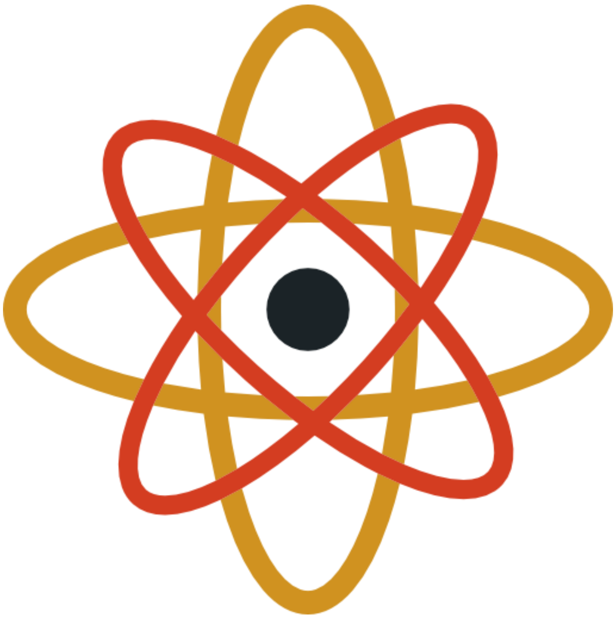

CHEMISTRY

B.Tech 1st Year

NOTES

Prepared By: TOPPERWORLD
LEARN & GROW

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UNIT 1

ATOMIC AND MOLECULAR STRUCTURES

MOLECULAR ORBITAL THEORY

Orbital: An Orbital is a three-dimensional space around nucleus where the probability of finding an electron is high. They represent the probability of finding an electron in any one place. They correspond to different energies. So, an electron in an orbital has definite energy. Each orbital is denoted by a number and a letter. The number denotes the energy level of the electron in the orbital. Thus 1 refers to the energy level closest to the nucleus; 2 refers to the next energy level further out, and so on. The letter refers to the shape of the orbital. The letters go in the order s, p, d, f, g, h, i, j, etc.

Atomic Orbitals: Atomic orbitals are regions of space around the nucleus of an atom where an electron is likely to be found. Atomic orbitals allow atoms to make covalent bonds. An atomic orbital can have a maximum of two electrons. Atomic orbitals are labelled as s, p, d, and f sublevels.

s Orbitals:

The s orbital is spherical and hold a maximum of two electrons. It has one sub-energy level.

The order of size is 1s < 2s < 3s < …, as shown below.

p Orbitals:

The p orbital is dumbbell shaped and can hold up to six electrons. It has three sub energy levels. These are given the symbols px, py and pz. The p orbitals at the second energy level

are called 2px, 2py and 2pz. There are similar orbitals at subsequent levels: 3px, 3py, 3pz,

4px, 4py, 4pz and so on.

D Orbitals

The d and f orbitals have more complex shapes. The d level has five sub-energy groups and holds up to 10 electrons, The five 3d orbitals are called 3dxy, 3dxz, 3dyz, 3dx^2 - y^2, 3dz^2

Molecular orbital (MO: Atoms join to form molecules. When two atoms move closer together to form a molecule, atomic orbitals overlap and combine to become molecular orbitals.

Molecular orbitals are regions around molecules where electrons are most likely to be found. The number of newly formed molecular orbitals is equal to the number of combined atomic orbitals. The molecular orbital surrounds the two nuclei of the atoms, and electrons can move around both nuclei. Similar to atomic orbitals, molecular orbitals maximally contain 2 electrons, which have opposite spins.

Molecular orbitals are of two types, bonding molecular orbitals and antibonding molecular orbitals. Bonding molecular orbitals contain electrons in the ground state and antibonding molecular orbitals contain no electrons in the ground state. Electrons may occupy in the antibonding orbitals if the molecule is in the excited state.

Molecular Orbital Theory

Valence Bond Theory fails to answer certain questions like Why He_2 molecule does not exist and why O_2 is paramagnetic Therefore in 1932 F. Hood and RS. Mulliken came up with theory known as Molecular Orbital Theory to explain questions like above. According to Molecular Orbital Theory individual atoms combine to form molecular orbitals, as the electrons of an atom are present in various atomic orbitals and are associated with several nuclei.

Molecular orbital (MO) theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.

Postulates of MOT are:

- Two atoms come together, interact and forms a bond. All the atomic orbitals on either nuclei mix together to form a new orbital called molecular orbital.

- The molecular orbitals are formed by mixing of the atomic orbitals of same energy level and symmetry.
- After formation of molecular orbital, the atomic orbitals lose their identity.
- Each and every electron in the molecular orbital belongs to all the nuclei of the molecules.
- Atoms have atomic orbitals with one nuclei and Molecules have molecular orbitals with n nuclei. Thus, atoms are monocentric while molecules are polycentric.
- The number of molecular orbitals formed is equal to the atomic orbitals mixing.
- Molecular orbitals can be bonding, anti-bonding, and non-bonding orbitals.
- Bonding molecular orbitals are lower in energy than the corresponding anti-bonding orbitals.
- Each molecular orbital is described by a wave function Ψ, which in turn is associated with a set of quantum number.
- Electrons fill up these orbitals in the same way as atomic orbitals in accordance to the 3 principles (Aufbau, Hund's and Pauli Principle).
- The Aufbau principle states that orbitals are filled with the lowest energy first.
- The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two, with opposite spins.
- Hund's rule states that when there are several MOs with equal energy, the electrons occupy the MOs one at a time before two occupy the same MO.

Electrons may be considered either of particle or of wave nature. Therefore, an electron in an atom may be described as occupying an atomic orbital, or by a wave function Ψ, which are solution to the Schrodinger wave equation. Wave function is a mathematical function related to probability of finding the particle in a particular region of space

Electrons in a molecule are said to occupy molecular orbitals. The wave function of a molecular orbital may be obtained by one of two methods:

1. Linear Combination of Atomic Orbitals (LCAO).

2. United Atom Method.

Linear Combination of Atomic Orbitals (LCAO)

As per this method the formation of orbitals is because of Linear Combination (addition or subtraction) of atomic orbitals which combine to form molecule. Consider two atoms A and B which have atomic orbitals described by the wave functions Ψ_A and Ψ_B . If electron cloud of these two atoms overlap, then the wave function for the molecule can be obtained by a linear combination of the atomic orbitals Ψ_A and Ψ_B i.e., by subtraction or addition of wave functions of atomic orbitals.

$\Psi_{MO} = \Psi_A + \Psi_B$

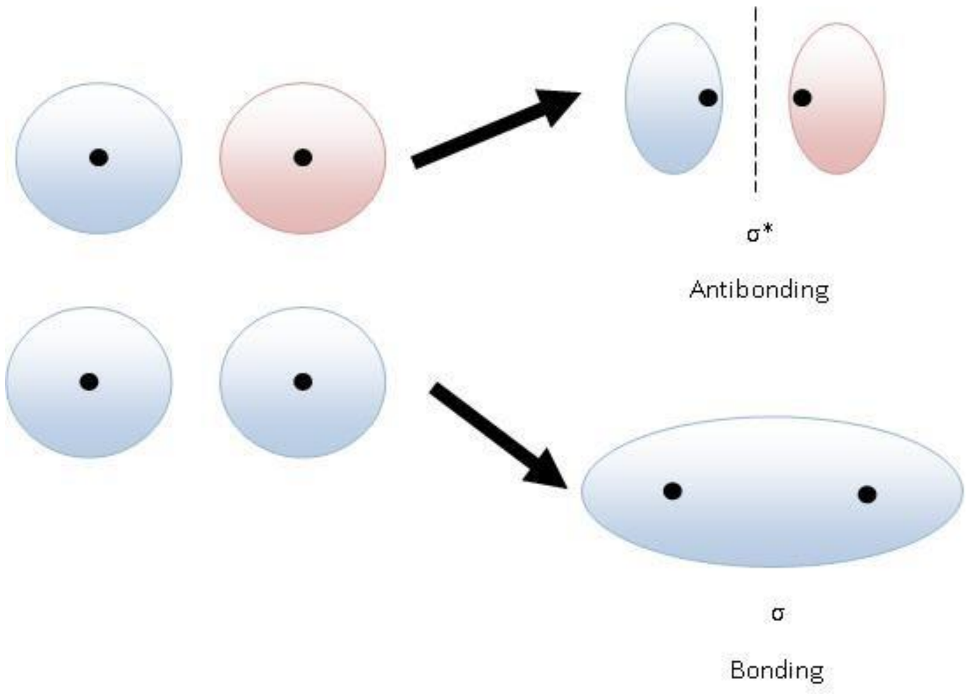
The above equation forms two molecular orbitals

Bonding Molecular Orbitals

When addition of wave function takes place, the type of molecular orbitals formed are called Bonding Molecular orbitals and is represented by $\Psi_{MO} = \Psi_A + \Psi_{B.}$ They have lower energy than atomic orbitals involved. It is similar to constructive interference occurring in phase because of which electron probability density increases resulting in formation of bonding orbital. Molecular orbital formed by addition of overlapping of two s orbitals shown in Figure 1. It is represented by s.

Anti-Bonding Molecular Orbitals

When molecular orbital is formed by subtraction of wave function, the type of molecular orbitals formed are called Antibonding Molecular Orbitals and is represented by $\Psi_{MO} = \Psi_A - \Psi_{B.}$



They have higher energy than atomic orbitals. It is similar to destructive interference occurring out of phase resulting in formation of antibonding orbitals. Molecular Orbital formed by subtraction of overlapping of two s orbitals. It is

represented by σ* (*) is used to represent antibonding molecular orbital) called Sigma Antibonding.

Therefore, Combination of two atomic orbitals results in formation of two molecular orbitals, bonding molecular orbital (BMO) whereas other is anti-bonding molecular orbital (ABMO). BMO has lower energy and hence greater stability than ABMO. First BMO are filled then ABMO starts filling because BMO has lower energy than that of ABMO. Formation of molecular orbitals occurs by the combination of atomic orbitals of proportional symmetry and comparable energy. Therefore, a molecular orbital is polycentric and atomic orbital is monocentric. Number of molecular orbitals formed is equal to the number of atomic orbitals.

Relative Energies of Molecular Orbitals

Bonding Molecular Orbitals (BMO) - Energy of Bonding Molecular Orbitals is less than that of Anti Bonding Molecular Orbitals because the attraction of both the nuclei for both the

electron (of the combining atom) is increased.

Anti-Bonding Molecular Orbitals (ABMO) - Energy of Anti Bonding Molecular Orbitals is higher than Bonding Molecular Orbitals because the electrons move away from the nuclei and are in repulsive state.

The Energies of Bonding Molecular Orbitals and Anti-Bonding Molecular Orbitals

Molecular orbitals of diatomic molecules:

Molecular Orbitals for diatomic Molecules formed from a Linear Combination of Atomic Orbital.

Filling Electrons in MO Diagrams

The next step in constructing an MO diagram is filling the newly formed molecular orbitals with electrons. Three general rules apply:

•The Aufbau principle states that orbitals are filled starting with the lowest energy

•The Pauli exclusion principle states that the maximum number of electrons. Occupying an orbital is two, with opposite spins.

•Hund's rule states that when there are several MOs with equal energy, and the electrons occupy the MOs one at a time before two occupy the same MO.

The filled MO that is highest in energy is called the Highest Occupied Molecular Orbital, or HOMO; the empty MO just above it is the Lowest Unoccupied Molecular Orbital, or LUMO. The electrons in the bonding MOs are called bonding electrons, and any electrons in the antibonding orbital are called antibonding electrons. The reduction these electrons' energy is the driving force for chemical bond formation.

Energy Level Diagram

The factors upon which relative energies of molecular orbitals depend are:

(i) Energies of the Atomic orbitals combining to form Molecular Orbitals.

(ii) The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs

1s Atomic Orbitals (AOs) of two atoms form two Molecular Orbitals (MOs) designated as s1s and s *1s. The 2s and 2p orbitals (eight AOs of two atoms) form four bonding MOs and four anti-bonding MOs as:

Bonding MOs: σ 2s, σ 2pz, $\pi\ 2p_x$, $\pi\ 2p_y$

Anti – Bonding MO: $\sigma\ {}^*2s$, $\sigma\ {}^*2p_z$, $\pi\ {}^*2p_x$, $\pi\ {}^*2p_y$

The order of increasing energy of molecular orbitals obtained by combination of 1s, 2s and

2p orbitals of two atoms is →

$\sigma 1s$, $\sigma\ {}^*1s$, $\sigma\ 2s$, $\sigma\ {}^*2s$, $\sigma\ 2p_z$, $\pi\ 2p_x = \pi\ 2p_y$, $\pi\ {}^*2p_x = \pi\ {}^*2p_y$, $\sigma\ {}^*2p_z$

(Energy Increases from left to right)

Bond order:

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

Bond order (B.O.) = (No. of electrons in BMO - No. of electrons in ABMO)/ 2.

Those with positive bonding order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

Magnetic Behavior: If all the molecular orbitals in species are spin paired, the substance is diamagnetic. But if one or more molecular orbitals are singly occupied it is paramagnetic.

Molecular orbital energy level diagram of Nitrogen molecule (N_2)

The electronic configuration of nitrogen atom is $1s^2\ 2s^2\ 2p\ ^1 2\ ^1 2p\ ^1$and N molecule has 14 electrons. The Molecular orbital diagram.

The molecular orbital electronic configuration of the molecule is:

N_2: KK $(\sigma 2s)^2 < (\sigma^*2s)^2 < (\text{Л}\ 2p_x)^2 = (\text{Л}2p_y)^2 < (\sigma 2p_z)^2$

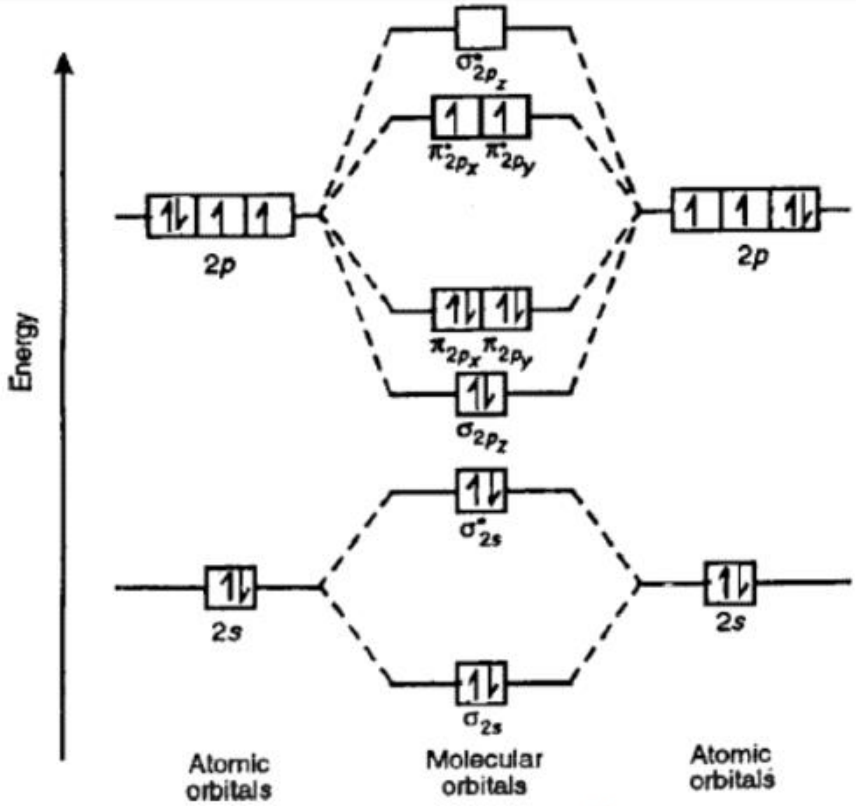
Bond Order= 8-2/2 =3

Thus, oxygen molecule has two bonds one σ and one π Further, in accordance with Hund's rule, the last two electrons in π^*2p_x and π^*2p_y orbitals will remain unpaired. Therefore, the molecule has paramagnetic character due to the presence of two unpaired electrons. These facts are in accordance with experimental observations. The bond dissociation energy in O_2 molecule is 498 kJ $mol^{-1}$and bond length is 121 pm.

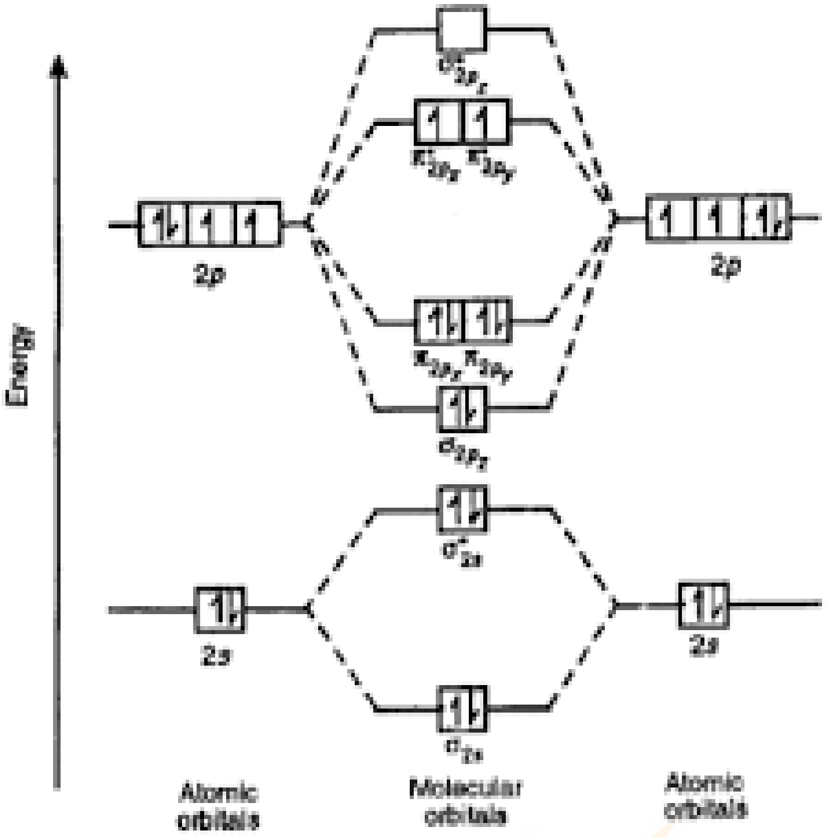
Metallic Bonding:

The force that holds the atoms of pure metal together in a crystal as a result of the attraction between positive ions and surrounding freely mobile delocalized electrons is known as metallic bond.

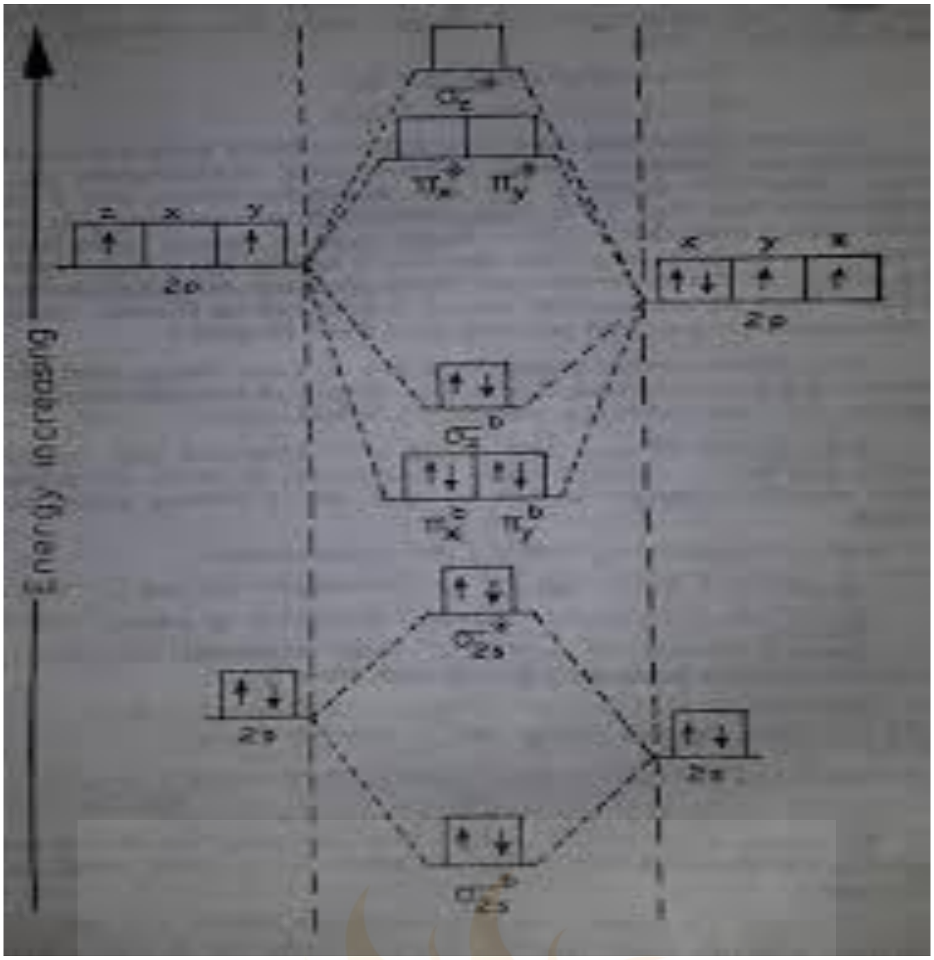
Molecular Orbital Energy Level Diagram of O2



Molecular Orbital Energy Level Diagram N2



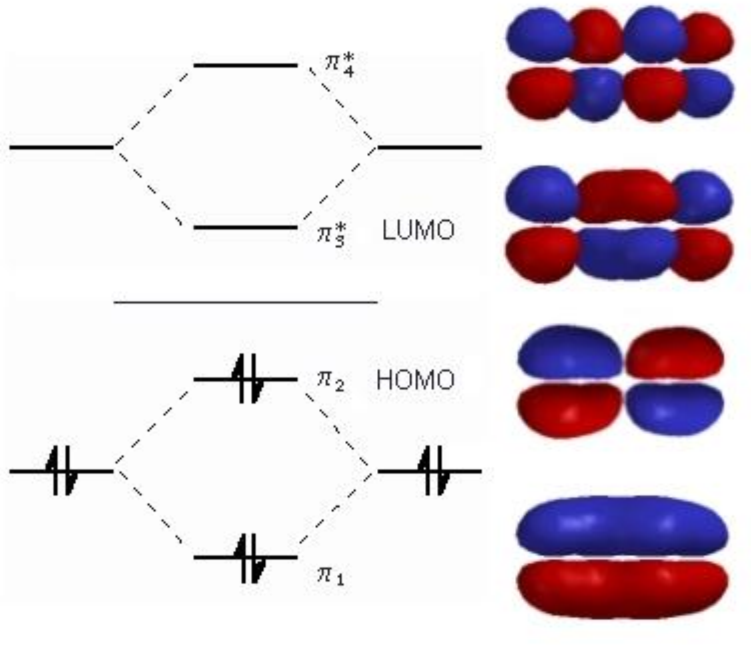
S Molecular Orbital Energy Level Diagram CO



π Molecular Orbitals of 1,3-Butadiene

- 1,3-Butadiene contains two double bonds that are conjugated.

- It is "built" from 4 sp^2 hybridsed C atoms, each contributing a p atomic orbital containing 1 electron.
- An alternative way to consider "building" the π molecular orbitals is by combining the π molecular orbitals of two ethene molecules.
- This requires that we make an in-phase and an out-of-phase combination for both the π and π* of ethene.
- Either way, we end up with the same set of 4 π molecular orbitals.



The diagram to the right shows the relative energies of the π molecular orbitals of 1,3-butadiene (derived from ethene) and the electron configuration.

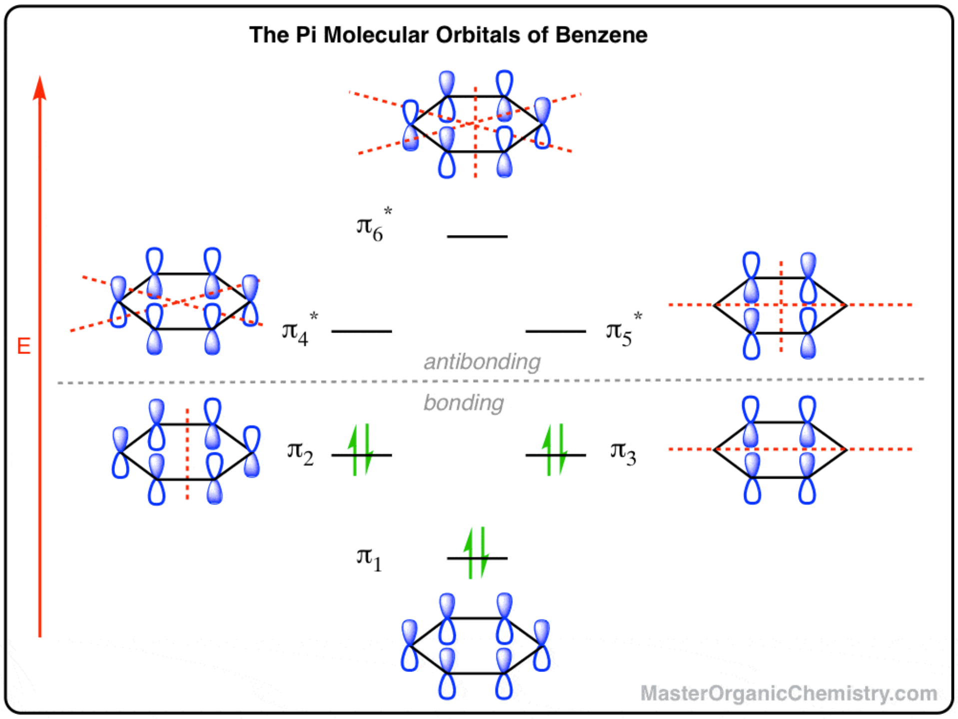
The horizontal center line denotes the energy of a C atomic p orbital. Orbitals below that line are bonding those above are anti-bonding.

We now have 4 electrons to arrange, 1 from each of the original atomic p orbitals. These are all paired in the two stabilized pi bonding orbitals, π1 and π2. The highest occupied molecular orbital or **HOMO** is π2 in 1,3-butadiene (or any simple conjugated diene).

In contrast, the anti-bonding π* orbitals contain no electrons. The lowest unoccupied orbital or **LUMO is** π3 in 1,3-butadiene (or any simple conjugated diene).

The Pi Molecular Orbitals of Benzene

Today, let's go through how to draw out the molecular orbitals of benzene. We'll compare them with the molecular orbitals for (linear) hexatriene. The big takeaway is that from contrasting the molecular orbitals of these two 6-electron pi systems, we will unlock the deep, mysterious riddle of why benzene is so unusually stable.



The necessary conditions for any system to be aromatic are planar, conjugated ring system with delocalization of (4n+2) π electrons, where, n is an integer.

Valence bond theory

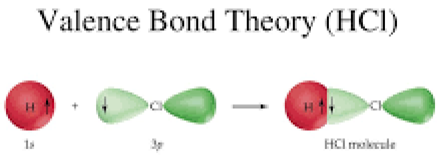
Valence bond theory explains the geometry of the complex compound using the concept of hybridization. This theory is a chemical bonding theory that explains the bonding between two atoms is caused by the overlap of half-filled atomic orbitals. The two atoms share each other's unpaired electron to form a filled orbital to form a hybrid orbital and bond together. According to this theory, a covalent bond is formed between the two atoms by the overlap of half-filled valence atomic orbitals of each atom containing one unpaired electron.

Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond and a pi bond. The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis is known as a sigma bond.

According to VBT theory, a coordination entity is formed as a result of coordinate covalent bond formation by electron pairs from ligands (Lewis bases) through overlap of appropriate atomic orbitals (usually hybrid orbitals) of the metal (Lewis acid) and ligand.

A coordination entity is composed of central atom, usually that of metal, to which is attached a surrounding array of other atoms or group of atoms, each of which is called ligand.

Hypothetical sequence of steps for the formation of a coordination entity;



Limitation of the VBT:

1.Fail to explain the colour & characteristics of absorption spectra of complex compounds.

2.Orbital contribution and temperature dependency on magnetic moment of coordination complex are not properly explained by VBT.

3.It is not helpful to predict the mystery of formation of outer or inner orbital coordination complex.

4.VBT fails to predict any distortion in the shapes of the coordination complexes from regular geometry.

Crystal Field Theory:

Coordination compounds /Complex compounds

They are molecular compounds which retain their identities even when dissolved in water and their properties are completely different from those constituents.

Ex. $[K_4Fe(CN)_6]$ is a complex compound.

Compounds containing complex ions are called complex compounds. These complex ions have coordinated bonds in their structure and known as coordinate ions and the compounds are called coordinate compounds.

Central ion. The cation to which one or more neutral molecules or anions are attached is called central ion

Ligands. Any atom or ion or molecule which is capable of donating a pair of electrons to the central metal atom are called ligands.

The particular atom which donates pair of electrons is called a donor atom.

Ex. Donor atoms-N, O, S and halogens

Unidentate ligands. The ligands containing one donor atom is called unidentate ligand.

Ex. F^-, Cl^-, Br^-, I^-, CN^-.

Bidentate ligands. The ligands which contain two donor atoms are called bidentate ligands.

Ex. Ethylene diamine

Coordination Number The total number of ligands attached to the central atom is called coordination number

Ex. $[Ag(NH_3)_2]^{2+}$ / CN-2 ; $[Cu(H_2O)_4]^{2+}$ / CN-4

Crystal field theory is very much different from valence bond theory. According to valence bond theory, bonding between the metal ion and the ligands is purely covalent, while according to crystal field theory, the interaction between the metal ion and ligands, is purely electrostatic, i.e., metal-ligand bonds are 100% ionic.

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. This theory was developed by Hans Bethe and John Hasbrouck van Vleck.

Crystal Field Theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, coordination,).

Salient features of crystal-field theory are:

1.The transition metal ion is surrounded by the ligands with lone pairs of electrons and the complex is a combination of central ion surrounded by other ions or molecules or dipoles i.e., ligands.

2.All types of ligands are regarded as point charges.

3.The ionic ligands, like F-, Cl-, CN-, etc., are regarded as negative point charges, or point charges and the neutral ligands, like H_2O, NH_3, etc., are regarded as point dipoles or just dipoles. (CFT regards neutral ligands as dipolar) If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal atom.

4. The interactions between the metal ion and the negative ends of anion (or ion dipoles) are purely electrostatic, i.e., the bond between the metal and ligand is considered 100 percent ionic.

5. The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly d-orbitals.

6. In the case of free metal ion, all the five d-orbitals have the same energy. Such orbitals having the same energies are called degenerate orbitals.

Crystal field splitting of d orbitals:

In a free transition metal or ion, there are five d-orbitals which are dxy, dyz , dzx , dz^2 and d (x^2 -y^2). These are divided into 2 sets based on their orientation in space:

•**t2g:** The 3d-orbitals (dxy, dyz and dzx) which orient in the regions between the coordinate axes. These are non-axial orbitals. t_{2g} are three-fold degenerate.

•**eg :** the other two orbitals (dz^2 and d (x^2 -y^2)) which orient along the axis. These are two-fold degenerate and also known as axial orbitals.

In an isolated gaseous atom, all the five-d orbital are degenerate. (They have same energy).

On the approach of the ligands in a complex, the electrons in the d orbital of the central ion are repelled by the lone pairs of the ligands. This repulsion will raise the energy level of the d orbitals. All the ligands approaching the energy of each orbital will increase by the same amount. In other words, they will remain degenerate. Since d-orbitals differ in their orientation, those orbitals lying in the direction of the ligands is raised to a larger extent than the others. So, five degenerate d-orbitals will split into two sets, having different number of energies. This splitting of five degenerate d-orbitals of the metal ion under the influence of approaching ligands, into two sets of orbitals having different energies is called as Crystal- field splitting.

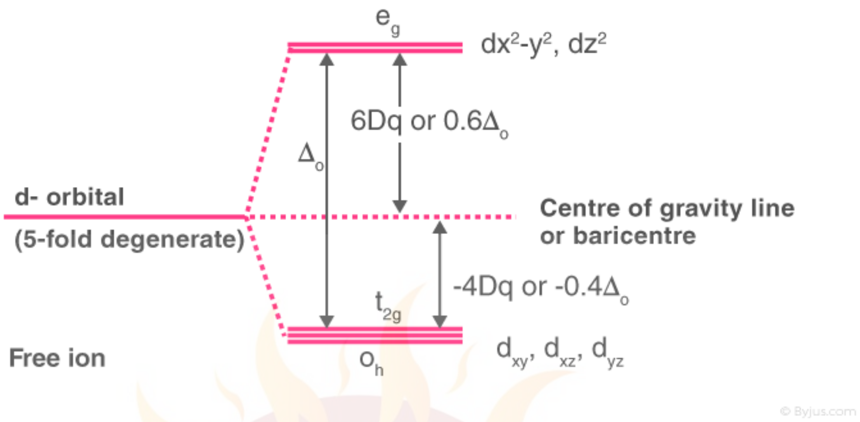
Crystal Field Splitting in Octahedral Complex

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.

- Hence, they have higher energy than average energy in the spherical crystal field.
- On the other hand, d_{xy}, $d_{yz,}$ and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

- *t_{2g}– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with lower energy*
- *e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy*



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Crystal Field Splitting in Tetrahedral Complex

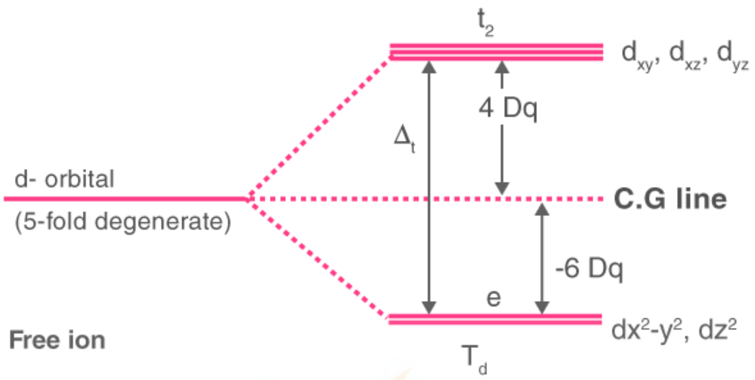
The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital sets are raised while that of the $d_{x^2-y^2}$ and d_{z^2} orbitals are lowered.

- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.

Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

- ***t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy***
- ***e – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with lower energy***

The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be -6Dq and the destabilizing effect of t_2 set will be +4Dq



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Spectrochemical Series

A **spectrochemical series** is a list of ligands ordered by ligand "strength", and a list of metal ions based on oxidation number, group and element.

I^- < Br^- < S^{2-} < SCN− (S–bonded) < Cl− < N3− < F−< NCO− < OH− < C2O42− < O2−< H2O < acac− (acetylacetonate) < NCS− (N–bonded) < CH3CN < gly (glycine) < py (pyridine) < NH3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < NO2− (N–bonded) < PPh3 < CN− < CO

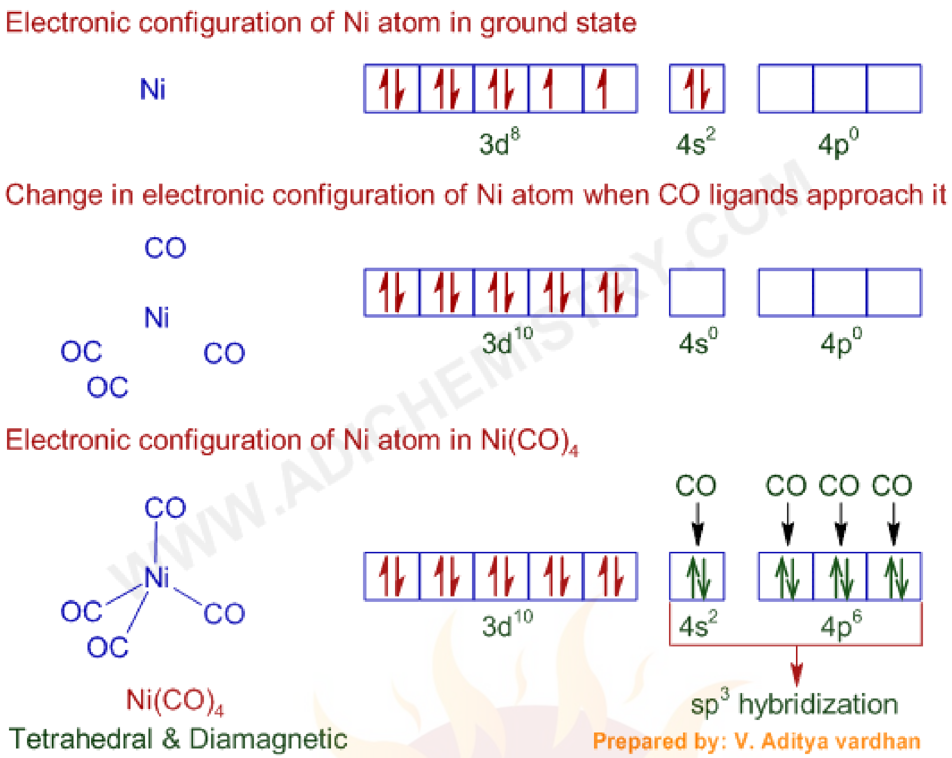
Weak field ligands: H_2O, F^-, Cl^-, OH^-

Strong field ligands: CO, CN^-, NH_3, PPh_3

Ni $(CO)_4$

* The valence shell electronic configuration of ground state Ni atom is $3d^8$ $4s^2$.

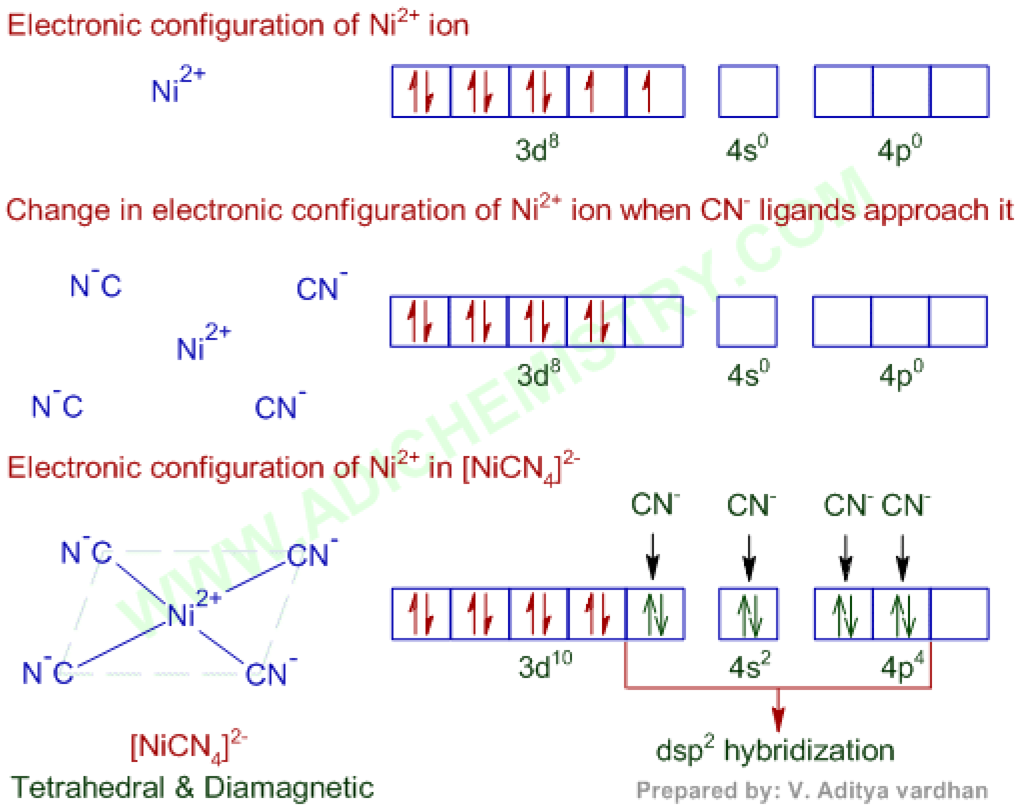
* All of these 10 electrons are pushed into 3d orbitals and get paired up when strong field CO ligands approach Ni atom. The empty 4s and three 4p orbitals undergo sp^3 hybridization and form bonds with CO ligands to give Ni $(CO)_4$. Thus Ni $(CO)_4$ is diamagnetic.



$[Ni(CN)_4]^{2-}$

* In $[Ni(CN)_4]^{2-}$, there is Ni^{2+} ion for which the electronic configuration in the valence shell is $3d^8\ 4s^0$.

* In presence of strong field CN^- ions, all the electrons are paired up. The empty 3d, 3s and two 4p orbitals undergo dsp^2 hybridization to make bonds with CN^- ligands in square planar geometry. Thus [Ni (CN)4]2- is diamagnetic. It is said to be a low spin inner orbital complex.



Band Structure Of Solid

Band theory of solids describes the quantum state that an electron takes inside a metal solid. Every molecule comprises various discrete energy levels. The way electrons behave inside a molecule is well explained through band theory. Band Theory was developed from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch applied quantum theory to solids.

In atoms, electrons are filled in respective energy orbits following Pauli's exclusion principle. Two atomic orbitals combine to form a molecular orbit with two distinct energy levels. In solids, 10^{23} stacked up lines confined in a tiny space would look like a band. Thereby forming an energy continuum called energy bands. Band theory helps to visualize the difference between a conductor, semiconductor, and an insulator by plotting available energies for an electron in a material.

In the band theory of solids, there are many energy bands but the following are the three most important energy bands in solids:

- Valence Band
- Conduction Band
- Forbidden Band

Valence band

The energy band that consists of valence electrons energy levels, is known as the valence band. The valence band is present below the conduction band and the electrons of this band are loosely bound to the nucleus of the atom.

Conduction band

The energy band that consists of free electrons energy levels, is known as the conduction band. For electrons to be free, external energy must be applied such that the valence electrons get pushed to the conduction band and become free.

Forbidden band

The energy gap between the valence band and the conduction band is known as the forbidden band which is also known as the forbidden gap. The electrical conductivity of a solid is determined by the forbidden gap and also the classification of the materials as conductors, semiconductors, and insulators.

Intrinsic Semiconductor

A semiconductor material in its pure form is known as an **intrinsic semiconductor**. Thus, the intrinsic semiconductors are chemically pure, i.e. they are free from impurities.

In case of intrinsic semiconductors, the number of charge carriers, i.e., holes and electrons are determined by the properties of the semiconductor material itself instead of the impurity. Also, the number of free electrons is equal to the number of holes in the intrinsic semiconductor. The common examples of the intrinsic semiconductors are germanium (Ge) and silicon (Si).

Extrinsic Semiconductor

When a small amount of chemical impurity is added to an intrinsic semiconductor, then the resulting semiconductor material is known as **extrinsic semiconductor**. The extrinsic semiconductor is also known as **doped semiconductor**. The process of adding impurity in the intrinsic semiconductor is known as **doping**. The doping of semiconductors increases their conductivity

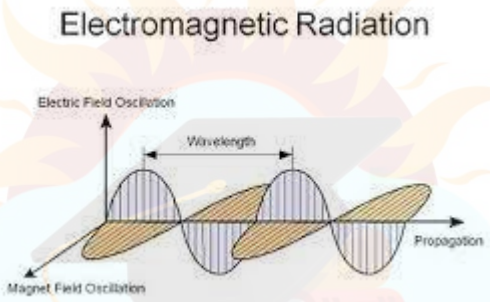
Based on the type of doping, the extrinsic semiconductors are classified into two types viz. **N-type semiconductors** and **P-type semiconductors**. When a pentavalent impurity is added to an intrinsic semiconductor, then the resulting semiconductor is termed as N-type semiconductor. On the other hand, when a trivalent impurity is added to a pure semiconductor, then the obtained semiconductor is known as P-type semiconductor.

UNIT 2

SPECTROSCOPIC TECHNIQUE AND APPLICATIONS

Electromagnetic radiation

Molecules and their energy levels are one main ingredient of spectroscopy. The other main ingredient is the electromagnetic radiation that induces transitions between different energy levels. Let us therefore briefly recall what electromagnetic radiation is. There are two general ways of describing electromagnetic radiation: as a wave and as a particle. Some aspects of an experiment are best explained by the wave concept, but others by the particle concept. We will use both views to explain the interaction of matter with radiation.



EMR

electromagnetic radiation (EMR) consists of waves of the electromagnetic (EM) field, which propagate through space and carry momentum and electromagnetic radiant energy.It includes radio waves, microwaves, infrared, (visible) light, ultraviolet, X-rays, and gamma rays. All of these waves form part of the electromagnetic spectrum.

Introduction

To Recapitulate the Wave parameters

The electromagnetic radiation can be described in a number of properties of parameters

Wavelength

It is the distance between the two adjacent crests (C-C) or troughs (T-T) in a particular wave. It is denoted by the letter , λ(lam da)

Units used for wave length are:

Angstrom(A^0) = 10^{-10}m = 10^{-8} cms

Micrometer (μm) = 10^{-6}m

Nano meter (nm) = 10^{-9}m

Frequency (ν)

Frequency may be defined as the number of waves which can pass through a point in one second (i.e., number of vibrations in unit time) of an electromagnetic radiation.

Frequency (ν) = Velocity of light / Wavelength

$$\nu = \chi/\lambda$$

Velocity of light c = 3×10^{10} cm/sec

Wavelength λ in cm

Wave number ()

The number of waves per unit length is known as **wave number** and is expressed as the reciprocal of wave length.

Wave number is expressed as the waves per cm (cm^{-1}). This unit is also called Kayser (K).

ELECTROMAGNETIC RADIATION

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities. It takes many forms, the most easily recognizable being light and radiant heat. Less obvious manifestations include X-ray, Ultraviolet, microwave and radio radiations.

The electromagnetic radiation is found to have dual nature - the particle nature (*photons)* and wave nature.

The principles and laws that govern the absorption of radiation apply to all wavelengths form X-ray to radiofrequency. The absorption measurements involve the determination of the reduction in power suffered by a beam of radiation as it passes through an absorbing medium of known dimensions.

INTRODUCTION TO SPECTROSCOPY

All chemical species interact with the electromagnetic radiation and in doing so, diminish the intensity or the power of the radiant beam. Absorption spectroscopy is based upon the measurement of this decrease in power (or attenuation) of the radiation brought about by the analyte.

It is convenient to characterize absorptiometric methods according to the type of electromagnetic radiation employed. They are X-rays, Ultraviolet, Visible, Infrared, microwave and radio-frequency radiation.

A white source (electromagnetic radiation) is focused on to a narrow slit and then made to pass through the sample. The light is absorbed by the sample and this is separated into its constituent frequencies by a filter and then sent to the recorder. At this point it may be helpful to consider what happens to the energy absorbed in the above process.

A given sample continues to absorb energy and show an absorption spectrum as long as we irradiate it. i.e. a finite number of molecules appear to be capable of absorbing an infinite amount of energy. Plainly the molecules should get rid of the absorbed energy.

A possible mechanism for this is by thermal collision. An energized molecule collides with its neighbors and gradually **loses its excess energy to them as kinetic energy**. The sample as whole becomes warm.

Another mechanism is that the energy gained from radiation is lost as radiation once more. A molecule in the ground state absorbs energy at frequency and its energy is raised an amount E = hv above the ground state. It is thus in an excited, unstable condition, but **by emitting radiation** of frequency v again, it can revert to the ground state.

The spectrum obtained could be either due to the excess radiation which is not absorbed or due to the emitted radiation.

The study of spectroscopy can be carrie out under the following two heads:

Atomic Spectroscopy

Interaction of electromagnetic radiation with **atoms** which are most commonly in their lowest energy state (ground state) resulting in electronic transitions is called atomic spectroscopy. The spectrum obtained is a line spectrum.

Molecular spectroscopy

Interaction of electromagnetic radiation with **molecules** is called Molecular spectroscopy. This may result in transitions between rotational, vibrational energy levels and electronic transitions. The spectrum obtained is a complicated spectrum.

Differences between Atomic and Molecular spectra		
	Atomic spectra	**Molecular spectra**
1	It is produced due to interaction of atoms with electromagnetic radiation	It is obtained from the interaction of molecules with electromagnetic radiation.

2	Atomic spectra are Line spectra.	Molecular spectra are complicated spectra.
3	It is obtained due to electronic transition in an element	It is produced due to vibrational, rotational and electronic transition in a molecule.

Absorption spectroscopy

If electromagnetic radiations of certain wavelength range are passed through the substance under analysis, radiations of certain wavelengths are absorbed by the substance. The study of this is called the absorption spectroscopy. The wavelength absorbed characterizes some specific functional group of the compound or the compound itself.

Emission spectroscopy

If electromagnetic radiation is passed through a substance or thermal energy is given to the substance under analysis, the energy is absorbed by the atom. The electrons in the ground state get excited to higher energy metastable states. These excited electrons are short lived. So, they emit energy to return to the stable state. The study of this is called the emission spectroscopy. The spectrum obtained is called the emission spectrum.

Fluorescence

The electron in the excited level return to its ground state either directly or in steps with the emission of certain amount of energy. When this **emission of light is instantaneous** the phenomenon is known as **fluorescence**

Phosphorescence

When the electron in the excited level return to its ground state with the **emission of light after some time lag**, it is known as **phosphorescence**

Ultra violet Spectroscopy

Introduction

UV consists of broad absorption bands which have greater utility for quantitative analysis. When polychromatic UV and Visible radiation is passed through a medium containing particle, they interact with the species and electronic transitions occur by the excitation of electrons from the ground state to the excited state. UV and visible radiation have sufficient energy to ensure transitions of the outermost or bonding electrons only.

Singlet set: On excitation the spins of the electrons in the molecular orbitals are paired.

Triplet set: On excitation the spins of electrons in the molecular orbital is unpaired or anti parallel

According to molecular orbital theory, the interaction of atomic orbitals leads to the formation of bonding and antibonding molecular orbitals. They may be classified as

Sigma (σ): The electron density is concentrated along the internuclear axis.

Pi (π) type: The electron density is concentrated above and below the internuclear axis.

Chromophores: **The part of the molecule having n or** π electrons which is essentially for absorption,

Example C=C, C=O, N=N

Auxochromes: **Polar groups having lone pair of electrons.**

Example –OH, OR, -NH_2, -SH etc

Instrumentation for UV and Visible spectroscopy

Principle

When UV-Visible radiations (wavelength range – 200-800nm) are absorbed by atom / molecules, the transition of valence electrons from lower electronic energy level to higher electronic energy level occurs. The amount of energy required for the transition depends on the difference in energy levels of ground state and excited state.

$$E_1 - E_0 = h\nu.$$

When excitation occurs, an electron from one of the filled σ, π or n molecular orbitals get excited to the vacant σ^* or π^* (antibonding) molecular orbitals. Corresponding to possible excitations, there are various absorptions.

$\sigma \rightarrow \sigma^*$ $\pi \rightarrow \sigma^*$ $n \rightarrow \sigma^*$

$\sigma \rightarrow \pi^*$ $p \rightarrow \pi^*$ $n \rightarrow \pi^*$

σ electrons require higher energy for excitation to σ^* or π^* than the excitation of π electrons which in turn is greater than n electrons.

The order of decreasing energy for the transition is

$$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* = \pi \rightarrow \sigma^* > n \rightarrow \sigma^* = \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Working

In a UV-Visible spectrometer, a beam of light is split into two halves. One half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analysed and one-half (the reference beam) is directed through an identical cell that contains the solvent or blank solution. The intensities of the two beams at each wavelength of the region is compared. If the compound absorbs light at a particular wavelength, then intensity of the sample beam will be less than that of the reference beam.

The motor light attenuator drives an **optical edge** into the reference beam until the detector receives light of equal intensity from sample and reference beam. The detector converts UV radiation into electrical signals and sends it to recorder. The output graph obtained is a plot of the wavelength of the entire region versus the absorbance of the light at each wavelength.

INFRARED SPECTROSCOPY

Introduction

The atoms in a molecule do not remain in fixed relative positions but vibrate about some mean position. This fact is used in the IR spectroscopy. The infrared region in the electromagnetic spectrum extends from the red end of the visible spectrum to the microwave region. The region includes radiation at wavelengths between 0.7 and 500 —m or, in wave numbers, between 14000 and 20 cm^{-1}. The spectral region is split into three regions

Near IR (12,500 - 4000 cm^{-1})

The absorption bands resulting from harmonic overtones of fundamental bands and combination bands are present. This region is used for quantitative work

Principle

The IR spectra are given by diatomic molecules with permanent dipole moments, i.e. heteronuclear atomic molecules and polyatomic molecules. When IR radiations (wavelength range –14000 – 20cm^{-1}) are absorbed by atom / molecules, the atoms/ molecules vibrate and undergo transition between vibrational levels. The transitions in the vibrational energy levels are also accompanied by transitions in the rotational energy levels. (So, IR is also called as Rotational – Vibrational spectra). These results in the absorption bands that is characteristic to the atoms / molecules.

Selection or Transition Rule

Selection rule decide whether transition is allowed or not (Forbidden)

Rule 1:

Change in energy level or transition in any energy level. (PRINCIPLE QUANTUM NUMBER)

Rule 2:

Laporte's Rule

Change in orbital angular momentum.

Orbitals change like s,p,d,f

s-p = allowed s-d = not

p-d = allowed p-f = not

d-f = allowed

Rule 3:

Spin selection rule

Delta s = 0 (allowed)

Spin multiplicity of electron should not change

Rule 4:

Total angular momentum change rule

Delta J = 0, +1, -1 (allowed)

Rule 4:

Symmetry selection rule

Sigma to sigma star (allowed)

Pi to pi star (allowed)

NMR Spectroscopy

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy, most commonly known as **NMR spectroscopy** or **magnetic resonance spectroscopy** (**MRS**), is a spectroscopic technique to observe local magnetic fields around atomic nuclei.The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio waves into nuclear magnetic resonance, which is detected with sensitive radio receivers. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups. As the fields are unique or highly characteristic to individual compounds, in modern organic chemistry practice, NMR spectroscopy is the definitive method to identify monomolecular organic compounds.

NMR Spectroscopy Principle

Many nuclei have spin, and all nuclei are electrically charged, according to the NMR principle. An energy transfer from the base energy to a higher energy level is achievable when an external magnetic field is supplied.

- All nuclei are electrically charged and many have spin.
- Transfer of energy is possible from base energy to higher energy levels when an external magnetic field is applied.
- The transfer of energy occurs at a wavelength that coincides with the radio frequency.
- Also, energy is emitted at the same frequency when the spin comes back to its base level.
- Therefore, by measuring the signal which matches this transfer the processing of the NMR spectrum for the concerned nucleus is yield.

NMR Spectroscopy Working

- Place the sample in a magnetic field.
- Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
- These NMR signals are detected with sensitive radio receivers.
- The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
- This gives details of a molecule’s individual functional groups and its electronic structure.

- Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
- This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

Chemical Shift in NMR Spectroscopy

A spinning charge generates a magnetic field that results in a magnetic moment proportional to the spin. In the presence of an external magnetic field, two spin states exist; one spin up and one spin down, where one aligns with the magnetic field and the other opposes it.

Chemical shift is characterized as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule. Nuclear magnetic resonance chemical change is one of the most important properties usable for molecular structure determination. There are also different nuclei that can be detected by NMR spectroscopy, 1H (proton), 13C (carbon 13), 15N (nitrogen 15), 19F (fluorine 19), among many more. 1H and 13C are the most widely used. The definition of 1H as it is very descriptive of the spectroscopy of the NMR. Both the nuts have a good charge and are constantly revolving like a cloud. Through mechanics, we learn that a charge in motion produces a magnetic field. In NMR, when we reach the radio frequency (Rf) radiation nucleus, it causes the nucleus and its magnetic field to turn (or it causes the nuclear magnet to pulse, thus the term NMR).

MRI

Magnetic Resonance (MR) spectroscopy is a noninvasive diagnostic test for measuring biochemical changes in the brain, especially the presence of tumors. While magnetic resonance imaging (MRI) identifies the anatomical location of a tumor, MR spectroscopy compares the chemical composition of normal brain tissue with abnormal tumor tissue. This test can also be used to detect tissue changes in stroke and epilepsy.

Advantages:

- Excellent soft tissue contrast - ideal for brain imaging.
- Non-ionising radiation (radio waves).
- Can also provide functional information (metabolism (MRS), diffusion (DWI), activation (fMRI), tissue perfusion (DCE/DSC/ASL).

Disadvantages:

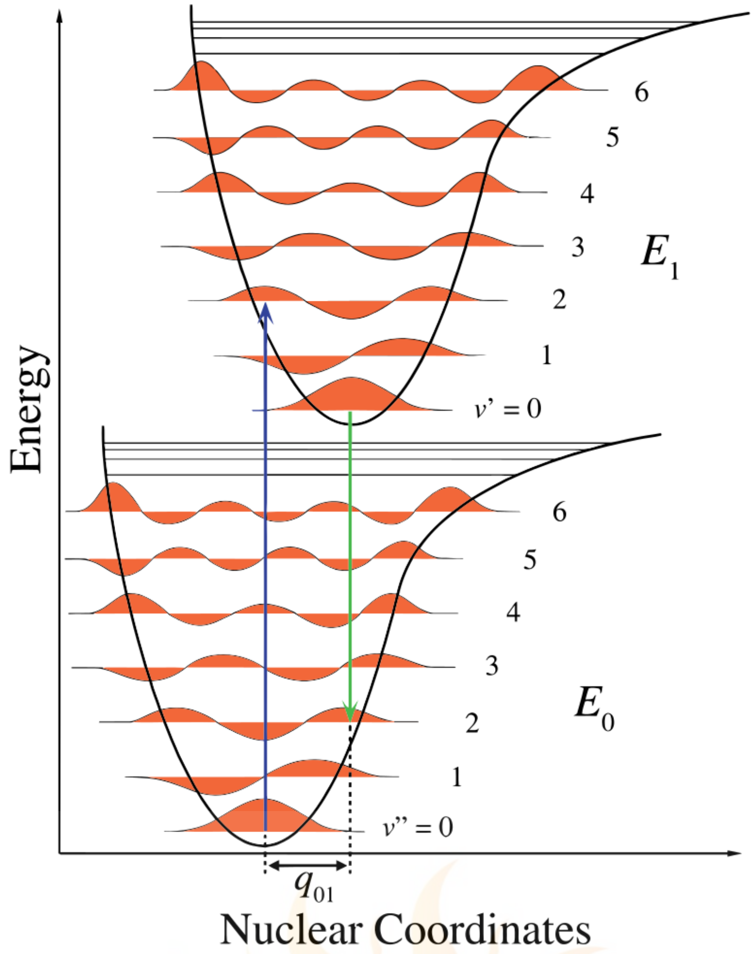
- Time consuming, scans are typically 1h - not so good for emergencies - trauma, stroke...
- Expensive, need special rooms to prevent interference.
- Complex safety protocols (no metal implants, quenching procedure...)

Applications

MR spectroscopy can be used to determine tumor type and aggressiveness, and distinguish between tumor recurrence and radiation necrosis.

The Franck-Condon Principle

The Franck-Condon Principle describes the intensities of vibronic transitions, or the absorption or emission of a photon. It states that when a molecule is undergoing an electronic transition, such as ionization, the nuclear configuration of the molecule experiences no significant change. This is due in fact that nuclei are much more massive than electrons and the electronic transition takes place faster than the nuclei can respond. When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.



The nuclear axis shows a consequence of the internuclear separation and the vibronic transition is indicated by the blue and green vertical arrows. This figure demonstrates three things:

1. An absorption leads to a higher energy state,
2. fluorescence leads to a lower energy state, and
3. the shift in nuclear coordinates between the ground and excited state is indicative of a new equilibrium position for nuclear interaction potential. The fact that the fluorescence arrow is shorter than the absorption indicates that it has less energy, or that its wavelength is longer.

Vibrational and Rotational Spectroscopy of Diatomic Molecules

Spectroscopy is an important tool in the study of atoms and molecules, giving us an understanding of their quantized energy levels. These energy levels can only be solved for analytically in the case of the hydrogen atom; for more complex molecules we must use approximation methods to derive a model for the energy levels of the system. In this paper we will examine the vibration-rotation spectrum of a diatomic molecule, which can be approximated by modeling vibrations as a harmonic oscillator and rotations as a rigid rotor. We will use these models to understand the features of the vibration-rotation spectrum of HCl, allowing us to use the spectrum to learn about properties of the molecule.

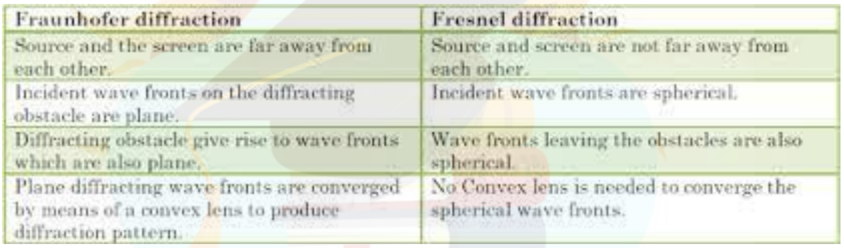
Diffraction and Scattering

Diffraction

The bending of light, or other waves, into the region of the geometrical shadow of an obstacle. More exactly, diffraction refers to any redistribution in space of the intensity of waves that results from the presence of an object that causes variations of either the amplitude or phase of the waves.

Diffraction is a phenomenon of all electromagnetic radiation, including radio waves; microwaves; infrared, visible, and ultraviolet light; and x-rays.

There are two main classes of diffraction, which are known as Fraunhofer diffraction and Fresnel diffraction



Fraunhofer diffraction	Fresnel diffraction
Source and the screen are far away from each other.	Source and screen are not far away from each other.
Incident wave fronts on the diffracting obstacle are plane.	Incident wave fronts are spherical.
Diffracting obstacle give rise to wave fronts which are also plane.	Wave fronts leaving the obstacles are also spherical.
Plane diffracting wave fronts are converged by means of a convex lens to produce diffraction pattern.	No Convex lens is needed to converge the spherical wave fronts.

Scattering

Light can be examined entirely from its source. When light passes from one medium to another, say air, a glass of water, then a part of the light is absorbed by particles of the medium, preceded by its subsequent radiation in a particular direction. This phenomenon is termed a scattering of light.

The intensity of scattered light depends on the size of the particles and the wavelength of the light.

Shorter wavelength and high-frequency scatter more due to the waviness of the line and its intersection with a particle. The wavier the line, the more the chance it intersects with a particle. On the other hand, longer wavelengths have low frequency, they are straighter, and the chances of colliding with the particle are less, so the chances are less.

The bending of multicoloured light can be seen in the afternoon due to the refraction and total internal reflection of light. The wavelength of the sunlight forms different colours in different directions. Rayleigh scattering theory is reasoned for the red colour of the sun in the morning and the blue colour of the sky.

UNIT 3

USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

Definitions:

- System: The part of the Universe that we choose to study
- Surroundings: The rest of the Universe
- Boundary: The surface dividing the System from the Surroundings

Systems can be:

- Open: Mass and Energy can transfer between the System and the Surroundings
- Closed: Energy can transfer between the System and the Surroundings, but NOT mass
- Isolated: Neither Mass nor Energy can transfer between the System and the Surroundings

Two classes of Properties:

- Extensive: Depend on the size of the system (n, m, V,)
- Intensive: Independent of the size of the system (T, p, V = V …)

The State of a System at Equilibrium

Defined by the collection of all macroscopic properties that are described by State variables (p, n, T, V…) [INDEPENDENT of the HISTORY of the SYSTEM]

- For a one-component System, all that is required is “n” and 2 variables. All other properties then follow.

$$V = f(n, p, T) \text{ or } p = g(n, V, T)$$

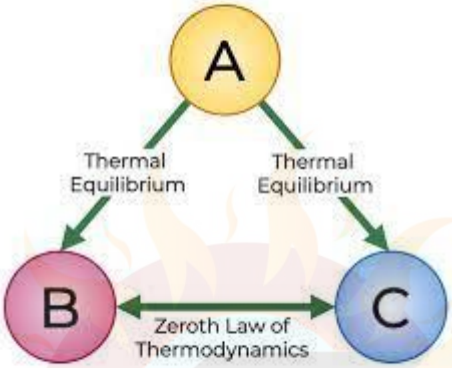
Thermal Equilibrium

When a hot object is placed in thermal contact with a cold object, heat flows from the warmer to the cooler object. This continues until they are in thermal equilibrium (the heat flow stops). At this point, both bodies are said to have the same "temperature".

This intuitively straightforward idea is formalized in the 0th Law of thermodynamics and is made practical through the development of thermometers and temperature scales.

Zero'th LAW of Thermodynamics

If B A and B C are in thermal equilibrium and and are in thermal equilibrium, then A and C are in thermal equilibrium.



Work

Whenever a system interacts with its surroundings, it can exchange energy in two ways- work and heat. In mechanics, work is defined as the product of the force and the displacement in the direction of the force.

Consider a gas in a container with a movable piston on top. If the gas expands, the piston moves out and work is done by the system on the surroundings.

Alternatively, if the gas inside contracts, the piston moves in and work is done by the surroundings on the system.

Why would the gas inside contract or expand? It would if the external pressure,and the internal pressure, were different.

To calculate the work done in moving the piston, we know that the force = pressure times area and then work equals pressure times area times distance or work equals pressure times the change in volume.

$$dW = F\,dl$$

$$dW = F\,dl = PA\,(dl) = P\,dV$$

$$W = \int p\,dV$$

Heat

Heat Heat like work, is a form of energy. The energy transfer between a system and its surroundings is called heat if it occurs by virtue of the temperature difference across the boundary. The two modes of energy transfer – work and heat- depend on the choice of the system. Heat energy moves from a hotter body to a colder body upon contact of the two bodies. If two bodies at different temperatures are allowed to remain in contact, the system of two bodies will eventually reach a thermal equilibrium (they will have the same temperature). A body never contains heat. Rather heat is a transient phenomenon and can be identified as it crosses the boundary.

THE FIRST LAW OF THERMODYNAMICS

So far, we have considered various forms of energy such as heat Q, work W, and total energy E individually, and no attempt is made to relate them to each other during a process.

The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and energy interactions.

Based on experimental observations, the first law of thermodynamics states that energy can be neither created nor destroyed during a process; it can only change forms. Therefore, every bit of energy should be accounted for during a process

(Total energy entering the system) – (Total energy leaving the system)=(Change in the total energy of the system)

REVERSIBLE AND IRREVERSIBLE PROCESSES

A process is reversible if, after the process occurs, the system can be returned to its original state without any net effect on the surroundings. This result occurs only when the driving force is infinitesimally small. Otherwise, the process is said to be irreversible. All real processes are irreversible; however, reversible processes are essential for approximating reality.

HEAT CAPACITY

The heat capacity at constant volume, cv, can be defined as

$$cv \equiv (\partial u / \partial T)\ v$$

From this, it is clear that

$$\Delta u = \int cv\ dT$$

The heat capacity at constant pressure, cP, can be defined as

$$cp \equiv (\partial h / \partial T)$$

From this, it is clear that

$$\Delta h = \int cp\ dT$$

REVERSIBLE, ISOBARIC PROCESS

Since pressure is constant:

$$W = -P\Delta V$$

We then have the following relationships for enthalpy:

$$QP = \Delta H$$

$$\Delta H = \int CP \; dT$$

$$\Delta H = \Delta U + P\Delta V$$

REVERSIBLE, ISOCHORIC PROCESS

Since volume is constant:

$$W = 0$$

We then have the following relationships for the internal energy:

$$QV = \Delta U$$

$$\Delta U = \int CV \; dT$$

$$\Delta H = \Delta U + V\Delta$$

REVERSIBLE, ISOTHERMAL PROCESS

If one is dealing with an ideal gas,

ΔU and ΔH are only functions of temperature, so $\Delta U = \Delta H = 0$ Due to the fact that

$$\Delta U = Q + W,$$

$$Q = -W$$

For an ideal gas, integrate the ideal gas law with respect to V to get

$$W = -nRT \ln (V2 / V1) = nRT \ln (P2 / P1)$$

REVERSIBLE, ADIABATIC PROCESS

By definition the heat exchange is zero, so:

$$Q = 0$$

Due to the fact that

$$\Delta U = Q + W,$$

$$W = \Delta \mathrm{U}$$

Entropy

Entropy Is defined in terms of the heat absorbed during a hypothetical reversible process:

$$ds \equiv \delta q\text{rev} /\text{T}$$

The Second Law of Thermodynamics

The Second Law of Thermodynamics says that the entropy of the universe increases for all real, irreversible processes (and does not change for reversible processes).

By stating,

$$\Delta s\text{univ} = \Delta s\text{sys} + \Delta s\text{surr}$$

the Second Law would read

$$\Delta s\text{univ} \geq 0$$

IRREVERSIBLE PROCESSES FOR IDEAL GASES

A general expression can be written to describe the entropy change of an ideal gas.

Two equivalent expressions are:

$$\Delta s = \int cV/ T *dT + R \ln (V2/ V1)$$

And

$$\Delta s = \int cP /T *dT - R \ln (P2 /P1)$$

In order to find the entropy, change of the universe, one must think about the conditions of the problem statement. If the real process is adiabatic, then $q$surr = 0 and then Δssurr = 0 such that Δsuniv = Δs.

If the real process is isothermal, note that $q = w$ from the First Law of Thermodynamics (i.e., $\Delta u = 0$) amd that due to conservation of energy $q$surr = $-q$. Once $q$surr is known, simply use Δssurr = $q$surr $/T$. The entropy change in the universe is then Δsuniv = Δs + Δssurr.

Internal Energy

Through, Joule experiment what happen to energy between time it is added to water as work, and time it is extracted to heat? Logic suggests that this energy contained in the water in another form which called internal energy.

Internal energy refers to energy of molecules of substance which are ceaseless motion and possess kinetics energy. The addition of heat to a substance increases this molecular activity, and thus causes an increase in its internal energy. Work done on the substance can have the same effect, as was shown by Joule. Internal energy cannot be directly measured; there are no internal-energy meters.

As a result, absolute values are unknown. However, this is not a disadvantage in thermodynamic analysis, because only changes in internal energy are required.

Gibbs Free Energy Equation

Gibbs free energy is equal to the enthalpy of the system minus the product of the temperature and entropy. The equation is given as;

$$\mathbf{G = H - TS}$$

Where,

G = Gibbs free energy

H = enthalpy

T = temperature

S = entropy

OR

or more completely as;

$$\mathbf{G = U + PV - TS}$$

Where,

- U = internal energy (SI unit: joule)
- P = pressure (SI unit: pascal)
- V = volume (SI unit: m^3)
- T = temperature (SI unit: kelvin)

- S = entropy (SI unit: joule/kelvin)

Variations of the Equation

Gibbs free energy is a state function hence it doesn’t depend on the path. So change in Gibbs free energy is equal to the change in enthalpy minus the product of temperature and entropy change of the system.

$$\Delta G = \Delta H - \Delta(TS)$$

If the reaction is carried out under constant temperature$\{\Delta T=O\}$

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

This equation is called the Gibbs Helmholtz equation.

$\Delta G > 0$; the reaction is non-spontaneous and endergonic

$\Delta G < 0$; the reaction is spontaneous and exergonic

$\Delta G = 0$; reaction is at equilibrium

Standard Energy Change of Formation

We can say that the standard Gibbs free energy of formation of a compound is basically the change of Gibbs free energy that is followed by the formation of 1 mole of that substance from its component element available at their standard states or the most stable form of the element which is at 25 °C and 100 kPa. Its symbol is $\Delta_f G^\circ$.

All elements in their standard states (diatomic oxygen gas, graphite, etc.) have standard Gibbs free energy change of formation equal to zero, as there is no change involved.

$$\Delta_f G = \Delta_f G^\circ + RT \ln Q_f,$$

where Q_f is the reaction quotient.

At equilibrium, $\Delta_f G = 0$, and $Q_f = K$, so the equation becomes

$$\Delta_f G^\circ = -RT \ln K,$$

where K is the equilibrium constant.

Relationship Between Free Energy and Equilibrium Constant

The free energy change of the reaction in any state, ΔG (when equilibrium has not been attained) is related to the standard free energy change of the reaction, ΔG° (which is equal to the difference in the free energies of formation of the products and reactants both in their standard states) according to the equation.

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

Where Q is the reaction quotient.

At equilibrium,

$\Delta G=0$ and Q become equal to the equilibrium constant. Hence the equation becomes,

$$\Delta G^\circ = -RT\ \mathrm{In}\ K(eq)$$

$$\Delta G^\circ = -2.303\ RT \log K(eq)$$

- R = 8.314 J mol-1 K-1 or 0.008314 kJ mol-1 K-1.
- T is the temperature on the Kelvin scale

In a reversible reaction, the free energy of the reaction mixture is lower than the free energy of reactants as well as products. Hence, free energy decreases whether we start from reactants or products i.e, ΔG is -ve in backward as well as forward reactions.

Relationship Between Gibbs Free Energy and EMF of a Cell

In the case of galvanic cells, Gibbs energy change ΔG is related to the electrical work done by the cell.

$$\Delta G = -nFE(cell)$$

Where, n = no. of moles of electrons involved

F = the Faraday constant

E = emf of the cell

F=1 Faraday =96500 coulombs

If reactants and products are in their standard states,

$$\Delta G^\circ = -nFE^\circ cell$$

$\Delta G^\circ$and equilibrium

EMF of the cell

The electromotive force of a cell or EMF of a cell is the maximum potential difference between two electrodes of a cell. It can also be defined as the net voltage between the oxidation and reduction half-reactions. The EMF of a cell is mainly used to determine whether an electrochemical cell is galvanic or not.

Electrochemical Series

Likewise, the standard potential values of different metals are calculated and arranged in the increasing order of the potential, we obtain the electrochemical series.

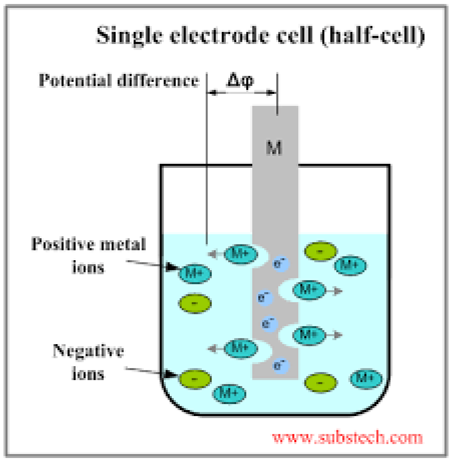
Electrochemical series are essential for the determination of cell potential. It also helps in selecting electrode metals for the construction of a cell.

The electrochemical series table shows the arrangement of a few elements based on the increasing order of their reduction potential. Lithium usually has the least reduction potential and fluorine has the most. Hydrogen has a zero-reduction potential. This is because all other elements are compared against hydrogen to obtain their standard electrode potential.

Electrode Potential

When a metal electrode is immersed in a solution containing its own ions, a potential difference is set up across the interface. This potential difference is called the electrode potential.

Consider the case of the zinc electrode immersed in a zinc sulfate solution. The zinc metal gets oxidized by releasing two electrons and becomes and is dissipated in the solution. The presence of electrons in the electrode and ions in the solution creates a potential difference. Same way, copper develops a positive potential. The combination of these two cells owing to the cell potential.



The standard cell potential (ΔE^o) of a galvanic cell can be calculated by considering the standard reduction potentials of the two half cells E^o.

$$E^o_{cell} = E^o_{red} + E^o_{ox}$$

Or

$$E^o_{cell} = E^o_{Cathode} + E^o_{Anode}$$

Nernst equation relates the equilibrium state potential of a half cell with the standard electrode potential of the half-cell, temperature, reaction coefficients as well as activity of the reacting species.

For an electrode reaction $M^{n+} + n\,e^- \rightarrow M_{(s)}$;

The equilibrium state EMF is given by;

$$E_{M^{n+}\,|\,M} = E^0_{M^{n+}\,|\,M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

PERIODIC PROPERTIES

Effective Nuclear Charge

- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- The nuclear charge that an electron “feels” depends on both factors.
- It’s called Effective nuclear charge.
- electrons in lower energy levels “shield” outer electrons from positive charge of nucleus.

The effective nuclear charge, Zeff, is:

Zeff = Z − S

Where: Z = atomic number

S = screening constant,

usually close to the number of inner (n-1) electrons.

Valence electrons

Many chemical properties depend on the valence electrons. Valence electrons:

The outer electrons, that are involved in bonding and most other chemical changes of elements. Rules for defining valence electrons.

1. In outer most energy level (or levels)
2. For main group (representative) elements (elements in s world or p world) electrons in filled d or f shells are not valence electrons
3. For transition metals, electrons in full f shells are not valence electrons.

Shielding Effect

When the number of inner electrons is greater, they shelter the outermost electron from the nucleus, allowing it to neglect the nuclear pull to some extent. This is referred to as the shielding or screening effect.

1.It is the repulsion of valence electrons that counteracts the attraction between these electrons and the nucleus.
2.The shielding effect increases when elements move down the group in the periodic table because of an increase in the number of inner orbits around the nucleus.
3.The outermost electrons of the high atomic number elements experience the low electrostatic force of attraction due to the repulsion that decreases the shielding effect.
4.The shielding effect for a period is constant because each period has a fixed number of orbits around the nucleus.
5.The order of the shielding effect in the sub-shell is: $s>p>d>f$ because the orbitals form diffuse shapes as the effect decreases.

Penetration

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom. Electrons in different orbitals have different wavefunctions and therefore different radial distributions and probabilities (defined by quantum numbers n and m_l around the nucleus). In other words, penetration depends on the shell (n) and subshell (m_l). For example, we see that since a 2s electron has more electron density near the nucleus than a 2p electron, it is penetrating the nucleus of the atom more than the 2p electron. The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell.

Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

$$s>p>d>f$$

And for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

1s>2s>2p>3s>3p>4s>3d>4p>5s>4d>5p>6s>4f....

and the energy of an electron for each shell and subshell goes as follows...

1s<2s<2p<3s<3p<4s<3d<4p....

The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. If we imagine a dartboard that represents the circular shape of the s-orbital and if the darts landed in correlation to the probability to where and electron would be found, the greatest dart density would be at the 50 points region but most of the darts would be at the 30 point region. When considering the 1s-orbital, the spherical shell of 53 pm is represented by the 30 point ring.

Electrons which experience greater penetration experience stronger attraction to the nucleus, less shielding, and therefore experience a larger *Effective Nuclear Charge* (Zeff), but shield other electrons more effectively.

Electronic Configuration

The electron configuration of an element describes how electrons are distributed in its atomic orbitals. Electron configurations of atoms follow a standard notation in which all electron-containing atomic subshells (with the number of electrons they hold written in superscript) are placed in a sequence. For example, the electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$.

Neon	$1s^2 2s^2 2p^6$		
Aluminum	$1s^2 2s^2 2p^6 3s^2 3p^1$	Becomes	[Ne] $3s^2 3p^1$
Ar gon	$1s^2 2s^2 2p^6 3s^2 3p^6$		
Calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	Becomes	[Ar] $4s^2$

Shells

The maximum number of electrons that can be accommodated in a shell is based on the principal quantum number (n). It is represented by the formula $2n^2$, where ‘n’ is the shell number. The shells, values of n, and the total number of electrons that can be accommodated are tabulated below.

Shell and ‘n’ value	**Maximum electrons present in the shell**
K shell, n=1	$2*1^2 = 2$
L shell, n=2	$2*2^2 = 8$
M shell, n=3	$2*3^2 = 18$
N shell, n=4	$2*4^2 = 32$

Subshells

- The subshells into which electrons are distributed are based on the azimuthal quantum number (denoted by ‘l’).
- This quantum number is dependent on the value of the principal quantum number, n. Therefore, when n has a value of 4, four different subshells are possible.
- When n=4. The subshells correspond to l=0, l=1, l=2, and l=3 and are named the s, p, d, and f subshells, respectively.
- The maximum number of electrons that can be accommodated by a subshell is given by the formula $2*(2l + 1)$.
- Therefore, the s, p, d, and f subshells can accommodate a maximum of 2, 6, 10, and 14 electrons, respectively.

All the possible subshells for values of n up to 4 are tabulated below.

Principle Quantum Number Value	**Value of Azimuthal Quantum Number**	**Resulting Subshell in the Electron Configuration**
n=1	l=0	1s
n=2	l=0	2s

	l=1	2p
n=3	l=0	3s
	l=1	3p
	l=2	3d
n=4	l=0	4s
	l=1	4p
	l=2	4d
	l=3	4f

Thus, it can be understood that the 1p, 2d, and 3f orbitals do not exist because the value of the azimuthal quantum number is always less than that of the principal quantum number.

Notation

- The electron configuration of an atom is written with the help of subshell labels.
- These labels contain the shell number (given by the principal quantum number), the subshell name (given by the azimuthal quantum number) and the total number of electrons in the subshell in superscript.
- For example, if two electrons are filled in the ‘s’ subshell of the first shell, the resulting notation is ‘$1s^2$’.
- With the help of these subshell labels, the electron configuration of magnesium (atomic number 12) can be written as $1s^2\ 2s^2\ 2p^6\ 3s^2$.

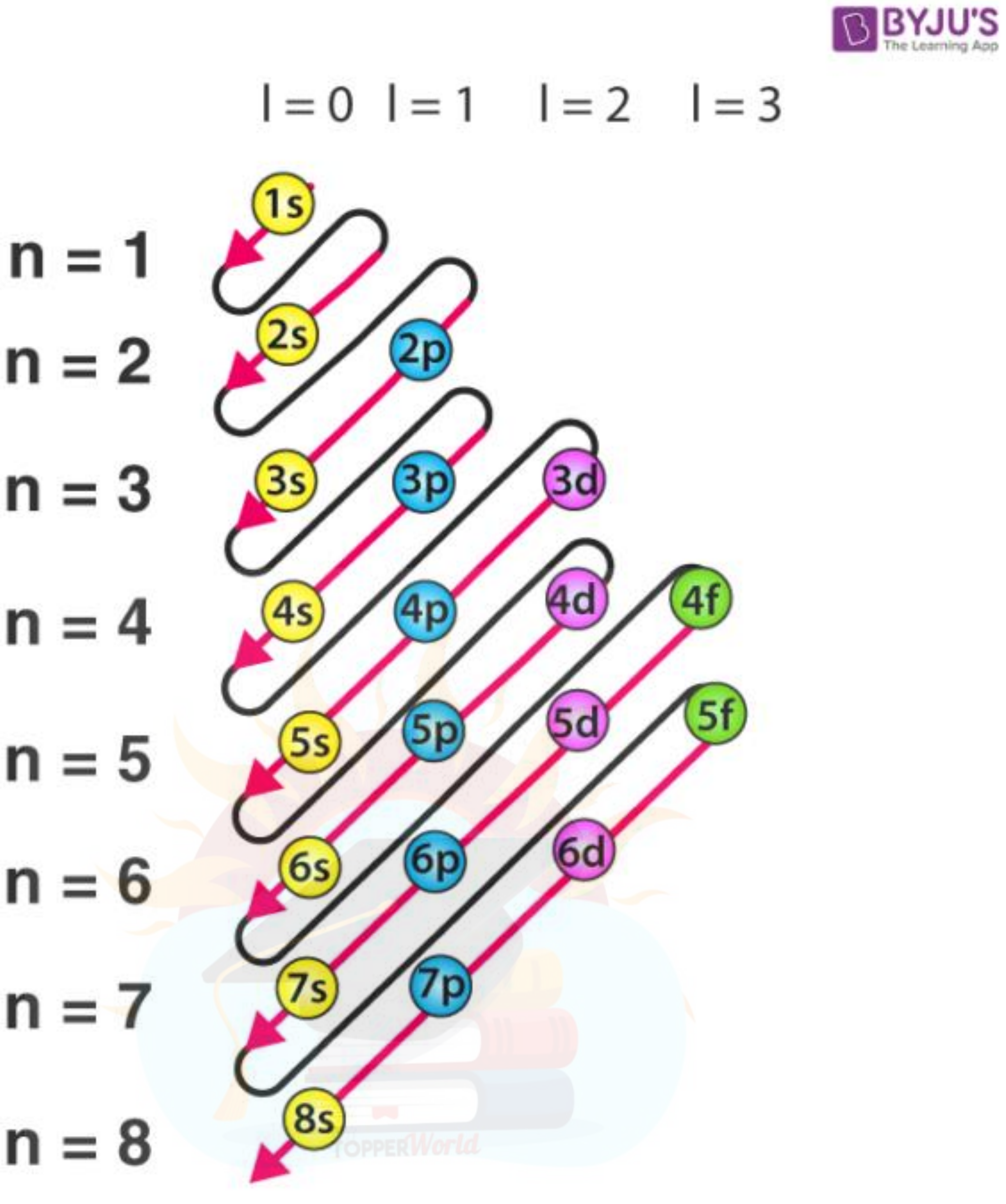
Filling of Atomic Orbitals

Aufbau Principle

- This principle is named after the German word ‘Aufbeen’ which means ‘build up’.
- The Aufbau principle dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals.
- The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.

- According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…

The order in which electrons are filled in atomic orbitals as per the Aufbau principle is illustrated below.



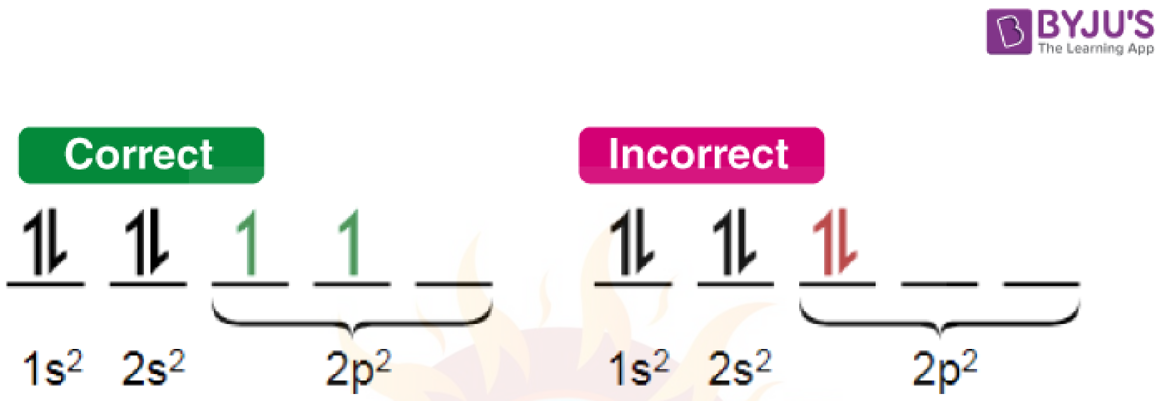
Pauli Exclusion Principle

- The Pauli exclusion principle states that a maximum of two electrons, each having opposite spins, can fit in an orbital.

- This principle can also be stated as “no two electrons in the same atom have the same values for all four quantum numbers”.
- Therefore, if the principal, azimuthal, and magnetic numbers are the same for two electrons, they must have opposite spins.

Hund’s Rule

- This rule describes the order in which electrons are filled in all the orbitals belonging to a subshell.
- It states that every orbital in a given subshell is singly occupied by electrons before a second electron is filled in an orbital.
- In order to maximize the total spin, the electrons in the orbitals that only contain one electron all have the same spin (or the same values of the spin quantum number).



An illustration detailing the manner in which electrons are filled in compliance with Hund’s rule of maximum multiplicity is provided above.

Representation of electronic Configuration of Atom
The electron configurations of a few elements are provided with illustrations in this subsection.

PERIODIC TRENDS

Electronegativity Trend

- From left to right across a period of elements, electronegativity increases. If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.
- From top to bottom down a group, electronegativity decreases. This is because atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.
- Important exceptions of the above rules include the noble gases, lanthanides, and actinides. The noble gases possess a complete valence shell and do not usually attract electrons. The lanthanides and actinides possess more complicated chemistry that does not generally follow any trends. Therefore, noble gases, lanthanides, and actinides do not have electronegativity values.
- As for the transition metals, although they have electronegativity values, there is little variance among them across the period and up and down a group. This is because their metallic properties affect their ability to attract electrons as easily as the other elements.

Ionization Trend

Ionization Energy is the energy required to remove an electron from a neutral atom in its gaseous phase. Conceptually, ionization energy is the opposite of electronegativity.

The lower this energy is, the more readily the atom becomes a cation. Therefore, the higher this energy is, the more unlikely it is the atom becomes a cation.

Ionization energies decrease as atomic radii increase.

- Across a period, Zeff *increases* and n (principal quantum number) *remains the same*, so the ionization energy *increases*.
- Down a group, n *ncreases* and Zeff *increases slightly;* the ionization energy *decreases*

Electron Affinity Trends

As the name suggests, electron affinity is the ability of an atom to accept an electron. Unlike electronegativity, electron affinity is a quantitative measurement of the energy change that occurs when an electron is added to a neutral gas atom. The more negative the electron affinity value, the higher an atom's affinity for electrons.

- Electron affinity increases from left to right within a period. This is caused by the decrease in atomic radius.
- Electron affinity decreases from top to bottom within a group. This is caused by the increase in atomic radius.

Atomic Radius Trends

The atomic radius is one-half the distance between the nuclei of two atoms (just like a radius is half the diameter of a circle). However, this idea is complicated by the fact that not all atoms are normally bound together in the same way. Some are bound by covalent bonds in molecules, some are attracted to each other in ionic crystals, and others are held in metallic crystals. Nevertheless, it is possible for a vast majority of elements to form covalent molecules in which two like atoms are held together by a single covalent bond. The covalent radii of these molecules are often referred to as atomic radii. This distance is measured in picometers. Atomic radius patterns are observed throughout the periodic table.

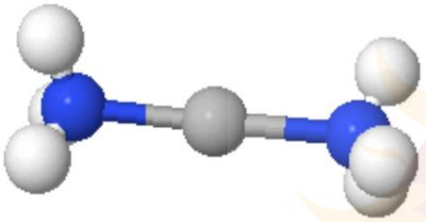
Atomic size gradually decreases from left to right across a period of elements. This is because, within a period or family of elements, all electrons are added to the same shell. However, at the same time, protons are being added to the nucleus, making it more positively charged. The effect of increasing proton number is greater than that of the increasing electron number; therefore, there is a greater nuclear attraction. This means that the nucleus attracts the electrons more strongly, pulling the atom's shell closer to the nucleus. The valence electrons are held closer towards the nucleus of the atom. As a result, the atomic radius decreases.

Coordination Numbers and Geometry

The total number of points of attachment to the central element is termed the coordination number and this can vary from 2 to as many as 16, but is usually 6. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion.

Coordination Number 2

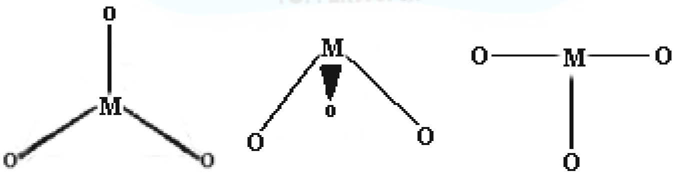
This arrangement is not very common for first row transition metal ion complexes and some of the best-known examples are for Silver(I). In this case we have a low charge and an ion at the right-hand side of the d-block indicating smaller size



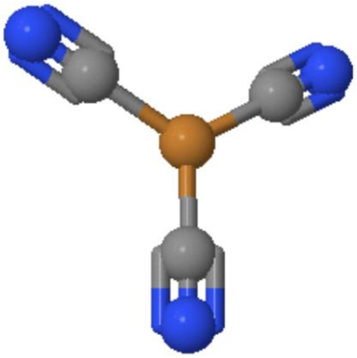
The linear [Ag (NH$_3$)$_{2]}$ $_{+}$ ion

Coordination Number 3

Once again, this is not very common for first row transition metal ions. Examples with three different geometries have been identified:



- **Trigonal planar Geometry**: Well, known for main group species like CO_3^{2-} etc., this geometry has the four atoms in a plane with the bond angles between the ligands at 120 degrees.

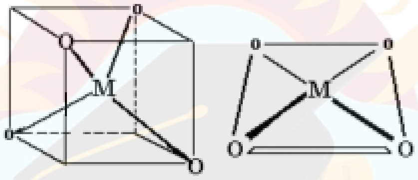


The Trigonal planar $[Cu\ (CN)_3]^{2-}$ system

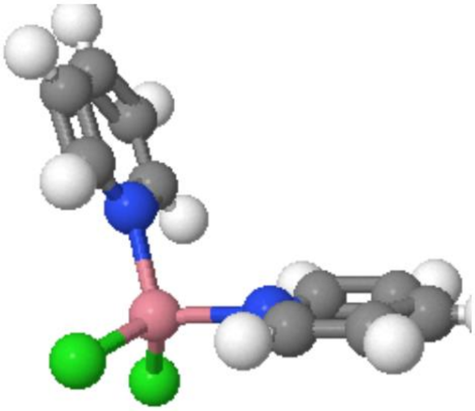
- **Trigonal pyramid Geometry**: More common with main group ions.
- **T-shaped**: The first example of a rare T-shaped molecule was found in 1977.

Coordination Number 4

Two different geometries are possible. The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.

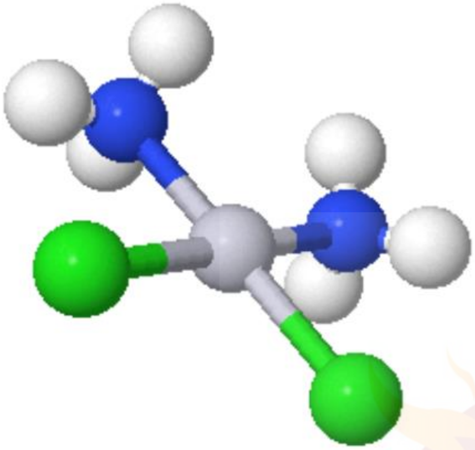


- **Tetrahedral Geometry**: The chemistry of molecules centered around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co. There are large numbers of tetrahedral Cobalt (II) complexes known.



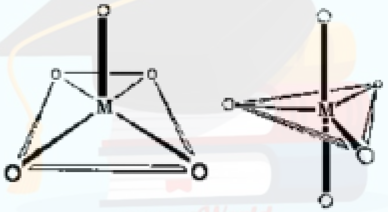
$CoCl_2pyr_2$

- **Square Planar Geometry:** This is fairly rare and is included only because some extremely important molecules exist with this shape.



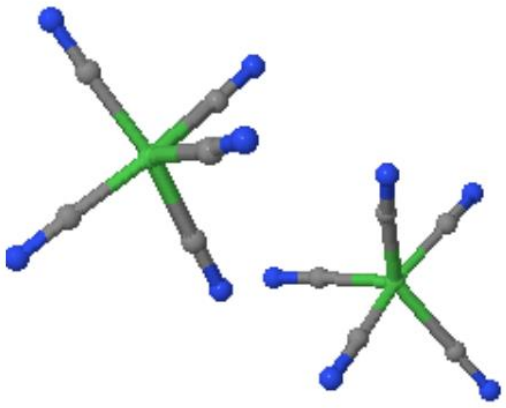
cisplatin - cis-$PtCl_2(NH_3)_2$

Coordination Number 5



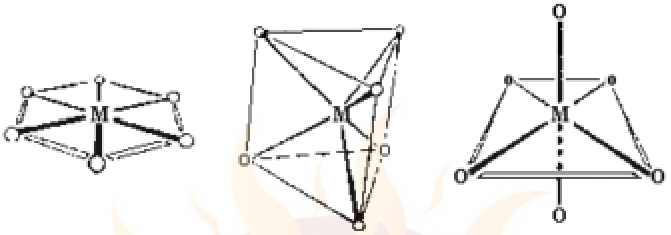
- **Square pyramid Geometry:** Oxovanadium salts (Vanadyl, VO^{2+}) often show square pyramidal geometry, for example, $VO(acac)_2$. Note that the Vanadium (IV) can be considered coordinatively unsaturated and addition of pyridine leads to the formation of an octahedral complex.

- **Trigonal Bipyramid Geometry:** The structure of $[Cr(en)_3][Ni(CN)_5]$ 1.5 H_2O was reported in 1968 to be a remarkable example of a complex exhibiting both types of geometry in the same crystal. The reaction of cyanide ion with Ni^{2+} proceeds via several steps:

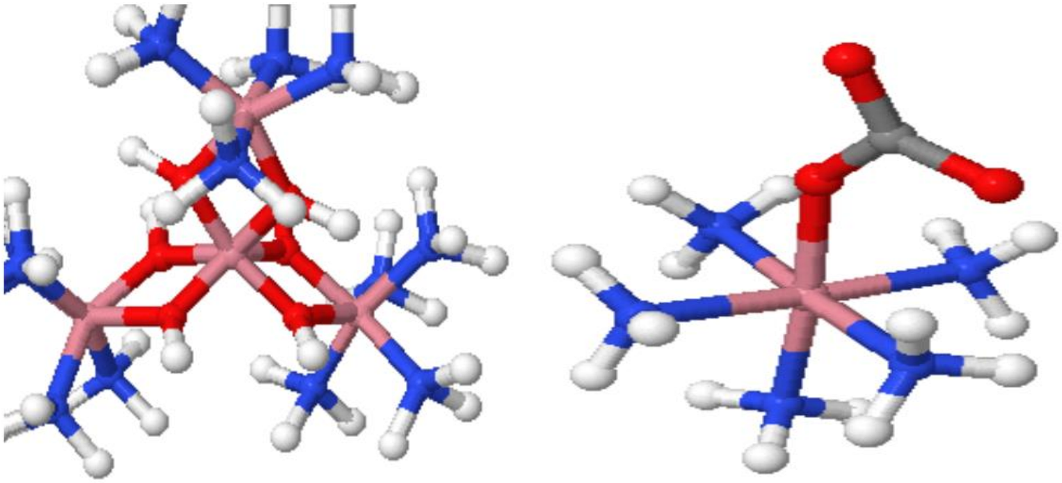


$[Ni(CN)_5]^{3-}$

Coordination Number 6



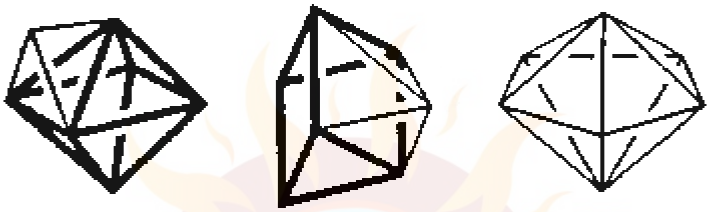
- **Hexagonal planar Geometry**: Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.
- **Trigonal prism Geometry**: Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral (Oh):** The most common geometry found for first row transition metal ions, including all aqua ions. In some cases, distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.



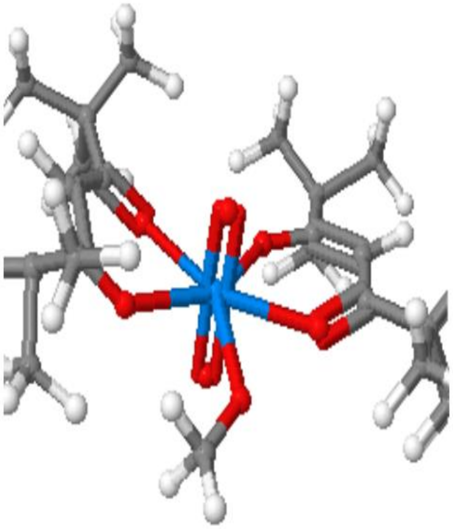
$[Co(en)_3]Cl_3$(left) and $[CoCO_3(NH_3)_5]^+$ (right)

Coordination Number 7

Not very common for 1st row complexes and the energy difference between the structures seems small and distortions occur so that prediction of the closest "idealized" shape is generally difficult. Three geometries are possible:

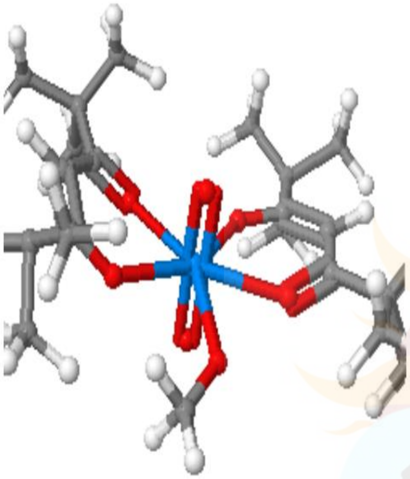


- **Capped octahedron (C_{3v}) Geometry**



$K_3[NbOF_6]$

- **Capped trigonal prism (C_{2v})**
- **Pentagonal Bipyramid (D_{5h})**



bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium

UNIT 4

STEREOCHEMISTRY

STEREOCHEMISTRY:

The branch of chemistry which deals with three-dimensional structure of molecule and their effect on physical and chemical properties is known as stereochemistry.

OPTICAL ACTIVITY:

We know that ordinary lights are composed of rays of different wavelengths vibrating in all directions perpendicular to the path of its propagation. These vibrations can be made to occur in a single plane by passing ordinary light through the polarizing Nicol prism. Such light whose vibrations occur in only one plane is called plane polarized light

Compounds which rotate the plane of polarized light are called optically active compounds and this property is known as optical activity. Rotation of plane of polarized light can be of two types.

- **Dextrorotatory:** If the compound rotates the plane of polarization to the right(clockwise) it is said to be dextrorotatory (Latin: dexter-right) and is denoted by (+), or 'd'
- **Laevorotatory :** If the compound rotates the plane of polarization to the left(anticlockwise) it is said to be laevorotatory (Latin: laevus-left) and is denoted by (-) or 'l'

The change in the angle of plane of polarization is known as optical rotation. The optical rotation is detected and measured by an instrument called polarimeter.

CHIRALITY

The term Chiral- The word chiral (Greek word Chier,meaning hand) is used for those objects which have right-handed and left-handed forms, i.e., molecules which have "handedness" and the general property of "handedness" is termed chirality. An object which is not superimposable upon its mirror image is chiral

The term Achiral-Object and molecules which are superimposable on their mirror images is achiral. Achiral molecule has internal plane of symmetry, a hypothetical plane which bisects an object or molecule into mirror-reflactive halves. An object or molecule with an internal plane of symmetry is achiral.

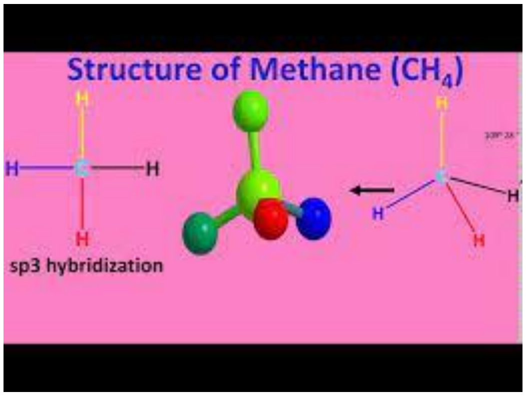
The term Asymmetric center and chiral center- Three terms are used to designate, a carbon atom bonded tetrahedrally to four different substituents in a chiral molecule: Asymmetric atom, chiral center or stereocenter.

REPRESENTATION OF THREE-DIMENSIONAL MOLECULES

FLYING-WEDGE OR WEDGE-DASH PROJECTION

The Flying-Wedge Projection is the most widely used three-dimensional representation of a molecule on a two-dimensional surface (paper). This kind of representation is usually done for molecule containing chiral centre. In this type of representation three types of lines are used.

• A solid wedge or thick line () - it represents bond projection towards the observer or above the plane of paper. • A continuous line or ordinary line () - it represents bond in the plane of paper. • A dashed wedge or broken line () - it represents bond projection away from the observer or below the plane of paper. Example: - CH4 (methane)

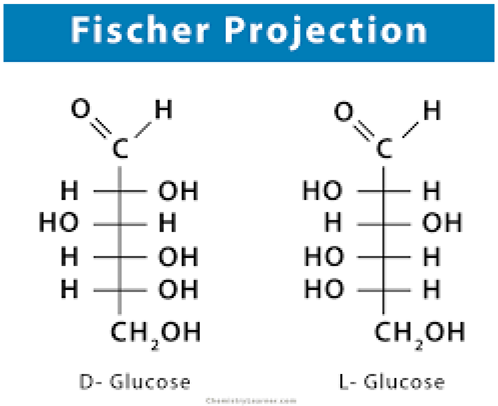


FISCHER PROJECTION

Fischer projection provide an easy way to draw three-dimensional molecule on two-dimensional paper and all the bonds are drawn as solid lines around asymmetric carbon atom.

The Fischer rules for showing the arrangement around asymmetric carbon.

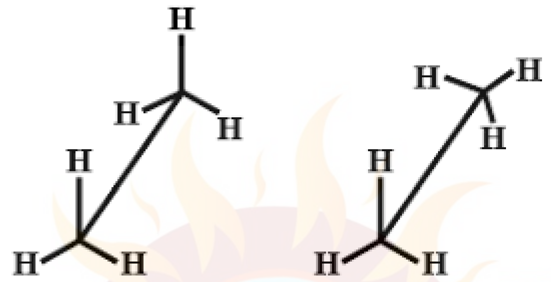
- The carbon chain of the compound is projected vertically, with the most oxidized carbon at the top or place the carbon number one at the top (as defined by nomenclature rule).
- The chiral carbon atom lies in the plane of the paper and usually omitted. The intersection of cross lines represents asymmetric carbon.
- The horizontal bonds attached to the chiral carbon are considered to be above the plane of paper or point towards the observer.
- The vertical bonds attached to the chiral carbon are considered to be below the plane of paper or point away from the observer.



D- Glucose L- Glucose

SAWHORSE FORMULA

The sawhorse formula indicates the arrangement of all the atoms or groups on two adjacent carbon atoms. The bonds between the two carbon atoms are drawn diagonally and of relatively greater length for the sake of clarity. The lower left-hand carbon is taken as the front carbon or towards the observer and the upper right-hand carbon as the back carbon or away from the observer.



(i) Eclipsed (ii) Staggered

Sawhorse projections of ethane

NEWMAN PROJECTION

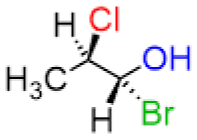
Newman devised a very simple method of projecting three dimensional formulas on two-dimensional paper which are known as Newman projection.

- In these formulae the molecule is viewed from the front or along the axis of a carbon-carbon bond.

- The carbon nearer to the eye is represented by a point and the carbon atom towards the rear by circle.

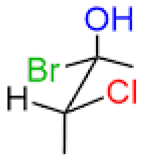
- The three atoms or groups on the carbon atoms are shown as being bonded to dot or circle by an angle of 1200 to each other.

- In Newman formula all parallel bonds are eclipsed or all anti parallel or opposite bonds are staggered.



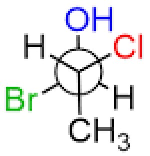
Bond-line

≡



Sawhorse

≡



Newman

NOMENCLATURE OF OPTICAL ISOMERS

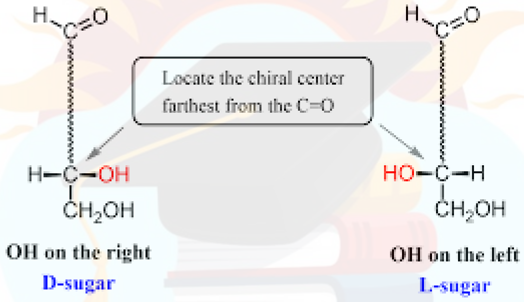
D, L SYSTEM OF NOMENCLATURE

This nomenclature is mainly used in sugar chemistry or optically active polyhydric carbonyl compounds. This is a relative nomenclature because all the configurations described with respect to glyceraldehydes.

All sugars whose Fischer projection formula shows the OH group on the right-hand side of the chiral atom belong to the D-series.

Similarly, if OH is on the left-hand side, then the sugar belongs to the L-series.

D and L Configuration of Carbohydrates



R.S. NOMENCLATURE

The order of rearrangement of four groups around a chiral carbon is called the absolute configuration around that atom. This system is known as (R) and (S) system or the Cahn-Ingold Prelog system. The letter (R) comes from the Latin rectus (means right) while (S) comes from the Latin sinister (means left). Any Chiral carbon atoms have either an (R) configuration or a (S) configuration.

Therefore, one enantiomer is (R) and the other is (S). A recemic mixture may be designated as (RS), meaning a mixture of the two.

The R, S nomenclature involves two steps:

Step I: The four ligands (atom or groups) attached to the chiral centre are assigned a sequence of priority according to sequence rules.

Rule 1: If all the four atoms directly attached to the chiral carbon are different, priority depends on their atomic number. The atom having highest atomic number gets the highest priority, i.e., (1). The atom with lowest atomic number is given lowest priority, i.e. (2), the group with next higher atomic number is given the next higher priority (3) and so on.

Rule 2: if two or more than two isotopes of the same element are present, the isotope of higher mass receives the higher priority.

Rule 3: if two or more of the atoms directly bonded to the chiral carbon are identical, the atomic number of the next atom is used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at the first point of difference along the chain. The atom that has attached to it an atom of higher priority gets the higher priority.

Rule 4: If a double or a triple bond is linked to chiral centre, the involved electrons are duplicated or triplicated respectively.

STEP-II: The molecule is then visualised so that the group of lowest priority (4) is directed away from the observer (at this position the lowest priority is at the bottom of the plane). The remaining three groups are in a plane facing the observer. If the eye travels clockwise as we look from the group of highest priority to the group of second and third priority (i.e., 1 2 3 with respect to 4) the configuration is designated R. If arrangement of groups is in anticlockwise direction, the configuration is designated as S.

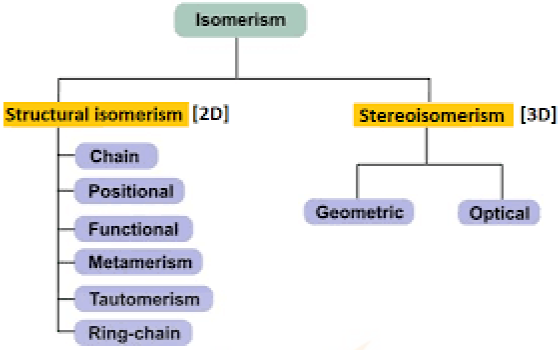
Case-I: R and S nomenclature from Fischer projection formula (Golden rule): If in a Fischer projection, the group of lowest priority (4) is on a vertical line, then the assignment of configuration is R for a clockwise sequence of 1 to 2to 3 and S for anticlockwise sequence.

Case-II: R, S- nomenclature from flying-wedge formula.

If the group of the lowest priority is away from the observer (i.e., bonded by dashed line) and the priority sequence (1 2 3) is clockwise, then the configuration is assigned as R. If the priority sequence is anticlockwise then the configuration is S.

ISOMERS

Chemical compounds that have identical chemical formulae but differ in properties and the arrangement of atoms in the molecule are called **isomers**. Therefore, the compounds that exhibit isomerism are known as isomers.

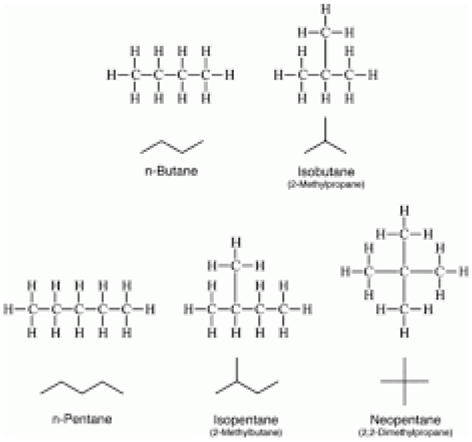


Structural Isomerism

Structural isomerism is commonly referred to as constitutional isomerism. The functional groups and the atoms in the molecules of these isomers are linked in different ways. Different structural isomers are assigned different IUPAC names since they may or may not contain the same functional group.

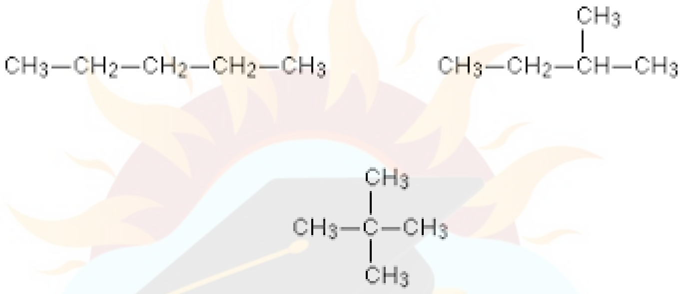
Chain Isomerism

- It is also known as skeletal isomerism.
- The components of these isomers display differently branched structures.
- Commonly, chain isomers differ in the branching of carbon
- An example of chain isomerism can be observed in the compound C_5H_{12}, as illustrated below.



Position Isomerism

- The positions of the functional groups or substituent atoms are different in position isomers.
- Typically, this isomerism involves the attachment of the functional groups to different carbon atoms in the carbon chain.
- An example of this type of isomerism can be observed in the compounds having the formula C_3H_7Cl.



$CH_3-CH_2-CH_2-CH_2-CH_3$

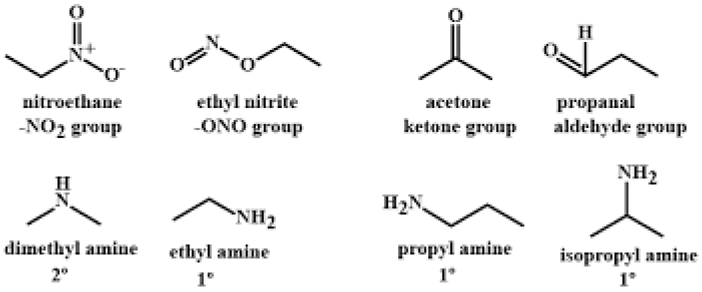
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

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

Functional Isomerism

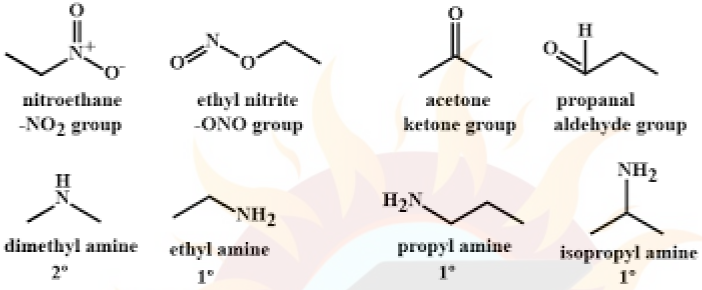
- It is also known as functional group isomerism.
- As the name suggests, it refers to the compounds that have the same chemical formula but different functional groups attached to them.

- An example of functional isomerism can be observed in the compound C_3H_6O.



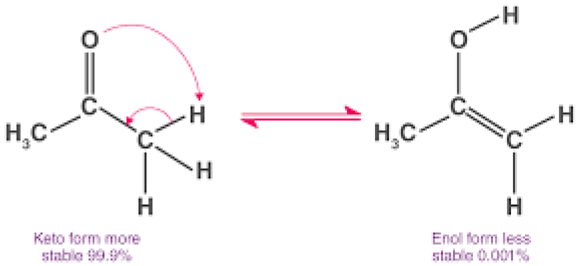
Metamerism

- This type of isomerism arises due to the presence of different alkyl chains on each side of the functional group.
- It is a rare type of isomerism and is generally limited to molecules that contain a divalent atom (such as sulphur or oxygen), surrounded by alkyl groups.
- Example: $C_4H_{10}O$ can be represented as ethoxyethane ($C_2H_5OC_2H_5$) and methoxy-propane ($CH_3OC_3H_7$).



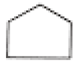
Tautomerism

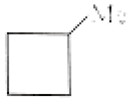
- A tautomer of a compound refers to the isomer of the compound which only differs in the position of protons and electrons.
- Typically, the tautomers of a compound exist together in equilibrium and easily interchange.
- It occurs via an intramolecular proton transfer.
- An important example of this phenomenon is Keto-enol tautomerism.



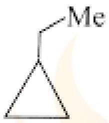
Ring-Chain Isomerism

- In ring-chain isomerism, one of the isomers has an open-chain structure whereas the other has a ring structure.
- They generally contain a different number of pi bonds.
- A great example of this type of isomerism can be observed in C_3H_6. Propene and cyclopropane are the resulting isomers, as illustrated below.

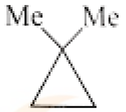
1.

Cyclopentane

2.


1-Methyl cyclobutane

3.


1-Ethyl cyclopropane

4.


1,1-Dimethyl cyclopropane

Stereoisomerism

This type of isomerism arises in compounds having the same chemical formula but different orientations of the atoms belonging to the molecule in three-dimensional space. The compounds that exhibit stereoisomerism are often referred to as stereoisomers. This phenomenon can be further categorized into two subtypes. Both these subtypes are briefly described in this subsection.

Geometric Isomerism

- It is popularly known as cis-trans isomerism.
- These isomers have different spatial arrangements of atoms in three-dimensional space.

- An illustration describing the geometric isomerism observed in the acyclic But-2-ene molecule is provided below.

Optical Isomerism

- Compounds that exhibit optical isomerism feature similar bonds but different spatial arrangements of atoms forming non-superimposable mirror images.
- These optical isomers are also known as enantiomers.
- Enantiomers differ from each other in their optical activities.
- Dextro enantiomers rotate the plane of polarized light to the right whereas laevo enantiomers rotate it to the left, as illustrated below.

Conformational Isomers

Let us understand the fundamentals of conformation with the example of ethane. If we observe the ball and stick model of ethane and rotate one carbon atom keeping another carbon atom stationary about the C-C axis. We will observe that the rotations will result in an infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These different arrangements are better known as **conformational isomers** or **conformers**.

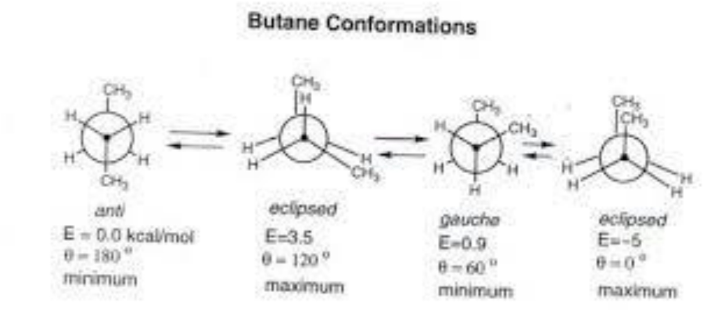
Predominantly, these can be broadly classified into two different cases

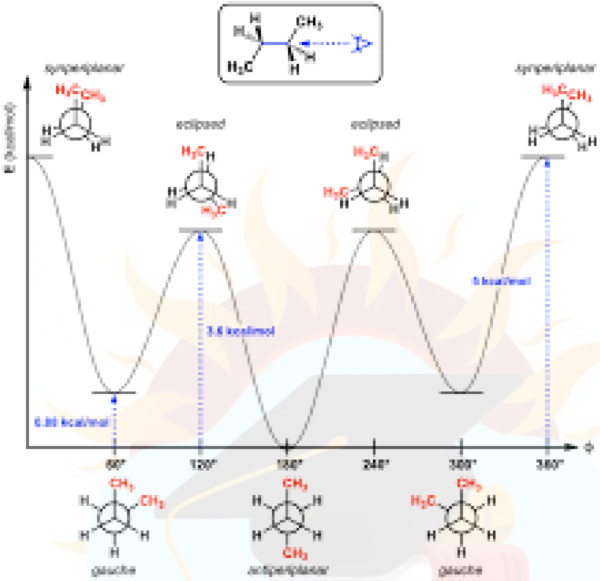
Eclipse conformation
Conformation in which hydrogen atoms are attached to two carbons stay nearest to each other as possible is known as eclipsed

Staggered conformation
Confirmation in which hydrogen atoms attached to two carbons are as far as possible with respect to each other is known as staggered The staggered conformation is thus relatively more stable in comparison to eclipse conformation as there are minimum repulsive forces, minimum energy due to many separations between the electron clouds of C-H bonds.

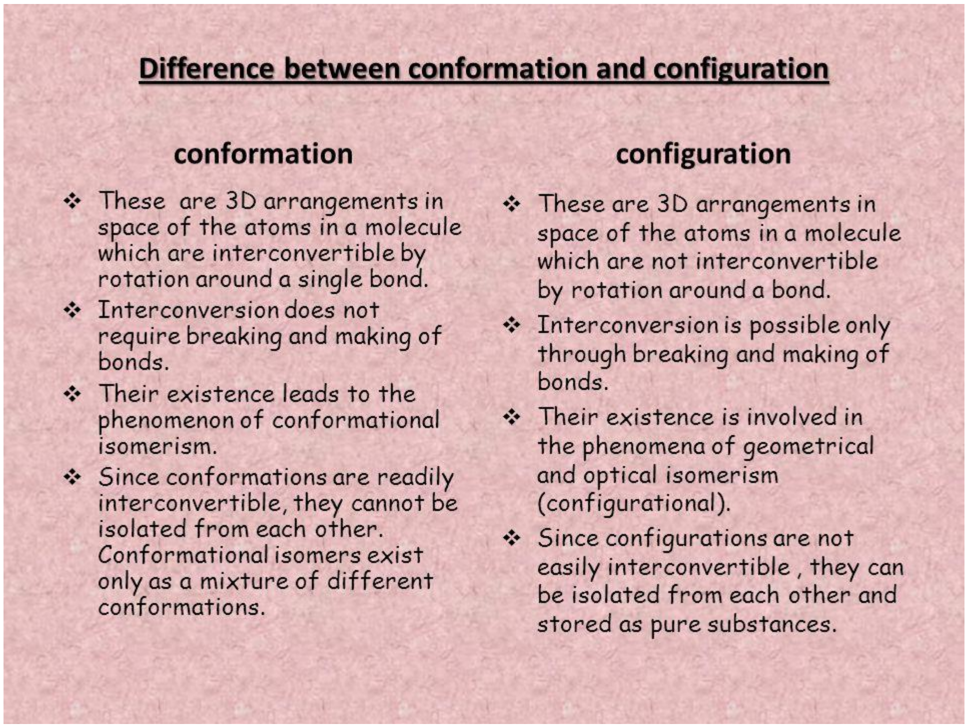
Conformational Analysis of Butane

Butane is an alkane with the presence of C-C bonds. Normally, when we rotate the molecule of butane at the axis of the C-C bond, it shows different conformation isomerism. Generally, Butane has four conformation isomers which are fully eclipsed, gauche, eclipsed, and anti butane conformational isomers.





Difference between Conformation and configuration



Difference between conformation and configuration

conformation	configuration
These are 3D arrangements in space of the atoms in a molecule which are interconvertible by rotation around a single bond.	These are 3D arrangements in space of the atoms in a molecule which are not interconvertible by rotation around a bond.
Interconversion does not require breaking and making of bonds.	Interconversion is possible only through breaking and making of bonds.
Their existence leads to the phenomenon of conformational isomerism.	Their existence is involved in the phenomena of geometrical and optical isomerism (configurational).
Since conformations are readily interconvertible, they cannot be isolated from each other. Conformational isomers exist only as a mixture of different conformations.	Since configurations are not easily interconvertible , they can be isolated from each other and stored as pure substances.

ORGANIC REACTION AND SYNTHESIS OF DRUGS

Organic Reactions

Organic reactions are the chemical reactions that are undergone by organic compounds (the chemical compounds containing carbon)

There are mainly five types of organic reactions:

1.Substitution reaction

2.Elimination reaction

3.Addition reaction

4.Radical reactions

5.Oxidation-Reduction Reactions

Substitution Reactions

In a substitution reaction, one atom or a group of atoms is substituted by another atom or a group of atoms to form a new substance.

For example, the conversion of methane to chloromethane is a substitution reaction as hydrogen atoms are replaced by chlorine atoms.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Substitution Reactions are of two types naming nucleophilic reaction and electrophilic reactions. These two types of reactions mainly differ in the kind of atom which is attached to its original molecule.

Nucleophilic Substitution Reaction:
Nucleophiles are those species in the form of an ion or a molecule which are strongly attached to the region of a positive charge.

S_N1 Reaction – Mechanism of S_N1 Reaction
There are certain factors that affect the S_{N1} reaction as well. A few are discussed below:

- Instead of two concentrations only one i.e., the substrate affects the rate of reaction.
- The rate equation for the above reaction is written as Rate = k[Sub].
- The reaction rate is determined by its slowest step. Therefore, the leaving group leaves at a particular rate which helps in determining the reaction speed.
- It is considered that the weaker the conjugate base, the better is the leaving group.
- S_N1 reactions can be determined by bulky groups that are attached to the carbocations.
- The reaction of the tertiary carbocation is faster than secondary carbocation which is faster than primary carbocation.
- The nucleophile is not required in the rate-determining step.

S_N2 Reaction – Mechanism of S_N2 Reaction

In this reaction, the elimination of the leaving group and the addition of the nucleophile occur simultaneously. S_N2 takes place where the central carbon atom has easy access to the nucleophile.

In S_N2 reactions, the rate of the reaction is affected by a few conditions. They are discussed below:

- The numerical value 2 in S_N2 states that there are two concentrations of substances which affect the rate of reaction, viz. nucleophile and substrate.
- The rate equation for the above reaction is written as Rate = k [Sub][Nuc].
- An aprotic solvent such as acetone, DMSO, or DMF is suited best for the S_N2 reaction as they do not add the H^+ ions in the solution.
- In case if there are protons present, they react with the nucleophile to critically limit the rate of reaction. It is a one-step reaction and the reaction speed is driven by the steric effects. During the intermediate step, the position of the leaving group is inverted whereas the nucleophile is 180°.
- Nucleophilicity also affects the reaction rate.

Electrophilic Substitution Reactions:

The electrophilic substitution reaction involves the electrophiles. Electrophiles are those which donate a pair of electrons in the formation of a covalent bond. The Electrophilic reactions occur mostly with the aromatic compounds.

Electrophilic Aromatic Substitution

In this type of electrophilic substitution, an atom attached to the aromatic ring which is mostly hydrogen is substituted by an electrophile. The reactions that occur are aromatic halogenation, alkylating Friedel-Crafts reactions, aromatic nitration, and aromatic sulfonation and acylation. It further comprises acylation and alkylation.

Electrophilic Aliphatic Substitution

In this type of electrophilic substitution reaction, an electrophile dislocates one functional group. The four electrophilic aliphatic substitution reactions which are similar to counterparts of nucleophile S_N1 and S_N2 are as follows – S_E1, S_E2(front), S_E2(back) and S_Ei (Substitution Electrophilic). During the S_E1 reaction, the substrate ionizes to a carbanion briskly recombines with the electrophile. During the S_E2 reaction, a single transition state occurs where the old and newly formed bond are present.

The other types of substitution reactions include radical reactions and organometallic substitution reaction. For more details on aromatic and aliphatic electrophilic substitution checkout the Electrophilic substitution reaction mechanism.

Elimination reaction

There are some reactions which involve the elimination or removal of the adjacent atoms or group of atoms. After this multiple bonds are formed and there is a release of small molecules as products.

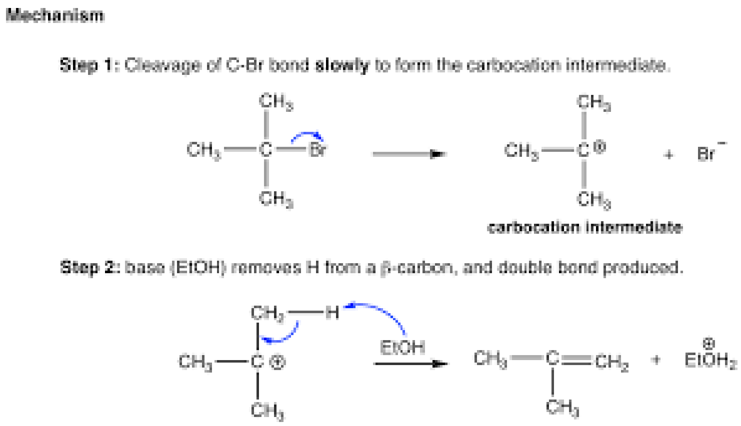
One of the examples of elimination reaction is the conversion of ethyl chloride to ethylene.

$CH_3CH_2Cl \rightarrow CH_2=CH_2 + HCl$

In the above reaction, the eliminated molecule is HCl, which is formed by the combination of H^+ from the carbon atom which is on the left side and Cl– from the carbon atom which is on the right side.

E1 Reaction

- In the E1 mechanism which is also ***known as unimolecular elimination***, there are usually two steps involved – ionization and deprotonation.
- During ionization, there is a formation of **carbocation as an intermediate**. In deprotonation, a proton is lost by the carbocation.
- This happens in the presence of a base which further leads to the formation of a pi-bond in the molecule.
- In E1, the reaction rate is also proportional to the concentration of the substance to be transformed.
- It exhibits ***first-order kinetics***.



Mechanism

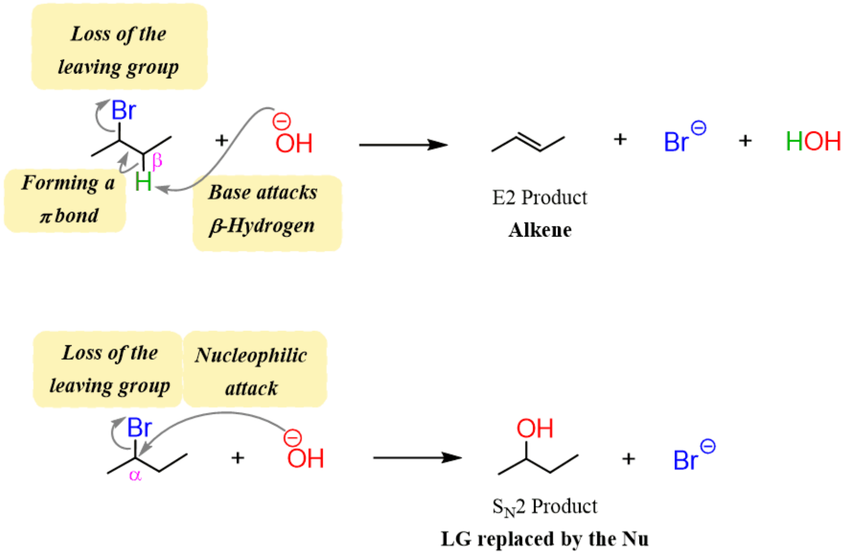
Step 1: Cleavage of C-Br bond **slowly** to form the carbocation intermediate.

Step 2: base (EtOH) removes H from a β-carbon, and double bond produced.

E2 Reaction

- In an E2 mechanism which refers to ***bimolecular elimination*** is basically a one-step mechanism.
- Here, the carbon-hydrogen and carbon-halogen bonds mostly break off to form a new double bond.
- However, in the E2 mechanism, a base is part of the rate-determining step and it has a huge influence on the mechanism.
- The **reaction rate is mostly proportional to the concentrations of both the eliminating agent and the substrate.**
- It exhibits ***second-order kinetics***.

The mechanisms of E2 Elimination and S_N2 Nucleophilic Substitution Reactions



Addition reactions

An addition reaction occurs when two or more reactants combine to form a product without the loss of any atoms present in the reactants. Addition reaction is common in compounds that have unsaturated C-C bonds, like double (alkene) and triple (alkyne) bonds. The weaker π bond is converted into two new stronger σ bonds.

$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$

Radical reactions

Many of the organic reactions involve radicals. The addition of a halogen to a saturated hydrocarbon involves a free radical mechanism. There are three stages involved in a radical reaction i.e. initiation, propagation, and termination. Initially when the weak bond is broken initiation of the reaction takes place with the formation of free radicals. After that when the halogen is added to the hydrocarbon a radical is produced and finally, it gives alkyl halide.

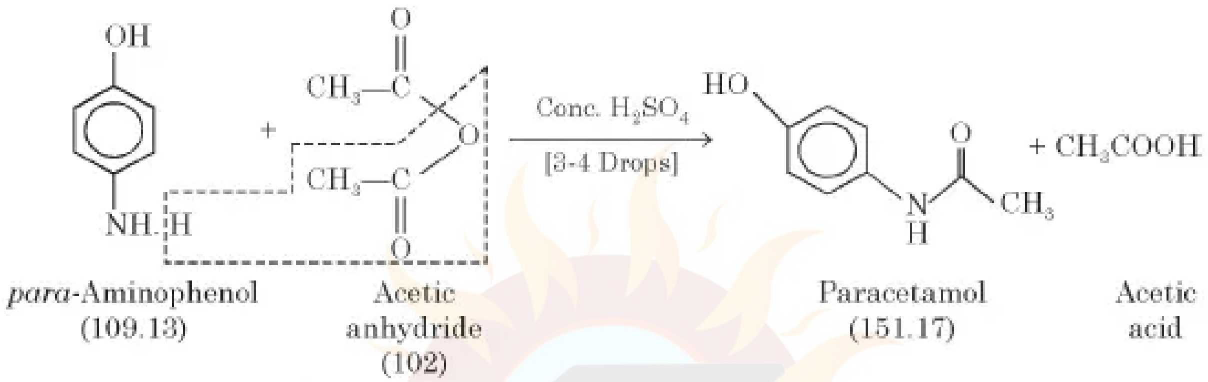
Oxidation – Reductio Reaction

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

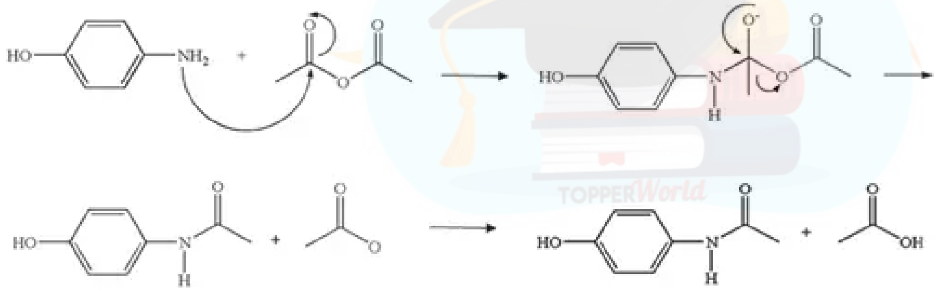
Synthesis of drugs

Paracetamol

Organic Reaction



Mechanism

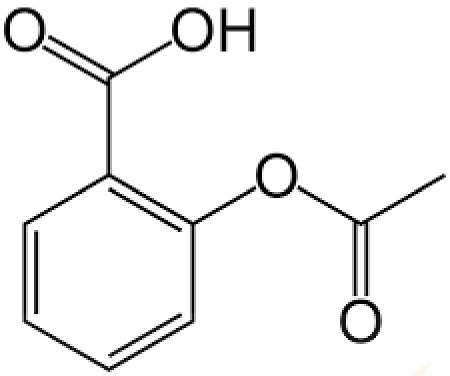


It is also found to be useful in diseases accompanied by pain, discomfort, and fever, for instance the common cold and other viral infections.

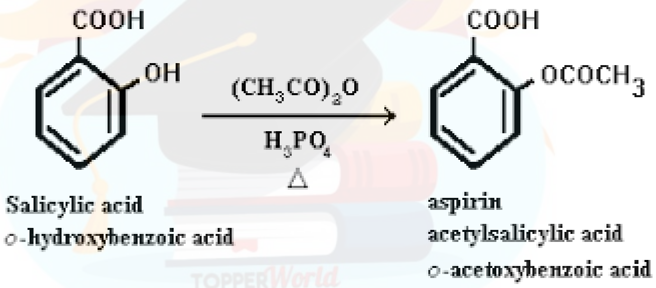
Aspirin

It is also known as ***aspirin or 2-Acetoxybenzoic acid.*** It appears as a crystalline powder which is colourless to white. Generally, it has no smell but when in moist air it acquires a smell of acetic acid. It has a flashpoint of 482° F. It is most widely used in medication to treat pain, inflammation, and fever.

Structure of Aspirin



Organic Reaction



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