that complex give optical isomerism:-



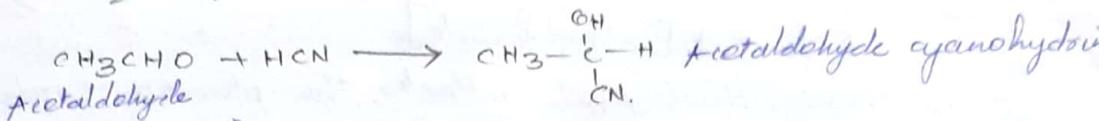
QX

Types of Organic Reactions:-

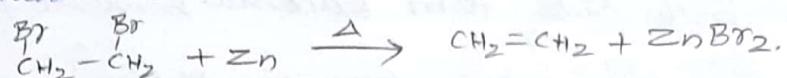
1) Substitution rxn:-



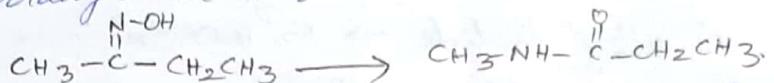
2) Addition rxn:-



3) Elimination rxn:-

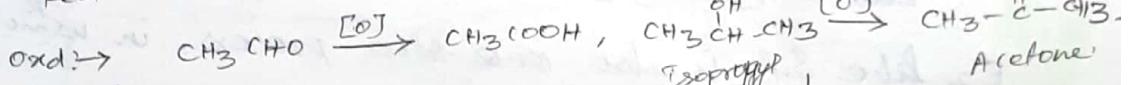
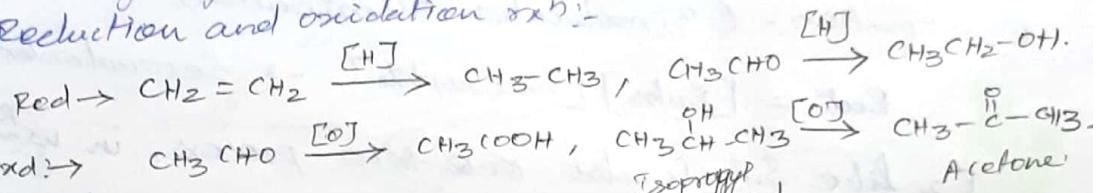


4) ~~Rearrangement rxn:-~~



methyl ethyl ketoxime N-methyl propanamide.

5) Reduction and oxidation rxn:-

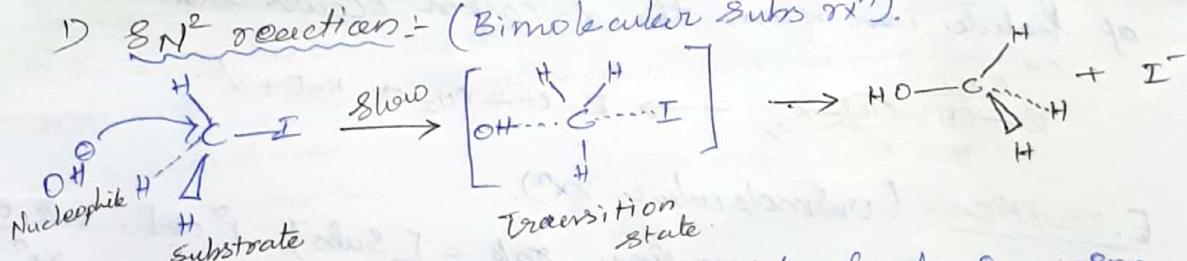


Isopropanol

Acetone

Mechanism of Nucleophilic Substitution rxn:-

1) S_{N}^2 reactions:- (Bimolecular Subs rxn).



→ Backside attack of nucleophile leads to inversion in configuration. (Walden Inversion).

→ Nucleophile approaches the substrate at 180° from the leaving group.

→ No intermediate formation but the reaction proceeds through transition state [T.S.]

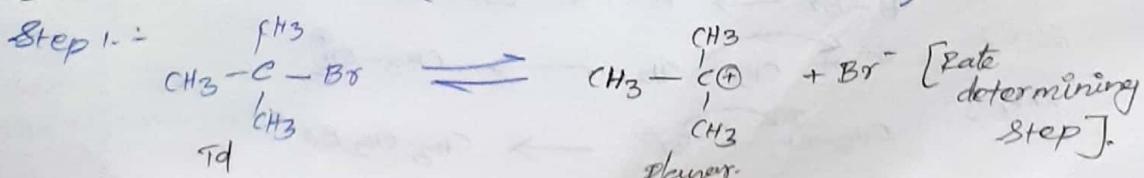
→ Hybridisation of substrate and product are sp^3 (Td), whereas T.S. is sp^2 (planar).

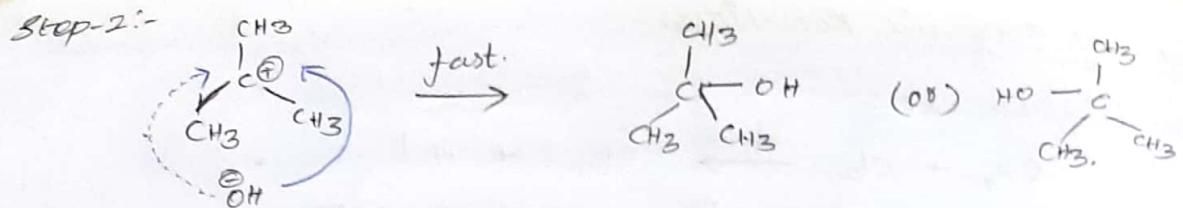
→ Rate = $k [\text{Substrate}] [\text{Nucleophile}]$.

→ Order of rxn is 2 (Ex) rate of rxn is 1st order w.r.t each substrate and nucleophile. Overall order is 2.

→ Coordination of carbon at T.S. is 5

2) S_{N}^1 reactions:- (Unimolecular Subs rxn)





→ Step 1 involves the formation of carbocation which is slow ~~is~~ ionisation of substrate and rate determining.

$$\text{Rate} = k[\text{Alkyl halide}]$$

Step.

→ In step 2, Nucleophile attacks the planar carbocation from the both side form Racemic mixture of compound

→ $^1\text{°}$ alkyl halide $\rightarrow \text{Sn}^2$, $^3\text{°}$ alkyl halide $\rightarrow \text{Sn}'$
 $^2\text{°}$ alkyl halide $\rightarrow \text{Sn}'$ (or) Sn^2 .

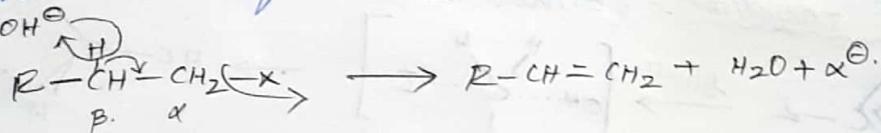
Mechanism of Elimination rxn:-

E₂-reaction:- (Bimolecular elimination)

~~Qix~~ Rate = [Subs] [nucleophile]. \rightarrow Second order rxn.

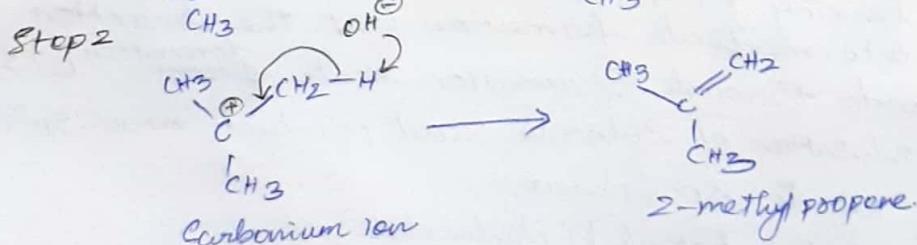
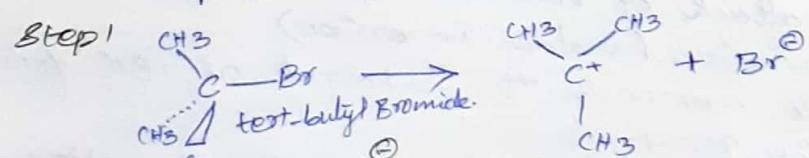
E₂ like Sn² is also one step process, in which

the abstraction of proton from β -carbon and expulsion of halide ion from the α -carbon occurs simultaneously



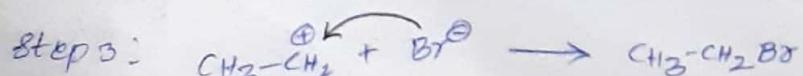
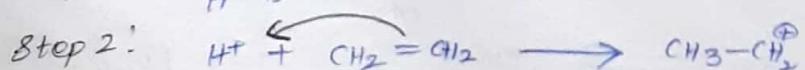
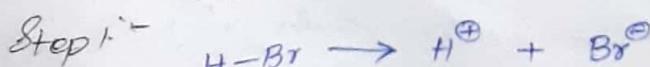
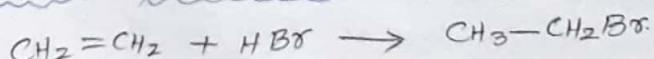
E₁-reaction:- (Unimolecular rxn).

Two step reaction, rate = [Subs]. 1^{st} order rate of rxn.

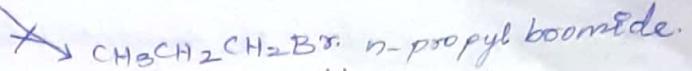
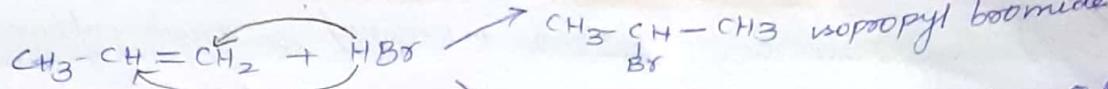


Mechanisms of Addition reaction:-

i) Electrophilic Addition rxn:-

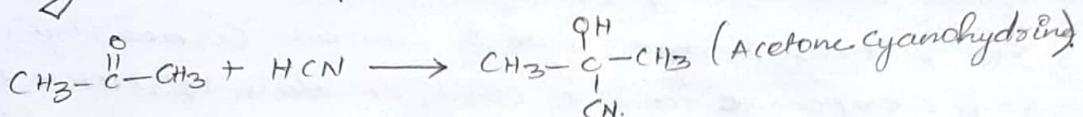
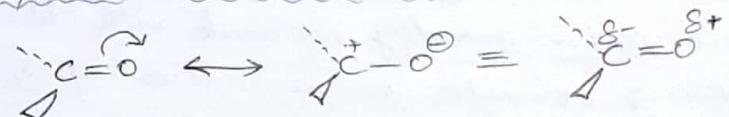


Eliminating	Substituting
Cone OH ⁻	dilute OH ⁻
alcohol	water
Less polar solv	More polar solv
① high temp	② Room temp



When an unsymmetrical reagent adds to an unsymmetrical double bond, the ~~more~~ part of the reagent becomes attached to the double bonded carbon atom which bears the greatest no. of hydrogen atom. (Markovnikov Rule).

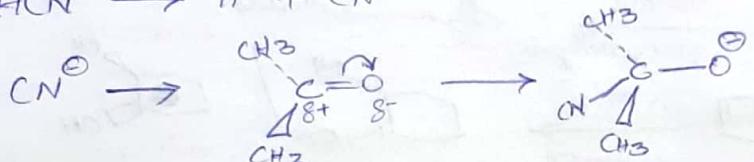
Nucleophilic Addition rxn:-



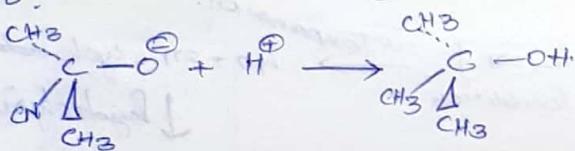
Step 1:-



Step 2:-



Step 3:-

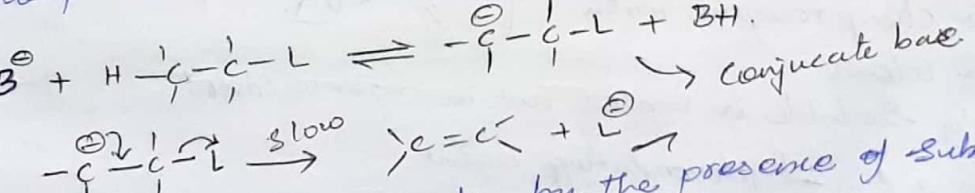


E₁CB Mechanism:- [E₁ conjugate base]

→ In E₁ mechanism, the bond to the leaving group breaks during the first step to give carbocation and the bond to the hydrogen breaks in a second step.

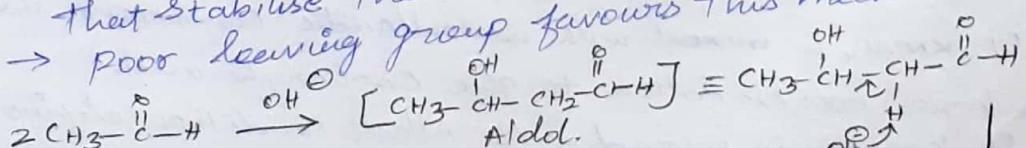
→ In E₂ mechanism, both bonds are broken in the single step.

→ But in E₁CB, the bond to the hydrogen breaks during the first step to give a carbanion and the bond to the leaving group breaks in a second step.

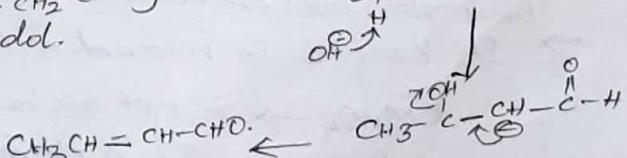
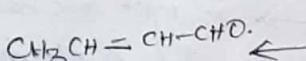


→ This mech dominates by the presence of substituents that stabilise the intermediate carbanion.

→ Poor leaving group favours this mechanism



E ₁	E ₁ CB
* C ⁺	* C ⁻
* unimolecular	* unimolecular
* First order	* First order
* LGP 1 st	* B-H 1 st
B-H 2 nd	LGP 2 nd .
* Good LGP	* poor LGP



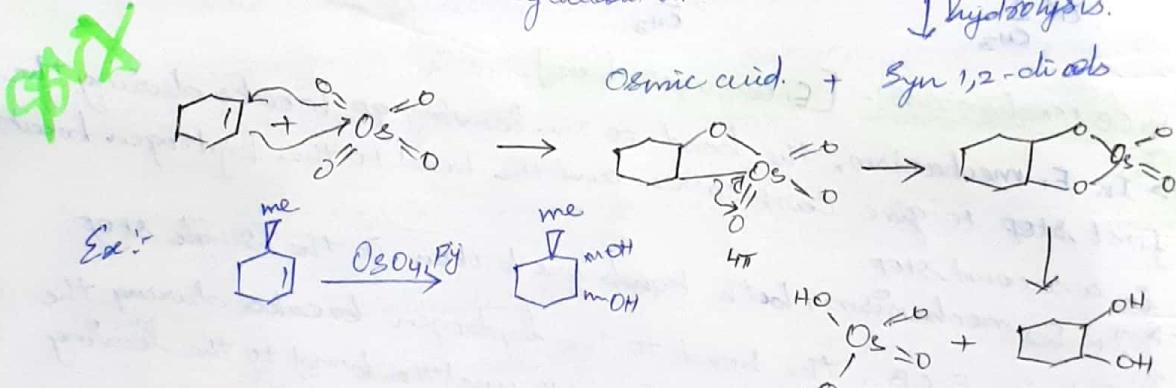
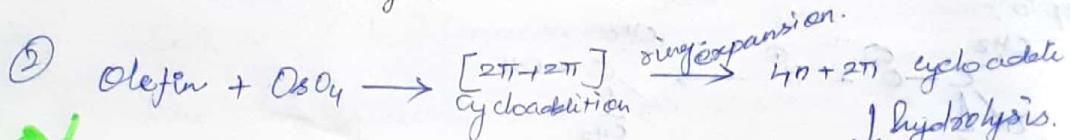
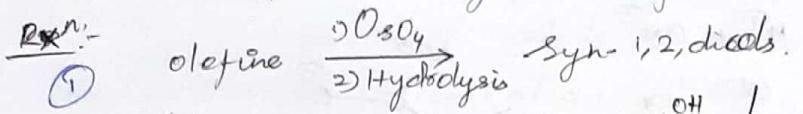
Oxidation reaction: Addition of oxygen/Loss of hydrogen/loss of e⁻

Oxidizing agents: The reagent used for oxidation on substrate is known as 'oxidizing agent'.

→ KMnO₄, O₂O₄, K₂Cr₂O₇, PCC

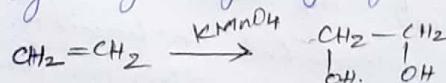
O₂O₄: Oxidation state of O₂ is → VIII (+8). $\left[\begin{matrix} \text{O} & \text{O} \\ \text{O} & \text{Os}=\text{O} \end{matrix} \right]$.

- It is a colourless solid reagent in pure form.
- Its monoclinic crystal symmetry molecule with chlorine colour.
- Yellow colour of O₂O₄ is due to contamination of O₂O₂. Impurity.
- It's a toxic reagent affects human "cornea" (eye).
- It is a explosive reagent. Easily soluble in H₂O, Acetone, Alcohol, Ether.



KMnO₄: O.S of Mn is ⇒ +7 $\left[\begin{matrix} \text{K}^+ & \text{O}^- \\ \text{O} & \text{Mn}=\text{O} \end{matrix} \right]$.

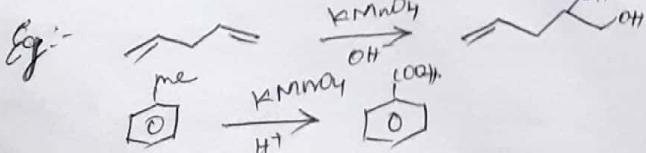
- It is cheap reagent with Purple colour.
- Easily soluble in water not in organic solvent.
- It is a syn-hydroxylating agent.



→ If KMnO₄ is mixed with neutral/Acidic conditions, olefins undergoes over oxidation to give carboxylic acid.

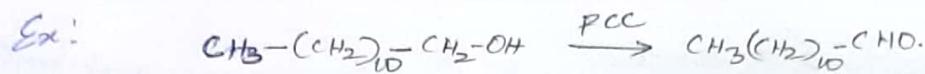
→ If KMnO₄ is mixed with Alkali condition olefins gives 1,2-dicols.

KMnO₄ → is not a chemoselective reagent
O₂O₄ → Is a chemoselective reagent.



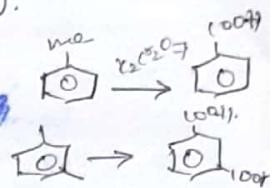
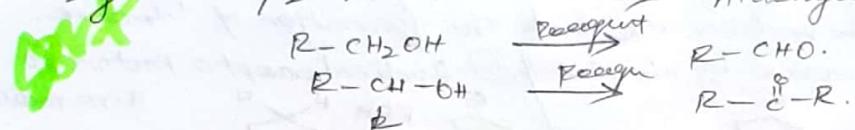
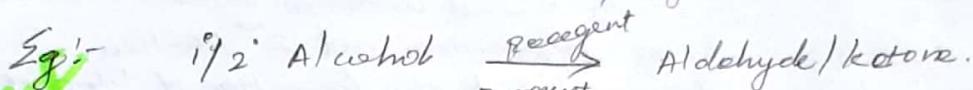
PCC [Pyridinium chloro chromate] \rightarrow $\text{CrO}_3 + \text{Py} + \text{aq. HCl}$

- It is acidic reagent, It is not a hygroscopic in nature.
- Easy to prepare in lab and easy to store.
- No over oxidation of 1° alcohols.



Cr(VI) reagent (or) $\text{K}_2\text{Cr}_2\text{O}_7$ (selective oxidising).

- Cr(VI) reagent is a Inorganic reagent
- It is soluble in water & organic solvents.



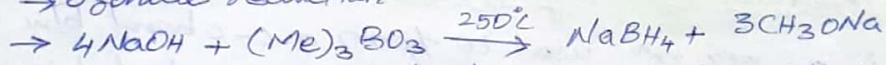
Reduction reactions:- Removal of O_2 (or) addition of H_2 (or) gain of e^- .

Reducing agent:-

$[\text{LiAlH}_4, \text{NaBH}_4,$
Raney Ni, Li/Na,
liq NH_3]

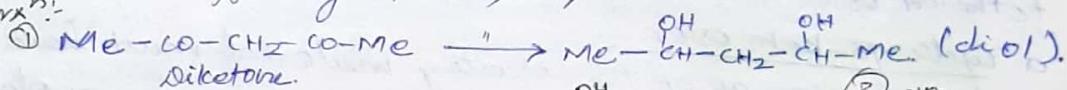
NaBH_4 :- in ether (or) isopropanol:-

→ Ozone reduction

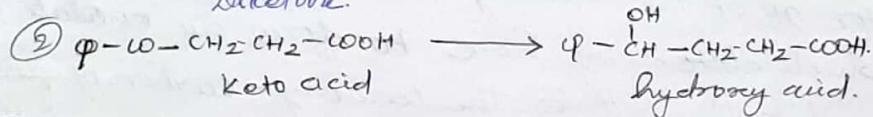


→ without affecting other X=O , ester, amide, nitrile, nitro..etc.

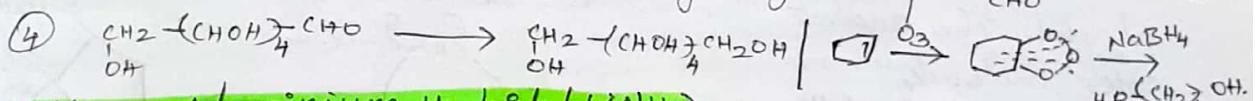
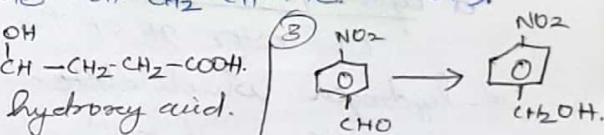
Some rxn:-



Diketone.

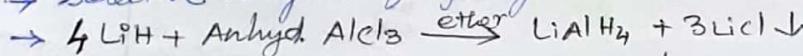


Keto acid



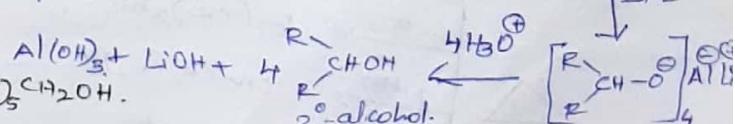
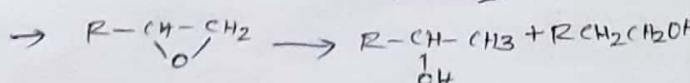
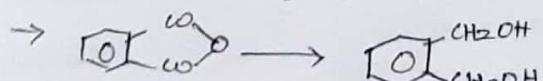
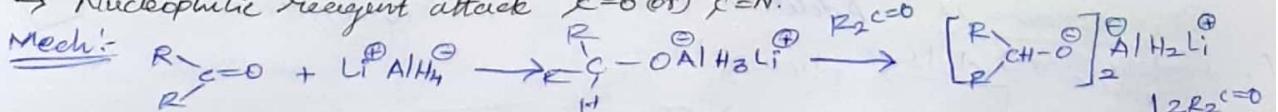
Lithium Aluminium Hydride (LiAlH_4).

→ Selective reagent for fn grps.



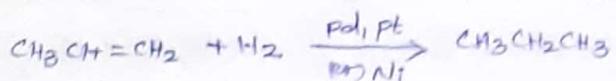
→ Dissolved in ether (or) THF as catalyst.

→ Nucleophilic reagent attack X=O (or) $\text{X}\equiv\text{N}$.



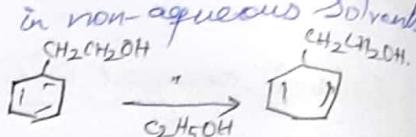
$\left. \begin{array}{l} \text{Mitro (NO}_2\text{)} \\ \text{Azide (-N}_3\text{)} \\ \text{Cyanide (-CN)} \\ \text{oxime (=N-OH)} \end{array} \right\} \rightarrow 1\text{-amine}$

Raney-Ni: less reactive than H₂/Pt.

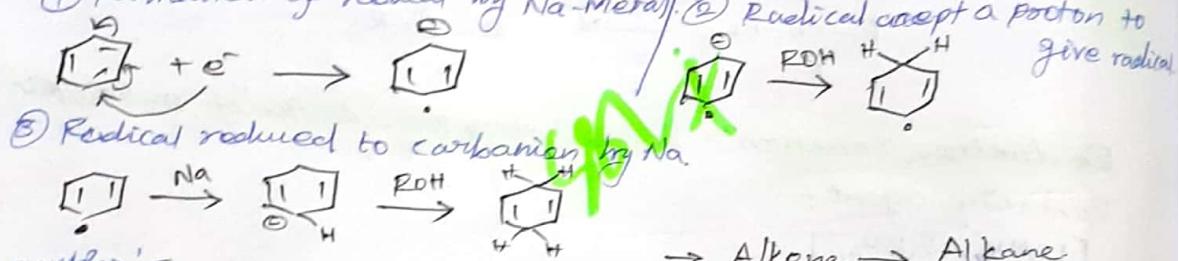


I₂/Na in lig. NH₃ (or) Birch reduction:-

- partial reduction of aromatic ring in non-aqueous solvents.
- Dissolving metal reduction.
- OH, O⁻, COO⁻, NH₂, don't interfere.
- =bond not ~~not~~ conjugated with ring → Birch reduction.
- C=O gp is conjugation with =bond undergoes Birch reduction.
- Proton abstraction only at -6-position not 2nd position.



Mech: ① Formation of radical by Na-Metal. ② Radical accepts a proton to



Examples:-



→ Alkene → Alkane

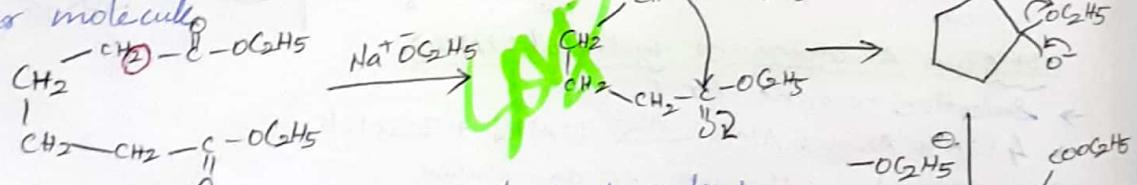
RCONH₂ → RCHO + NH₃.

Cyanide → Amine.

Dieckmann condensation (cyclization).

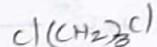
D.C. is an org oxn used to form a C-C bond b/w two tethered ester gps using an alkoxide base in alcohol to make a cyclic β -keto ester.

One ester gp of the starting material must have an α -hydrogen which abstracts by base to form an enolate and alcohol. The enolate then attacks the carbonyl-carbon of another ester molecule.



R²Ring opening rx?:- Addition of Cr₂O₇²⁻/H₂SO₄/H₂ to cyclopropane

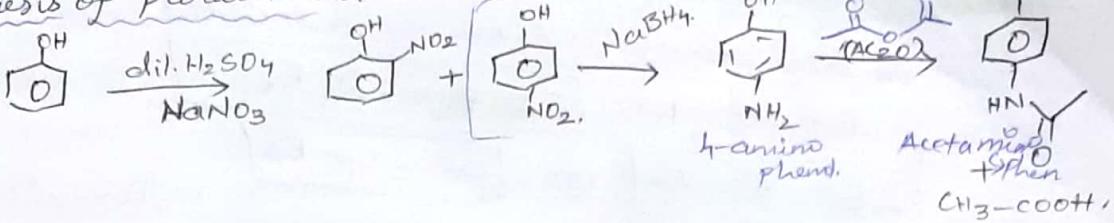
(electrophilic addition rxn) Cl₂/dark



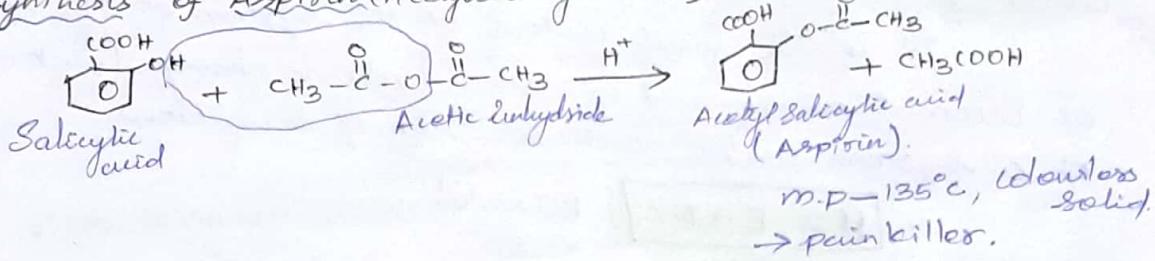
- + Br₂ → Br(CH₂)₃Br
- + HBr → CH₂CH₂CH₂Br
- + Ni, H₂ 120°C → CH₃CH₂CH₂
- + H₂SO₄ → CH₂CH₂CH₂HSO₄
- HJ → CH₃CH₂CH₂J

Drug molecules:-

Synthesis of paracetamol:-



Synthesis of Aspirin (Acetylsalicylic acid):-



Chemical Thermodynamics

It deals with relationship b/w $\xrightarrow{\text{Heat}}$ motion \rightarrow Heat of motions, deals with interconversion of energy to other energy (electrical, chemical).

Terminology of Thermodynamics:-

1) System:-

A system usually has a definite amount of a specific substance. $\xrightarrow{\text{Heat}}$ The remaining part of the universe is called surroundings.

3) Boundary:-

\rightarrow The region or interface separating the system from surroundings is called boundary.

Types of System:-

1) Isolated system:- A system which cannot exchange both energy and matter with its surroundings.

2) closed system:- A system which can exchange energy but not matter with its surroundings.

3) open system:- A system which can exchange energy as well as matter with its surroundings.

4) Homogeneous \rightarrow when a system is completely uniform throughout.

5) Heterogeneous \rightarrow when a system is not uniform.

Properties of a system:-

Intensive properties:- The prop which don't depend on the amount of substance but depend only on nature of the subs present in the system are called intensive properties. Ex Temp, P, Conc, densi.

Extensive properties:- The prop which depend on the amount of subs present in the system are called extensive prop. Mass, vol, I.E, Enthalpy (H), free enrgy (G).

Process and their types:-

1) Isothermal process:- Temp const $dT=0$.

2) Adiabatic process:- No heat change. $dq=0$.

3) Isobaric process:- pressure const $dP=0$.

4) Isochoric process:- Volume const $dV=0$.

5) Cyclic process:- When initial and final states of syst are same $dE=0, dH=0$.

Internal Energy (E) (or) U :-

The total amount of energy associated with the given substance. (or) $E = E_v + E_{rt} + E_t \dots$

$$\Delta E = E_f - E_i \quad (\text{or}) \quad \Delta E = E_p - E_i$$

Enthalpy (or) Heat content of a system (H) :-

It is "the heat content of the system (or) the sum of Internal energy and Pressure-volume change (work done) of a system, under particular set of conditions.

$$H = E + PV \quad \text{kJ mole}^{-1}$$

Enthalpy change :- (ΔH) :-

$$\Delta H = H_f - H_i \quad (\text{or}) \quad \Delta H = H_p - H_i$$

w.k.t. $H = E + PV$ then $\Delta H = E_2 + PV_2 - (E_1 + PV_1)$
then $= (E_2 - E_1) + P(V_2 - V_1)$

Zero-law of thermodynamics :- $\Delta H = \Delta E + P\Delta V$ at $\text{const } V$

When two bodies at two different temp are brought into contact with each other, after sometimes they attain a equal temp & thermal equilibrium exists.

First law of thermodynamics :-

Energy can neither be created nor destroyed, but it can be converted from one form to another form.

$$E_2 = E_1 + q - w \rightarrow E_2 - E_1 = q - w \quad \because w = p\Delta V$$

Need for the second law :-

$\{\text{change in}\}_{\text{Int. Energy}} = \{\text{Heat supplied to the system}\} - \{\text{Work done by the system}\}$

- The second law predict the feasibility of a process.
- It explains why its not possible to convert heat into an equivalent amount of work.
- The second law is able to predict the direction of Energy transformed and also the direction of Spontaneous process.

Second law of thermodynamics :-

This law introduces two new thermodynamic functions Entropy and free energy. to explain the Spontaneity of the processes.

It States that work can always be converted into heat, but heat cannot be completely converted into work, only a fraction of heat can be converted into work and the rest remains unavailable and unconverted.

Entropy :-

Entropy is a measure of degree of disorder (or) randomness in a molecular system. It is also considered as a measure of unavailable form of energy.

Mathematical Expressions for Entropy :-

The change in entropy (ΔS) of a system is equal to the ratio of heat change (q) to the temp (T) of the reversible cyclic process.

$$\boxed{\Delta S = \frac{q_{rev}}{T}} \quad \text{cal/deg (or) } \text{J K}^{-1} \text{ mole}^{-1}$$

Spontaneous process :-

A process which proceeds on its own, without any outside assistance is termed as a Spontaneous (or) natural process.

Criteria for the Spontaneous process (or) Gibbs free energy and Spontaneity :-

According to SLT a process is said to be spontaneous only when ΔS_{tot} is +ve. i.e. entropy of the universe (sys + surroundings) increases. The entropy of surroundings is difficult to measure. So we need a criteria, which does not involve the entropy of surroundings. The Gibbs free energy provides such criteria.

$$\boxed{\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surrounding.}} \quad \text{--- ①}$$

The amt of heat transferred by the system to surr. is given by $\Delta S_{sys} = (-\frac{q_p}{T})_{sys}$ If a rxn carried out at const $T \& P$.

The amount of heat taken by the surroun. is equal to $\Delta S_{sur} = (+q_p)_{surround}$

$$\therefore (q_p)_{sur} = -(q_p)_{sys} = -\Delta H_{system.}$$

Since, the surroundings is large area, the temp of the surroundings remains constant, so we have

$$\boxed{\Delta S_{surround} = \frac{-(q_p)_{sys}}{T} = -\frac{\Delta H_{sys}}{T}} \quad \text{--- ②}$$

on subs ① in ② $\Delta S_{tot} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$

$$\textcircled{1} T \Rightarrow T \Delta S_{tot} = T \Delta S_{sys} - \Delta H_{sys.}$$

$$\boxed{T \Delta S = \Delta H - \Delta G} \quad (\because \Delta G = \Delta H - T \Delta S)$$

Eq ④ is introduce in eq ⑤.

$$T \Delta S_{sys} = \Delta H_{sys} - \Delta G - \Delta H_{sys}$$

$$\textcircled{4} \quad T \Delta S = \Delta H - \Delta G$$

$$\therefore \Delta G = -T \Delta S_{tot} \quad \text{--- ⑤}$$

ΔH	ΔS	$\Delta G = \Delta H - TS$	Conclusion
- (exothermic)	+	-	Spontaneous
(-)	-	- (at low T). (+) (at high T)	Spontaneous Non-spont.
+ (endothermic)	+	+ (at low T) (-) (at high T)	Non-spont. Spontaneous.
+ (endothermic)	-	+	Forbidden in the forward direction.

If ΔG is -ve the reaction is Spontaneous.

If ΔG is +ve non-spont - concns.

Free Energies (or) New thermodynamic function:-

Need for new thermodynamic functions:-

$$S.L.T \quad \Delta S_{\text{TOT}} = \Delta S_{\text{sys}} + \Delta S_{\text{surv.}}$$

If ΔS_{TOT} is > 0 , i.e. spontaneous.

In order to find out the spontaneity of a process, we have to see the change in entropy of the sys as well as Surv. It is very difficult to find out the change in entropy of Surv every time. Therefore use the following function :-

1) Helmholtz free energy (A) (or) Helmholtz work function.

2) Gibbs free energy (or) Free energy.

3) Helmholtz work function (A):-

We know that a part of I.E of a system can be used at constant temperature to do some useful work. This part of I.E (E), which is Isothermally available is called "work function" (A) of the System.

$$A = E - TS$$

Significance of the work function (A):-

$$A = E - TS \quad \text{--- (1)}$$

for a small change in a reversible sys at const T $\rightarrow \Delta A = \Delta E - T \Delta S$. (2)

$$\text{but, } \Delta S = \frac{q_{\text{rev}}}{T} \Rightarrow T \Delta S = q_{\text{rev}} \quad \text{--- (3)}$$

$$\text{Subs (3) in (1)} \quad \Delta A = \Delta E - q_{\text{rev}} \quad \text{--- (4)}$$

AC. to 1st law of thermodynamics $\Delta E = q - w \Rightarrow \Delta E - q = -w$ (5)

$$\text{comp eq (4) & (5)} \quad \Delta A = -w \quad (\text{or})$$

$$w_{\text{max}} = -\Delta A$$

The decrease the work function ($-\Delta A$) of a process at const Temp gives a maximum work obtained from the system.

Gibbs free Energy (G) (or) Thermodynamic potential

The Isothermally available energy present in a system is called free energy (G_f).

$$G_f = H - TS$$

Available Energy (G_f)	$=$	Total energy (H)	-	Unavailable Energy
				TS

Significance of Gibbs free energy (G_f).

Free energy (or) Gibbs free energy (or) is the total available Energy present in a reversible system at const temp & pressure as useful work. $G_f = H - TS \rightarrow ①$

For a small change in a reversible system at constant temp. $\Delta G_f = \Delta H - T\Delta S \rightarrow ②$

But we know that the enthalpy change ΔH is $\Delta H = \Delta E + P\Delta V \rightarrow ③$,

Subs ③ in ②

$$\Delta G_f = \Delta E + P\Delta V - T\Delta S \quad \text{But } \Delta A = \Delta E - T\Delta S$$

$\downarrow ④$

$$\Delta E = \Delta A + T\Delta S.$$

Hence eq ④ may be written as

$$\Delta G_f = \Delta A + P\Delta V. \rightarrow ⑤$$

Since $\Delta A = -W_{max}$

$$\therefore \Delta G_f = -W_{max} + P\Delta V.$$

$\downarrow ⑥$

$$\Delta G_f = W_{max} - P\Delta V.$$

where

$P\Delta V$ = work done by expansion

W_{max} = maximum work that is obtained from the system

$W_{max} - P\Delta V$ = net work (or) useful work.

Hence. $\boxed{\Delta G_f = W_{useful}}$

The decrease of free energy ($-\Delta G_f$) of a process at constant temperature and pressure is equal to the useful work obtainable from the system.

Gibb's- Helmholtz Equation (or) Relation b/w ΔG_f & ΔH .

Consider the following relations.

$$G_f = H - T\Delta S \quad (\text{Gibbs free energy}). \rightarrow ①$$

$$H = E + PV \quad (\text{enthalpy}). \rightarrow ②$$

Subs eq ② in ① $\boxed{\therefore G_f = E + PV - TS.} \rightarrow ③$

for infinitesimal change

$$dG_f = dE + PdV + VdP - TdS - SdT \rightarrow ④$$

But A.C to 1st & 2nd law of thermodynamics.

$$dE = dq - PdV \quad (\text{first law}).$$

$$dq = TdS \rightarrow (\text{second law}).$$

$$\therefore dE = Tds - pdv \quad \text{--- (B)}$$

Subs eq (B) in (4) $\rightarrow dG_1 = Tds - pdv + pdv - Tds - sdT$

$$\therefore dG_1 = sdT \quad \text{--- (6)}$$

At const pressure $dp = 0$, eq (6) becomes.

$$dG_1 = -sdT \quad \text{--- (7)}$$

$$\left(\frac{\partial G_1}{\partial T}\right)_P = -s \quad \text{--- (8)}$$

Subs eq (8) in (1) $\rightarrow G_1 = H + \left(\frac{\partial G}{\partial T}\right)_P \quad \text{(or)} \quad \boxed{G_1 - T\left(\frac{\partial G}{\partial T}\right)_P = H}$

~~(9)~~ This is one form of Gibbs-Helmholtz eq.

For any two states of the system the eq (7) may

$dG_1 = -s_1 dT$ (Initial state) be written as

$dG_2 = -s_2 dT$ (Final state)

To get the change.

$$dG_2 - dG_1 = -s_2 dT - (-s_1 dT)$$

$$d(\Delta G) = -\Delta s dT \quad \text{--- (10)}$$

At const pressure the eq (10) becomes.

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta s \quad \text{--- (11)}$$

But A.C to definition of free energy.

$$\Delta G = \Delta H - T\Delta S \quad \text{(or)} \quad -\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{--- (12)}$$

Subs eq (12) in (11)

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad \text{(or)}$$

$$\Delta G - \Delta H = T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P$$

$$\therefore \boxed{\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P} \quad \text{--- (13)}$$

$\therefore \Delta A = \Delta E + T \left[\frac{\partial(\Delta A)}{\partial T} \right]_V$ may be derived.

This is another form of Gibbs-Helmholtz eq.

$$\left(\frac{dG}{dT} \right)_P = -V$$

Electrochemistry:-

- production of electricity during spontaneous chem rxn and use of electrical energy to bring about non-spontaneous chemical transformation.
- It deals with redox rxn

Spontaneous $\Rightarrow \Delta G = -ve$

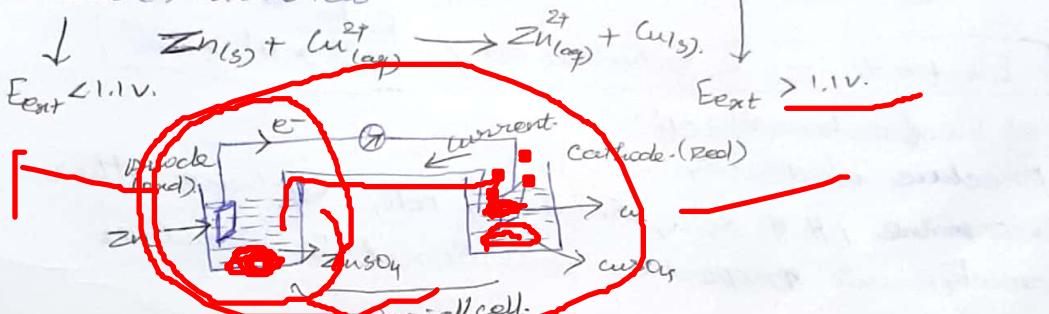
non-spontaneous $\Rightarrow \Delta G = +ve$

Cells

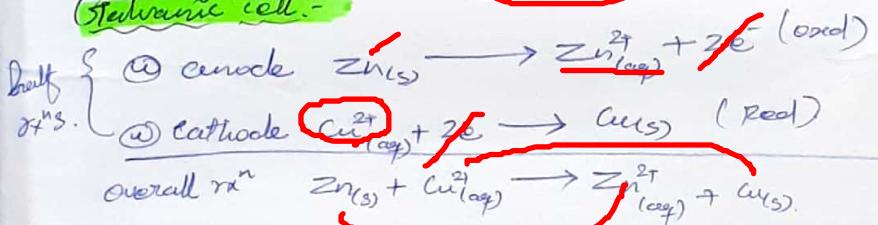
Electrochemical cells.
(It produce Electricity).
also called

Galvanic or voltaic cell

Electrolytic cells.
(It use electricity)



Galvanic cell:-



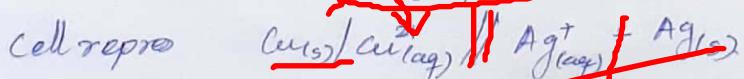
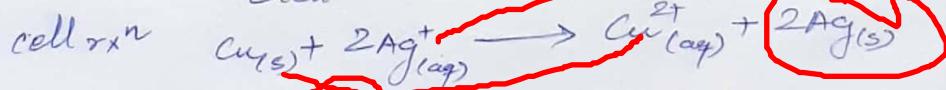
→ Two half cell connected externally through salt bridge.

→ A potential difference develops b/w the electrode and electrolyte which is called Electrode potential.

→ When the conc. of all the species involved in a half-cell is unity then the electrode potential is known as S.E. Potential.

→ The potential difference b/w two electrodes of a galvanic cell is called cell potential. It is the difference b/w the electrode potential of (reduction potential) the cathode and anode.

$$E_{cell} = E_R - E_L$$



$$\therefore E_{cell} = E_R - E_L = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$$

Measurement of Electrode potential:-

→ Potential of individual cannot measure

→ If we take one reference electrode then their the other can be determined w.r.t this

at 298 K the emf of the cell \Rightarrow SHE // second half cell

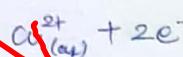
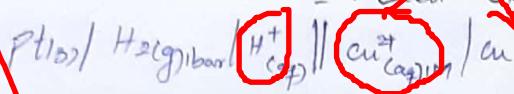
$$E_{\text{cell}} = E_R - E_L$$

cathode
SHE // cathode

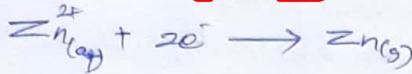
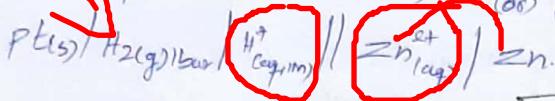
E_L for SHE = 0
(or.)

$$\therefore E_{\text{cell}} = E_R - 0$$

SHE // cathode



$E_{\text{cell}} = E_{\text{Cu}/\text{Cu}} - 0$
It indicates Cu^{2+} ion
reduce easily compare to H^+ ion.



$E_{\text{cell}} = 0.34$
 H^+ cannot oxidise Cu
It indicate Zn^{2+} ion
difficult to reduce
compare to H^+ ion.

$$\therefore E_{\text{cell}} = E_R - E_L = 0.34 - (-0.76) = 1.1 \text{ V.}$$

Electrode pot = reduction pot.

Reduction order:
 $\text{Cu}^{2+} > \text{H}^+ > \text{Zn}^{2+}$

use of Electrochemical cell:-

→ produce electricity.

→ determine pH of soln, solubility pdt, eq const, other
thermodynamic properties, potentiometric titrations.