

10/05/2022

## SYLLABUS

### UNIT-I ATOMIC AND MOLECULAR STRUCTURE (QUANTUM CHEMISTRY)

- Postulates of quantum chemistry
- Schrödinger equation
- Particle in a box solutions
- Molecular orbitals of diatomic molecules and Plots of multicenter orbitals.
- Equation of atomic and molecular orbitals
- Energy level diagrams of diatomic
- Pi-molecular orbitals of butadiene and benzene
- Band structure of solids and the role of doping on band structures.

### UNIT-II SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

- Principles of spectroscopy and selection rules
- Electronic spectroscopy
- Fluorescence and its applications in medicine
- Vibrational and rotational spectroscopy of diatomic molecules.
- Applications
- Nuclearmagnetic resonance and magnetic resonance imaging
- Surface characterization techniques.

### UNIT-III CHEMICAL EQUILIBRIA, INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

- Use of free energy in thermodynamic functions
- Energy, entropy and free energy.
- Estimations of entropy and free energies
- Free energy and emf
- Cell potentials, the Nernst equation and applications
- Use of free energy considerations in metallurgy through Ellingham diagram.

- Evaluations of state of real gases and critical phenomena.

## UNIT-IV PERIODIC PROPERTIES (INORGANIC CHEMISTRY)

- Effective nuclear charge
- Penetration of orbitals
- Variations of s,p,d and f orbital energies of atoms in the periodic table
- Electronic configurations
- Atomic and ionic sizes
- Ionization energies
- Electron affinity & Electronegativity
- Polarizability, oxidation states, coordination numbers and geometries
- Hard soft acids and bases, molecular geometries,
- Born-Haber cycle, The uses of reduction potentials
- Properties of ionic and covalent compounds.

## UNIT-V STEREOCHEMISTRY, ORGANIC REACTIONS AND SYNTHESIS OF A DRUG MOLECULE (ORGANIC CHEMISTRY)

- Representations of 3 dimensional structures
- Structural isomers and stereoisomers
- Configurations and symmetry and chirality
- Enantiomers, diasteromers, optical activity
- Absolute configurations and conformational analysis
- Introduction to reactions involving substitution, addition, elimination, oxidation, reduction, cyclizations
- Ring openings synthesis of a commonly used drug molecule.

## II. SPECTROSCOPY

→ Identification of organic compound



Classical method or Technique



Qualitative elemental test



Quantitative elemental test



Empirical Formula



Molecular mass



Molecular formula of compound.

Qualitative	Quantitative
It relates just to the identity of the material question. <u>Ex:</u> Identification of a powder may release the presence of Heroin and Quinine.	The determination of the percentage combination of the components of substance. <u>Ex:</u> Indicates 10% heroin & 90% quinine.

→ DISADVANTAGES OF ABOVE METHOD:

- It needs specific chemical reaction.

- It is a time taking process.

- Wastage of compound

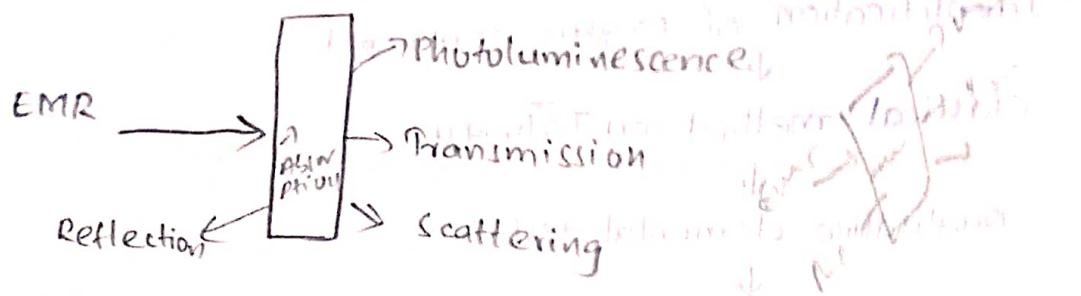
- Not comfortable

- Lack of accuracy

- The instrument needed is expensive

\* SPECTROSCOPY

It is a modern technique, in which "electromagnetic radiation of particular wavelength is used for qualitative and quantitative analysis of matter."



- Based on interaction, it has classified into 3 types of spectroscopy:-

- \* Absorption based spectroscopy
- \* Emission based spectroscopy
- \* Scattering based spectroscopy

### ① ABSORPTION BASED SPECTROSCOPY:

The main principle is that, "atom can absorb light at a specific, unique wavelength." When this specific wavelength of light is provided, the energy is absorbed by the atom. Electrons in the atom move from the ground state to an excited state.

- Available non-degenerate multienergy level states are;
- Electronic energy state
- Vibrational energy state
- Rotational energy state
- Spin energy state.

#### → Electronic Energy state spectroscopy

The method of determining the energy with which electrons are bound in chemical species by measuring the kinetic energies of the electrons emitted upon bombardment of the species with "x-ray or ultraviolet radiation."

#### → Vibrational Energy Spectroscopy

"Infrared spectroscopy (or) Vibrational spectroscopy" that deals with the infrared region of Electro magnetic spectrum, that is light in longer wavelength & lower

frequency than visible light.

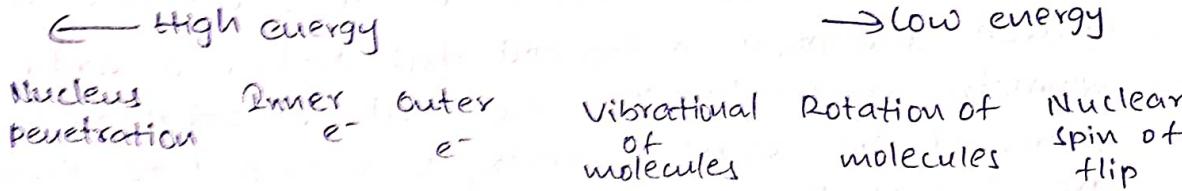
### → Rotational Energy Spectroscopy

Rotational spectroscopy is the part deals with "the measurement of the energies of transition between quantized rotational states of molecules in the gas phase." The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy (or) by far infrared spectroscopy.

### → Spin Energy Spectroscopy

It is present in "NMR spectroscopy".

Electro-magnetic spectrum  
Gamma - X-rays - U.V-visible - IR - Micro - Radio  
rays wave wave



### → SPECTROSCOPIC SELECTION RULES

When light falls on certain molecule (Atom) species it will absorb the light or not depends on certain rules called "spectroscopic selection rules".

These rules helps us to differentiate between allowed and forbidden transition. These rules are divided into two types. They are:

\* Spin Selection Rule

\* Laporte selection rule

### → SPIN SELECTION RULE

It states that transition from lower to higher energy state (or) electronic energy level of molecules may occur, provided that two energy level involved in transition are of same multiplicity.

11

E-3

1

$$\Delta \zeta \leq 0$$

Number of unpaired electrons are same.

- while number of unpaired  $e^-$  changes on going from lower to higher energy level (or state), that transition (or) Multiplicity is called "spin forbidden (or) Multiplicity forbidden".

$$\frac{1}{11} \quad 0.0909\ldots$$

- Spin selection rule :  $\Delta S = 0$

-allowed transitions : singlet-singlet (or) Triplet-Triplet  
 -forbidden transitions : singlet-Triplet (or) triplet-singlet.

- forbidden transitions: singlet-triplet (or) triplet-singlet.

## LAPORTE SELECTION RULE

The Laporte rule is a "selection rule" in electron absorption spectroscopy that applies to centrosymmetric molecules. It says that transitions between states of the same symmetry with respect to inversion are forbidden.

The transition which allowed in it i.e.,  $\sigma \neq 0$  are called "laporte transition";

Exhibit 40 ~~42~~ shows certain of the above mentioned

$$\text{Ex: } Ca_{20} = [Ar]_{18}^{45^2}, \text{ where } l_1 = l_2 - l_1 \text{ and } m_{l_1} = \{1^1, 2^1, 3^1, 4^1, 5^1\}$$

The transition which do not involve change in secondary (or) subsidiary Quantum number,  $\Delta l = 0$  are "forbidden transitions". The forbidden is called "laporte forbidden".

Ex: If  $n^e$  undergo transition from one d-level to another d-level, then metal complexes are not allowed.

$$\text{allowed: } \Delta l = d - d' = 2 - 2 = 0 \quad (\text{so no light is lost in the double slit})$$

- This way of 'relaxing' the orbital selection rule is not available in octahedral complexes.

- In general, no mixing of the 'd' & 'p' orbitals is possible if the molecule has a centre of inversion (Laporte rule).

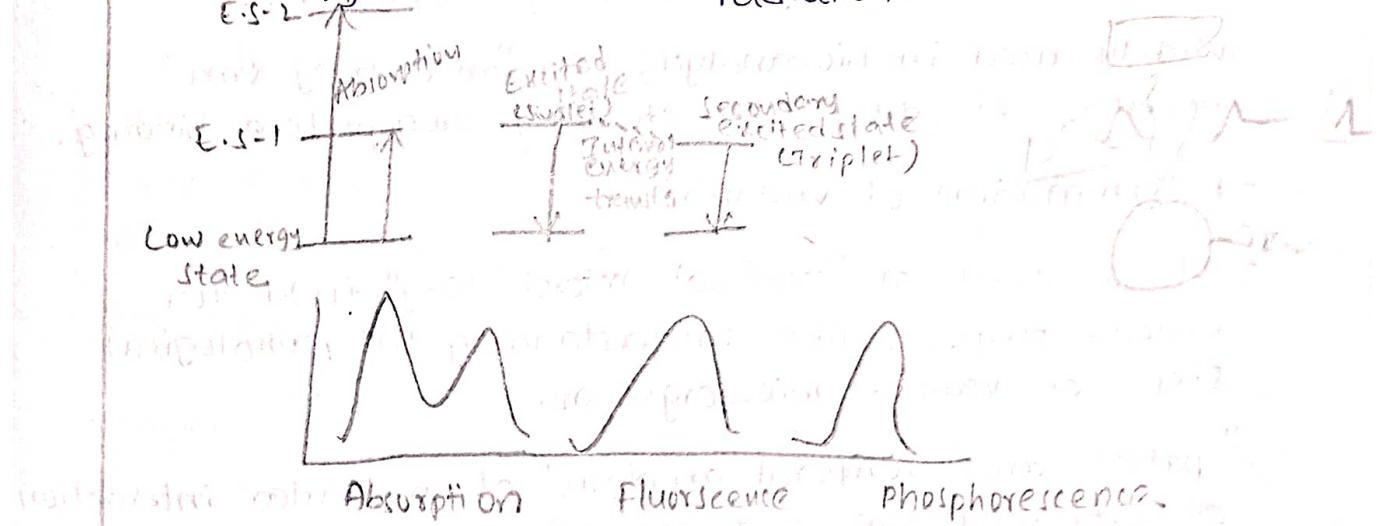
## \* FLOURESCENT SPECTROSCOPY

- Fluorescence spectroscopy (also known as fluorimetry) is a type of electromagnetic spectroscopy that analyses "fluorescence" from a sample.

- At a particular wavelength many compounds absorb UV visible light under electronic transition from low ground state to excited state. This "incident re-emission" of the absorbed energy is called "Fluorescence".

- While the "delayed re-emission" of the absorbed energy is called "Phosphorescence".

- The energy of radiation emitted is always less than the energy of the incident radiation.



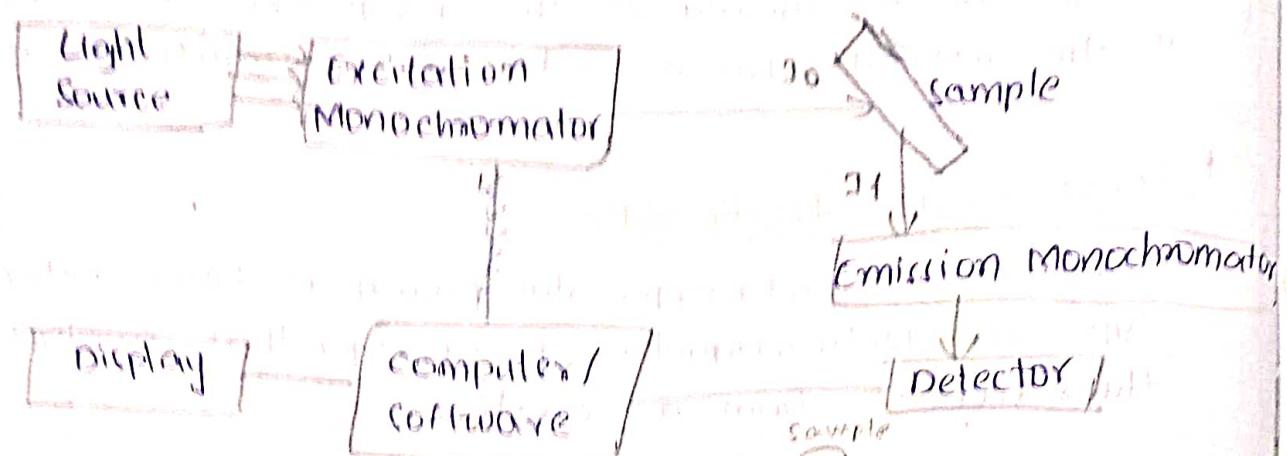
- The absorbed radiation can produce more than one excited state depending on energy radiation.

- The emission can follow two pathways: FLOURESCENCE when it goes from the excited state to the lower energy state.

- On the other hand when an internal energy transfer occurs from the initial excited state to second internal excited state and later the molecule goes back to the lower

state by emitting light, is called "PHOSPHORESCENCE".

### Instrumentation of Fluorescence spectrometry:



### Applications:

- Fluorescence spectroscopy is an "emerging diagnostic tool" for various medical diseases like multi-system cancer and pre-malignant and lesions and early cancer detection.
- Monitoring and "conformational changes" in protein
- Effect of solvent, pH and temperature on protein structure, studying ligand bonding to proteins.
- Widely used in bio-analysis for "measuring small amounts of drug" for studying drug-protein binding.
- Determination of vitamin-c.
- It is used in "medical microbiology" field for various purposes like understanding the pathological steps of various microorganisms.
- "spatial and temporal analysis" of molecular interaction of extremely low concentrated biomolecules in solution.
- It is used to detect and analyze biofilms and their derivatives such as deposits of dental calculus.
- It can distinguish from healthy tissues to damaged tissues.

## \* NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR spectroscopy is a spectroscopy technique used to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains "nuclei possessing spin".

Ex: NMR can analyse mixtures containing known compounds.

Ex: In  $\text{H}_2\text{O}$ ,  $\text{H}_2$  is in a higher energy state than  $\text{O}$ .  $\text{H}_2$  is in a lower energy state than  $\text{O}$ .

IP<sup>+</sup>

(IP)

stable state

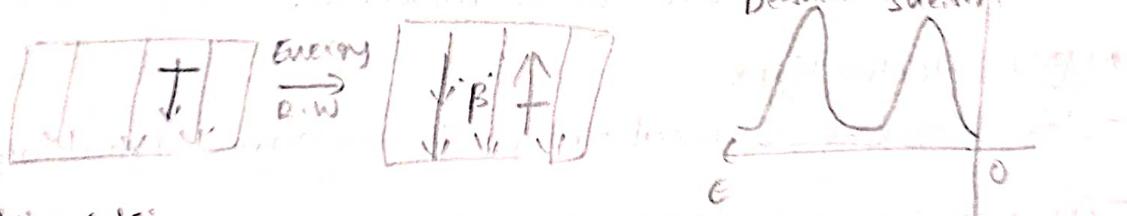


NMR

Machine

- When shielded, less energy is required.

- Not shielded, more energy is required to rearrange.



### \* Principle

The principle behind NMR is that "many nuclei have spin and all nuclei are electrically charged". If an external magnetic field is applied, an energy transfer is possible between the base energy to higher energy level.

### \* Working

Working principle of nuclear magnetic resonance is based on the spins of atomic nuclei. Nuclei with odd mass and odd atomic number have "nuclear spin".

- Since a nuclei is a charged particle, in motion, it will develop a magnetic field. When the nuclei with non-zero spin is placed in a strong magnetic field with respect to the applied magnetic field with the supply of appropriate energy, these nuclei flip to a higher energy state from lower energy state.

- The energy difference between the two states depends on the applied field.

# Magnetic Resonance

- The energy absorbed during this transition is a function of nucleus type and its chemical environment in the molecule.
- The magnetic field is increased and the excitation (or) flipping of nuclei from one orientation to another is detected as an individual voltage resulting from the absorption of energy from the radio frequency field.
- The free induction decay, which is in time domain gives its equivalent frequency domain signal on Fourier transformation.
- The area under a peak is proportional to the number of nuclei "flipping" and by observing the field strength at which protons absorb energy, one can know about the structure of a molecule.

## NMR Applications:

- Life Sciences: Clinical magnetic resonance Imaging (MRI)
- Agriculture and Food sciences: Identifying food additives.

Biotechnology: Using NMR probes during formula processing.

- Spectroscopy: Analysis of unknowns
- Material science: Identifying nanotechnology composites of silicon and different polymers.

## Solution structure

- Molecular Dynamics
- Protein Folding
- Ionization state
- Weak Intermolecular Interactions
- Protein Hydration
- Hydrogen bonding
- Drug screening and design
- Native membrane
- Metabolite Analysis

## \* MAGNETIC RESONANCE IMAGES

- MRI is the important application of NMR technique.
- Magnetic resonance imaging (MRI) is a medical imaging technique used in radiology to form pictures of the anatomy and the physiological processes of the body.
- MRI scanners use strong magnetic field gradients, and radio waves to generate images of the organs in the body.
- MRI does not involve x-rays or the use of ionizing radiation, which distinguishes it from CT and PET scans.
- MRI is a medical applications of nuclear magnetic resonance which can also be used for imaging in other NMR applications, such as NMR spectroscopy.
- NMR spectroscopy is used to form cross sectional images of body parts in living subjects by displaying the intensity of particular MRI transition as the function of the coordinates in cross sectional planes.
- This technique is used in diagnoses of cancer diseases, signals generated from the soft tissues of brain, eye and spinal columns etc.

## \* SURFACE CHARACTERIZATION TECHNIQUES

- Properties associate with surface, Typically measurement of surface area, surface roughness, pore size and reflectivity constitutes. Information on surface characteristics is very important for the possible applications of surface as semiconductors, heterogeneous catalysts and also in biological research.
- There are different methods used to measure different surface properties, i.e., they are sensitive to the outermost atomic layers of the bulk solids.

## Surface characterization techniques

### Classical Methods

- Langmuir's Model

- BET method

### Instrumental methods

- Spectroscopic methods

- Microscopic method.

### SPECTROSCOPIC METHODS

These methods make use of the principle that when a beam of electrons or high-energy radiation are bombarded at the surface, the surface electrons from the upper layer of are ejected. These electrons are called "secondary electrons".

Since the energy of these electrons is very low, these are assumed to be produced from only a few layers of the surface. Electrons of this energy (10-30 eV) cannot reach the surface from underlying layers. In spectroscopic methods, surfaces are analyzed by capturing secondary electrons of different energies, which are characteristic of their environment. Based on spectroscopic theory, some of the techniques are discussed below:

\* X-ray photoelectron spectroscopy (XPS)

\* Auger Electron Spectroscopy (AES)

\* Low energy Electron Diffraction (LEED)

\* X-ray Photoelectron Spectroscopy (XPS)

This technique provides a wide range of information regarding atomic composition, oxidation states, and chemical structures.

- Because of its versatility it is also called "Electron spectroscopy for chemical Analysis (ESCA)".

Basic principle of this technique is based on phenomena called "Photoelectric effect".

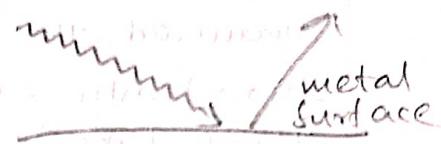
- When photons of known energy knock the surface, an electron from K-shell is knocked out; kinetic energy of this electron is measured in the spectroscopy.
- The spectrum is given as the binding energy as the function of electron counting rate.
- Binding is one unique character of different elements.
- Binding energy of an atom can be calculated from the following equation.

$$\text{Binding energy (eV)} B.E = h\nu - K.E - W$$

where,  $\nu$  = Incident energy

K.E = Kinetic Energy of ejected electron

W = work function.



In the XPS spectrum, the innermost orbital appears at higher energy than outer orbital. Binding energies of orbital increase with atomic number.

#### Applications:

- Surface analysis for elemental composition.
- To determine different oxidation states of the elements.
- For structural analysis of molecules.
- It is also useful for qualitative analysis of the surfaces.

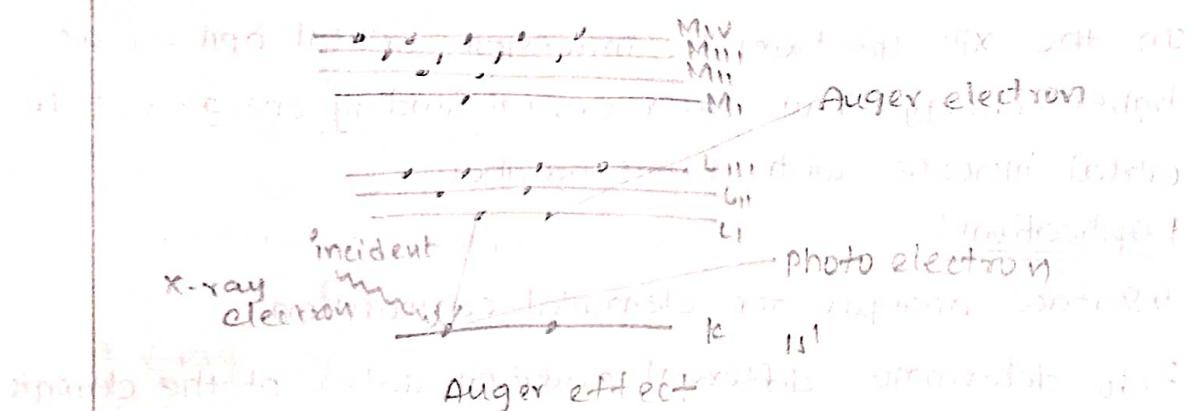
#### AUGER ELECTRON SPECTROSCOPY:

When a core electron of an atom is ejected by the action of an incident x-ray, an energetic electron "an electron" from higher level will drop to fill the vacancy. The energy released in this transition is sufficient to remove another electron from the same shell in the atom.

This secondary electron is called "Auger electron"; and this effect is known as "Auger effect". The Auger electron may originate from the same level (or) from a level having lower B.E.

- If a 'K' electron is ejected in the primary event an 'L' electron may take its place in the 'K' shell while at the same time a second 'L' electron is ejected from the atom.
  - If the Auger electron has sufficient K.E., it will be ejected into the vacuum and its K.E. can be measured. The energies of the secondary electrons are characteristic of the material present and hence Auger effect takes a "finger print" of the material".

A schematic representation of Auger process is shown in figure.



The K.E.E.A of an Auger electron from 'L' shell is given by,

The most pronounced Auger transitions observed in AES involved blw electrons of neighbouring orbitals such as KLL, LMM, MNN, Nnn etc.

The most prominent KLL transitions occur for elements with  $Z = 3$  to  $14$  LMM

14 to 40 MNN and 40 to 79 and

No transition for heavier elements.

In Auger process at least two energy states and three electrons must take part. Hydrogen & He atoms cannot give rise to Auger electrons.

#### \* APPLICATIONS OF AES:

- 1, Qualitative analysis of solid surfaces.
  - 2, Depth profiling of solids.
  - 3, Line scanning.
- (5) LOW ENERGY ELECTRON DIFFRACTION (LEED)

This technique is especially used in crystallography.

- If a crystal is cut along a plane, then the atoms near the surface may be distributed from their equilibrium positions. Such changes can be explored with LEED.
- The surface crystallography structures can be determined by bombarding the surface with low energy electrons (10-200 eV) and diffracted electrons are observed as spots on a phosphorescent screen. The relative position of the spots on the screen shows the surface crystallographic structure.
- The diffracted spots move as the energy of the incident electron changes and the intensity of the spots as function of incident electron energy reveals much about surface reconstruction. In order to determine the true structure, much computer analysis to be done.

#### Applications:

This instrument is basically used for crystallographic surface analysis.

## \* MICROSCOPIC METHOD:

Even microscopic methods make use of more or less the same principles, but these methods are generated by bombarding the surface with high-energy electrons, which are then multiplied several times so as to produce a magnified image of the surface on the fluorescent screen.

\* Scanning Electron Microscope (SEM)

\* Scanning Tunneling Microscope (STM)

\* Atomic Force Microscope (AFM)

## chemical shift

The variation in nuclear magnetic resonance frequencies of the same type of nucleus due to change in electronic configuration is called chemical shift. It depends on the nature of the molecule, its environment, presence of substituents, etc. It is also dependent on the frequency of the applied magnetic field. The variation in frequency is proportional to the square of the magnetic field.

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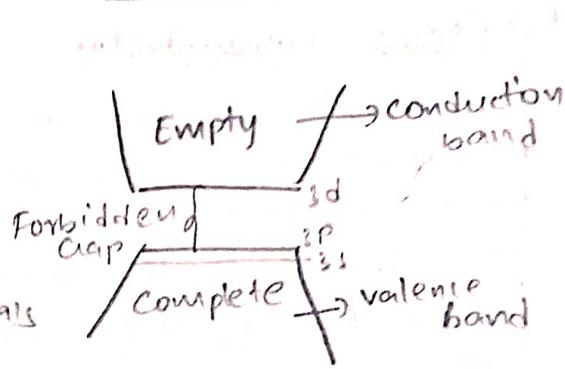
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# I. ATOMIC AND MOLECULAR STRUCTURE

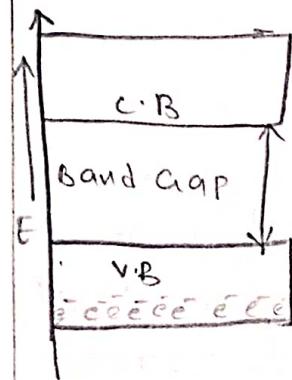
## \* Bond theory:

solid → Conduction Band  
Valence Band

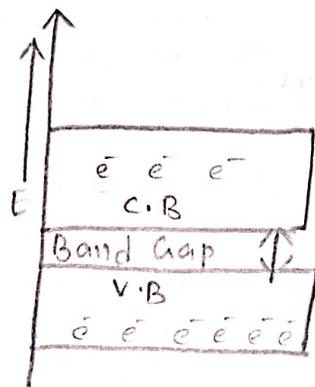
Ex:  $\text{Si}_{14} = 1s^2 2s^2 2p^6 3s^2 3p^2$  3d orbitals



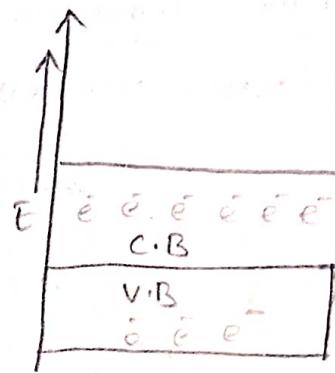
## \* Insulators



## \* SEMICONDUCTORS



## \* CONDUCTORS



\*

## SEMICONDUCTOR

### Intrinsic Semiconductor

Pure form of  
Ge, Si  
( $n_e = n_h = n_i$ )

### Extrinsic semiconductor

#### N-Type

Pentavalent impurity  
P, As, Sb etc.

Donor impurity-ND

( $n_e >> n_h$ )

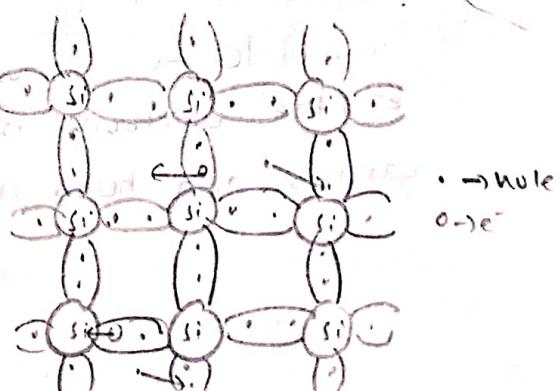
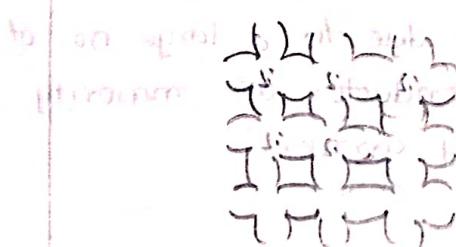
#### P-Type

Trivalent impurity  
Ga, B, In, Al

Acceptor impurity-NA

## \* Intrinsic Semiconductor:

An intrinsic type of semiconductor material is made to be very pure chemically. It is made up of only a single type of element.

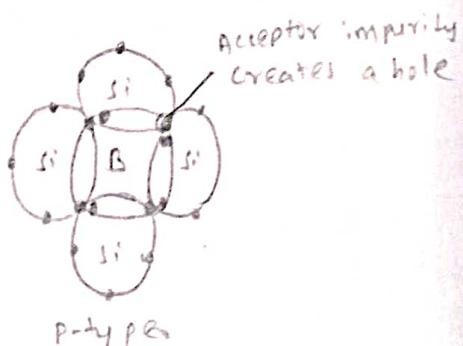
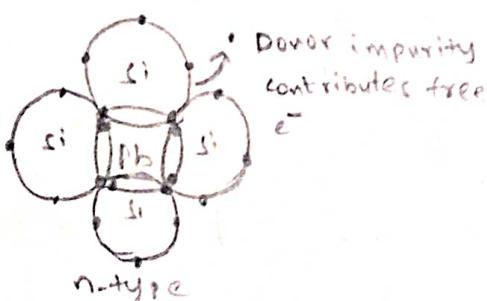


## \* Extrinsic Semiconductor:

The conductivity of semiconductors can be greatly improved by introducing a small number of suitable replacement atoms called "IMPURITIES." The process of adding impurity atoms to the pure semiconductor is called "Doping." An extrinsic semiconductor can be further classified into:

- N-type semiconductor
- P-type semiconductor

### -> Extrinsic Semiconductors



## \* N-Type Semiconductor:

- Mainly due to electrons
- Majority ' $e^-$ ' & Minority 'holes'
- When a pure semiconductor (Si or Ge) is doped by Pentavalent impurity (P, As, Sb, Bi) then, four electrons out of five valence electrons bonds with the four electrons of Ge or Si. The fifth electron of the dopant is set free. Thus, the impurity atom donates a free  $e^-$  for conduction in lattice and is called "Donor".
- Since, the number of free  $e^-$  increases by addition of impurity, the -ve charge carriers increases. Hence, it is called n-type semiconductor.
- Crystal as a whole is neutral, but ~~donor atom becomes an~~ ~~an~~ becomes an immobile -ve ion. As conduction is due to a large no. of  $e^-$ , the electrons in n-type semiconductor are majority carriers and holes are the minority carriers.

- \* P-Type Semiconductor:
  - Mainly due to holes.
  - When a pure atom is doped with trivalent impurity ( $\text{B}, \text{Al}, \text{In}, \text{Ga}$ ) then, three valence  $e^-$  of the impurity bonds with three of the four valence  $e^-$  of semiconductor.
  - This leaves an absence of  $e^-$  in the impurity. These impurity atoms which are ready to accept bonded  $e^-$  are called "Acceptors".
  - With increase in the number of impurities, holes are increased. Hence, it is called p-type semiconductor.
  - Crystal as a whole is neutral, but acceptors become an immobile -ve ion. As conduction is due to the large no. of holes, the holes in the p-type semiconductor are "MAJORITY CARRIERS" and  $e^-$  in the p-type semiconductor are "MINORITY CARRIERS".

#### \* MOLECULAR ORBITAL THEORY:

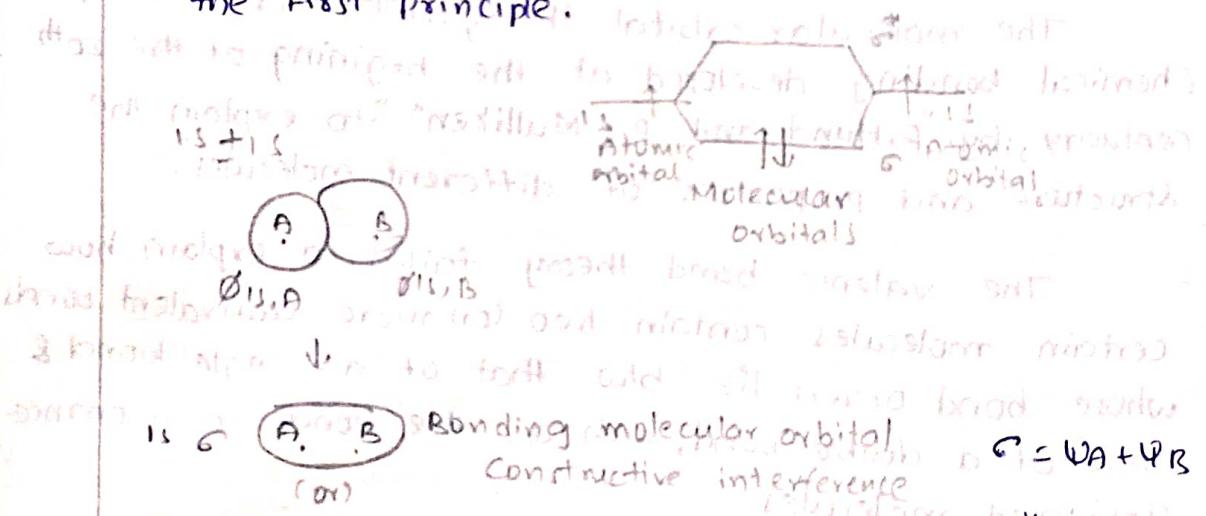
The molecular orbital theory (MOT) is a theory on Chemical bonding developed at the beginning of the 20<sup>th</sup> century by "F. Hund and R.S. Mulliken" to explain the structure and properties of different molecules.

- The valence band theory failed to explain how certain molecules contain two or more equivalent bonds whose bond orders lie b/w that of a single bond & that of a double bond, such as the bonds in resonance-stabilized molecules.

#### \* Features of MOT:

- The atomic orbitals overlap to form new orbitals called "Molecular Orbitals". When two atomic orbitals overlap they lose their identity and form new orbitals called "Molecular orbitals".
- The  $e^-$  in the molecules are filled in the new states called the "Molecular orbitals" similar to the  $e^-$  in atom being filled in an energy state called atomic

- The  $\sigma$  MO has lower energy & greater stability than the corresponding  $\pi$  MO.
- The  $\sigma$  like AOs are filled by Aufbau principle obeying Orbitals'. Pauli's exclusion principle and Hund's rule of maximum multiplicity.
- The probability of finding the  $e^-$  in a molecule around its group of nuclei is given by the molecular orbital. An atomic orbital gives the electron probability distribution around a single nucleus. The two combining atomic orbitals should possess energies of comparable value and similar oscillation frequencies.
- For example,  $1s$  can combine with  $1s$  & not with  $2s$ .
- The number of molecular orbitals formed is equal to the number of atomic orbitals combining when two atomic orbitals combine, they form new orbitals called  $\sigma$  MOs.
- The shape of molecular orbitals formed depends upon the shape of the combining atomic orbitals.
- Just as letters  $\sigma$ ,  $\pi$  &  $\delta$  used to denote AOs, Greek letter  $\zeta$  ( $H_2$ ) are used to denote  $\sigma$  MOs.
- Ex: Each Hydrogen atom has a single valence orbital, that is being the  $1s$  orbital. Two molecular orbitals may be formed by the constructive and destructive overlap of these two atomic orbitals. So if you have two  $1s$  atomic orbitals you can only make two molecular orbitals from them. This is the First Principle.



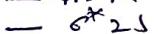
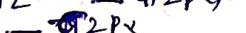
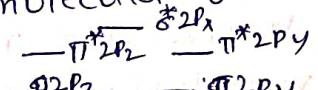
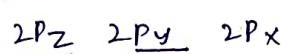
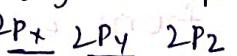
- According to MOT, the two molecular orbitals that form are called  $\sigma$  (sigma-bonding) and  $\sigma^*$  (sigma star anti-bonding).
- In the case of  $H_2$  both the valence  $e^-$  that form the bond between the hydrogens fill the bonding  $\sigma$  orbital. (Note: valence and bonding electrons are the same in  $H_2$ ).

- According to M.O.T, the filling of orbitals takes place according to the following rules:

\* AUFBAL's Principle: Molecular orbitals are filled in the increasing order of energy levels.

\* PAULI's Principle: In an atom or a molecule, no two  $e^-$  can have same set of four quantum numbers.

\* HUND's Rule of Maximum multiplicity: Pairing of  $e^-$  doesn't take place until all the atomic (or) molecular orbitals are singly occupied.



\* BOND ORDER: The bond order for a molecule can be determined as follows:

$$\text{Bond order} = \frac{1}{2} [\text{Bonding } e^- - \text{Anti-bonding } e^-]$$

-  $\text{H}_2$  molecule has a bond order of  $\frac{1}{2}(2-0) = 1.0$

- In other words, there is a single bond connecting the two  $\text{H}$  atoms in the  $\text{H}_2$  molecule. In the case of  $\text{He}_2$ , on the other hand, the bond order is  $\frac{1}{2}(2-2) = 0$ . This means that  $\text{He}_2$  is not a stable molecule.

Bonding Molecular Orbitals

NOT

Anti-bonding molecular orbital

Molecular orbitals formed by the additive effect of the atomic orbitals is called "Bonding molecular orbitals".

- Probability of finding the  $e^-$  is more in case of B.M.O.s.

Molecular orbitals formed by the subtractive effect of atomic orbitals is called "Anti-bonding molecular orbital".

- probability of finding  $e^-$  is less in anti-bonding molecular orbitals. There is also a node b/w A.B.M.O.s b/w the nuclei where the electron density is zero.

- These are formed by the combination of + and - and with  $\perp$  part of  $\psi$  waves.
- The  $\psi$  density in the bonding molecular orbitals in the inter-nuclear region, is high.
- The nuclei are shielded from each other and hence the repulsion is very less.
- These are formed by the overlap of + with - part of  $\psi$  waves.
- The  $\psi$  density in the A-B-M.O in the inter-nuclear region is very low.
- The nuclei are directly exposed to each other. The Nuclei are less shielded from each other.

### \* Bonding in Homonuclear Diatomic molecules:

- The molecules which are composed of two identical atoms are called "homonuclear diatomic molecules".

Ex:  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$  etc;

- As we already know that, formation of molecular orbitals by the combination of atomic orbitals is the central idea of bonding according to MOT.

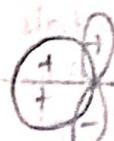
- For the effective combination of atomic orbitals, the following conditions must be satisfied:

\* The energies of combining atomic orbitals, should be nearly same/comparable.

\* The extent of overlapping should be large.

\* The symmetry of the combining atomic orbitals around the inter-nuclear axis should be the same.

Ex:



+ 2p<sub>z</sub> + 2p<sub>x</sub>



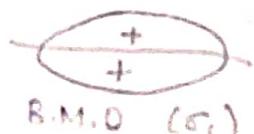
- 2p<sub>z</sub> - 2p<sub>x</sub>

Effective overlap & Bonding

\* Combination of s-s atomic orbitals:



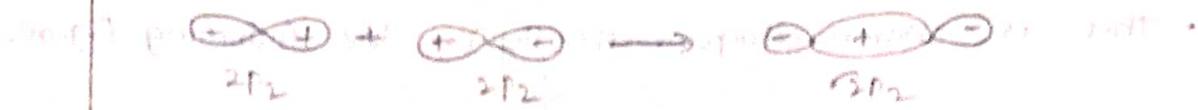
+ 1s + 1s



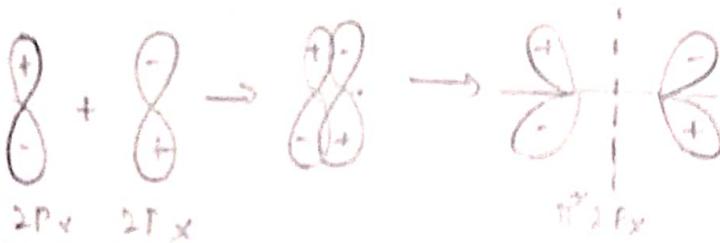
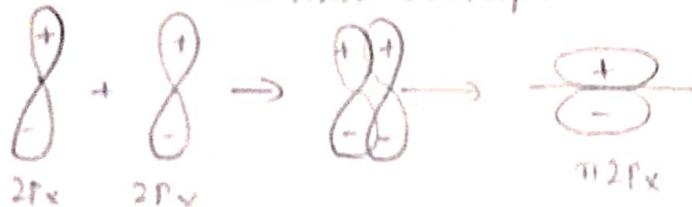
B.M.O ( $\sigma$ )



- By convention the z-axis is assumed as the inter-nuclei axis. The  $2p_z$  atomic orbitals overlap along the inter nuclear axis to form  $\sigma$  &  $\sigma^*$  M.O whereas  $2p_x$  &  $2p_y$  orbitals overlap side to side to form  $\pi$  &  $\pi^*$  M.O.



(a) Axial overlap.



- In a similar way  $2p_y$  orbitals also combine but their orientation is fixed along the y-axis.

#### \* Energy of molecular orbitals:

The molecular orbitals obtained by the combination of  $1s, 2s$  &  $2p$  atomic orbitals can be arranged in the increasing order of energy as follows.

$$\sigma_1, \sigma_1^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p_z}, \pi_{2p_x} = \pi_{2p_y}, \pi_{2p_x}^* = \pi_{2p_y}^*, \sigma_{2p_z}^*$$

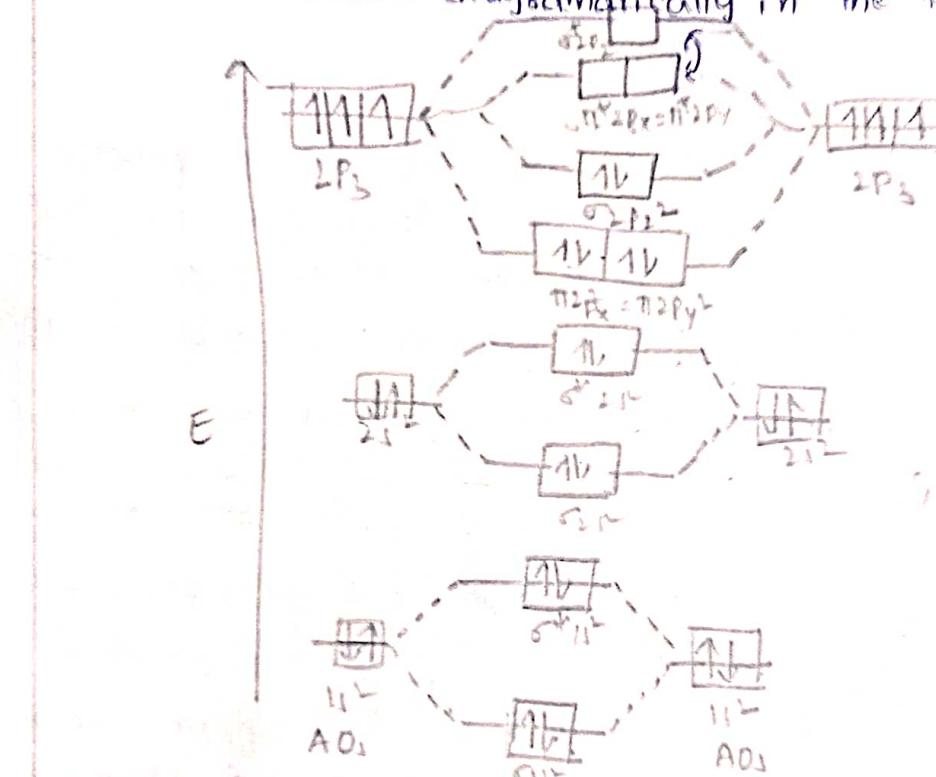
The energy of bonding  $\pi_{2p_x}$  &  $\pi_{2p_y}$  MOs is exactly similar & they are said to be doubly degenerate. Similarly,  $\pi_{2p_x}^*$  &  $\pi_{2p_y}^*$  MOs also have the same energy and are doubly degenerate. The molecular orbitals of  $O_2, F_2$  follow above-mentioned energy order.

### \* Energy level diagram of $\text{N}_2$

A nitrogen atom has '7' electrons with the following configuration.  $\text{N} = 1s^2 2s^1 2p^3$ .

Thus,  $\text{N}_2$  molecule contains 14 electrons. These are arranged in MOs as;  
 $\text{N}_2 = 14 = \sigma_{1s}^2, \sigma_{1s}^2, \sigma_{2s}^2, \sigma_{2s}^2, \sigma_{2p_x}^2, \sigma_{2p_y}^2, \sigma_{2p_z}^2, \pi_{2p_x}^4, \pi_{2p_y}^4, \pi_{2p_z}^4$

This is shown diagrammatically in the following figure.



Thus total bonding MOs = 8 and antibonding MOs = 8

$$\text{Bond order} = \frac{\text{No. of bonding MOs} - \text{No. of antibonding MOs}}{2} = \frac{8 - 8}{2} = 0$$

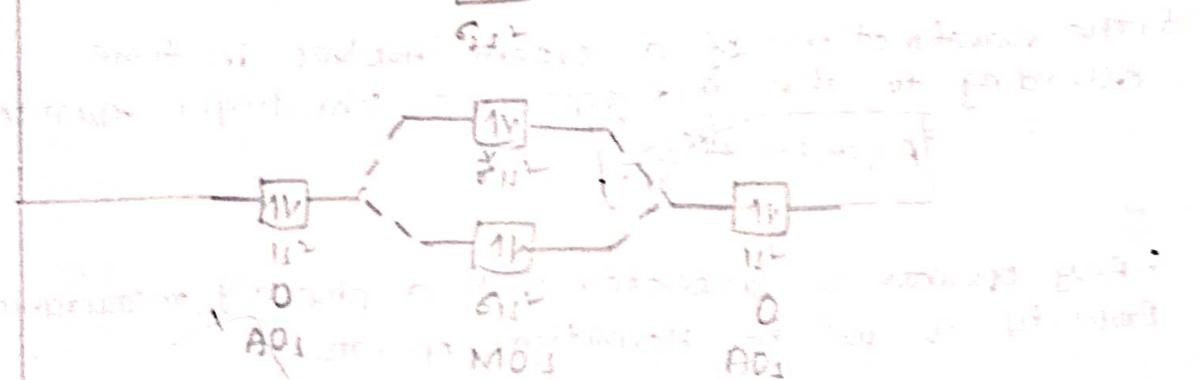
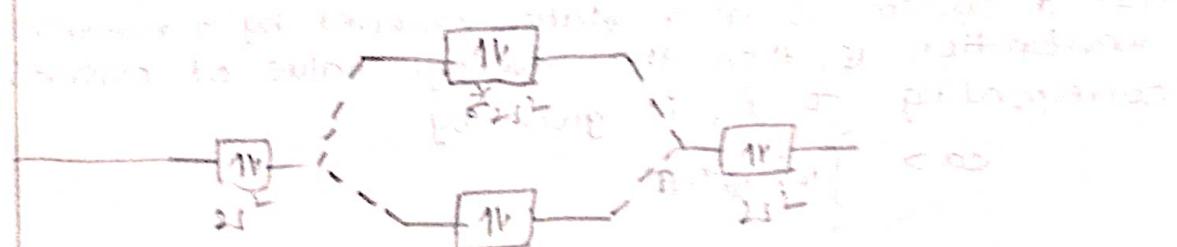
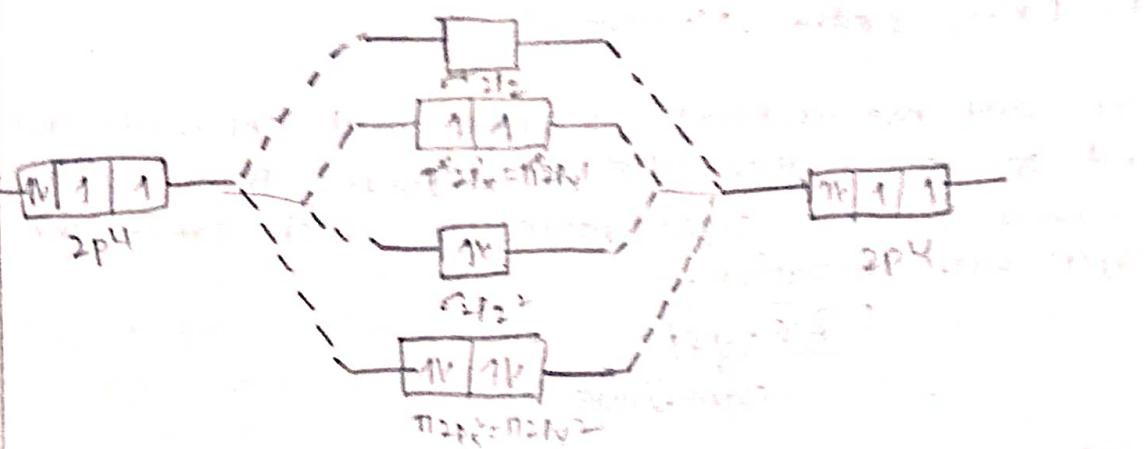
### \* Energy level diagram of $\text{O}_2$

A oxygen atom has '8' electrons with the following configuration.  $\text{O} = 8 = 1s^2 2s^2 2p^4$ .

Thus  $\text{O}_2$  molecule contains 16 electrons. These are arranged in MOs as;  
 $\text{O}_2 = 16 = \sigma_{1s}^2, \sigma_{1s}^2, \sigma_{2s}^2, \sigma_{2s}^2, \sigma_{2p_x}^2, \sigma_{2p_y}^2, \sigma_{2p_z}^2, \pi_{2p_x}^4, \pi_{2p_y}^4, \pi_{2p_z}^4$

This is shown diagrammatically in the following figure.

This is shown diagrammatically in the following figure.



$$\text{- Bond order} = \frac{\text{No. of bonding electrons} - \text{No. of antibonding electrons}}{2} = \frac{10 - 6}{2} = 2$$

Thus, there are two bonds in the oxygen molecule, one  $\sigma$  & one  $\pi$  bond.

It has two unpaired electrons in  $\pi^*_{2p_x}$  &  $\pi^*_{2p_y}$  orbitals, which makes the molecule paramagnetic.

#### \* Important postulates of quantum Mechanical Model:

1) The state of a quantum mechanical system is specified by the wave functions  $\Psi(x, t)$  that depends upon the coordinates of particle and time.

This wave function  $\Psi(x, t)$  must be "well defined".

2) For every observable in classical mechanics, there exists an operator in quantum mechanics.

**Observable:** A measurable dynamical variable is called.

an observable, e.g., position, momentum etc. "dynamical" is any property of the system.  
Ex: Energy, Position, Momentum etc.,

3) If any measurement is done with observable associated with operator  $\hat{A}$ , then the only values that will ever be observed are the eigen values  $a$ , which satisfy the eigen value equation.

$$[\hat{A}\Psi = a\Psi]$$

eigen value

4) If a system is in a state described by a normalized wavefunction  $\Psi$ , then the average value of observable corresponding to  $\hat{A}$ , is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \Psi \hat{A} \Psi^* d\mathbf{r}$$

5) The wavefunction of a system involves in time according to the time-dependent Schrödinger equation.

$$[\hat{A}(\Psi_{\text{out}}, t) = i\hbar \frac{d\Psi}{dt}]$$

6) Any operator  $\hat{Q}$  associated with a physically measurable property  $'a'$  will be Hermitian operators.

7) The wave function must be antisymmetric with respect to the interchange of all the coordinates of one fermion with another fermion.

Explanation: Pauli's exclusion principle is a direct result of anti-symmetry principle.

Consider two electrons having same quantum numbers. Then the wavefunction of the system will be

$$\Psi = \psi_1 \psi_2$$

where  $\psi_1$  &  $\psi_2$  are the wavefunctions of the two electrons. Now if we interchanged the positions of the two electrons, the wavefunction will change to

$$\Psi' = \psi_2 \psi_1$$

Now the wavefunction  $\Psi'$  is antisymmetric with respect to the interchange of the two electrons. This is because

$$\Psi' = \psi_2 \psi_1 = -\psi_1 \psi_2 = -\Psi$$

which is impossible. Hence the wavefunction must be symmetric with respect to the interchange of the two electrons.

## SCHRODINGER WAVE EQUATION

The Schrodinger equation is the fundamental equation of quantum mechanics. The solutions to the Schrodinger equation are called "wave functions". Wave functions gives a complete description of any system. In this section, we shall present and discuss the version of the Schrodinger equation that does not contain time as a variable. Solutions to this time-independent Schrodinger equation are called "stationary state wave functions" because they are independent of time. Many problems of interest to chemists can be solved using time-independent Schrodinger equation. Let us try to derive it.



- Consider a small particle of mass 'm'. The fundamental equation describing the behaviour of its wave motion along the 'x' direction with wavelength 'λ' is given by  $\psi = A \sin \frac{2\pi}{\lambda} x$  — (1)

where,  $\psi$  = wave function &  $A$  = a constant.

- The above equation is generally known as equation for a standing wave.

- Let us do the double differentiation of (1) wrt  $x$ :

$$\frac{d\psi}{dx} = \frac{d}{dx} \left( A \sin \frac{2\pi}{\lambda} x \right)$$

$$\frac{d\psi}{dx} = A \cdot \frac{2\pi}{\lambda} \cdot \cos \frac{2\pi}{\lambda} x$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \cdot A \cdot \sin \frac{2\pi}{\lambda} x$$

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

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \psi = 0$$
 — (2)

The K.E. of a moving particle of mass 'm' & velocity  $v$  is given by  $K.E. = \frac{1}{2}mv^2$  — (3)

- According to de Broglie Eq:

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

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

$$m v^2 = \frac{h^2}{\lambda^2} \quad \text{--- (4)}$$

From (3) & (4)  $K.E = \frac{h^2}{2m\lambda^2} \quad \text{--- (5)}$

- If the particle moves in a field whose potential Energy is  $V$  then,  $K.E = E - V$

where  $E = \text{Total energy}$ .

- By substituting the value of  $K.E$  in (5) it becomes:

$$E - V = \frac{h^2}{2m\lambda^2}$$

$$\frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2} \quad \text{--- (6)}$$

From (2) & (6) we can write;

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (7)}$$

The above equation is the Schrödinger equation in one dimension.

- In three dimensions it becomes;

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (8)}$$

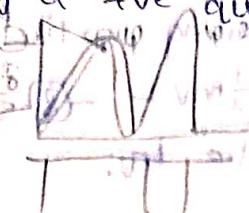
$$(n^2 m^2 A) \frac{\partial^2 \psi}{\partial r^2}$$

\* Significance of  $\psi$  &  $\psi^2$

- A wave function ' $\psi$ ' is a mathematical function that contains detailed information about the behaviour of a particle.

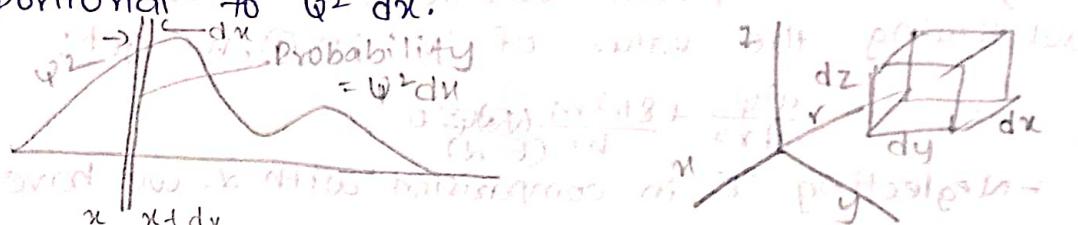
- The wave functions in general have regions of +ve & -ve sign. They may be complex number functions also.

There is no direct significance in the -ve value of a wave function. Only a +ve quantity has direct physical significance.



Value of the first derivative  
at position r

- Thus, the wave function  $\psi$  has no direct visualizing meaning, but the square of the wave function  $\psi^2$  has the physical significance. Because the square of any no. is +ve, we don't have to worry about ' $\psi$ ' having a -ve sign in some regions of space;  $\psi^2$  is never -ve. And also, if ' $\psi$ ' is a complex function then the corresponding ' $\psi^2$ ' is real.
- $\psi^2$  is called "probability density". The probability that the particle will be found in a small region divided by the volume of the region is called "probability density".
- For one dimensional system, if the wave function of a particle has the value ' $\psi$ ' at some point ' $x$ ', then the probability of finding the particle b/w  $x$  &  $x+dx$  is proportional to  $\psi^2 dx$ .
- For three dimensional system, if the wave function of a particle has the value ' $\psi$ ' at some point - say  $r$ ; then the probability of finding the particle surrounding to the point in an infinitesimal volume  $dr = dx dy dz$  is proportional to  $\psi^2 dr$ .
- Wherever  $\psi$ , and hence  $\psi^2$ , is zero, the particle has zero probability density. A location where  $\psi$  passes through zero is called a node of the wave function so we can say that a particle has zero probability density wherever the wavefunction has nodes.
- Wherever  $\psi^2$  is large, the particle has a high probability density, wherever  $\psi^2$  is small, the particle has only a low probability density.
- The presence of +ve & -ve regions of a wave function ' $\psi$ ' is of great indirect significance, bcz it gives rise to the possibility of constructive & destructive interference b/w different wave functions.



## Particle in a Box

Consider a particle with mass  $m$ , that is free to move back and forth along one dimension between the values  $x=0$  and  $x=L$ . We will assume that the P.E. of the particle is zero, within the region  $x=0$  to  $x=L$ , and outside this region the P.E. is taken to be infinity. The particle is trapped in a 1D box with impenetrable walls.

The Schrödinger equation in 1D is given by;

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E-V)\psi = 0 \quad \text{--- (1)}$$

Case ①: Outside the box: Region I & III present outside of box with  $V=\infty$ . By substituting the value of 'V' in (1), we get;

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E-\infty)\psi = 0$$

Neglecting 'E' in comparison with  $\infty$ , we have

$$\frac{d^2\psi}{dx^2} - \frac{8\pi^2m}{h^2}\psi = 0$$

We conclude that  $\psi=0$  outside the box, in other words particle can't be found at outside the box.

Case ②: Inside the box: Region II represents inside of box with  $V=0$ . By substituting the value of 'V' in eq(1) we get,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{--- (2)}$$

where  $k^2$  is a constant.

The general solution of (2) is given by,

$$\psi(x) = A\sin kx + B\cos kx \quad \text{--- (2)}$$

wave function of particle is  $\psi(x)$

According to quantum mechanics,  $\psi$  must be a continuous function. Therefore, it must be consistent with the solution found for the outside of the box, hence at the walls of the box;

1st boundary condition:  $\psi=0$  at  $x=0$

2nd " " " :  $\psi=0$  at  $x=L$

• By applying first boundary condition, we get,  
or  $A \sin(0) = 0$

$$(A=0)$$

• By applying 2nd Boundary condition & value of  $B$  in ② we get

$$B \sin(kL) = 0$$

$$\sin(kL) = 0$$

• Calculating for  $kL = n\pi$ , we get,  $k = n\pi/L$

$$\boxed{k = \frac{n\pi}{L}} \quad -④$$

$$\therefore \psi(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad -⑤ \quad k = n\pi/L$$

The probability of finding the particle in the box must be equal to 1, bcz there is only one particle and at all times it is somewhere in the box.

$$\int_0^L [\psi(x)]^2 dx = 1$$

$$\int_0^L [A \sin\left(\frac{n\pi}{L}x\right)]^2 dx = 1$$

$$A^2 \int_0^L \left[ 1 - \frac{1 - \cos\left(\frac{n\pi}{L}x\right)}{2} \right] dx = 1$$

$$A^2 \cdot \left(\frac{1}{2}\right)_0^L = 1$$

$$A^2 \cdot \frac{L}{2} = 1$$

$$A^2 = \frac{2}{L}$$

$$\boxed{A = \sqrt{\frac{2}{L}}}$$

$$\therefore \boxed{\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)} \quad -⑥$$

with  $n = 1, 2, 3, \dots$

The above equation represents the complete solution to Schrödinger equation which is applied for a particle in a box.  $\psi_n(x)$  represents various wave functions, that are possible with the respective values of quantum number 'n'.

Energies of particle in a box:

$$E = \frac{8\pi^2 m E}{h^2}$$

$$\left(\frac{n\pi}{L}\right)^2 = \frac{8\pi^2 m E}{h^2}$$

$$\frac{n^2 \pi^2}{L^2} = \frac{8\pi^2 m E}{h^2}$$

$$E = \frac{n^2 h^2}{8mL^2}$$

with  $n=1, 2, 3, \dots$

So the energy of the particle is said to quantized.

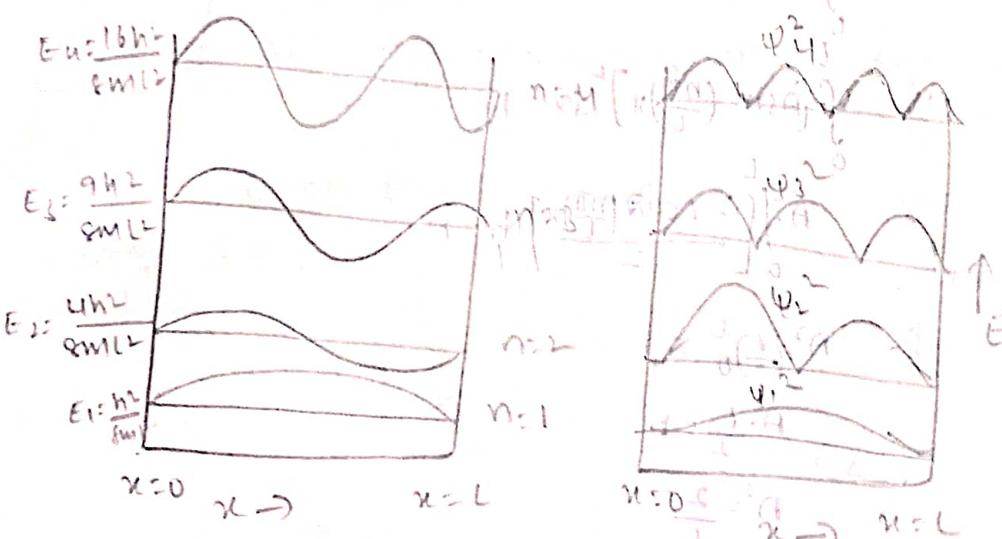
wavefunction      Energy

$$\psi_1 = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \quad E_1 = \frac{h^2}{8mL^2}$$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \quad E_2 = \frac{4h^2}{8mL^2}$$

$$\psi_3 = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) \quad E_3 = \frac{9h^2}{8mL^2}$$

$$\psi_4 = \sqrt{\frac{2}{L}} \sin\left(\frac{4\pi x}{L}\right) \quad E_4 = \frac{16h^2}{8mL^2}$$



wave functions

Probability densities

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

.....

Note that each wave function goes to zero at the edges of the box, as required by the boundary conditions. Also note that the probability distribution is significantly different for the four levels. For  $n=1$  the particle is found near the centre of the box. In contrast, for  $n=2$  the particle has zero probability of being found in the center of the box.

### chemical shift:

protons with no bonds

protons with one bond

protons with two bonds

protons with three bonds

protons with four bonds

protons with five bonds

protons with six bonds

protons with seven bonds

protons with eight bonds

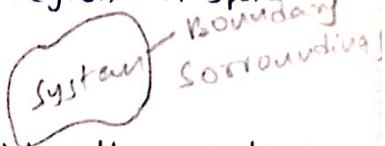
### 3. THERMODYNAMICS

(1)

→ Therms = Heat

→ Dynamics = Motion

SYSTEM: A quantity of matter or a region in space chosen for study.



SURROUNDINGS: The mass or region outside the system.

BOUNDARY: The real or imaginary surface that separate the system from its surroundings.

- Types of systems: There are 3 types of systems:

\* Open system

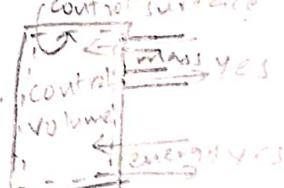
\* Closed system

\* Isolated system

- Open system: Both mass and energy can cross the selected boundary.

Ex: An cup of coffee.

- Have boundaries which are not closed.



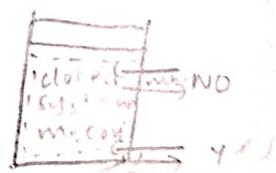
- Closed system: Only energy can cross the selected boundary.

- Cannot exchange mass with surroundings.

Ex: A tightly capped cup of coffee

- Mass of the system is constant.

- Boundaries are completely closed.



- Isolated system: Neither mass nor energy can cross the selected boundary.

Ex: Coffee in a closed, well-insulated thermos bottle.

- Mass and energy can't cross the boundary.



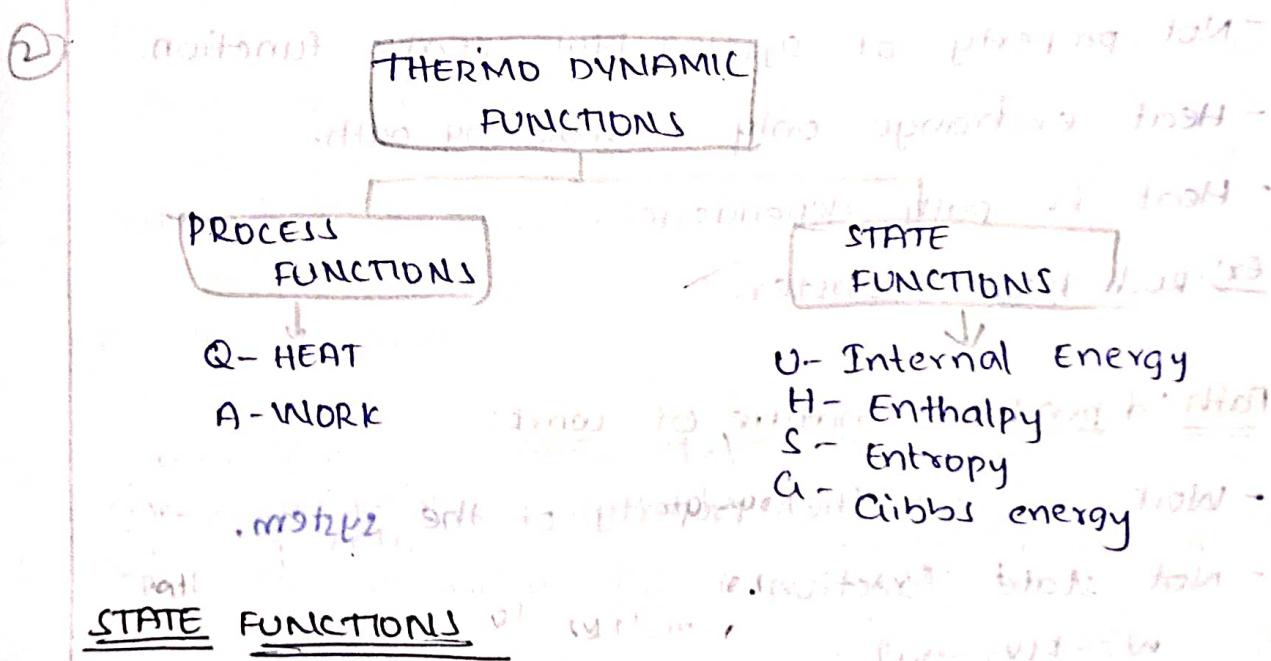
- \* Properties of a system:   
 Properties of a system is a measurable characteristic of a system that is in equilibrium.
- Properties may be intensive (or) extensive.

- \* Intensive: Are independent of the amount of mass:
- Ex: Temperature, Pressure and Density.

- \* Extensive: Varies directly with the mass.

Ex: Mass, Volume, energy, enthalpy, etc.

$m$	$\frac{1}{2}m$	$\frac{1}{2}m$	Extensive
$V$	$\frac{1}{2}V$	$\frac{1}{2}V$	
$T$	$T$	$T$	Intensive
$P$	$P$	$P$	
$P_1, P_2$	$P_1$	$P_2$	Path
$P$	$P$	$P$	



A state function is a property whose value does not depend on the path taken to reach that specific value.

In contrast, functions that depend on the path from two values are called "Path functions".

Both Path and state functions are often encountered in thermodynamics.

State functions depend only on the final and initial value and not on the object's history (or) the path taken to get from the initial to final value.

### WORK (W):

$$\text{Work} = F \cdot S$$

- Work is one of the ways by which a system can exchange energy with its surroundings by changing the state of the system.

Ex: Object move by applying force (object energy)

### HEAT (Q):

- Another way of exchanging energy, state & surroundings.
- Not property of system; Not state function.
- Heat exchange only possible by path.
- Heat is path dependence.

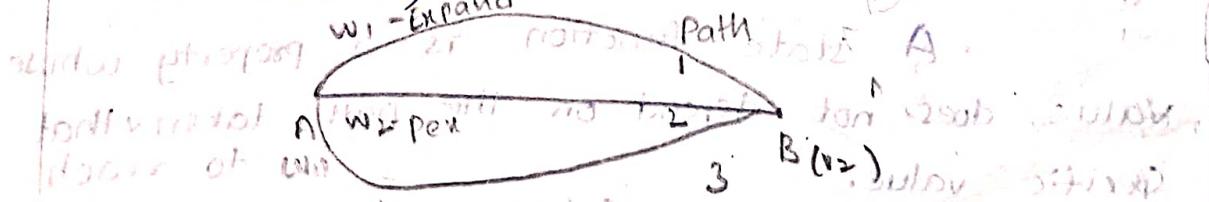
Ex: Rod heating transfer.

### Path dependence nature of work:

- Work is not the property of the system.
- Not state function.

$$W = -P(V_2 - V_1)$$

*w<sub>1</sub> - expand*



"Initial state" below is now constant.  $W_1 = P(V_2 - V_1)$

## - First Law of Thermodynamics!

The first law is usually referred to as the "Law of conservation of energy", i.e., "Energy can neither be created nor destroyed, but rather transformed from one state to another".

- The energy balance is maintained within the system being studied/defined boundary.
- The various energies associated are then being observed as they cross the boundaries of the system.

## \* INTERNAL ENERGY

In thermodynamics, the internal energy is one of the two cardinal state functions of the state variables of a thermodynamic system. It refers to energy contained within the system, while excluding the K.E. of motion of the system as a whole and the potential energy of the system as a whole due to external force fields. It keeps accounts of the gains and losses of energy of the system.

The change in internal energy of a system is equal to the heat added to the system, minus the work done by the system.

$$\Delta U = Q - W$$

The internal energy of a system can be changed by heating the system, or by doing work on it, or by adding or taking away matter. When matter transfer is prevented by impermeable

walls containing the system, it is said to be closed. Then the first law of thermodynamics states that the "increase in internal energy" is equal to the total heat added and work done on the system by the surroundings.

### \* LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

1) "NO restriction on the direction of the flow of heat": The first law of thermodynamics establishes equivalence b/w the quantity of heat used and the mechanical work but does not specify the conditions under which conversion of heat into work is possible, or the directions in which heat transfer can take place.

2) "Does not specify the feasibility (flexibility) of the reaction": First law does not specify that process is feasible or not. For example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3) Practically it is not possible to convert the heat energy into an equivalent amount of work.

### \* 2nd Law of Thermodynamics

- It indicates that "all heat cannot be converted into work".

- According to 2nd law of T.D, Heat will only be transferred from high temperature to lower temperature and not vice versa".

- Second law states that whether it is possible for energy transfer to proceed along a particular direction or not.

- A cycle can only occur if it satisfies both the first law and second law of thermodynamics.
  - First law of T-D is a "quantitative statement".
  - Second law of T-D is a qualitative statement.
- \* ENTHALPY:  $H = U + PV$

- Enthalpy represent total heat content of the system, at constant pressure.
- It is a state function and extensive property.
- Absorption of heat by system increases its enthalpy.

\* Extension of Enthalpy change:

$$H_1, U_1, P_1, V_1 \longleftrightarrow H_2, U_2, P_2, V_2$$

$$H_1 = U_1 + PV_1 \quad \text{&} \quad H_2 = U_2 + PV_2$$

$$\Delta H = H_2 - H_1$$

$$\Delta H = U_2 + P_2 V_2 - U_1 - P_1 V_1$$

$$= U_2 - U_1 + P_2 V_2 - P_1 V_1$$

$$\Delta H = \Delta U + \Delta P \cdot V \quad \text{or} \quad \Delta H = \Delta U + \Delta P \cdot V$$

\* ENTROPY:

- Entropy may be defined as the property of a system which measure the degree of disorder or randomness in the system.
- It is denoted by 's'.
- It can be expressed as  $s = Q/T$ .
- Entropy is mainly associated with heat and temperature.
- Like total energy & enthalpy, 'H', entropy 's' is a state function.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

- A comparison of the entropies of the solid, liquid, gaseous states of a substance. The crystalline solid is highly ordered and has a very low entropy.



- The liquid has a higher entropy because it is less ordered, but all particles are still found at one end of the container.

- The gas has the highest entropy bcz the particles are randomly distributed throughout the entire container.

### \* GIBBS FREE ENERGY

"Gibbs free energy is a measure of the potential for reversible or maximum work that may be done by a system at constant temperature and pressure." It is a thermodynamic property that was defined in 1876 by Josiah Willard Gibbs to predict whether a process will occur spontaneously in the reverse direction at constant temperature and pressure.

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$$

-  $\Delta G < 0$ , The reaction is spontaneous in the forward direction.

-  $\Delta G > 0$ , The reaction is non-spontaneous as written. The reaction is spontaneous in the reverse direction.

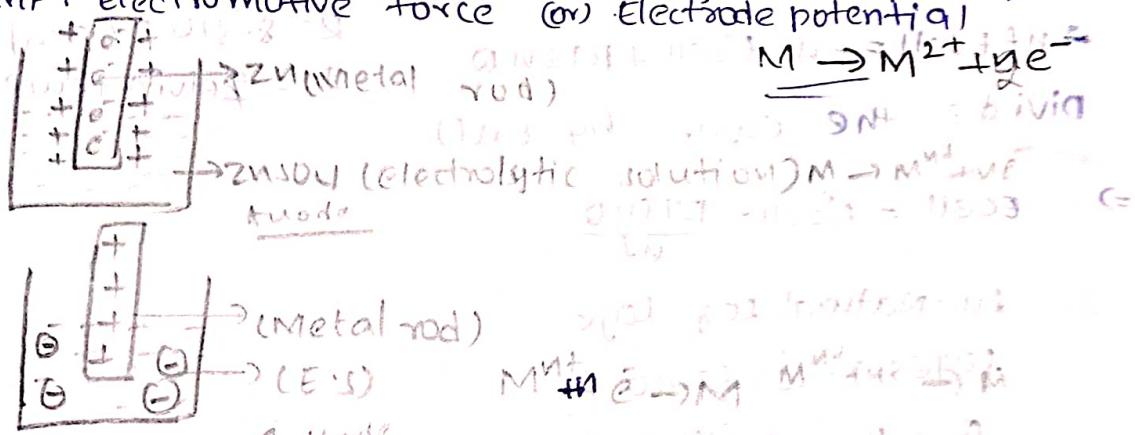
-  $\Delta G = 0$ , The reaction is at equilibrium.

$\Delta H$ ,  $\Delta S$  & sign of  $\Delta G$ ,  $\Delta G = \Delta H - T\Delta S$ .

sign of $\Delta H$	sign of $\Delta S$	sign of $\Delta G$	Type of Process
-ve	+ve	-ve	Spontaneous at all 'T'.
+ve	-ve	+ve	Non-spontaneous at all 'T'.
+ve	+ve	(-) cor (+)	Spontaneous if 'T' is high.
-ve	-ve	(+) cor (-)	Spontaneous if 'T' is low.

\* NERNST EQUATION → The Nernst Equation defines a relation between cell potential to standard potential and to the activities of the electrically active species.

EMF: Electromotive force (or) Electrode potential



The potential difference b/w the electrode (metal rod) and it's ions in electrolyte under equilibrium is called "electrode potential".

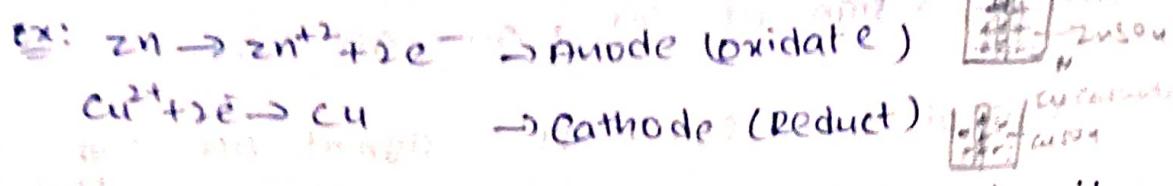
### \* EMF of Cell

At Non standard conditions  $\rightarrow T \neq 298, p \neq 1 \text{ atm}$ ,

At standard conditions  $\rightarrow T = 298, p = 1 \text{ atm} \& C = 1M$

$W = q \times V$ ,  $q = \text{charge of flow } e^- \text{ in the cell}$

$V = \text{Potential difference developed in the cell}$



- If  $n$  mole of  $\text{e}^-$  are flowing in the circuit  
then total charge;  $q = nt$

$$\Rightarrow V = \text{Voltage} = E_{\text{cell}}$$

$$W = nt E_{\text{cell}} \quad (W = V \times q)$$

$$W = -\Delta G_i$$

$$nt E_{\text{cell}} = -\Delta G_i$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$\text{- Charge on one mole e}^-$$

$$= 96500 \text{ C} = 1 \text{ F}$$

$$\rightarrow \Delta G_i = -nt E_{\text{cell}}$$

$$\Delta G_i^{\circ} = -nt E_{\text{cell}}^{\circ}$$

At standard conditions

Introduction of  $\Delta G$  equation from thermodynamics

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\Rightarrow nt E_{\text{cell}} = nt E_{\text{cell}}^{\circ} + RT \ln Q$$

Divide the eqn. by  $nt$ )

$$\left[ R = 8.314 \text{ J/Kcal} \right]$$

$T = \text{kelvin temp}$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT \ln Q}{nt}$$

$\ln = \text{Natural log} = \log_e$

$$\log_e = 2.303 \log_{10}$$

$Q = \text{Rxn coefficient}$

$$T = 298 \text{ K}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{8.314 \times 298 \times 2.303 \log_{10} Q}{10 \times 96500 \times n}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log_{10} Q$$

IDEAL GASES

Applications: It is frequently used to compute an electrochemical cell potential for any given pressure, reactant concentration & temperature.

IDEAL GAS EQUATION:

Boyle's law :  $V \propto \frac{1}{P}$  (at constant  $n \& T$ )

Charles' law :  $V \propto T$  (at constant  $n \& P$ )

Avagadro's law :  $V \propto n$  (at constant  $P \& T$ )

$$\frac{V = nRT}{P}$$

$\Rightarrow V = \text{constant} \times \frac{nRT}{P} = \frac{R^2 n T}{P}$

$$PV = nRT \quad (R^2 \text{ is the gas constant})$$

IDEAL GASES	REAL GASES
- Ideal gases obey all gas laws under all conditions of temperature and pressure.	- Real gases obey gas laws only at <u>low</u> pressures & <u>high</u> temperature.
- The volume occupied by the molecule is negligible as compared to the volume occupied by the gas.	- The volume occupied by the molecule is not negligible as compared to the total volume of the gas.
- The force of attraction among the molecules are negligible.	- The force of attraction are not negligible at all temperatures & pressures.
- obeys ideal gas equation $PV = nRT$ .	- obeys van der waals eqn. $(P + \frac{an^2}{V^2})(V - nb) = nRT$ .

→ To vanderwaals's correction either real gas equation fit a simple & universal one parameter that is applicable on

\* DERIVATION OF REAL GAS EQUATION - real gases called V.E.

→ volume correction: (b)

$v_{\text{gas}} = v_{\text{container}} \quad (\text{Ideal gas})$

$v_{\text{gas}} \neq v_{\text{container}} \quad (\text{Real gas})$

$$v_{\text{gas}} = v_{\text{container}} - v_{\text{molecule}} \quad (\text{a})$$

$$= v - b$$

For  $n$  moles,  $v_{\text{gas}} = v - nb \quad (\text{b})$



Significance: van der waals constant 'b': It is a measure of the effective size of the gas molecules. Its value is equal to four times the actual volume of the gas molecules. It is called "Excluded volume" or co-volume".

$$- b = 4 \text{N}_A \times \frac{4}{3} \pi r^3$$

$$\text{units} = \text{L} \cdot \text{mol}^{-1}$$

and gas does not follow the gas law perfectly.  
pressure correction: (a)

$$- P_{\text{gas}} = P_{\text{external}} [1 - \text{ideal-gas}]$$

$$- P_{\text{gas}} = P_{\text{external}} + P_{\text{internal}} [\text{real gas}]$$

$$- \text{conc. of 'A' type molecules} = \frac{n}{V}$$

$$- \text{conc. of 'B' type molecules} = \frac{n}{V}$$

$$- P_{\text{gas}} = P_{\text{ext}} + P_{\text{internal}} = P_{\text{ext}} + \frac{n^2}{V^2} \cdot a$$

$$P_{\text{gas}} \propto \frac{n^2}{V^2}$$

$$P_{\text{gas}} = \frac{an^2}{V^2}$$

Significance: van der waals constant 'a' is a measure of the magnitude of the attractive forces among the molecules of the gas.

. There would be large intermolecular forces of attraction if the value 'a' is large.

### ④ Critical Constants:

#### - Critical Temperature: ( $T_c$ )

It is the temperature above which a gas cannot be liquefied by applying pressure.

$$T_c = \frac{8a}{27Rb}$$

(i) Inert gases:  $T_c = 0^\circ\text{C}$

(ii)  $N_2: T_c = 128.2^\circ\text{K}$

CRITICAL PRESSURE ( $P_c$ ): It is the minimum pressure required to cause liquefaction at critical temperature,  $T_c$ .

$$P_c = \frac{a}{27b^2}$$

\* CRITICAL VOLUME ( $V_c$ ):

It is the volume occupied by one mole of a gas at  $T_c$  &  $P_c$ .

$$V_c = 3b$$

\* DERIVATION OF CRITICAL CONSTANTS:

- Consider van der waal's equation,

$$(P + \frac{a}{V^2})(V - b) = RT$$

- For one mole

$$(P + \frac{a}{V^2})(V - b) = RT \quad \text{--- (1)}$$

$$\Rightarrow PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0 \quad \text{--- (2)}$$

$$\textcircled{2} \times \frac{V^2}{P} \Rightarrow \frac{V^2}{P}[PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT] = 0$$

$$V^3 - V^2b + \frac{aV}{P} - \frac{ab}{P} - \frac{V^2RT}{P} = 0 \quad \text{--- (3)}$$

$$\Rightarrow V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \text{--- (4)}$$

- The above eqn. is an cubic equation of  $V$ , which can have three roots.

- At critical point all three values of  $V$  are equal to the critical volume  $V_c$ . i.e.,  $V = V_c$ .

$$V = V_c$$

$$V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$V^3 - V_c^3 - 3V^2V_c + 3VV_c^2 = 0 \quad \text{--- (5)}$$

Eq (4) & Eq (5) are identical, with

Comparing 'v' terms in ⑦ & ⑥

$\sqrt{2} \Rightarrow$

$$-3V_C V^2 = -\left(\frac{RT_C}{P_C} + b\right) V^2$$

$$3V_C = \frac{RT_C}{P_C} + b \quad \text{--- ⑦}$$

$$"v" \Rightarrow 3V_C^2 = \frac{a}{P_C} \quad \text{--- ⑧}$$

$$"c" \Rightarrow V_C^3 = \frac{ab}{P_C} \quad \text{--- ⑨}$$

Divide ⑨ by ⑦

$$\frac{V_C^3}{3V_C^2} = \frac{ab/P_C}{a/P_C}$$

$$V_C = 3b$$

$$⑦ \Rightarrow 3V_C^2 = \frac{a}{P_C}$$

$$P_C = \frac{a}{3V_C^2}$$

$$P_C = \frac{a}{27b^2}$$

$$T_C = \left(\frac{a}{P_C}\right)^{\frac{1}{2}}$$

$$⑦ \rightarrow T_C = (a - b)(\frac{a}{b})^{\frac{1}{2}}$$

$$a = \left\{ \left( 1 - \frac{b}{a} \right)^{\frac{1}{2}} \cdot \frac{a}{b} + ab - b^2 \right\}^{\frac{1}{2}} \cdot \left( 1 - \frac{b}{a} \right)^{\frac{1}{2}} \times ②$$

Substituting  $V_C$  &  $P_C$  in ⑥

$$⑥ \Rightarrow 3(3b) = \frac{RT_C}{q} + b \cdot \frac{dP}{q} = \frac{8b}{q} + 2b\sqrt{\left(\frac{a}{b} + d\right)} \cdot \frac{d}{\sqrt{b}}$$

$$3 \times 3b \times \frac{q}{27b^2} = RT_C + b \quad 9b - b = \frac{RT_C}{a/27b^2}$$

$$RT_C = \frac{a - b}{27b}$$

$$\frac{8a}{27b} = RT_C$$

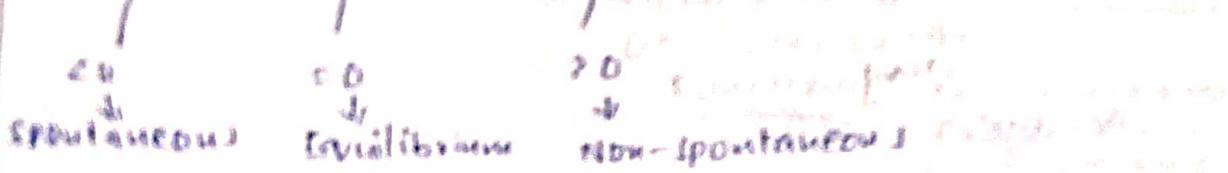
$$T_C = \frac{8a}{27Rb}$$

$$\therefore a = 3V_C^2 P_C$$

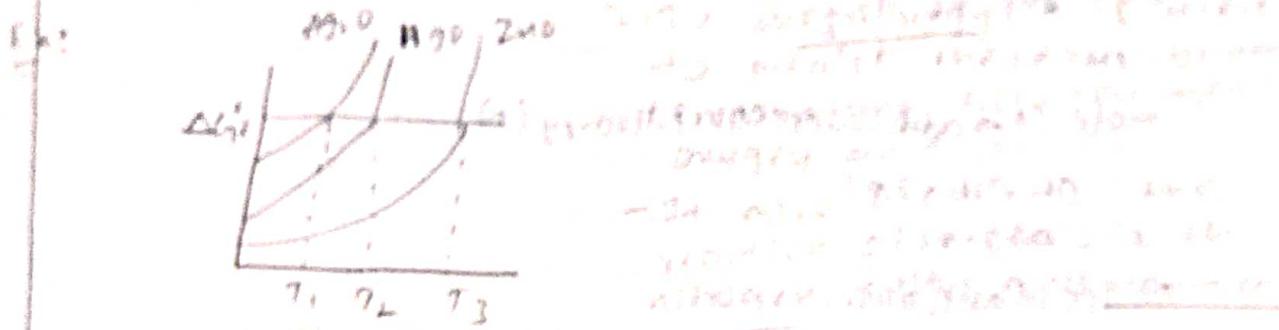
$$b = V_C/3 \quad //$$

## ELECTRODE POTENTIAL OF OXIDATION

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  For  $\Delta G^\circ < 0$ , reaction is spontaneous  
graph showing that  $\Delta G^\circ$  is different at different temperatures.

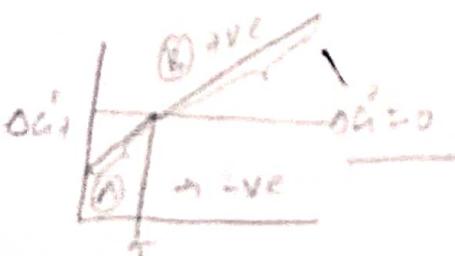


\* OGRVIT - To find the best reducing agent.



- $\text{Ag}_2\text{O} \xrightarrow{\Delta} \text{Ag} + \frac{1}{2}\text{O}_2(\text{g})$
- $\text{HgO} \xrightarrow{\Delta} \text{Hg} + \frac{1}{2}\text{O}_2(\text{g})$  { low temperature decomposes
- $\text{ZnO} \xrightarrow{\Delta} \text{Zn} + \frac{1}{2}\text{O}_2(\text{g})$  { high temperature decomposes.
- $\text{ZnO} + \text{C} \xrightarrow{\Delta} \text{Zn} + \text{CO}$

### \* METALLURGICAL APPLICATIONS



- A part:-



$\Delta E^\circ = -ve$

$\Rightarrow$  Spontaneous reaction



$\Delta E^\circ = +ve$

$\Rightarrow$  Non-spontaneous reaction.  $\Rightarrow$  Spontaneous reaction.

- B part:

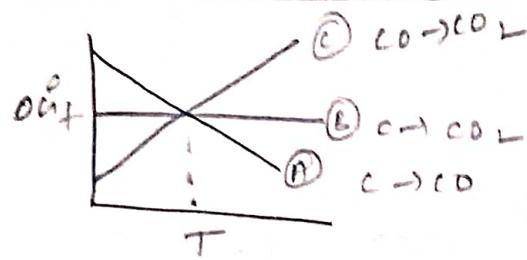


$\Delta E^\circ = +ve$

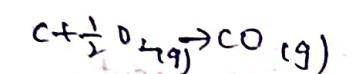
$\Rightarrow$  Non-spontaneous reaction.



$\Delta E^\circ = -ve$



\* At part A:  $C \rightarrow CO_2$



$$\Delta H^\circ_f = \Delta H^\circ_p - \Delta H^\circ_f = 1 - \frac{1}{2} = \frac{1}{2}$$

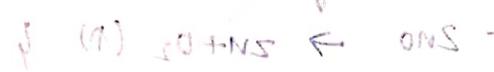
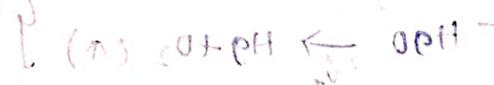
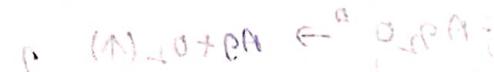
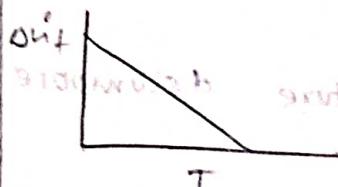
$\Delta S^\circ > 0$

∴ mole (↑) randomness ( $\Rightarrow$ ) Entropy ( $\uparrow$ )

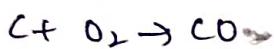
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Rightarrow \Delta G^\circ = -ve$$

$\Rightarrow$  spontaneous.



\* At part B:  $c \rightarrow CO_2$

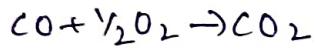


$$\Delta H^\circ_f = \Delta H^\circ_p - \Delta H^\circ_f = 1 - 1 = 0$$

$$\Rightarrow \Delta S^\circ = 0 \Rightarrow \Delta G^\circ = 0$$

$\Rightarrow$  Equilibrium reaction

\* At part C:



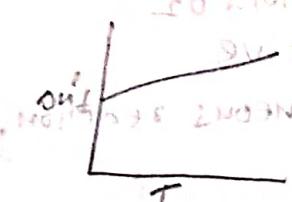
$$\Delta H^\circ_f = \Delta H^\circ_p - \Delta H^\circ_f = 1 - \frac{3}{2} = -\frac{1}{2}$$

- Moles ( $\downarrow$ )  $\Rightarrow$  randomness ( $\downarrow$ )  $\Rightarrow$  Entropy ( $\downarrow$ )

$$\Delta H^\circ_f = \Delta H^\circ_p - T\Delta S^\circ$$

$\Rightarrow \Delta G^\circ$  is  $+ve$ .

$\Rightarrow$  Non-spontaneous reaction.



## 4 PERIODIC PROPERTIES

The periodic table is a tabular arrangement of the chemical elements by increasing atomic number which displays the elements so that one may see trends in their properties.

### - TRIAD LAW:-

- Triad law was given by "Dobenier".
- Triad law states that "Arithmetic mean of the atomic masses of the first and third element in a triad would be approximately equal to atomic mass of the second element in that triad".

Ex: Lithium, Sodium, Potassium

- Calcium, Strontium, Barium.
- Chlorine, Bromine, Iodine.
- Iron, Cobalt, Nickel.

### - OCTAVE LAW:-

- It was given by Newland.
- If the chemical elements are arranged according to increasing atomic weight, those with similar physical and chemical properties occur after each interval of seven elements.

Ex: Potassium, lithium, sodium.

- Fluorine, chlorine.

### - Mandaleev's definition:-

- Periodic table is an arrangement of elements in an increasing atomic mass order in a tablet form.

### - Moseley Periodic table:-

- Periodic table is an arrangement of elements in an increasing order of atomic numbers.

- Elements present in the same group have similar properties.

- Modern law: The elements are arranged according to their "Electronic configuration":

↳ Elements arranged in a table showing MELT

Periodic table consists of periods and groups.

\* There are 7 periods.

\* First period:- (shortest period) - 2 elements

\* 2<sup>nd</sup> & 3<sup>rd</sup> " :- (short period) - 8 "

\* 4<sup>th</sup> & 5<sup>th</sup> " :- (Long period) - 18 " and 18 "

\* 6<sup>th</sup> " :- (Longest " ) - 32 "

\* 7<sup>th</sup> " :- (Incomplete " ) - Transuranium element

\* There are 18 groups.

\* There are 4 block elements.

\* s, p, d, f.

\* Classification of Elements in Blocks :-

- There are four blocks:-

i, s-block elements:-

The elements in which the last electron enters the outermost s-orbital.

- Group 1 & 2 elements of the modern periodic table are called s-block elements.

- Group-1, alkali metals of configuration  $ns^1$ .

- Group-2, alkaline earth metals of configuration  $ns^2$ .

ii, p-block elements :-

The elements in which the last electron enters outermost p-orbital.

- Groups 13 to 18 elements of the modern periodic table are called p-block elements.

- GROUP - 13 :- Boron family  $ns^2 np^1$
- " - 14 :- Carbon family  $ns^2 np^2$
- " - 15 :- Nitrogen family  $ns^2 np^3$
- " - 16 :- Oxygen family (Chalcogens)  $ns^2 np^4$
- " - 17 :- Fluorine family (Halogens)  $ns^2 np^5$
- " - 18 :- Neon family (Inert gases)  $ns^2 np^6$
- Configuration of p-block elements:  $ns^2 n'p^6$

#### iii) d-block elements :-

- Last electron enters into the outermost d-orbital.
- ~~Excluding~~ Groups from "3-12" are p-block elements.
- These are also called as "transition elements", as the atom has partially filled d-subshell.
- Configuration  $\rightarrow (n-1)d^{1-10} ns^{1-2}$

#### iv) f-block elements :-

- Last electron enters into the outermost f-orbital.
- These are also called as "inner transition metals", as they provide a transition in 6th & 7th row of periodic table, which separates s&p block elements.
- "4f" series  $\Rightarrow$  Lanthanides [57-71]
- "5f" series  $\Rightarrow$  Actinides [89-103]
- Configuration:  $(n-2)f^{1-14}(n-1)d^{0-1} ns^{1-2}$

#### \* ATOMIC RADIUS :-

Radius of the atom is the distance between the center of the nucleus and electron in the outer most orbit.

Four widely used definitions of atomic radius are It is also known as covalent radius, Ionic radius, Van der Waals radius, depending on the type of bond formed.



- Valence particle trend
- In a group, while moving from top to bottom it decreases/increases.
- It decreases from left to right across a period.

### IONIZATION ENERGY

Amount of energy required to remove an electron from isolated gaseous atom is called "Ionization Energy".



~~Electron + Na(g) → Na<sup>+</sup> + e<sup>-</sup>~~ Work required to remove one electron from the atom.

- In a group, while moving from top to bottom it decreases, i.e. valence and inner shell electrons decrease.
- It increases from left to right across a period.
- Factors effecting the IE are:

\* size of the atom

\* screening effect

\* effective nuclear charge

### ELECTRON AFFINITY

The energy released when an extra electron is taken up by neutral gaseous atom from an ion is called its "Electron affinity".

Electron + e<sup>-</sup> → energy

- units : ev/atom, kJ/mole.

negative values indicate that it is endothermic.

- In a group, while moving from top to bottom it decreases.

- It increases from left to right across a period.

## ELECTRONEGATIVITY:-

The tendency of a atom in a compound to attract pair of bonded electrons towards itself is known as Electronegativity.

- EA & EN both measure the electron attraction power but former (EA) refers to an isolated gaseous atom while the latter (EN) refers to an atom in a compound
- EA - attraction of single electron
- EN - attraction of pair of electrons/bonded electron
- In a group, EN decreases.
- In a period, EN Increases.
- Since EN is relative property, it has no units. It will be expressed in the following three scales.

## Mullikan's Scale :-

EN is the average value of IP & EA of a atom.

$$\boxed{EN = \frac{IP + EA}{2}}$$

## Aller-Rochow Scale :-

EN as the electrostatic force exerted by the nucleus on valence electron.

$$\boxed{X_A = \frac{0.395Z}{r^2} + 0.744}$$

- where, 'Z' is the effective nuclear charge and 'r' is the radius of atom in Å.

## Pauling Scale :-

- Excess bond energies

$$\boxed{X_A - X_B = 0.208 \sqrt{\Delta E}}$$

$\Delta E$  = Actual bond energy -  $\sqrt{E_A - A \times E_{B-B}}$

## \* Penetration of orbitals :-

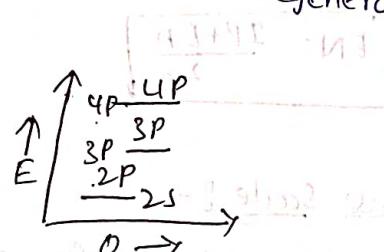
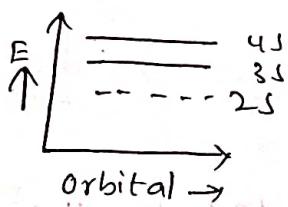
- Nodal point / plane separates one orbital from another.
- where node means zero probability of finding e<sup>-</sup>.
- penetration of orbitals is due to attraction of nucleus (only to orbitals close to nucleus), that increases shielding effect.

## \* Variation of energies on <sup>Si</sup> and <sup>Li</sup> orbitals :-

- The orbital energy is dependent upon the principle quantum number as well as azimuthal quantum number.
- The order of increase in energy along the various orbitals is stated as :-

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f.$$

degenerate orbitals.



- Single e<sup>-</sup> system

- degenerate orbitals

- Multi-e<sup>-</sup> system

- Non-degenerate orbitals.

- The lower value of ( $n\ell$ ) for an orbital, the lower is its energy.

- If ( $n\ell$ ) value is same for two orbitals, consider ' $\ell$ ' with highest value.

DORADIXATION STATE (ON) :- It is the total no. of electrons it appears to have gained (or) lost.

Atomic configuration :-  $ns^2 np^6$  (octet)  
 $ns^2 np^4 nd^{10}$  (electron shell)  
 $(n-1)^2 np^6 d^{10}, ns^2$  (the inert pair)

Ex :- Group 1B2 :  $ns1 n(2)$  +1,+2

Group 13  $\overset{o}{\circ}-(ns^2 np^1)$  +1,+3

Group 14  $\overset{o}{\circ}-(ns^2 np^4)$  +2,+4,-4

Group 15  $\overset{o}{\circ}-(ns^2 np^5)$  +3,+5

Group 16  $\overset{o}{\circ}-(ns^2 np^6)$  +6,+2,-2,+4

\* POLARIZABILITY :-

Polarizability is "a measure of how easily an electron cloud is distorted by an electric field. Typically the electron cloud will belong to an atom or molecule or ion. The electric field could be caused, for example, by an electrode or a nearby cation or anion."

- If an electron cloud is easy to distort then the species it belongs to is polarizable.

- Polarizability, which is measured by the Greek letter alpha( $\alpha$ ), is experimentally measured as the ratio of induced dipole moment  $p$  to the electric field  $E$ .

$$\boxed{\frac{p}{E}}$$

units :-  $\text{cm}^3/\text{V}$

## Factors that influence polarizability :-

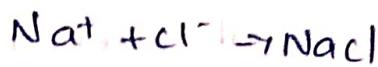
The relationship b/w polarizability and the factors of electron density, atomic radii, and molecular orientation is as follows:

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.
2. The greater the distance of  $e^-$  from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.
3. Molecular orientation with respect to an electric field can affect polarizability, except for molecules that are: tetrahedral, octahedral. This factor is more important for unsaturated molecules that contain areas of electron-dense regions, such as 2,4-hexadiene. Greatest polarizability in these molecules is achieved when the electric field is applied parallel to the molecule rather than perpendicular to the molecule.

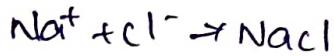
## BORN-HABER CYCLE :-

- The Born-Haber cycle is an approach to analyze reaction energies.
- Born Haber cycle helps to determine lattice enthalpy of ionic compound as well as  $e^-$  gain enthalpy of different elements.

## Lattice Energy = $LE^{\circ}$



- Amount of energy released when one mole of an ionic compound is formed from its gaseous cation and anion is lattice energy.



- Amount of energy is required to break one mole of ionic compound into its gaseous cation and anion.



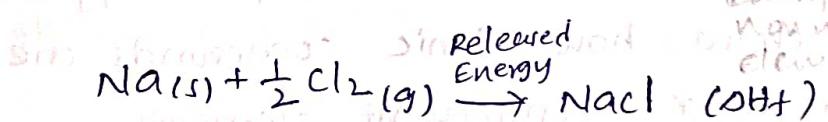
- Determination of lattice energy (Indirect method)

By Born-Haber Cycle:-

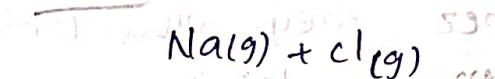
- Heat of formation  $\Delta H_f$  (Enthalpy of formation):-

Amount of heat released when one mole of compound is formed from its elements in pure and stable state is called "heat of formation".

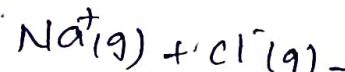
Ex<sup>o</sup>: NaCl



S.E



$\downarrow I.E(+)$  and  $\downarrow E.A(-)$



Step 2: Add the energy required to turn one atom of the element into its gaseous state, and then add the same for other element.

Step 3: Add the energy required to change a molecule into atoms.

Step 4: Add the I.E value and subtract the E.A value.

Step 5: Subtract the L.E value.

where, S.E  $\Rightarrow$  Sublimation energy

I.E  $\Rightarrow$  Ionisation energy

B.D.E  $\Rightarrow$  Bond dissociation energy

E.A  $\Rightarrow$  Electron affinity

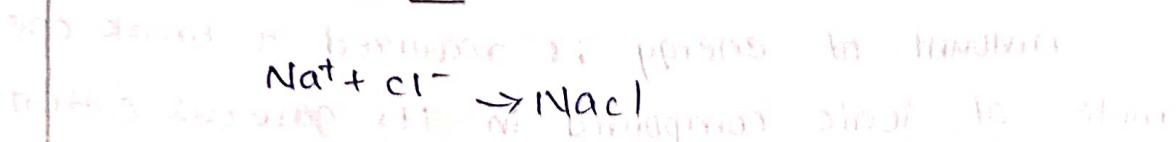
L.E  $\Rightarrow$  Lattice energy

Hess law: States that the overall change in energy in a process can be determined by breaking down into then adding the changes in energy at each stage if summation is equal when it is happened in one step (or) multiple steps.

$$\Delta H_f = S \cdot E + I \cdot E + B \cdot \frac{b}{2} E - E \cdot A - L \cdot E$$

Exothermic reaction

### \* Factors of L.E:



① charge,  $F = k \frac{q_1 q_2}{r^2}$

$L \cdot E \propto z^+$  [charge of ions]

② size :-  $L \cdot E \propto \frac{1}{\text{size}}$

$L \cdot E (\text{N}) \Rightarrow \text{size} (\text{N})$

Atomic size decreases with increasing

atomic number due to nuclear pull

\* Born-Haber cycle, definition:- Application:-

These cycles are simply energy/enthalpy cycles that show how ionic compounds are formed from their constituent elements.

They are useful bec they allow lattice enthalpies to be calculated theoretically using empirical data.

Properties with relation to Born-Haber cycle

→ Lattice enthalpy & B.H.C.

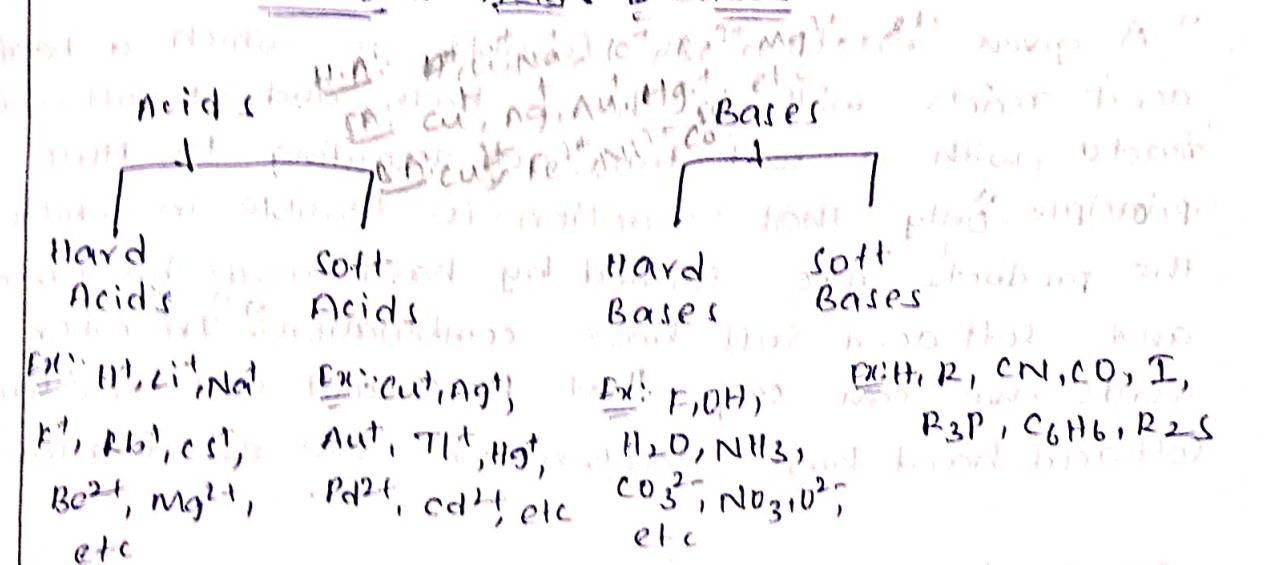
→ Born-Haber cycle & enthalpy of atomization

→ Born-Haber cycle & bond enthalpy

## Hard and soft Acids and Bases Theory :-

According to "Lewis", a base is an electron-pair donor and an acid is an electron-pair acceptor. They two combine to form an adduct.  $\text{A}+\text{B} \rightarrow \text{A}+\text{B}$

### Pearson's Acids & Bases



Border line Acids:  $\text{Fe}^{2+}, \text{CO}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+}, \text{SO}_2^{+}$ .

Border line Bases:  $\text{NO}_2^-, \text{SO}_3^{2-}, \text{N}_3^-, \text{Cl}^-, \text{C}_6\text{H}_5\text{N}, \text{SCN}^-$

### H-SAB Characteristics

#### - Hard Acid

- Small ionic radius
- High +ve charge
- Low electronegativity
- High energy LUMO
- Not easily oxidized.

#### - Hard Base

- Small radius
- High electronegativity
- weak polarizability
- High energy HOMO
- Not easily oxidized.

#### - Soft Acid

- Large ionic radius
- Low +ve charge
- Intermediate electronegativity
- Low energy LUMO
- Easily oxidised.

#### - Soft Base

- Large radius
- intermediate electronegativity
- high polarizability
- Low energy HOMO
- Easily oxidized.

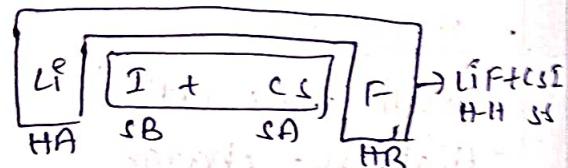
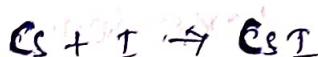
## Pearson's HSAB Principle :-

In 1963 Pearson proposed a rule for predicting the feasibility of a given reaction. This rule states:

"A given reaction is feasible in which a hard acid reacts with a hard base and a soft acid reacts with a soft base"; i.e., according to HSAB principle, "Only that reaction is feasible in which the products are formed by hard acids-hard base and soft acid-soft base combinations." In other words, we can say that hard acid-soft base (or) soft acid-hard base combinations are not feasible."

### Illustrative Examples :-

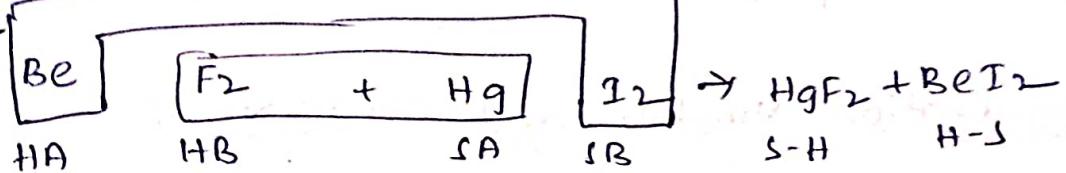
i) The following reaction is feasible, since a hard acid (Li<sup>+</sup>) combines with a hard base (F<sup>-</sup>) and a soft acid (Cs<sup>+</sup>) combines with a soft base (I<sup>-</sup>) to form LiF and CsI respectively.



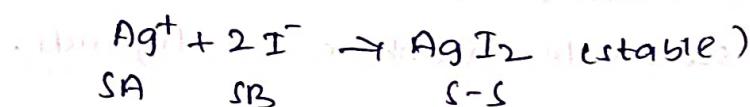
The reaction given above is feasible since the products (LiF & CsI), formed are HA-HB & SA-SB combinations.

### Non-Feasible Reaction:-

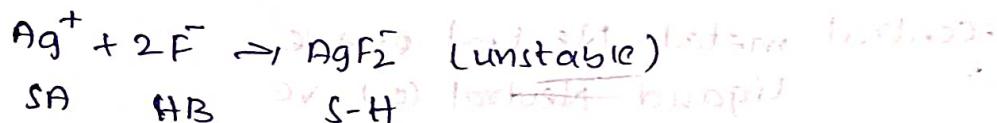
ii) The following is not feasible, since the products HgF<sub>2</sub> and BeI<sub>2</sub> (formed are SA-HB (Hg<sup>2+</sup>) - HB(F<sup>-</sup>)) and HA(Be<sup>2+</sup>) - SB(I<sup>-</sup>) combinations.



(iii) The following reaction is feasible.



(iv) The following reaction is not feasible.



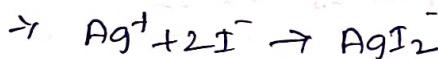
### Applications of Hard / Soft theory :-

1. Stability of a complex -

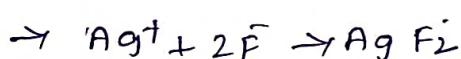
A complex would be more stable if metal & ligand, both are hard (or) soft.

Ex:-  $\text{AgI}_2$  is stable but  $\text{AgF}_2$  is not.

$\text{AgI}_2$  is stable.



• SA & SB [stable] complex

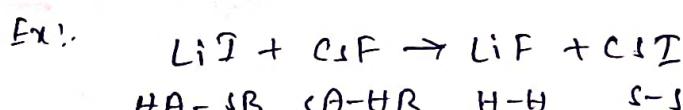


• SA & HB unstable

Lewis definition  
Polarisability  
characteristics  
Polaris H-S-H theory  
Enthalpies  
Application LST

2. Feasibility of a reaction :-

A reaction is feasible if the product follows H-S-A-B rule, like combinations.



3. Prediction of Hardness and softness of Acid-base

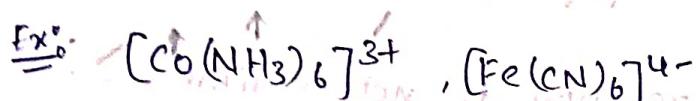
4. Order of stability of hydrogen halides.

5. Sequence of metals in nature.

## 6. Positioning of metal crystals.

### \* Coordination Number and geometries:-

- Complex ion: It is a +vely (or) -ve ly charged species which contains a central metallic atom surrounded by suitable number of ligands.



→ Central metal - Neutral (or) +ve

→ Ligand - Neutral (or) -ve

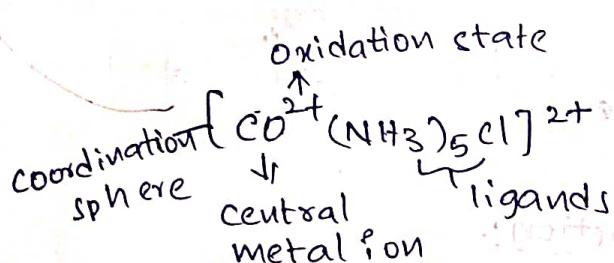
### \* Coordination Number (CN) of the central Metal:-

Number of atoms of the ligand which are directly attached with the metal atom (or) ion in coordination sphere is called CN.

Number of coordination bonds (or) sigma bonds are formed between the central atom (or) ion is CN.

Ex:- CN of  $\text{Ag}^+$  ion in  $[\text{Ag}(\text{CN})_2]^-$  is 2.

- CN of  $\text{Cr}^{3+}$  ion in  $[\text{Cr}(\text{en})_3]^{3-}$  is 6.

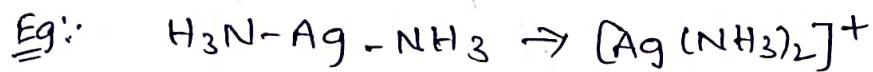


→ CN of  $\text{Co}^{2+}$  is 6.

Geometry: The ligands present in a complex adopt definite geometry around the central metal atom. Geometry adopted by the ligands is the geometry (stereochemistry) of the complex compound.

- complex with C.N = 2
  - 1. Linear geometry
  - 2. Bent geometry.

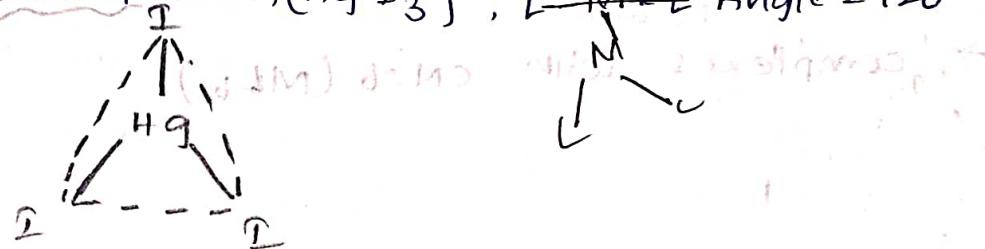
→ Linear structure -  $ML_2 \rightarrow L-M-L$



$$[L-M-L] \text{ Angle} = 180^\circ$$

- complexes with C.N = 3 [ML<sub>3</sub> Type]

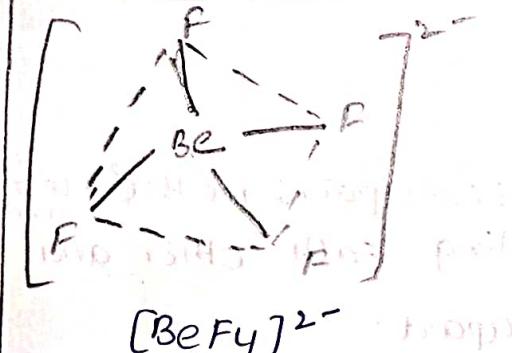
Eg: Trigonal planar,  $[HgI_3]^-$ ,  $L-M-L$  Angle =  $120^\circ$



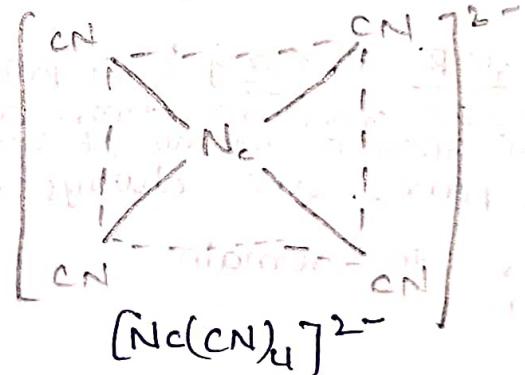
- complexes with C.N = 4 [ML<sub>4</sub> type]

- Two types of geometry 1. Tetrahedral -  $90^\circ$   
2. Square planar. -  $90^\circ$

### Tetrahedral

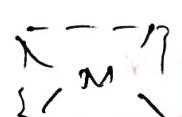


### Square planar



Angle:  $109^\circ$

Angle:  $90^\circ$

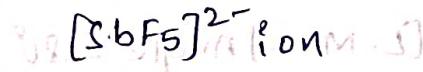
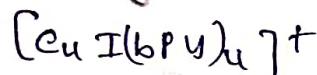
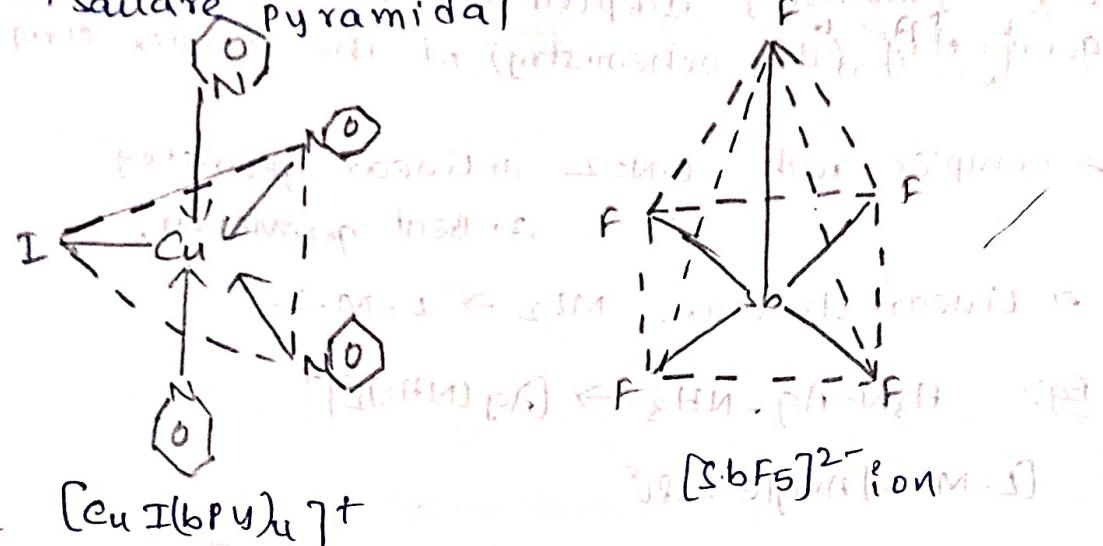


$$90^\circ + 90^\circ < 109^\circ + 109^\circ < 180^\circ$$

→ Complexes with  $C:N = 5$  ( $M_{15}$ )

1. Trigonal bipyramidal

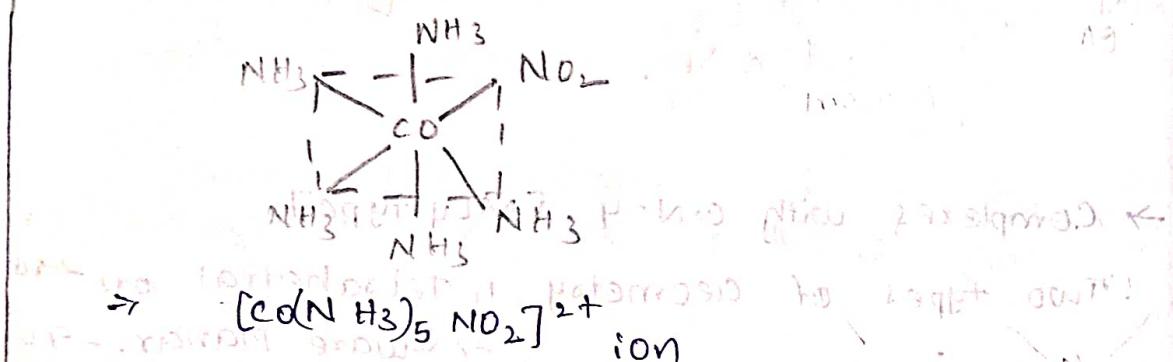
2. Square pyramidal



→ Trigonal bipyramidal & square pyramidal

→ Angle:  $90^\circ$  &  $120^\circ$ ,  $\{sp^3d\}$ ,  $\{sp^3d^2\}$

→ complexes with  $C:N = 6$  ( $M_{16}^6$ )



→ Octahedral structure.

→ Angle:  $90^\circ$  &  $180^\circ$

V.S.E.P.R Theory → It predicts

molecular structures from an examination of the no. of bonds & Lewis pairs in their Lewis structure

→ e<sup>-</sup> pairs are always repelling each other and tries to remain apart.

2. Different e<sup>-</sup> pair have different order of repulsion.

— Bond pair      ○ Lone pair.

$$L.P - L.P > L.P - B.P > B.P - B.P$$

- g. If lone pair is zero then geometry is the shape of the molecule.  
or else geometry  $\neq$  shape.

Ex: Methane - Geometry - Tetrahedral  
shape - Tetrahedral  $b_{L.P=0}$

4. Geometry depends on  $(B.P + L.P) = Z$ .

$Z = \frac{1}{2} (\text{no. of valence e}^- \text{ on central atom} + (-\text{ve charge}) + \text{no. of monovalent } - (+\text{ve charge}))$

$Z=2$   $\Rightarrow$  linear

$Z=3$  - Trigonal planar

$Z=4$  - Tetrahedral, Square planar

$Z=5$  - Trigonal bipyramidal, Square pyramidal

$Z=6$  - Octahedral

5. Shape depends on surrounding atoms (B.p only)

- shape = geometry if  $L.P = 0$

- shape  $\neq$  geometry if there is L.P

### Postulates

- The total number of valence shell electron pairs of each atom in a molecule decides the shape of the molecule.

$Z$	B.P	L.P	Geometry	shape	Hybridization
2	2	0	$-A-$	Linear	$sp$
2	1	1	$\text{O}-A-B$	$\text{V}$	$sp$
3	3	0	$\begin{array}{c} A \\   \\ \text{O} \end{array}$	$\angle 120^\circ$	$sp^2$
				Trigonal planar	sp <sup>2</sup>
3	2	1	$\begin{array}{c} A \\   \\ \text{O} \\   \\ B \end{array}$	$\angle >120^\circ$ $\angle <120^\circ$	$sp^2$
3	1	2	$\begin{array}{cc} A & \\   & \\ \text{O} & \\   & \\ B \end{array}$	$\angle <120^\circ$ $\angle >120^\circ$	$sp^2$
				Bent - angular	
				A $\ominus$ O	linear

4	4	0	$\text{A}^4$	$109^\circ.28'$	Tetrahedral	$\text{sp}^3$
4	3	1	$\text{A}_1^3 \text{B}^1$	$109^\circ.28'$	Pyramidal	$\text{sp}^3$
4	2	2	$\text{A}_1^2 \text{B}_2^2$	$109^\circ.28'$	Bentangular	$\text{sp}^3$
5	5	0	$\text{A}^5$	$90^\circ$ , $120^\circ$	Trigonal bipyramidal	$\text{sp}^3\text{d}$
5	4	1	$\text{A}_1^4 \text{B}^1$	$90^\circ$ , $120^\circ$	Axial position equatorial position	$\text{sp}^3\text{d}$
5	3	2	$\text{A}_1^3 \text{B}_2^2$	$90^\circ$ , $120^\circ$	Saw	$\text{sp}^3\text{d}$
5	2	3	$\text{A}_1^2 \text{B}_3^3$	$90^\circ$ , $120^\circ$	T-shape	$\text{sp}^3\text{d}$

	5	2	3	7	6	0	6	5	1	6	5	1	6	5	1
5	linear	sp <sup>2</sup> d <sup>2</sup>	sp <sup>3</sup> d <sup>2</sup>	square pyramidal	octahedral	square pyramidal	sp <sup>3</sup> d <sup>2</sup>								
2	linear	sp <sup>2</sup> d <sup>2</sup>	sp <sup>3</sup> d <sup>2</sup>	square pyramidal	octahedral	square pyramidal	sp <sup>3</sup> d <sup>2</sup>								
3	sp <sup>2</sup> d <sup>2</sup>	sp <sup>3</sup> d <sup>2</sup>													
7	sp <sup>3</sup> d <sup>2</sup>														
6	sp <sup>3</sup> d <sup>2</sup>														
0	sp <sup>3</sup> d <sup>2</sup>														
6	sp <sup>3</sup> d <sup>2</sup>														
5	sp <sup>3</sup> d <sup>2</sup>														

1. tetrahedral  
2. trigonal bipyramidal  
3. octahedral

1. trigonal bipyramidal  
2. octahedral

1. trigonal bipyramidal  
2. octahedral

## IONIC COMPOUND:

- Definition: Ionic compound is a chemical compound of ions held together by electrostatic forces termed ionic bonding. The compound is neutral overall, but consists of +vely charged ions called "cations" and -vely charged ions called "anions".

These can be simple ions such as the sodium ( $\text{Na}^+$ ) and chloride ( $\text{Cl}^-$ ) in sodium chloride, or polyatomic species such as the ammonium ( $\text{NH}_4^+$ ) & carbonate ( $\text{CO}_3^{2-}$ ).

An ionic bond is formed when there is a large electronegativity difference b/w the elements participating in the bond. The greater the difference, the stronger the attraction b/w the +ve ion & -ve ion.

### Characteristics of ionic bond:

- Three dimensional structure called an "ionic lattice".
- Soluble in water.
- High melting point & boiling point bcz a large amount of energy is required to break the electrostatic forces holding the lattice together
- They are compounds formed from metals and non-metals.
- In a solid state they do not conduct electricity, However, in a liquid state or when dissolved in water, they will conduct electricity well, bcz the ions are free to move.
- They contrast to the characteristics of a covalent bond.

## \* COVALENT COMPOUND :-

- Definition: A covalent compound is formed by equal sharing of electrons from both the participating atoms. The pair of electrons participating in this type of bonding is called "shared pair" (or) bonding pair and such type of compounds are called "covalent compounds". The covalent bonds are also termed as molecular bonds. Sharing of bonding pairs will ensure that the atoms achieve stability in their outer shell which is similar to the atoms of noble gases.

### CHARACTERISTICS:-

- Most covalent compounds have relatively low melting points and boiling points.
- Covalent compounds usually have lower enthalpies of fusion and vaporization than ionic compounds.
- Covalent compounds tend to be more flammable than ionic compounds.
- When dissolved in water, they don't conduct electricity.

### \* DIFFERENCES BLW IONIC AND COVALENT BOND

Highly Covalent Bonds & less Ionic Bonds :-

- A covalent bond is formed b/w two similar electronegative non-metals.
- This type of bond is formed b/w a metal & non-metal.

- Bonds formed from covalent bonding have a definite shape.
- Ionic Bonds have no definite shape.

- Low melting point & Boiling point.

- High melting point & Boiling point.

- Low polarity and more flammable.

- High polarity and less flammable.

\* Covalent bonds are in liquid (or) gaseous state at room temperature.

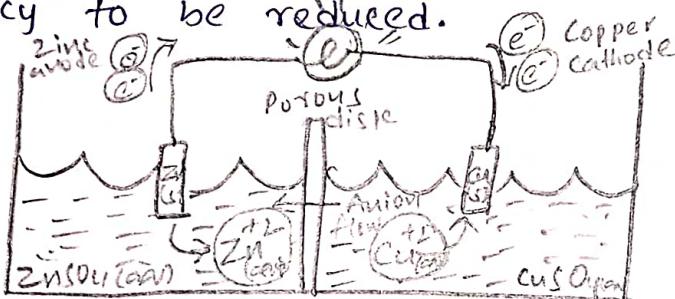
- At room temperature, ionic bonds have solid state.

Ex:- Methane, HCl

Ex:- NaCl, Sulfuric acid.

### \* REDUCTION POTENTIAL

It is a measure of the tendency of a chemical species to acquire electrons and thereby reduced. Reduction potential is measured in volts(v), (or) millivolts(mv). Each species has its own intrinsic reduction potential, the more positive the potential, the greater the species affinity for electrons and tendency to be reduced.



#### Applications

1. Reduction potential measures the intrinsic tendency for a species to undergo reduction, comparing standard reduction potential for two processes can be useful for determining how a reaction will proceed.
2. In field of Biochemistry: Enzymatic reactions.
3. In the field of environmental chemistry, the reduction potential is used to determine, if oxidizing or reducing conditions are prevalent in water or soil and to predict the states of different chemical species in the water.
4. To check the water quality.

## UNIT-5

\* Isomerism: It is a phenomenon where two (or more) compounds have the same chemical formula but different structural formulas, that is, different properties. This is mainly bcz of different structural (or) spatial arrangements. Isomers are the compounds exhibiting isomerism.

→ Types of Isomerism:

Basically, there are two types. They are:

1. Structural Isomerism.
2. Stereo Isomerism.

However, these are again of many subtypes as shown in the figure.

\* STRUCTURAL ISOMERISM: Isomers are structural isomers when they have same molecular formula but different structures, as in how they are linked to each other. Structural isomerism is further of the following types:

① Chain Isomerism: Isomers are chain isomers when two (or) more compounds have the same molecular formula but differ in the branching of carbon atoms. For example we can represent  $C_5H_{12}$  as three compounds:  $CH_3CH_2CH_2CH_2CH_3$ -pentane [or  $CH_3-CH_2-CH_2-CH_2-CH_3$ ]

② POSITION ISOMERISM: Isomers are position isomers when the two (or) more compounds differ in the position of the functional group (or) substituent atoms. For example, we can represent  $C_3H_7OH$  in two arrangements:  $CH_3-CH_2-CH_2OH \rightarrow$  propan-1-ol.

③ FUNCTIONAL ISOMERISM: Isomers are functional isomers when the two or more compounds have an identical molecular formula but differ in the functional group present. These isomers are the

functional isomers. For example, we can represent

$C_3H_6O$  as a "ketone" and as an "aldehyde".

④ METAMERISM: This is exhibited by compounds due to presence of "different alkyl chains on either side of the functional group. For example, we can represent  $C_4H_10O$  as "ethoxyethane" ( $C_2H_5OC_2H_5$ ) and "methoxy propane": ( $CH_3OC_3H_7$ )

⑤ TAUTOMERISM: Tautomerism is a special type of structural isomerism where the "isomers stay in dynamic equilibrium" with each other by simple proton transfer in an intramolecular fashion.

Ex: 2-butanone  
keto-form

2-butanol.  
enol-form.

### STEREOISOMERISM

Stereoisomerism is a phenomenon in which compounds have the same molecular formula but differ in the relative positioning (or orientation of atoms) in space! Stereoisomers are the compounds exhibiting stereoisomerism. We can further classify stereoisomerism into:

#### Stereo Isomerism

##### Conformational Isomerism

##### Configurational Isomerism

##### Geometrical Isomerism

##### Optical Isomerism

##### Enantiomers

##### Diastereomers

## \* Conformational Isomerism:-

Isomers which differs in the conformation are known as "conformational isomers" and the phenomenon is called conformational Isomerism.

Ex:- Alkanes, Cyclo alkanes.

- Rapidly interconverted at room temperature, not separable.
- Due to free rotation about c-c single bond.

\* Configurational Isomerism :- Differ in the configuration arrangement of substituents around central atom).

- Restricted rotation either due to =bond or cyclic structure, presence of chirality of molecule.
- Not readily interconverted at room temperature, separated.
- eis,trans isomers and optical isomers (chirality center)

## \* Configurational Isomers:-

- Two systems has been developed for the studying the configuration of organic compounds.

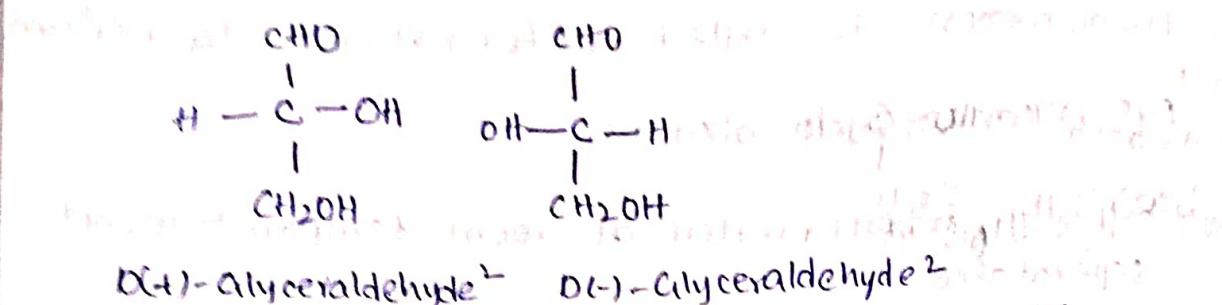
\* Relative configuration (D,L-Nomenclature)

\* Absolute configuration (R & S system of configuration)

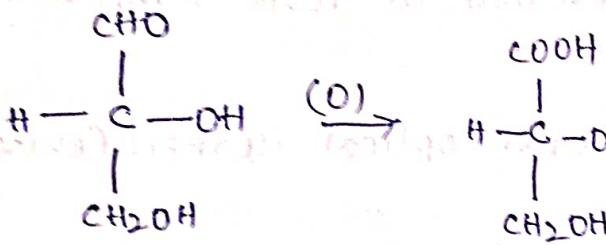
Relative configuration:(D,L-Nomenclature)

configuration of the compounds were studied with respect to glyceraldehyde, configuration of which was taken as an arbitrary standards (+)-glyceraldehyde having 'OH group on the right side and 'H' on the left side, CHO and CH<sub>2</sub>OH group being at Top & bottom respectively.

- Arbitrary configuration has been assigned as D<sub>+</sub> and minor image of compound is (-)-glyceraldehyde.



Any compound that can be prepared from, or converted into D(+)-glyceraldehyde will belong to the D-series, and similarly any compound that can be prepared from, or converted into L(-)-glyceraldehyde will belong to the L-series (relative configuration). For example "D-glyceraldehyde" can be converted to "glyceric acid" by simple oxidation and thus the configuration of glyceric acid obtained must be D.



D(+)-Glyceraldehyde

D(+)-~~Glyceraldehyde~~ glyceric acid.

\* Absolute configuration in R & S system of configuration.

To overcome the defect in D,L system like configuration of the same molecule may be related to D & L series. Moreover it is difficult to apply to molecule having complicated structure and compound having more than one asymmetric carbon atoms.

- Absolute configuration in stereochemistry is the arrangement of atoms (or) group of atoms that is described independently of any other atom (or) group of atoms in the molecule.

Cahn-Ingold and Prelog (1956, 1964) proposed rules based on the actual three-dimensional formula.

### SEQUENCE RULE

This system of assigning configuration involves the following steps:

Step-I: The four atoms or groups attached to the asymmetric or chiral carbon atom are assigned a sequence of priorities in accordance with a set of rules known as "sequence rules".

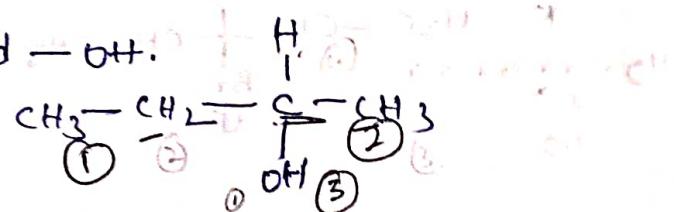
→ Sequence rule-1: In case all the four atoms directly attached to the chiral carbon atom are different from one another, sequence of priorities is determined by their "atomic numbers".

The atom of highest atomic number gets the highest priority while the atom having the lowest atomic number is given the least order of priority. Thus, the sequence of priority of the four atoms in bromochloroiodo methane ( $\text{BrCHClI}$ ) is:

"I-Br-Cl-H."

In case of the asymmetric centre I has two isotopic atoms, such as deuterium ( $\text{D}$ ) and hydrogen ( $\text{H}$ ). the "isotopes of higher H mass number gets higher priority".

→ Sequence rule-2: If two (or) more atoms directly attached to the asymmetric carbon atom have the same atomic number, the priority may be determined by comparing the next atom in the group. If even this does not solve the problem, the comparison is extended to next atom and soon. Let us consider the case of "sec-butyl alcohol" in which the four atoms (or) groups attached to the chiral centre are



→ Sequence rule: is a doubly or triply bonded atom 'X' is equivalent to two or three such atoms. Thus, if we compare the priority order of  $\text{—CH}_2\text{OH}$  and  $\text{—CH}_2\text{OHH}$ , the former (having C, O, OH) gets higher priority order than the  $\text{—CH}_2\text{OHH}$  (C, O, H, H) since the third atom in  $\text{—CHO}$  is 'O' while it is 'H' in  $\text{—CH}_2\text{OHH}$ .

→ Determination of priority between  $\text{—CH}=\text{CH}_2$  &  $\text{—CH}(\text{CH}_3)$

\* Step-II: After assigning the priorities to the four groups (or) atoms attached to the asymmetric (or) chiral carbon, the molecule is imagined to be in the position where the atom (or) group of lowest priority is directed away from the eye (or) it is brought in the vertical position in Fischer-projection formula.

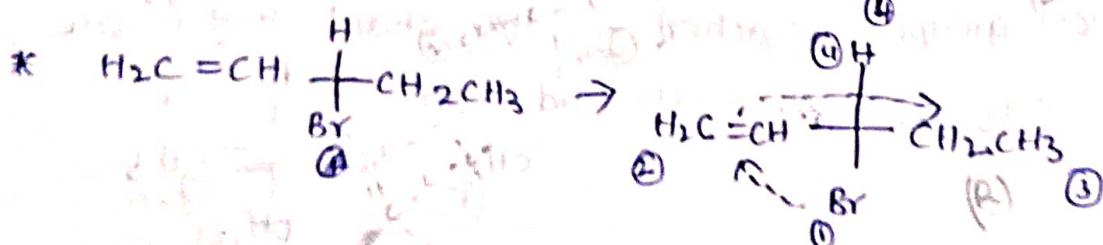
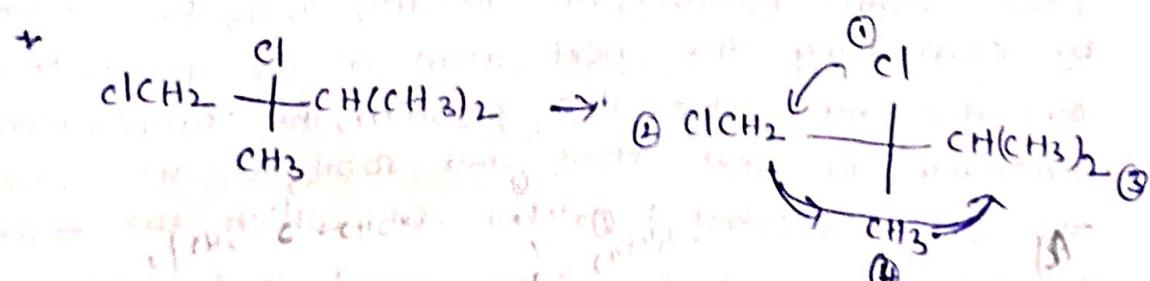
Now the arrangement of the remaining three groups is viewed in decreasing order of the priorities.

- In looking so, if the eye travels in the clockwise direction, the configuration is specified as 'R'.

- However, in looking so, if the eye moves in the anticlockwise direction, the configuration is specified as 'S'.

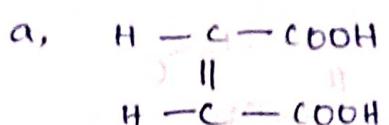
The following examples illustrate the above procedure of specifying R & S configuration to compounds containing an asymmetric (or) chiral carbon atom.

Illustration: Designate R (or) S configuration to the

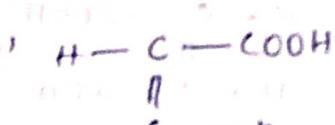


## Geometrical Isomerism :-

The isomers which posses the same structural formula but differ in the spatial arrangement of the groups around the double bond are known as geometrical isomers and the phenomenon is known as "Geometrical Isomerism". The isomerism is shown by alkenes (or) their derivatives. When the similar groups lies on the same side, it is the "cis-isomer", while when similar groups lie on the opposite sides, the isomer is "trans". For example:

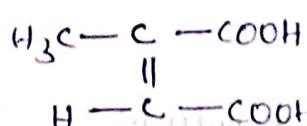


Maleic acid (cis)

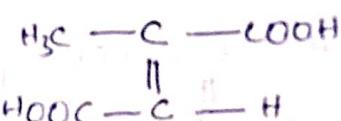


Fumaric acid (trans)

b,

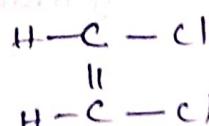


Citraconic acid (cis)

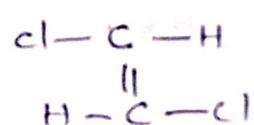


Mesaconic acid (trans)

c,

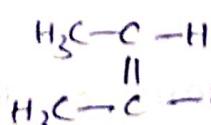


cis-1,2-Dichloroethylene



trans-1,2-Dichloroethylene

d,

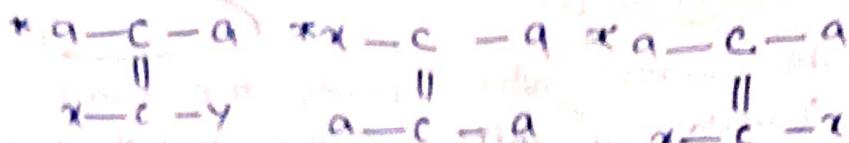


cis-Butene-2



trans-Butene-2

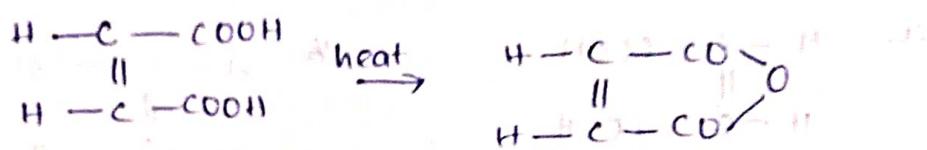
- Remember that geometrical isomerism is possible only when each of the doubly bonded carbon atom has two different groups. Thus the following type compounds will not show geometrical isomerism.



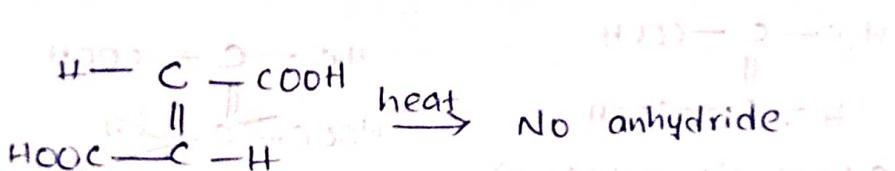
### Distinction between cis and trans-isomers:

#### ① "By cyclization method":

- Generally, the cis-isomer cyclizes on heating to form the corresponding anhydride while the trans-isomer does not form its anhydride at all.



- Note that the two reacting groups ( $-\text{COOH}$ ) are near to each other.

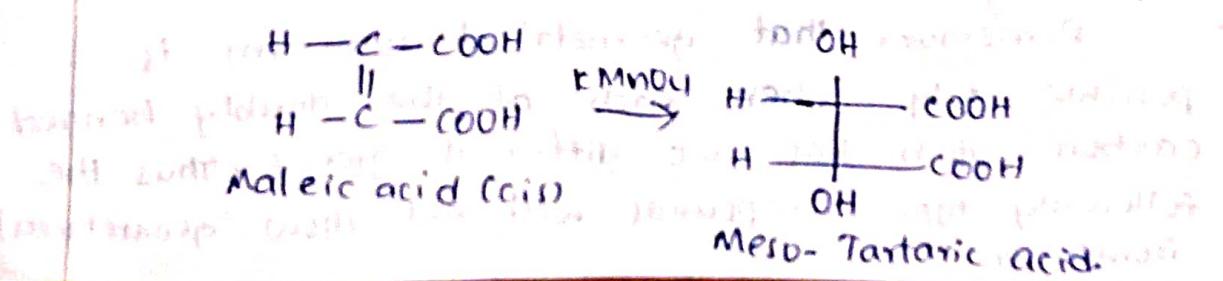


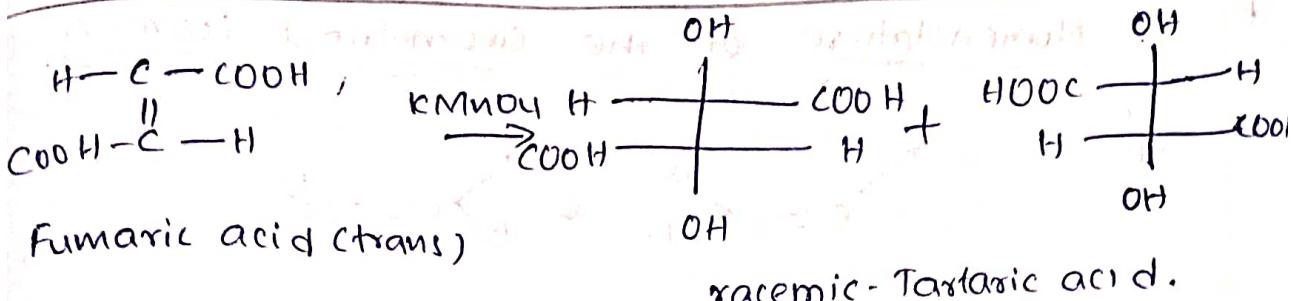
- Note that the two reacting groups ( $-\text{COOH}$ ) are quite apart from each other, hence cyclisation is not possible.

#### ② By Hydroxylation:

(Oxidation by means of  $\text{KMnO}_4, \text{OsO}_4$  or  $\text{H}_2\text{O}_2$  in presence of  $\text{OsO}_4$ ).

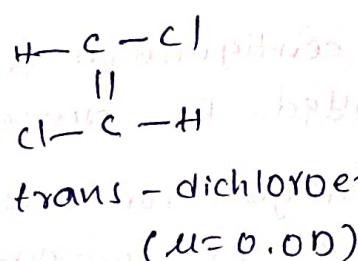
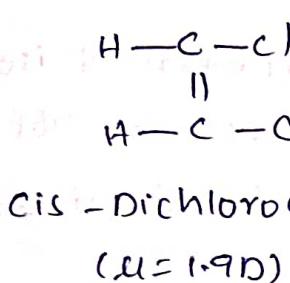
- Oxidation of alkenes by means of these reagents proceeds in the cis-manner. Thus, the two geometrical isomers of an alkene leads to different products by these reagents. For example:





③ By ~~measuring~~ studying their dipole moments :-

The cis-isomer of a symmetrical alkene has a definite dipole moment, while the trans-isomer has either zero dipole moment or less dipole moment than cis-isomer, for example, 1,2-dichloroethylene and butene-2.



④ By studying their physical properties ?-

a, the cis-isomer of a compound has higher boiling point due to higher polarity, higher density and higher refractive index than the corresponding trans-isomer. (Auwers-Skita rule).

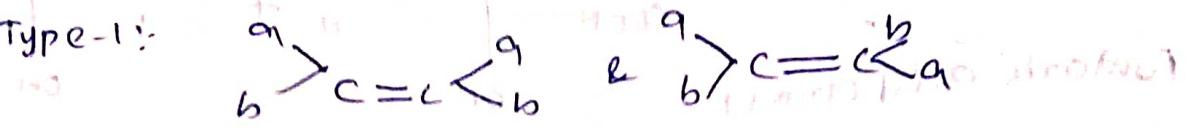
b, The trans-isomer has higher melting point than the cis-isomer due to its symmetrical nature and more close packing of the trans-isomer.

when a compound contains 'n' number of dissimilarly substituted double bonds, the number of geometrical isomers is  $2^n$ . e.g.

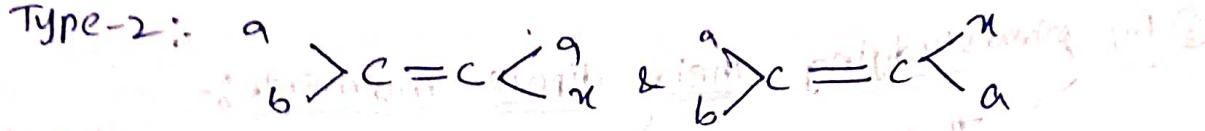
In case, the double bond is identically substituted as in  $\text{XCH}=\text{CH}-\text{CH}=\text{CHX}$ , then the number of geometrical isomers is  $2^{n-1} + 2^{\lfloor \frac{n}{2} \rfloor - 1}$ , when 'n' is even and  $2^{n-1} + 2^{\lfloor \frac{n}{2} \rfloor - 1/2}$ , when 'n' is odd.

## EZ Nomenclature of the Geometrical Isomers

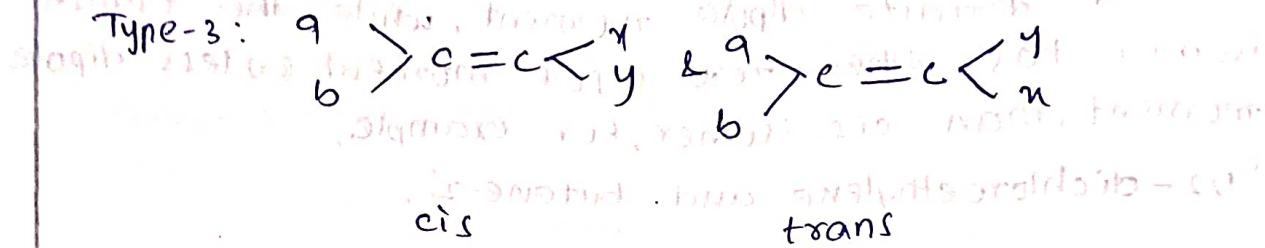
Type-1:



Type-2:



Type-3:



- The configuration assigned for geometrical isomers is called EZ nomenclature - developed in 1968.

- EZ configuration has been written based on the rules of RS configuration.

Sec-I: Assigning of priority order of the two groups attached to each doubly bonded carbon.

a) Based on atomic No, Mass No

b) Comparing the next atom in the group

(C, O, S, Cl, Br, F, H, N, P, As, Sb, Bi, I, At)

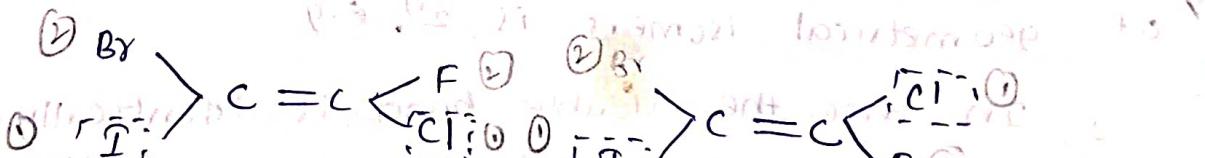
c) A double or triply bonded atoms

(C, O, S, Cl, Br, F, H, N, P, As, Sb, Bi, I, At)

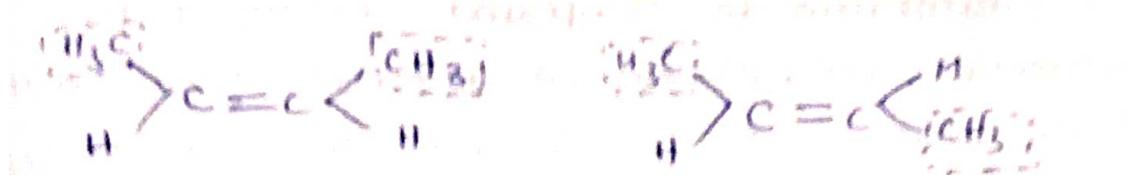
Sec-II: Higher priority on each carbon atom are on the same side of the double bond assigned as Z (zusammen-together).

- Higher priority on each carbon atom are on the opposite side of the double bond assigned as E (Entgegen-against).

② By

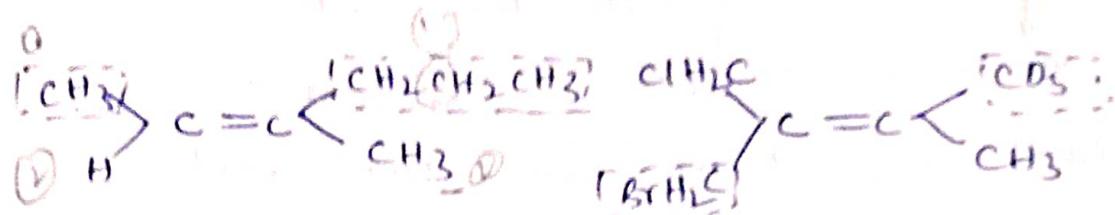


① By  $\text{I}^-$  >  $\text{Br}^-$  >  $\text{Cl}^-$  >  $\text{F}^-$  >  $\text{H}^-$  >  $\text{D}^-$  >  $\text{T}^-$  >  $\text{P}^-$  >  $\text{S}^-$  >  $\text{N}^-$  >  $\text{C}^-$  >  $\text{O}^-$  >  $\text{F}^-$  >  $\text{Cl}^-$  >  $\text{Br}^-$  >  $\text{I}^-$



2-2 Butene

E-2 Butene

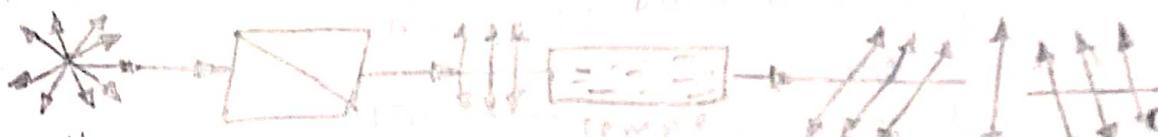


Z-isomer

E-isomer

### Optical isomerism

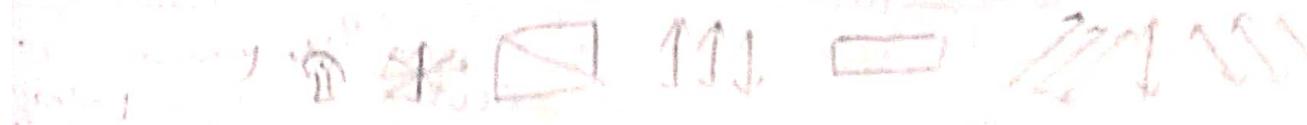
Optical isomerism :- Optical isomers have the ability to rotate PPL which the compound which is having same molecular formula, same structural formula and same physical and chemical properties but differ in their behaviour towards light (PPL) is called optical isomers. And the phenomena is known as optical isomerism and is related with PPL (Plane Polarized Light).



In all directions Nicol prism is optically inactive compounds. When a beam of PPL is passed through a sample solution, if it is unaffected, PPL, optically inactive compound.

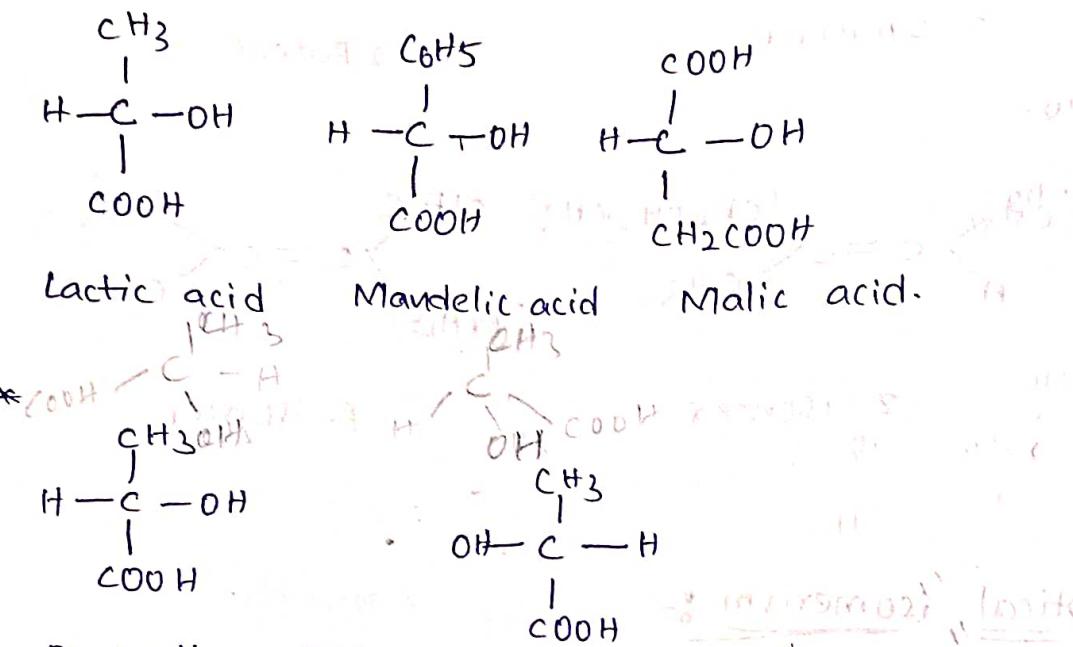
→ Clockwise rotation of PPL, optically active compound  
Right (+) - Dextrorotatory compound.

→ Anti clockwise rotation of PPL, optically active compound. → Left (-) - Levo rotatory compound.

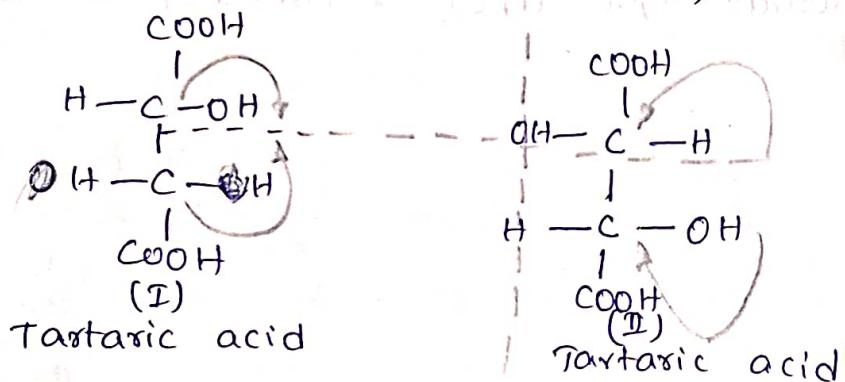


For many optically active substances

- \* Optical isomerism in compound containing one asymmetric (chiral) carbon atom (Ex - lactic acid)
- chiral carbon atom can exist three forms: (+), (-), (R), (S)

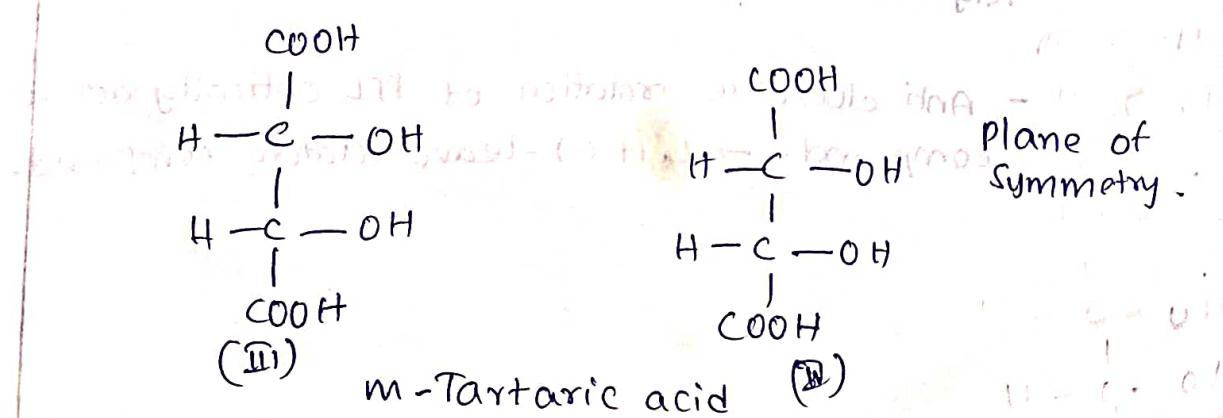


- D-Lactic acid → rotates in clockwise direction, left
- L-Lactic acid → rotates in anti-clockwise direction, right
- ④ → optical isomerism containing two or more chiral carbon atom (Tartaric acid)



Enantiomers are non superimposable

(i) & (ii) D & L tartaric acid structures are non superimposable to each other optically active compounds.



- (iii) Meso (or) M-tartaric acid, optically inactive compound due to superimposable mirror image of each other
- (iv) dl-(l) racemic mixture. Optically inactive due to External compensation.

~~Chirality and its representation by enantiomers~~

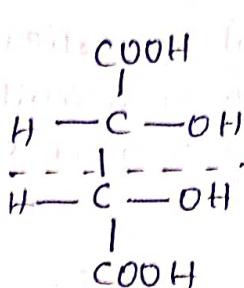
\* chirality and elementary of symmetry elements

1) Molecule has only one chiral center it always chiral.

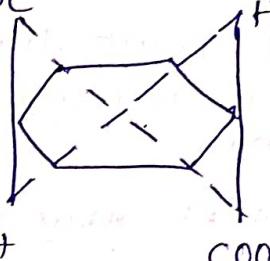
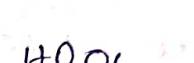
\* if it has more than one sometimes chiral or some achiral.

2) A molecule has chirality it will be neither plane of symmetry nor center of symmetry.

Ex:-



meso-Tartaric acid



trans-cyclohexane-1,4-di carboxylic acid

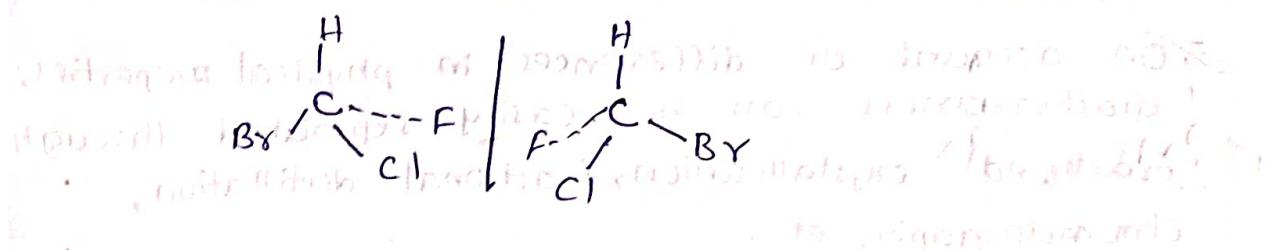
(Optically Inactive due to

presence of horizontal plane of symmetry)

Coptically inactive due to presence of centre of symmetry

Enantiomers (optically active isomers)

Isomers which are non-superimposable mirror images of each other are known as enantiomers.



- These compounds are optically active and can rotate the plane polarised light. Thus it is also known as optical isomerism. The isomer which can rotate the plane polarised light from left to right is known as "dextrorotatory" and which can rotate from right to left is known as

"Levorotatory". A equal mixture of two enantiomers is known as "racemic mixture". Such a mixture is optically inactive as they rotate the plane polarised light in opposite direction and thus cancel each other.

### \* Characteristics of Enantiomers and Diastereomers

- Enantiomers have identical physical properties like melting points, boiling points, densities, refractive indices etc. "they differ only in their action on plane polarised light, one of enantiomer rotates the plane polarised light to the right and the other to the same magnitude but to the left. The two enantiomers are designated as dextrorotatory (+) and levorotatory, (or) (-) respectively."

✓ Diastereomers have different physical properties such as melting points, boiling points, densities, solubilities, refractive indices, dielectric constants and specific rotations.

- Diastereomers may or may not be active.

- Diastereomers show similar, but not identical chemical properties. The rates of reactions of two diastereomers with a given reagent are generally different.

✓ Enantiomers have the same rates of reaction with a reagent provided the reagent is not optically active.

✓ On account of differences in physical properties, diastereomers can be easily separated through fractional crystallisation, fractional distillation, chromatography etc.

✓ Enantiomers cannot be separated by these techniques.

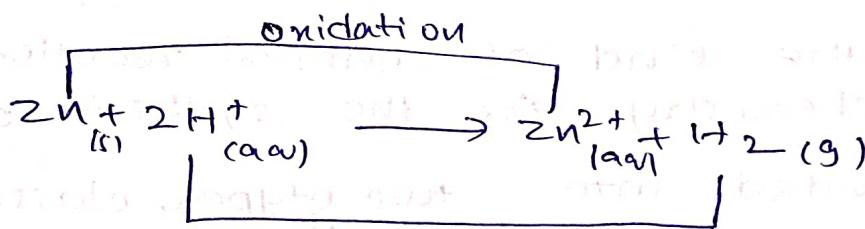
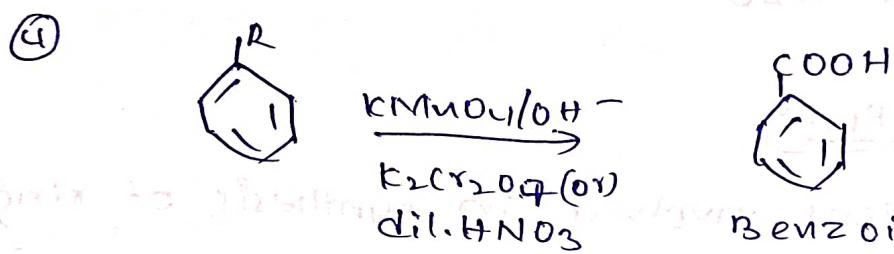
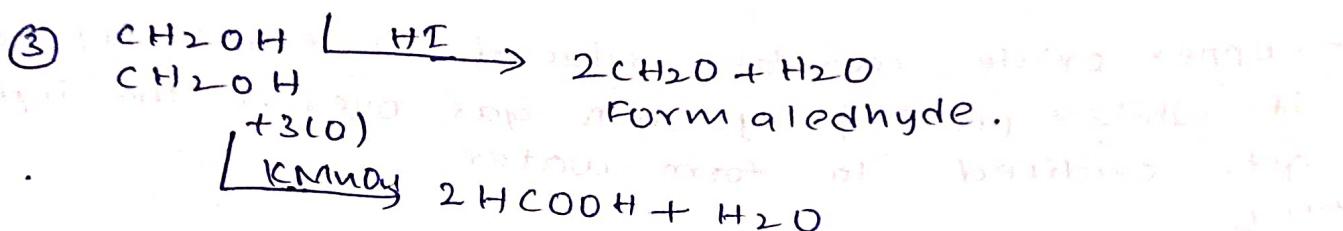
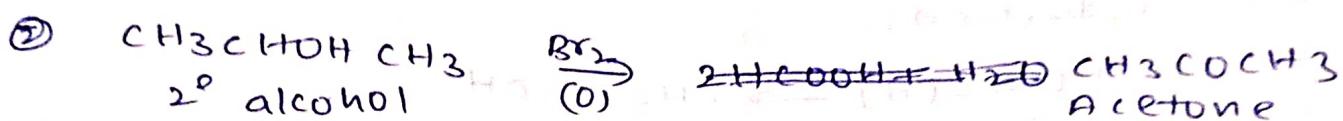
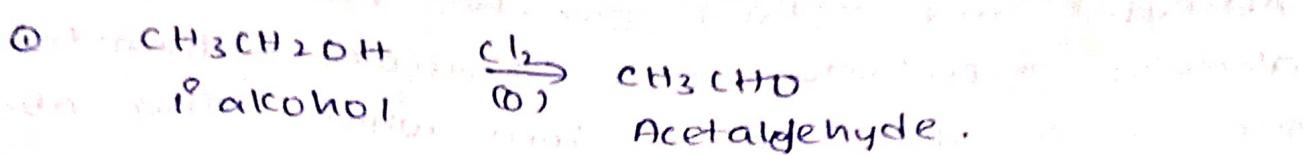
The following table shows the optical rotation values of some common organic compounds.

Oxidation: loss of hydrogen or loss of electron during a reaction by a molecule, atom, ion, etc.



- In this reaction hydrogen is being oxidized and fluorine being reduced.
- When oxygen is added to the compound which act as oxidizing reagent.

-  ${}^1\text{P}, {}^2\text{D}$  alcohol to aldehydes and ketone.



Reduction.

- Reduction can be considered as the removal of oxygen, the addition of hydrogen, or the gain of electrons.

Isotropy (प्रकृति नहीं बदलती है) (UP)

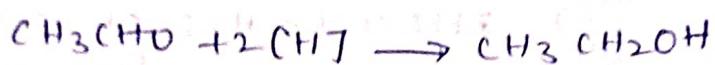
### → Removal of oxygen:

- Metal oxides which are oxides are reduced to the metal - this is how iron is made from iron oxide. The reducing agent is carbon monoxide.



### → Addition of hydrogen:

- Aldehydes and ketones can be reduced to  $\text{Pb}_2^{\circ}$  alcohols respectively using aqueous sodium borohydride. This is a source of  $\text{H}^-$  ions which bring about the reduction:



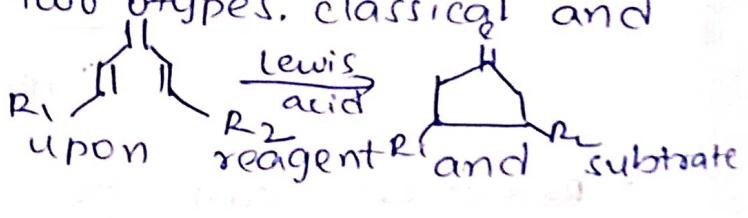
- Copper oxide can be reduced to copper by heating it while passing hydrogen gas over it. The hydrogen gets oxidised to form water.



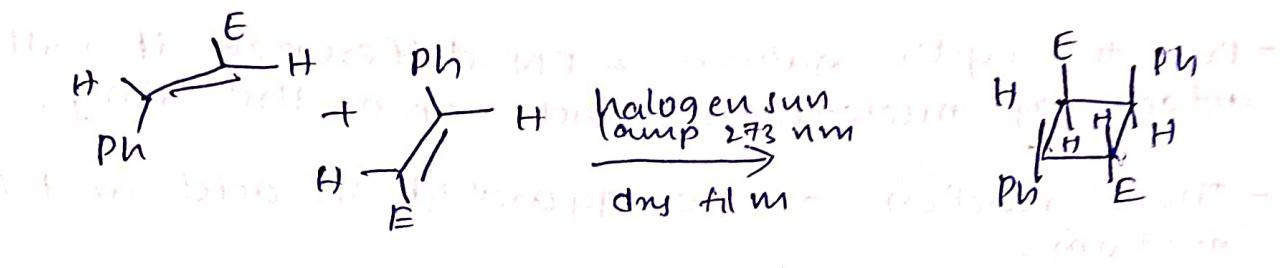
### → Cyclisation reaction:

- Importance: Reactions involved in synthesis of ring compounds.

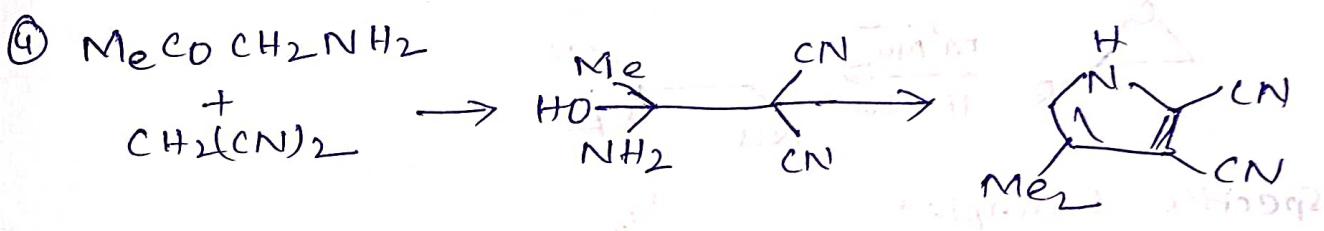
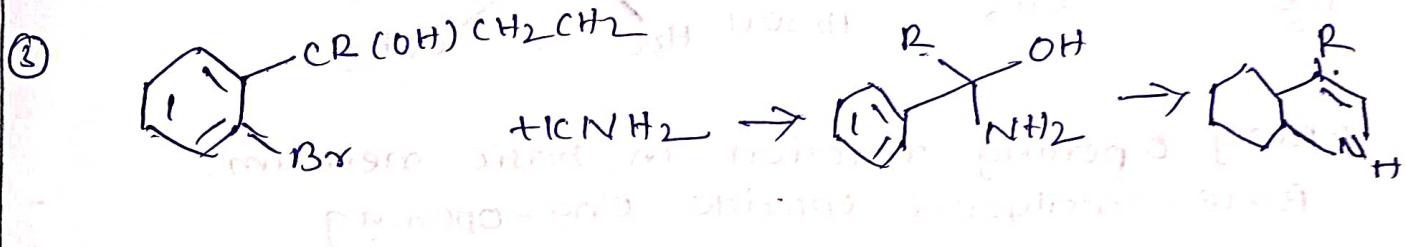
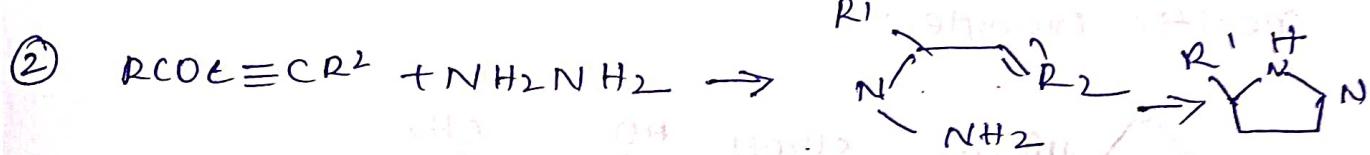
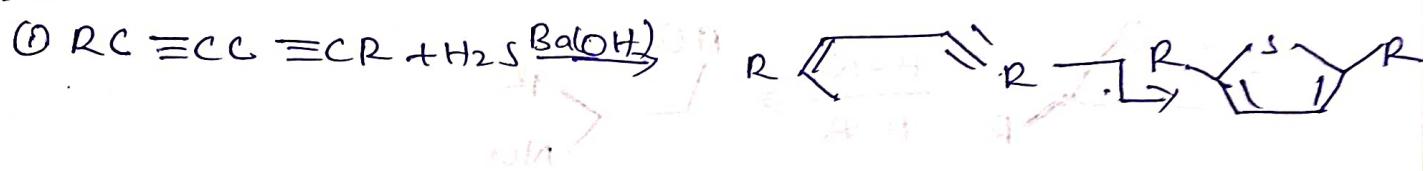
- This is the kind of chemical reactions used in organic chemistry for the synthesis of cyclopentane.
- It is divided into two types, classical and modern reactions.
- It can be depending upon Lewis acid reagent and substrate.
- It is discovered by Ivan Nikolaevich Nazarov in 1941 doing research on vinyl ketones.



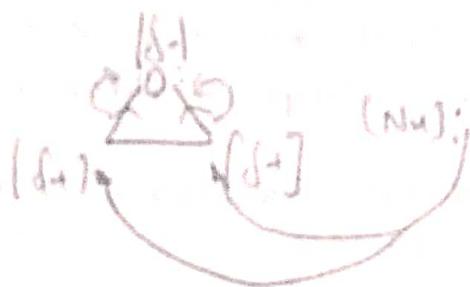
- conversion of one ring to other ring using the conditions like heat or irradiation of additional electrophilic and nucleophilic reagents.
- Any intermolecular conversion of comma sigma bond forming process.
- loss of two pi bonds and gain of two  $\sigma$  bonds



Ex:



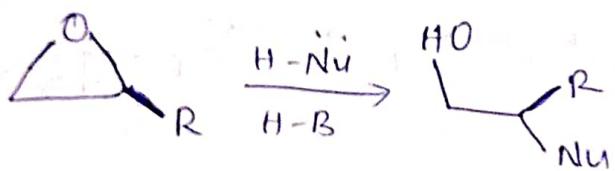
## \* RING OPENING REACTION:



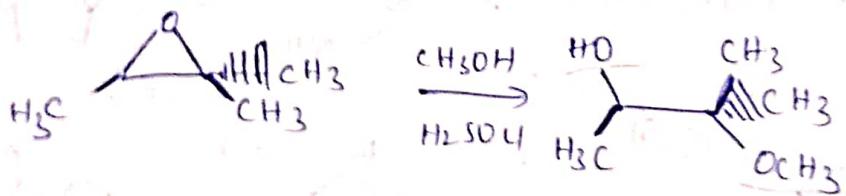
- Epoxide is cyclic ether and three membered ring which include with oxygen.
- Due to cyclic nature & EN difference it will attack by nucleophile and open the ring.
- These reaction are exaggerated in acid and base medium.

### \* Ring opening reaction in acidic medium:

general reaction:

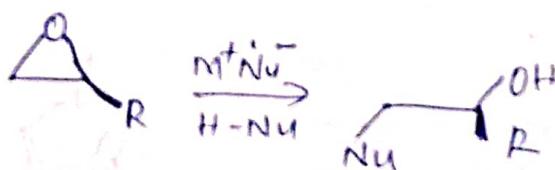


#### Specific Example:

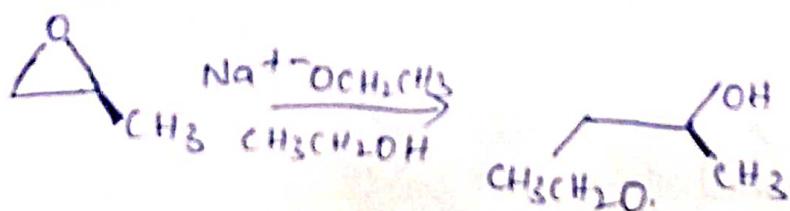


### \* Ring opening reaction in basic medium:

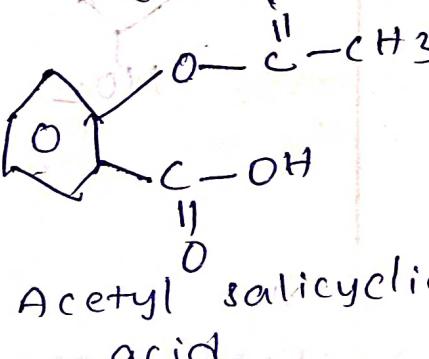
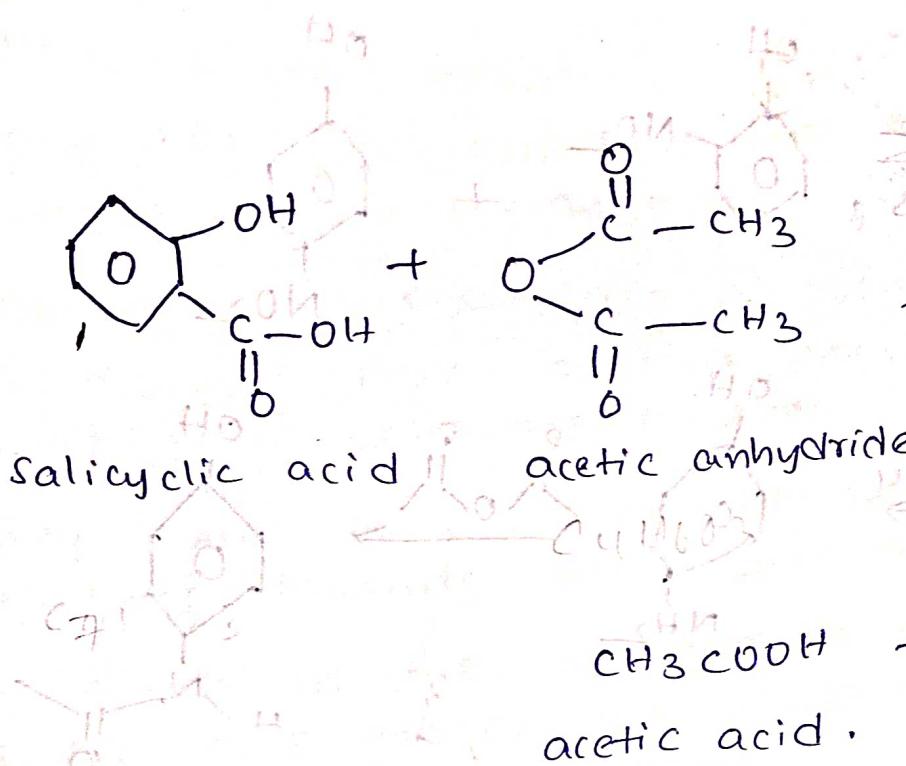
Base-catalyzed Epoxide Ring-opening



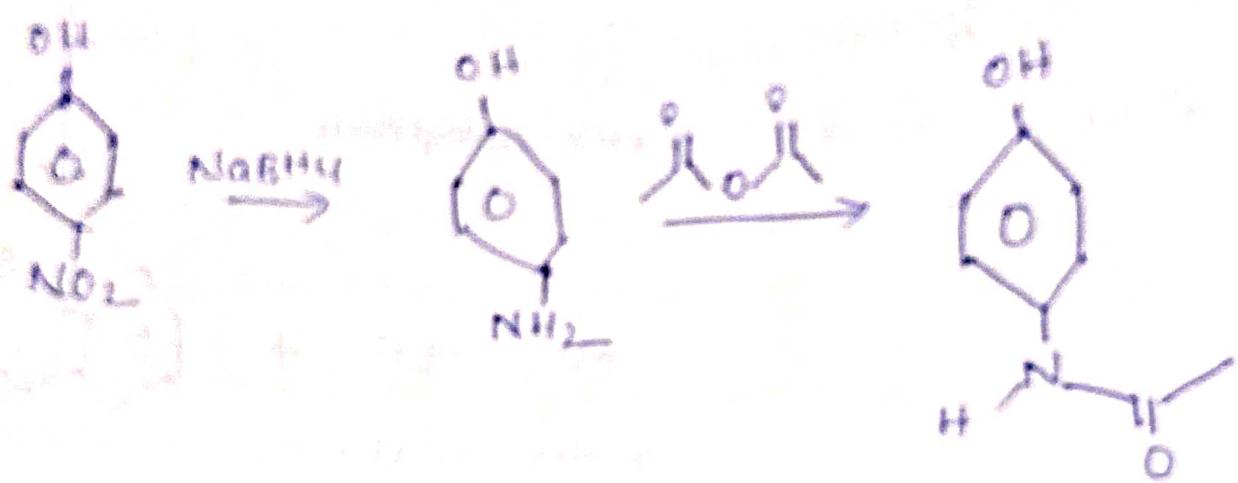
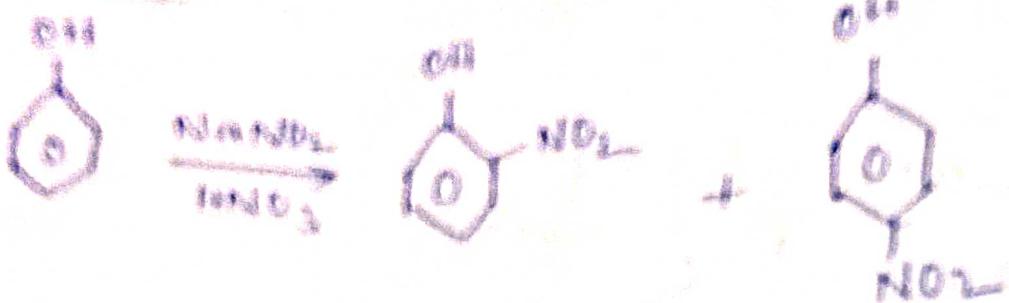
#### Specific Example:



## \* Aspirin synthesis :-



## Molecular weight



## Enantiomers :-

- They always exist as discrete pairs.
- Stable, isolable compounds that differ from one another in 3-D arrangement.
- Cannot be interconverted at room temperature.
- Enantiomers have identical properties in all respects except their behaviour towards the PPL.
- They have same MP, density, solubility, color and reactivity towards acids and bases.
- They differ in the direction in which they rotate the PPL. One rotates the plane to right and other to left, but of same extent.  
A mixture of equal amounts of two enantiomers is a racemic mixture. It is optically inactive.

## Diastereomers :-

- Diastereomers that are not mirror images of each other.
- They have different MP, BP, & solubilities. They will also have different reactivities towards most reagents.
- They are similar, but not identical and not mirror images.
- May or may not be active.
- The rate of reactions of two diastereomers with a given reagent are generally different.