

SRM INSTITUTE OF SCIENCE AND TECHNOLOGY
FACULTY OF ENGINEERING AND TECHNOLOGY
DEPARTMENT OF CHEMISTRY
18CYB101J-CHEMISTRY

PART-B

3 Mark Module Wise

Module-1

1. What is the Physical significance of Wave function?

The wave function ψ associated with a moving particle is not an observable quantity and does not have any direct physical meaning. It is a complex quantity. The complex wave function can be represented as $\psi(x, y, z, t) = a + ib$ and its complex conjugate as $\psi^*(x, y, z, t) = a - ib$.

2. Explain the term wave function?

A **wave function** is defined to be a **function** describing the probability of a particle's quantum state as a **function** of position, momentum, time, and/or spin. **Wave functions** are commonly denoted by the variable Ψ . A **wave function** may be used to describe the probability of finding an electron within a matter **wave**.

3. Define Eigen value and Eigen function?

A mathematical operation on a function if it gives any constant multiplied with the function itself then, the function is eigen function for corresponding operator and the constant value obtained is called eigen value. For example energy, you operate on the wavefunction with the quantum mechanical operator associated with that parameter. The operator associated with energy is the Hamiltonian, and the operation on the wavefunction is the Schrodinger equation.

$$H_{op}\psi_i = E_i\psi_i$$

4. Give any two applications of Schrodinger wave equation.

Schrodinger equation gives us a detailed account of the form of the wave functions or probability waves that control the motion of some smaller particles. The equation also describes how these waves are influenced by external factors. Moreover, the equation makes use of the energy

conservation concept that offers details about the behaviour of an electron that is attached to the nucleus.

Besides, by calculating the Schrödinger equation we obtain Ψ and Ψ^2 , which helps us determine the quantum numbers as well as the orientations and the shape of orbitals where electrons are found in a molecule or an atom.

- 5. Write down the one-dimensional Schrodinger time independent wave equation and the same for a free particle.**

Schrodinger time independent wave equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = E\psi$$

$$\hat{H}\psi = E\psi. \quad \hat{H} - \text{Hamiltonian operator}$$

Particle in a one dimensional box equation:

$$E = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, 4, \dots$$

- 6. What is the Normalization process and give a normalized wave function for an electron in one dimensional potential well of length “a” meter.**

To determine 'a', that the total probability inside the box is 1, there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are normalizing the wave function.

$$\int_0^L \psi^2 dx = 1$$

7. What is the Heisenberg uncertainty principle?

Uncertainty principle, also called **Heisenberg uncertainty principle** or **indeterminacy principle**, statement, articulated (1927) by the German physicist Werner **Heisenberg**, that the position and the velocity of an object cannot both be measured exactly, at the same time, even in theory.

$$\Delta X \times \Delta p \geq h/4\pi$$

Where,

ΔX – uncertainty in position

Δp – uncertainty in momentum

h – planck's constant

8. Give the plots of radial wave functions for hydrogen atoms.

The solutions to Schrödinger's equation for atomic orbitals can be expressed in terms of spherical coordinates: r , θ , and ϕ . For a point (r, θ, ϕ) , the variable r represents the distance from the center of the nucleus, θ represents the angle to the positive z -axis, and ϕ represents the angle to the positive x -axis in the xy -plane.

Because the atomic orbitals are described with a time-independent potential V , Schrödinger's equation can be solved using the technique of separation of variables, so that any wavefunction has the form:

$$\Psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$$

where $R(r)$ is the **radial wave function** and $Y(\theta,\phi)$ is the **angular wave function**:

$$Y(\theta,\phi)=\Phi(\theta)\Phi(\phi)$$

Each set of quantum numbers, (n, l, m_l) , describes a different wave function.

9. What is the significance of angular wave function?

The **angular wave function** describes the spherical harmonics of the electron's motion. Because orbitals are a cloud of the probability density of the electron, the square modulus of the **angular wave function** influences the direction and shape of the orbital.

10. What is Linear Combination of Atomic Orbitals (LCAO)? Give the wave function equations for the formation of molecular orbitals by the combination of atomic orbitals?

The Linear combination of atomic orbitals which is also known as LCAO is an approximate method for representing molecular orbitals. It's more of a superimposition method where constructive interference of two atomic wave functions produces a bonding molecular orbital whereas destructive interference produces non-bonding molecular orbital.

Conditions to be satisfied:

The conditions that are required for a linear combination of atomic orbitals are as follows:

- **Same Energy of combining orbitals** – The combining atomic orbitals must have same or nearly same energy. This means that the 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine as they have appreciable energy differences.
- **Same symmetry about the molecular axis** – The combining atoms should have same symmetry around the molecular axis for proper combination, otherwise, the electron density will be sparse.

For e.g. all the sub-orbitals of 2p have the same energy but still, the $2p_z$ orbital of an atom can only combine with a $2p_z$ orbital of another atom but cannot combine with $2p_x$ and $2p_y$ orbital as they have a different axis of symmetry.

In general, the z-axis is considered as the molecular axis of symmetry.

- **Proper Overlap between the atomic orbitals** – The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

11. Differentiate bonding and antibonding molecular orbital.

Bonding molecular orbital	Anti Bonding molecular orbital
Molecular orbitals formed by the additive effect of the atomic orbitals is called bonding molecular orbitals	Molecular orbitals formed by the subtractive effect of atomic is called anti-bonding molecular orbitals
Probability of finding the electrons is more in the case of bonding molecular orbitals	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
These are formed by the combination of + and + and – with – part of the electron waves	These are formed by the overlap of + with – part.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by σ , π , δ .	The corresponding anti-bonding molecular orbitals are represented by σ^* , π^* , δ^* .

12. Give the differences between atomic and molecular orbitals.

Differences between atomic orbital and molecular orbital are as follows.

Atomic orbital:

A region where there occurs a high probability of finding an electron in an atom is known as atomic orbital.

An electron cloud leads to the formation of atomic orbitals around the atom.

Single nucleus affects the electron cloud.

Atomic orbitals are monocentric because they are found around a single nucleus.

Molecular orbital:

A region where there is the highest probability of finding an electron in a molecule is known as molecular orbital.

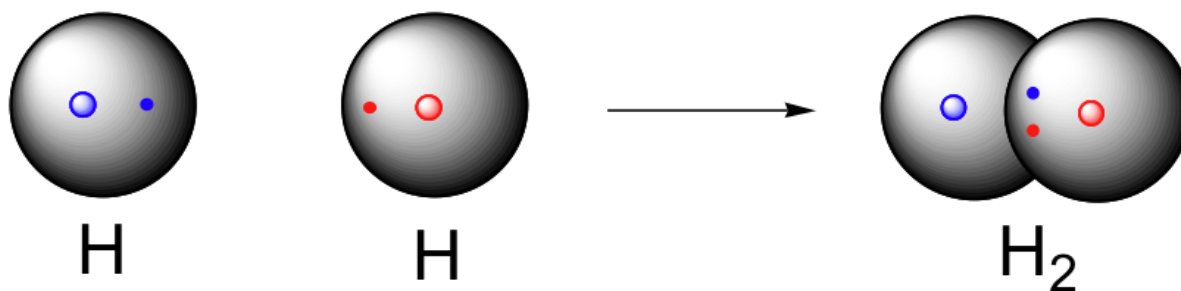
When fusion of atomic orbitals that have nearly the same energy take place then it tends to the formation of molecular orbitals.

In molecular orbitals, two or more nuclei affect the electron cloud.

Since, molecular orbitals are found around different nuclei. Hence, they are polycentric.

13. What is s-s orbital overlapping? Give examples.

When two half filled s - orbitals of two different atoms containing unpaired electrons with opposite spin overlap with each other it is called as s-s overlap. example, formation of Hydrogen molecule .



14. Give the Molecular orbital diagram for Carbon Monoxide molecule {N.B: Only the diagram is required} and calculate its bond order.

Molecular Orbital diagram of Carbon monoxide molecule (CO):

Total electrons: $6+8=14$

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

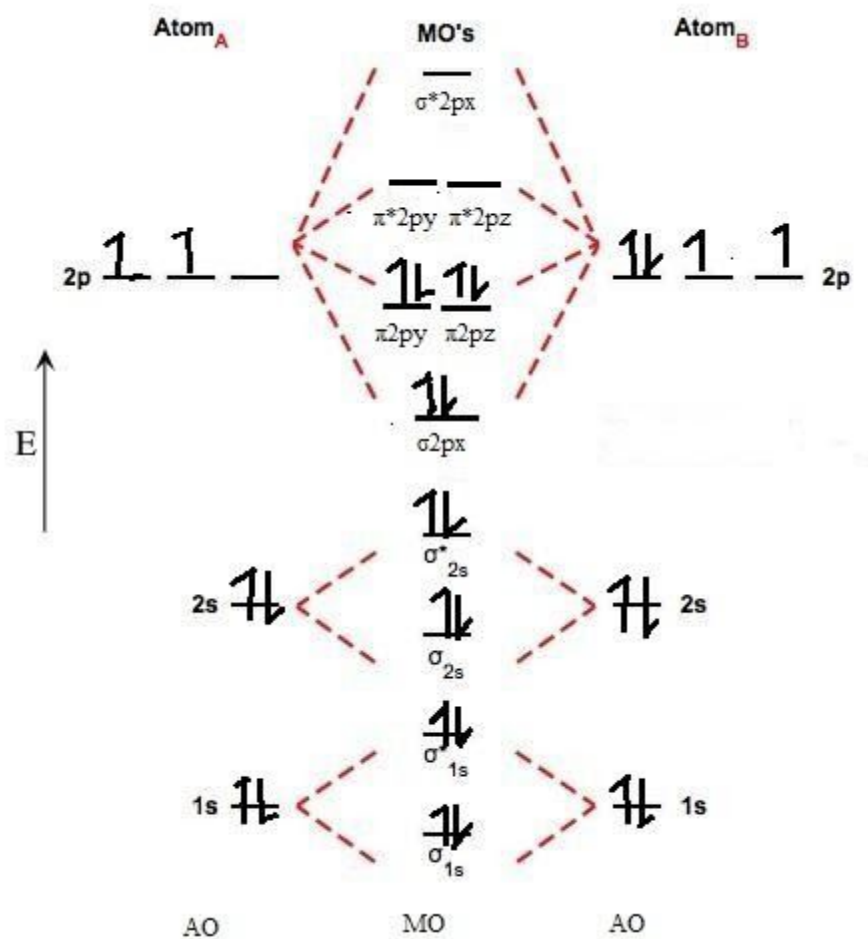
$Nb=10$

$Na=4$

$B.O = 0.5 (Nb - Na)$

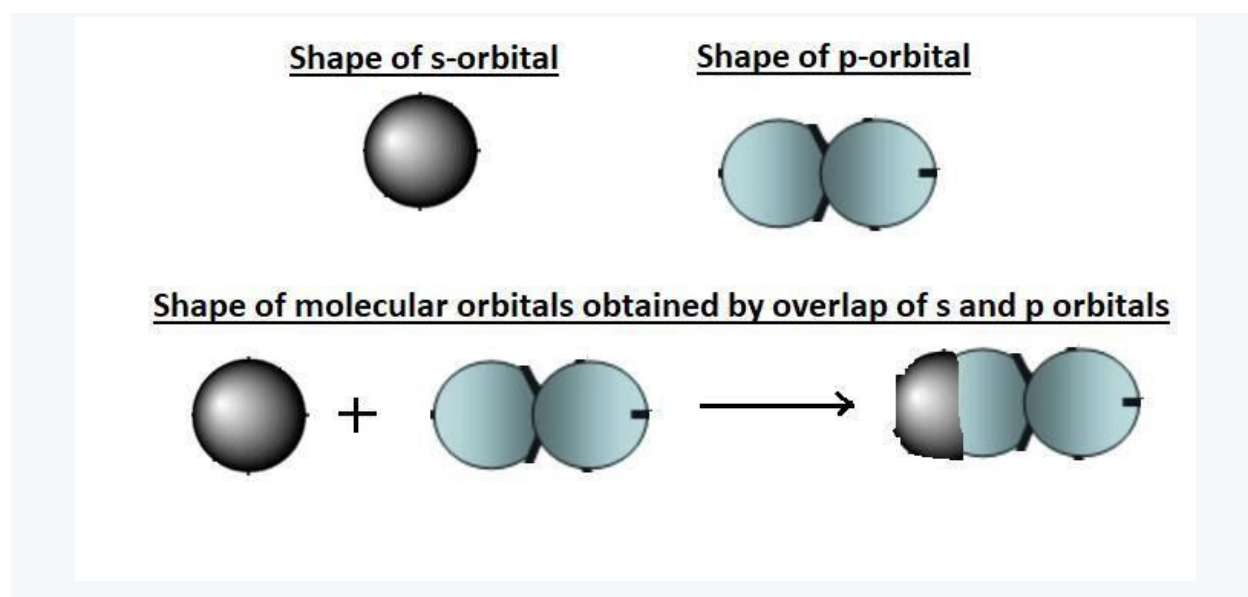
$B.O = 0.5(10 - 4)$

$B.O = 3$



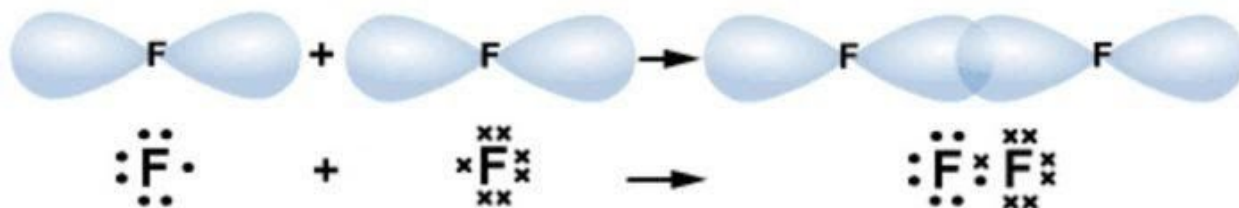
15. Draw the shape of Molecular Orbitals obtained by overlap of s-p orbitals.

- To draw the shape of molecular orbitals obtained by overlapping of s and p orbital, the shape of the s orbital and p orbital must be drawn first.
- The '*s*' orbital is *spherical* and can hold a maximum of *two electrons* in it.
- On the other hand, '*p*' orbital is *in shape in which two circles are overlapping each other* and it can hold a maximum of *six electrons*.
- When these two orbitals overlap each other it leads to the formation of sigma bonding and gives structure in which both the 's' and 'p' orbitals joined together.
- The shape of s orbital, p orbital and molecular orbitals obtained by overlap are given in the attachment.



16. What is p-p orbital overlapping? Give only the molecular orbital diagram taking an example.

The mutual **overlap** between two half-filled p-orbitals of two atoms is called **p-p overlap**. So the covalent bond formed is called a **p-p bond**. The formation of such a bond is also called axial **overlapping**. The two 'p' orbitals **overlap** each other when they acquire minimum potential energy.



17. Give the type of overlapping that the following molecules undergo? i. H₂ ii. O₂ iii.

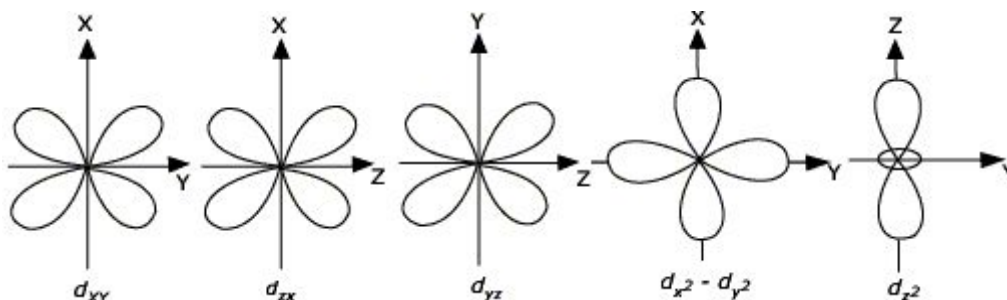
HF

- i. H₂ – S-S Overlapping
- ii. O₂ – S-P Overlapping
- iii. HF – S-P Overlapping

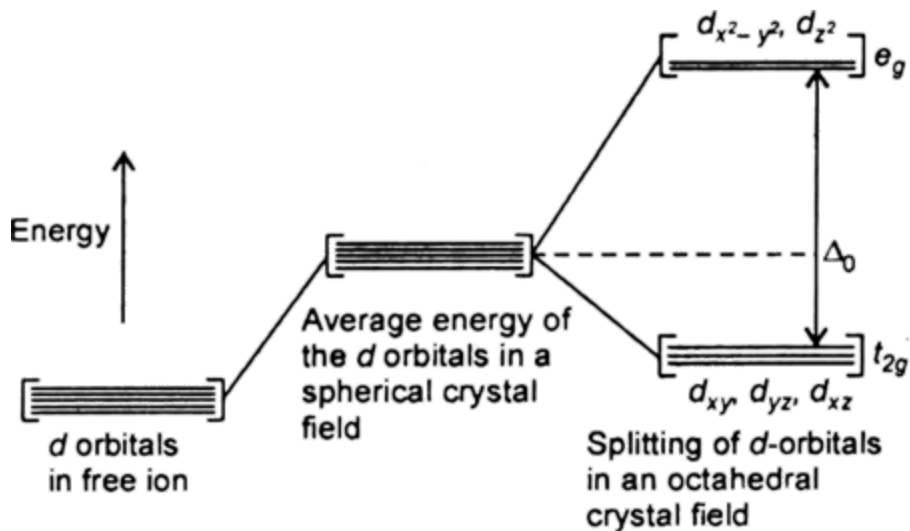
18. Calculate the bond order for i. Hydrogen molecule ii. CO and iii. He

- i. Hydrogen molecule – 1
- ii. Carbon monoxide – 3
- iii. Helium – 0

19. Give a neat sketch on five d-orbitals.



20. Give the splitting pattern of d-orbitals in Oh complexes in the presence of ligands.



21. What is CFSE? Give the formula for calculating it in Oh complexes.



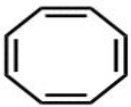
The **crystal field stabilization energy (CFSE)** is the stability that results from placing a transition metal ion in the **crystal field** generated by a set of ligands.

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ contains a d^7 metal ion with a weak field ligand. This complex is known to be high spin from magnetic susceptibility measurements, which detect three unpaired electrons per molecule. Its orbital occupancy is $(t_{2g})^5(e_g)^2$.

We can calculate the CFSE as $-(5)(2/5)\Delta_o + (2)(3/5)\Delta_o = -4/5 \Delta_o$.

22. What is Huckel's rule of aromaticity? Give an example.

According to **Huckel's rule**, all planar aromatic compounds must have $[4n+2]$ pi-electrons where n is an integer (i.e. $n = 0, 1, 2, 3, 4 \dots$ etc.). This **rule** estimates whether a planar ring compound will possess aromatic properties or not.

Summary: Anti-Aromaticity		
Aromatic	Anti-Aromatic	Non-Aromatic
<i>unusually stable</i>	<i>unusually unstable</i>	<i>everything else</i>
•Cyclic	•Cyclic	<i>Fails any one of the 4 criteria on the left</i>
•Conjugated	•Conjugated	
• $(4n+2)$ Pi electrons	• $(4n)$ Pi electrons	
•Flat	•Flat	
e.g. 	e.g. 	e.g. 
benzene (resonance energy of 36 kcal/mol)	cyclobutadiene (only stable below -100°C)	cyclooctatetraene (adopts a tub-like shape to "escape" anti-aromaticity)

23. Compare Non-aromatic with Anti-aromatic compounds.

Aromatic molecules are cyclic, conjugated, have $(4n+2)$ pi electrons, and are flat. **Antiaromatic** molecules are cyclic, conjugated, have $(4n)$ pi electrons, and are flat. **Non-aromatic** molecules are every other molecule that fails one of these conditions.

AROMATIC VS ANTIAROMATIC VS NONAROMATIC

Aromatic compounds are organic compounds composed of carbon and hydrogen atoms arranged in ring structures with delocalized pi electrons

Stable

Have delocalized pi electron system and $4n + 2$ pi electrons

Have $4n + 2$ pi electrons

Less reactive

Antiaromatic compounds are molecules that are cyclic, planar and completely conjugated but are consist of $4n$ pi electrons

Highly unstable

Have delocalized pi electron system and $4n$ pi electrons

Have $4n$ pi electrons

Highly reactive

Nonaromatic compounds are molecules that lack one or more of the requirements to be aromatic: being planar and cyclic structure, completely conjugated system

Unstable

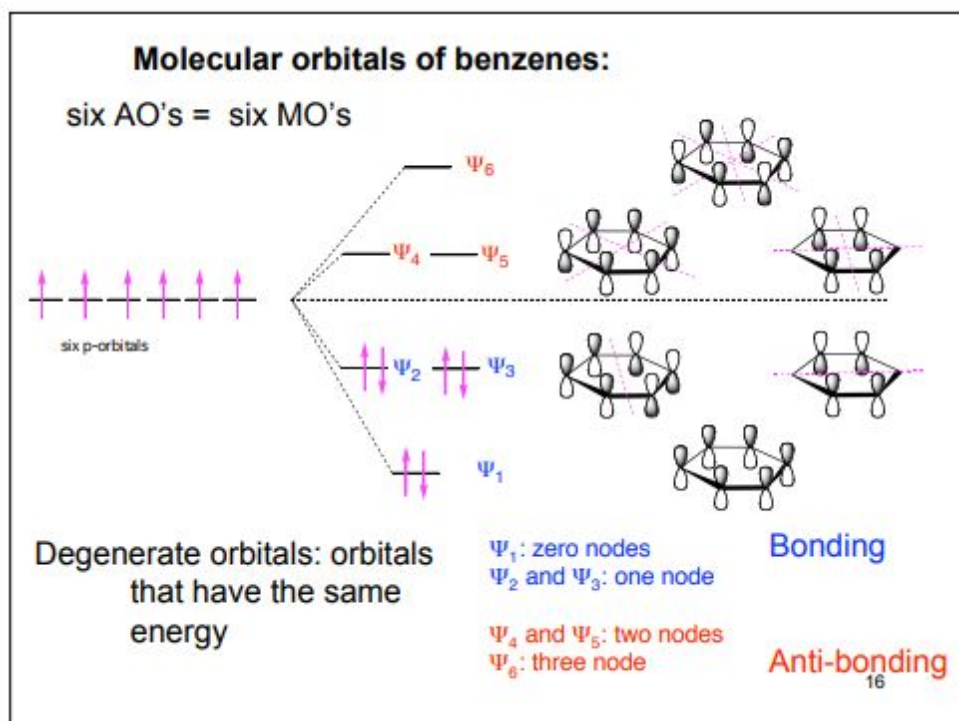
May or may not have delocalized pi electron system

Number of pi electrons is not applicable

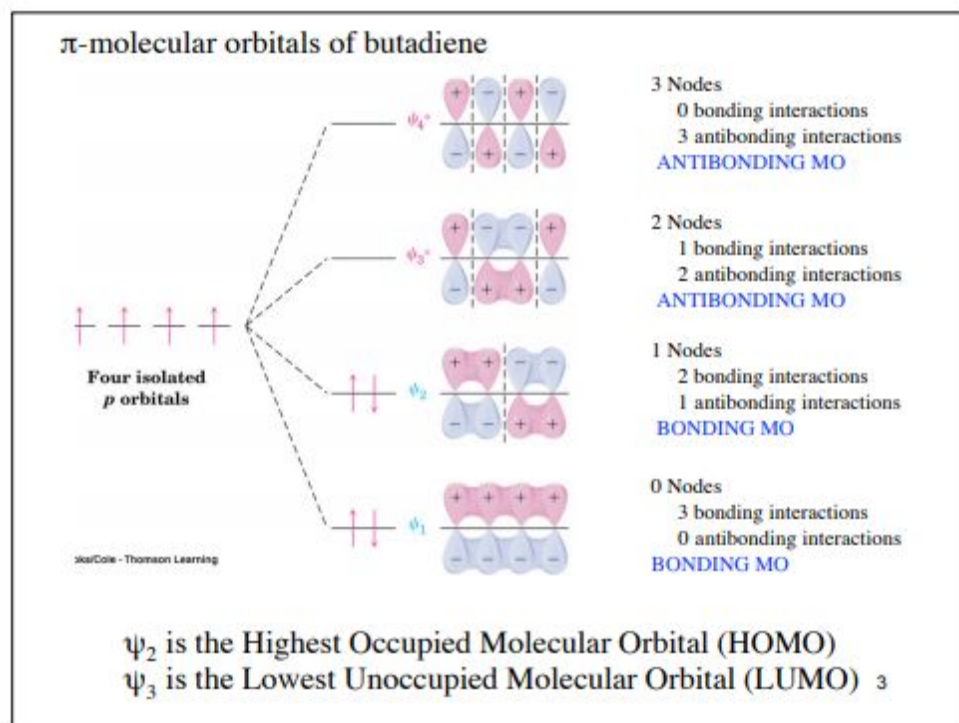
Less reactive

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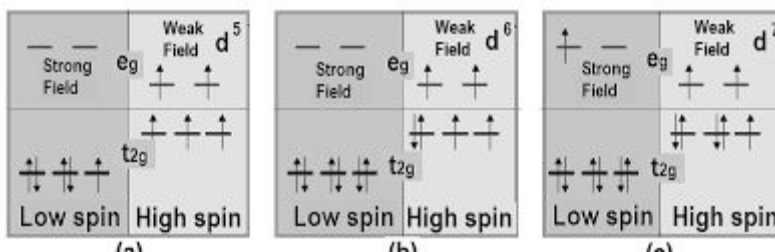
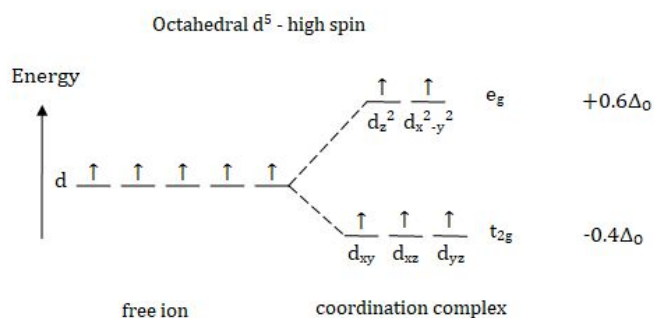
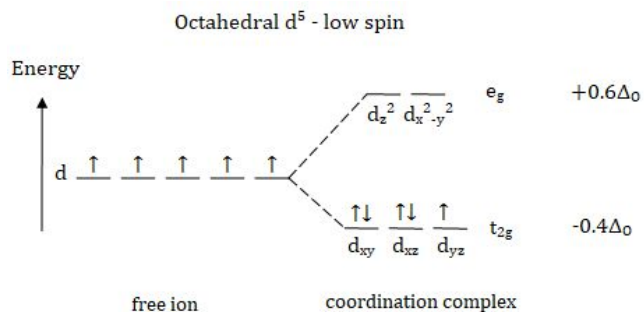
24. What is HOMO and LUMO in Benzene?



25. What is HOMO and LUMO for 1,3-butadiene molecules?

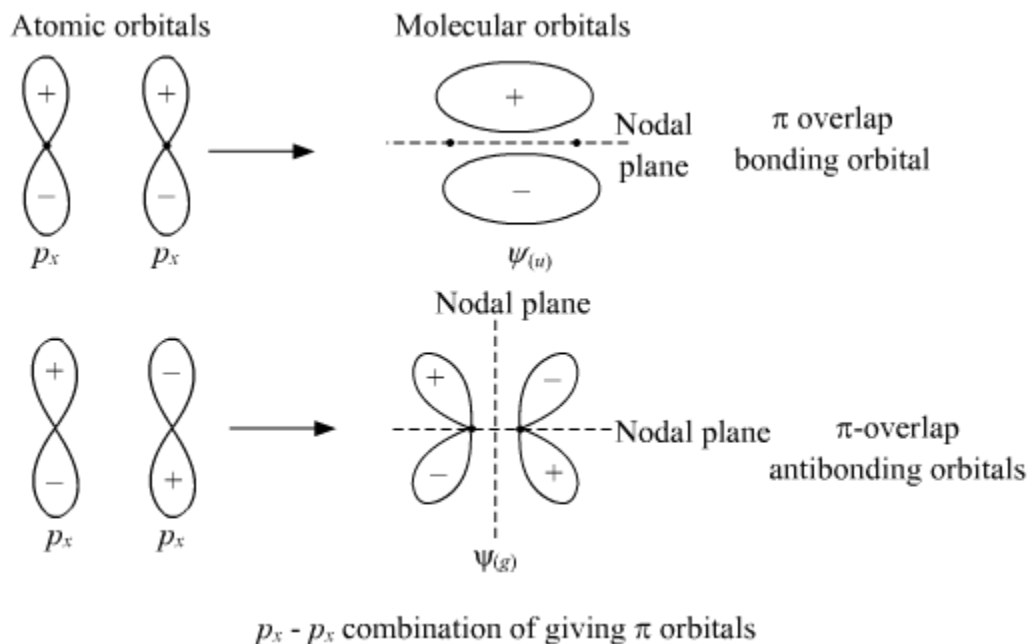


26. Calculate CFSE for high spin octahedral complexes having d5, d6 and d7 configurations.

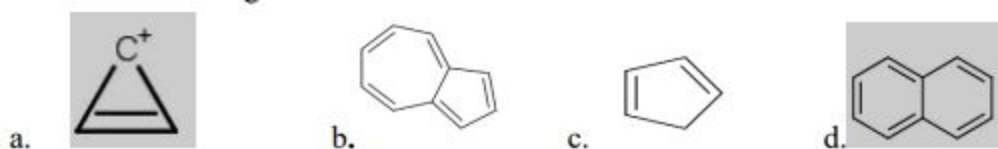


27. What is meant by a nodal plane? Explain with an example.

A **plane** passing through the nucleus on which the probability of finding electron is zero, is called a **nodal plane**. The number of **nodal planes** in an orbital is equal to azimuthal quantum number(*l*). Only option C has value *l*=1. Hence, **nodal plane** is found in L shell and p orbital.

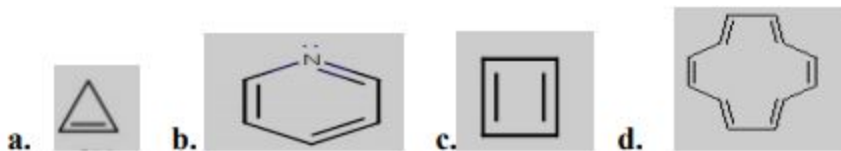


28. Identify aromatic, non-aromatic and anti-aromatic compounds using Huckel's rule from the following:



- Anti aromatic
- Aromatic
- Non aromatic
- Aromatic

29. Based on Huckel's rule, justify which of the following are aromatic, non aromatic and antiaromatic.



- Non aromatic
- Aromatic

- c. Anti aromatic
- d. Aromatic

30. Calculate CFSE for [Fe(CN)₆]³⁻ and [CoF₆]³⁻ ions.

In [Fe(CN)₆]⁴⁻, iron has 3d⁶,4s² system in ground state but in excited state it loses two electrons in the formation of ions and two electrons from 4s, so thus Cobalt gets 3d⁶ configuration. Now it is of low spin complex due to CN ligands so all 6 electrons will go to t_{2g} orbitals. and 0 electrons will be in e_g orbital. By applying formula,

$$\begin{aligned}\Delta &= \text{no. of electrons in } t_{2g} \cdot (-0.4) + \text{no. of electrons in } e_g (0.6) \\ &= 6(-0.4) + 0(0.6) \\ &= -2.4\Delta_0\end{aligned}$$

In [CoF₆]³⁻, cobalt has 3d⁷,4s² system in ground state but in excited state it loses three electrons in the formation of ions and two electrons from 4s and one from 3d orbital so thus Cobalt gets 3d⁶ configuration. Now it is of high spin so 4 electrons go to t_{2g} orbital and 2 electrons go to e_g orbital. By applying formula,

$$\begin{aligned}\Delta &= \text{no. of electrons in } t_{2g} \cdot (-0.4) + \text{no. of electrons in } e_g (0.6) \\ &= 4(-0.4) + 2(0.6) \\ &= -1.6 + 1.2 \\ &= -0.4\Delta_0\end{aligned}$$

Module-2

31. Give any two factors that influence crystal field splitting in octahedral complexes.

The factors which influence the splitting in octahedral complexes are

- the nature of the metal ion.
- the metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
- the arrangement of the ligands around the metal ion.
- the coordination number of the metal (i.e. tetrahedral, octahedral...)
- the nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy *d* groups.

32. What is Pairing energy (P)? Give the relation between crystal field splitting in octahedral complexes (Δ_o) and pairing energy (P).

Pairing energy, P, is the energy required to place two electrons in the same orbital. If the crystal field splitting (Δ) is small because of weak-bonding ligands, then the pairing energy will be larger, and the complex will be high-spin. If the crystal field splitting (Δ) is large because of strong-bonding ligands, then the pairing energy will be smaller, and the complex will be low-spin.

33. Give the splitting pattern of d-orbitals in Td complexes in the presence of ligands.

In a tetrahedral crystal field splitting, the d-orbitals again split into two groups, with an energy difference of Δ_{tet} . The lower energy orbitals will be d_{xy}^2 and $d_{x^2-y^2}^2$, and the higher energy orbitals will be d_{xy} , d_{xz} and d_{yz} - opposite to the octahedral case.

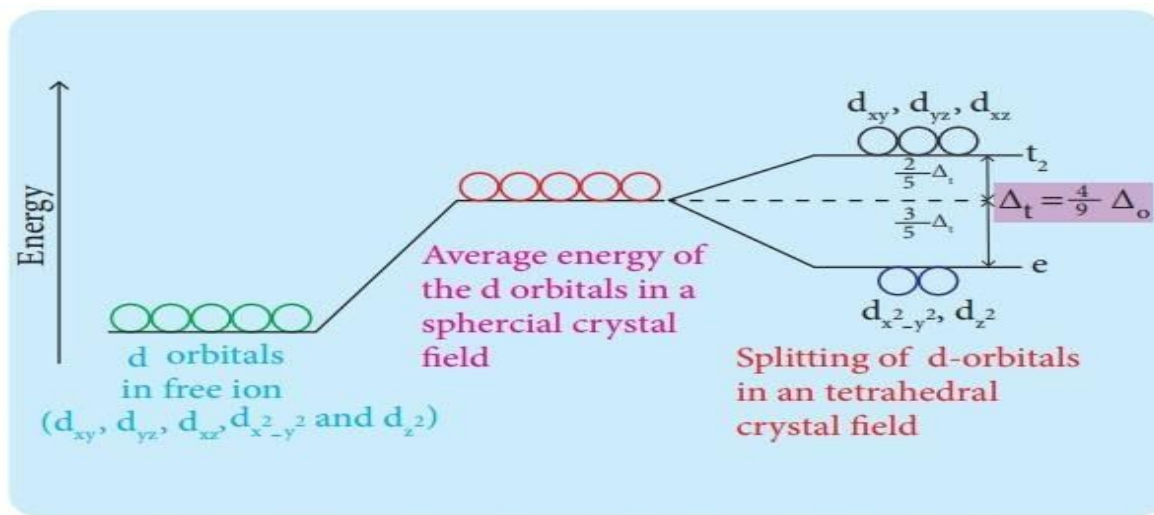


Figure: 5.13 - Crystal field splitting in tetrahedral field

34. Give the formula for calculating CFSE in Td complexes.

$$\Delta_t(CFSE) = \left[+\frac{2}{5}(m)t_2g - \frac{3}{5}(n)eg \right] \Delta_t + lP$$

OR

$$\Delta_t(CFSE) = [+0.4(m)t_2g - 0.6(n)eg] \Delta_t + lP$$

we know $\Delta_o = 10 Dq$ so that

$$\Delta_t(CFSE) = [+4(m)t_2g - 6(n)eg] \Delta_t + lP$$

Δ_t (del.tetra) = crystal field stabilisation energy for tetrahedral complexes

Calculation of crystal field stabilization energy for tetrahedral complexes

A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

Crystal Field Stabilization Energies for Tetrahedral Complexes of $d^1 - d^{10}$ Ions

# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6 \Delta_t$	6	$-0.6 \Delta_t$
2	$-1.2 \Delta_t$	7	$-1.2 \Delta_t$
3	$-0.8 \Delta_t$	8	$-0.8 \Delta_t$
4	$-0.4 \Delta_t$	9	$-0.4 \Delta_t$
5	zero	10	zero

35. Why does TD geometry favours to form High spin rather low spin complexes?

In a tetrahedral complex, Δ_t is relatively small even with strong-field ligands as there are fewer ligands to bond with. It is rare for the Δ_t of tetrahedral complexes to exceed the pairing energy. Usually, electrons will move up to higher energy orbitals rather than pairs. Because of this, *most tetrahedral complexes are high spin.*

36. What is a spectrochemical series? Mention its importance.

The **spectrochemical series** is a list of ligands (attachments to a metal ion) arranged in order of their field strength. The order of common ligands according to their increasing ligand field strength.

The ligands cyanide and CO are considered strong-field ligands and the halides are called weak-field ligands. Ligands such as water and ammonia are said to produce medium field effects.

37. Calculate CFSE for high spin Td complexes having d^5 , d^6 , d^7 , and d^8 configurations.

Calculation of crystal field stabilization energy for tetrahedral complexes			
A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:			
Crystal Field Stabilization Energies for Tetrahedral Complexes of $d^1 - d^{10}$ Ions			
# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6 \Delta_t$	6	$-0.6 \Delta_t$
2	$-1.2 \Delta_t$	7	$-1.2 \Delta_t$
3	$-0.8 \Delta_t$	8	$-0.8 \Delta_t$
4	$-0.4 \Delta_t$	9	$-0.4 \Delta_t$
5	zero	10	zero

38. Calculate the magnetic moment value for the following complexes and predict whether paramagnetic or diamagnetic.

i. Low spin Oh complex with d^7 and

$t_2g^5 e_g^2$ - paramagnetic

ii. High spin Td complex with d^4 configurations.

$e_g^4 t_2g^0$ - diamagnetic

39. Classify the following as high spin or low spin complexes and calculate the magnetic moment of the complexes.



$t_2g^4 e_g^2$ - paramagnetic



$e_g^2 t_2g^2$ - paramagnetic



$t_2g^6 e_g^0$ - diamagnetic

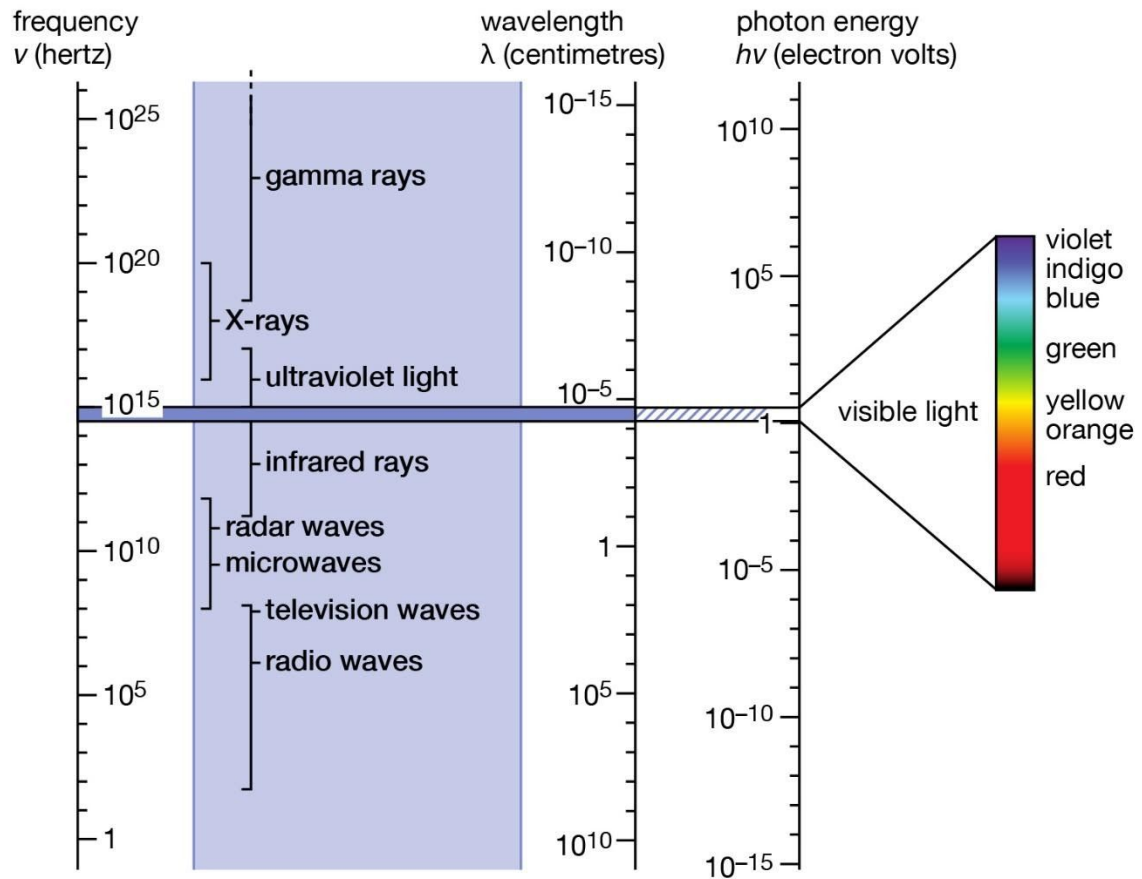


$e_g^2 t_2g^2$ - paramagnetic

40. What is the electromagnetic spectrum and give its different regions?

Electromagnetic spectrum, the entire distribution of electromagnetic radiation according to frequency or wavelength. Although all electromagnetic waves travel at the speed of light in a vacuum, they do so at a wide range of frequencies, wavelengths, and photon energies.

The electromagnetic spectrum comprises the span of all electromagnetic radiation and consists of many subranges, commonly referred to as portions, such as visible light or ultraviolet radiation. The various portions bear different names based on differences in behaviour in the emission, transmission, and absorption of the corresponding waves and also based on their different practical applications. There are no precise accepted boundaries between any of these contiguous portions, so the ranges tend to overlap.



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41. What is the significance of the selection rule in spectroscopy?

A **selection rule** describes how the probability of transitioning from one level to another cannot be **zero**. It has two sub-pieces: a **gross selection rule** and a **specific selection rule**. A gross selection rule illustrates characteristic requirements for atoms or molecules to display a spectrum of a given kind, such as an IR spectroscopy or a microwave spectroscopy. Once the atom or molecules follow the gross selection rule, the specific selection rule must be applied to the atom or molecules to determine whether a certain transition in quantum number may happen or not.

Selection rules specify the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation.

42. What are the criteria for a molecule to absorb in the Microwave region?

During a transition, the rotational quantum number must change by 1 unit only, i.e. **$\Delta J = \pm 1$ (angular momentum is conserved)**.

In other words, only transitions between neighbouring energy levels are possible.

43. Give examples for microwave active and inactive molecules.

Gross Selection Rule: molecules with permanent dipoles are microwave active (the molecule must be polar), e.g., heteronuclear diatomic - HCl, CO, NO, etc.

Homonuclear diatomics are microwave inactive (e.g., O₂, N₂, etc.)

In other words, a dipole must be present in the molecule for you to get a rotational spectrum.

44. Write a short note on the selection rule for Rotational (microwave) spectroscopy?

A photon contains one unit of angular momentum, so when it interacts with a molecule it can only impart one unit of angular momentum to the molecule. This leads to the selection rule that a transition can only occur between rotational energy levels that are only one quantum rotation level (J) away from another.

$$\Delta J = \pm 1$$

The transition moment integral and the selection rule for rotational transitions tell if a transition from one rotational state to another is allowed.

45. What are allowed and forbidden transitions in spectroscopy?

Selection rules, accordingly, may specify “allowed transitions,” those that have a high probability of occurring, or “forbidden transitions,” those that have minimal or no probability of occurring.

46. Define Hooke's law and give its significance in IR spectroscopy.

Hooke's Law states:

- The vibrational frequency is proportional to the strength of the spring; the stronger the spring, the higher the frequency.
- the vibrational frequency is inversely proportional to the masses at the ends of the spring; the lighter the weights, the higher the frequency.

Hooke's Law in IR spectroscopy means:

- stronger bonds absorb at higher frequencies.
- weaker bonds absorb at lower frequencies.
- bonds between lighter atoms absorb at higher frequencies.
- bonds between heavier atoms absorb at lower frequencies.

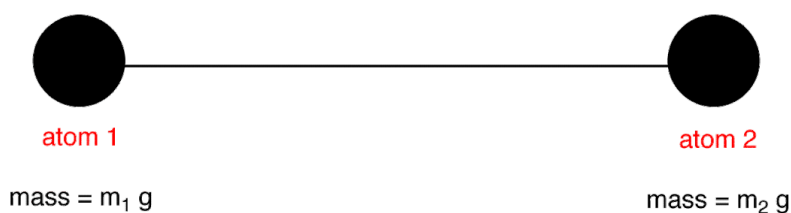
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$ = wave number, in cm^{-1} , corresponding to the vibrational frequency of the bond

c = speed of light in cm s^{-1}

K = force constant in dynes cm^{-1} (a measure of bond strength. The stronger the bond, the larger the K .)

μ = reduced mass in g atom^{-1}



$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

47. What are the criteria for a molecule to absorb in the IR region?

A criterion for IR absorption is a net change in dipole moment in a molecule as it vibrates or rotates. Using the molecule HBr as an example, the charge distribution between hydrogen and bromine is not evenly distributed

since bromine is more electronegative than hydrogen and has a higher electron density. HBr thus has a large dipole moment and is thus polar.

48. Give the selection rule for IR spectroscopy?

Selection rules for Infrared transitions

For a particular vibration to be infrared active there must be a change in the dipole moment of the molecule during the vibration. In other words, the transition dipole moment must not be zero.

$\Delta v = \pm 1$, transition can take place between Adjacent vibrational levels, 0 to 1, 1 to 2 etc.

49. What is an IR active and Inactive molecule? Give examples.

Homonuclear diatomic molecules are inactive in the infrared spectrum. They do not have a dipole moment to start with and during the vibration also the dipole moment is zero. e.g.: H_2 , O_2 , N_2 etc.

Heteronuclear diatomic molecules such as CO, NO are active in IR.

Symmetrical polyatomic molecules such as CO_2 , the symmetric stretching vibration is infrared inactive whereas the asymmetric stretching vibration is IR active.

50. What is the spin selection rule in electronic spectra?

The wave function of a single electron is the product of a space-dependent wave function and a spin wave function. Spin is directional and can be said to have odd parity. It follows that transitions in which the spin "direction" changes are forbidden. In formal terms, only states with the same total spin quantum number are "spin-allowed".

51. Write a note on Laporte or orbital selection rule.

The Laporte rule is a selection rule formally stated as follows:

In a centrosymmetric environment, transitions between like atomic orbitals such as $s-s$, $p-p$, $d-d$, or $f-f$, transitions are forbidden. The Laporte rule

(law) applies to electric dipole transitions, so the operator has u symmetry (meaning *ungerade*, odd). p orbitals also have u symmetry, so the symmetry of the transition moment function is given by the triple product $u \times u \times u$, which has u symmetry. The transitions are therefore forbidden. Likewise, d orbitals have g symmetry (meaning *gerade*, even), so the triple product $g \times u \times g$ also has u symmetry and the transition is forbidden.

52. Explain the criteria for a molecule to absorb radio frequency waves in the NMR region.

The NMR spectroscopy depends upon the fact that most isotopes of the elements possess gyromagnetic properties, which means that they behave like tiny spinning bar magnets. When a sample containing nuclei exhibiting this immutable gyro magnetism is placed in an appropriate DC magnetic field and is simultaneously irradiated by a weaker rotating radiofrequency magnetic field, the nuclei can be compelled to reveal their presence, identify themselves and describe the nature of their surroundings.

53. What is NMR active and inactive nuclei? Give examples.

The spin of atomic nuclei can be predicted based on the knowing the number of protons and neutrons in the nucleus:

- Even/Even. Nuclei that contain an even number of protons *and* an even number of neutrons have $I=0$ and are NMR silent.
- Examples: C^{12} , O^{16} and S^{32} .

All other nuclei are NMR active:

- Odd/Odd. Nuclei that contain an odd number of protons *and* an odd number of neutrons have I that are positive integers. Examples: H^2 ($I=1$), N^{14} ($I=1$) and B^{10} ($I=3$).
- Odd/Even & Even/Odd. All other nuclei (odd/even and even/odd) have spins that are half integral.
Examples: H^1 ($I=1/2$), B^{11} ($I=3/2$), C^{13} ($I=1/2$), O^{17} ($I=5/2$), F^{19} ($I=1/2$) and P^{31} ($I=1/2$).

54. What are the two scales used to calculate chemical shift values?

There are two chemical-shift scales, viz., the δ -scale and the ζ – scale is used in recording NMR signals. They are related by the expression

$$\delta + \zeta = 10$$
$$\text{i.e., } \zeta = 10 - \delta$$

Chemical shift δ is usually expressed in parts per million (ppm) by frequency, because it is calculated from

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\nu_{\text{ref}}},$$

where ν_{sample} is the absolute resonance frequency of the sample and ν_{ref} is the absolute resonance frequency of a standard reference compound, measured in the same applied magnetic field B_0 . Since the numerator is usually expressed in hertz, and the denominator in megahertz, δ is expressed in ppm.

55. Give any two references (or) standards used in NMR spectroscopy.

The detected frequencies (in Hz) for ^1H , ^{13}C , and ^{29}Si nuclei are usually referenced against TMS (tetramethylsilane), TSP (Trimethylsilylpropanoic acid), or DSS, which by the definition above have a chemical shift of zero if chosen as the reference.

56. What is the shielding and deshielding effect in NMR spectra?

The Nucleus feels a weaker magnetic field.

Shielding is a barrier made of inner-shell electrons and it decreases the nucleus' pull on the outer electrons. Shielding is defined as “a nucleus whose chemical shift has been decreased due to addition of electron density, magnetic induction, or other effects.”

The Nucleus feels a stronger magnetic field.

Deshielding is the opposite of shielding. When we say that an atom is deshielded, we mean that “A nucleus whose chemical shift has been increased due to removal of electron density, magnetic induction, or other effects.”

57. What is Larmor (or) precessional frequency?

The **Larmor or precessional frequency** in MRI refers to the rate of precession of the magnetic moment of the proton around the external magnetic field. The frequency of precession is related to the strength of the magnetic field, B_0 .

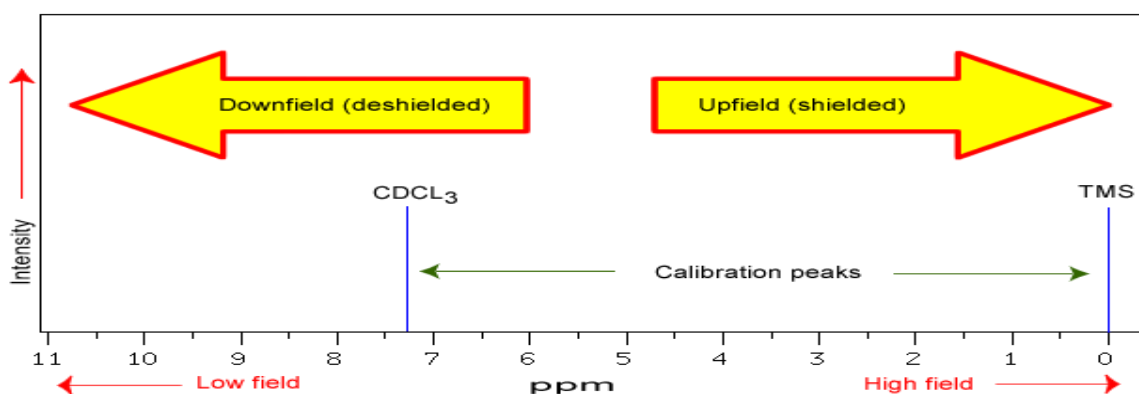
The **precessional frequency** of nuclei of a substance placed in a static magnetic field B_0 is calculated from the Larmor Equation:

$$\omega = \gamma B$$

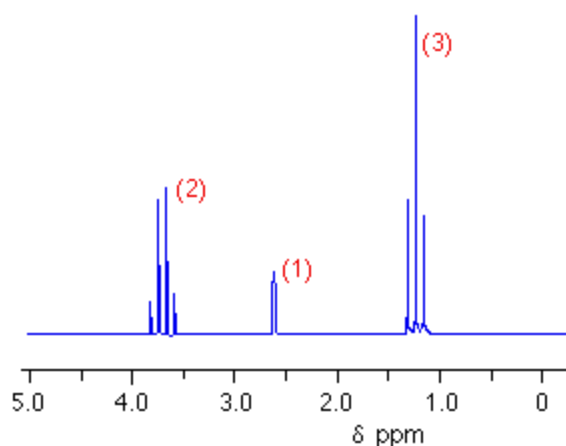
where ω is the Larmor frequency in MHz, γ is the gyromagnetic ratio in MHz/tesla and B is the strength of the static magnetic field in tesla.

58. Define the term chemical shift and give the model of NMR spectrum for ethanol molecules.

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.



nmr spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ - source SDBS



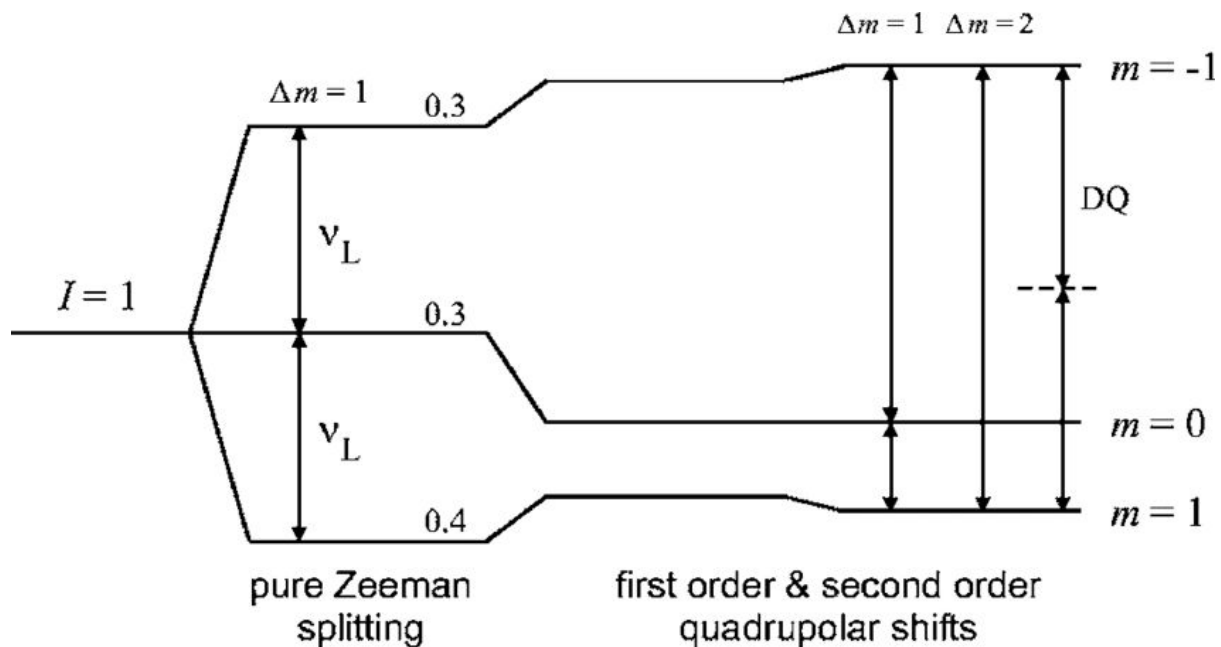
The left-hand cluster of peaks is due to the CH_2 group. It is a quartet because of the 3 hydrogens on the next door CH_3 group. You can ignore the effect of the $-\text{OH}$ hydrogen. Similarly, the $-\text{OH}$ peak in the middle of the spectrum is a singlet. It hasn't turned into a triplet because of the influence of the CH_2 group.

59. How many values can the magnetic quantum number have?

The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of orbital in space. Electrons in a particular subshell (such as s, p, d, or f) are defined by values of ℓ (0, 1, 2, or 3). The value of m_ℓ can range from $-\ell$ to $+\ell$, including zero. Thus, the s, p, d, and f subshells contain 1, 3, 5, and 7 orbitals each, with values of m within the ranges 0, ± 1 , ± 2 , ± 3 respectively. Each of these orbitals can accommodate up to two electrons (with opposite spins), forming the basis of the periodic table.

60. Write down possible values m can have for a nucleus with $I=1$. Draw the energy level diagram for it.

For the proton in a field of 1 T, $\nu_L = 42.576$ MHz, as the proton spin orientation flips from $+1/2$ to $-1/2$. This transition is in the radiofrequency region of the electromagnetic spectrum.



Module-3

61. Why is XPS a more qualitative than quantitative technique?

XPS is a more qualitative technique because the spectral interfaces are minimal. Since XPS peaks for the core electrons tend to be fairly widely separated, XPS elemental analysis is based on core electron peaks usually straightforward.

62. Give the number of electrons and best suitable pressure required for XPS measurement.

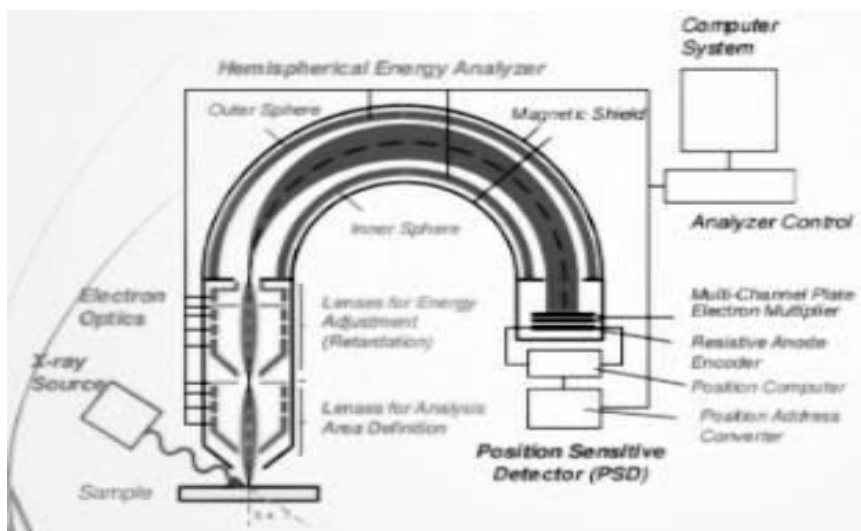
In XPS analysis the electrons emitted from atoms near the sample surface is 10-100 Angstroms and suitable pressure requires for high vacuum chamber is 10^{-6} pa, for ultra high Vacuum chamber is $P < 10^{-7}$ pa

63. What is the principle of XPS?

The working principle of XPS is the ejection of electrons from the surface of a sample in ultra high vacuum (UHV) condition. When an X ray (with energy $h\nu$) ejects out an electron (by energy B.E). The ejected electron is called a photoelectron and this effect is

called photoelectric effect. The element present in the sample can be identified on the basis of kinetic energy (K.E) and the binding energy (B.E) of their photo electron. The intensities of photoelectrons provide information about concentration of elements in a sample.

64. Give only a schematic diagram for XPS instrumentation.



65. What are the merits and demerits of XPS analysis?

Merits

- 1) XPS analysis is effective across a range of organic and inorganic materials.
- 2) XPS is a leading technique for analyzing stainless steel passivation.
- 3) XPS is also effective at identifying surface contaminants.

Demerits

- 1) Size matters.
- 2) Challenges with reproducibility.
- 3) Samples must be compatible with a high vacuum environment.

66. Define the terms: Binding energy and Work function in XPS analysis.

Electron Binding energy is a generic term for the minimum energy needed to remove an electron from a particular electron shell for an atom or ion,

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

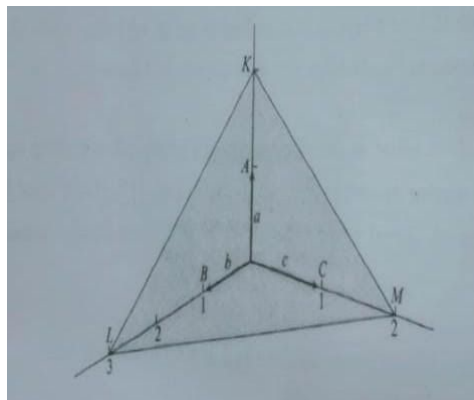
where E_{binding} is the binding energy (BE) of the electron measured relative to the chemical potential, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument

ϕ is the **Work function** for the specific surface of the material, which in real measurements includes a small correction by the instrument's work function because of the contact potential. The work function-like term can be thought of as an adjustable instrumental correction factor that accounts for the few eV of kinetic energy given up by the photoelectron as it gets emitted from the bulk and absorbed by the detector.

67. What are the applications of XPS? [Any two]

- i. It is used for the surface analysis of organic and inorganic materials
- ii. It is used to study the fiberglass surface
- iii. It is an unique approach in probing electronic structures.

68. Define Miller indices with examples.



Miller introduced a set of integers (hkl) to specify a plane of the crystal. This set of three numbers (hkl) is known as ‘Miller indices’ of a particular plane of a crystal. “The Miller indices (hkl) of a plane of a crystal are inversely proportional to the plane on the crystallographic axes”

- i. It is customary to describe crystal planes by a set of Miller indices.
- ii. Find the intercept on the crystal axes as multiples of the lattice constants a_1, b_2, c_3
- iii. Take reciprocals of these numbers and
- iv. Using an appropriate multiplier, convert the $1/\text{intercept}$ set to the smallest possible set of whole numbers
- v. Represent the above as a set of integers (hkl) for a given plane of a crystal.

69. For the intercepts x, y and z with values of 3,1 and 2 respectively, find the Miller indices [Give the steps].

- i. Intercepts : 3,1,2
- ii. Fractional intercepts: $1/3, 1/1, 1/2$ (reciprocal)
- iii. Miller indices: (263)

70. Compute the Miller Indices for a plane intersecting at $x=1/4, y=1$, and $z=1/2$. [Give the steps].

- i. Intercepts : $1/4, 1, 1/2$
- ii. Fractional intercepts: 4,1,2 (reciprocal)
- iii. Miller indices: (412)

71. Give the expression for Bragg’s law and explain the terms involved in it.

Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacings, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d .

When the scattered waves interfere constructively, they remain in phase since the difference between the pathlengths of the two waves is equal to an integer multiple of the wavelength. The path difference between two waves undergo interference is given by $2d \sin \theta$, where θ is the glancing angle

$$2d \sin \theta = n \lambda$$

where n is a positive integer and λ is the wavelength of the incident wave. A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern at the points where the scattering angles satisfy Bragg condition.

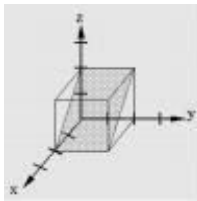
72. What is interplanar spacing in lattices? Give the expression taking an example.

The interplanar spacing or interplanar distance is the perpendicular distance between two successive planes in a family (hkl).

Interplanar Crystal spacing of cubic crystal families is defined as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

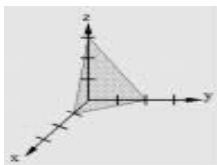
73. Determine the Miller indices (hkl) of the shaded planes below.



→ Intercepts: 2, ∞ , 2

Fractional intercepts: $1/2$, $1/\infty$, $1/2$

Miller indices: (101)



→ Intercepts: 1, 2, 3 :

Fractional intercepts: $1/1$, $1/2$, $1/3$

Miller indices: (632)



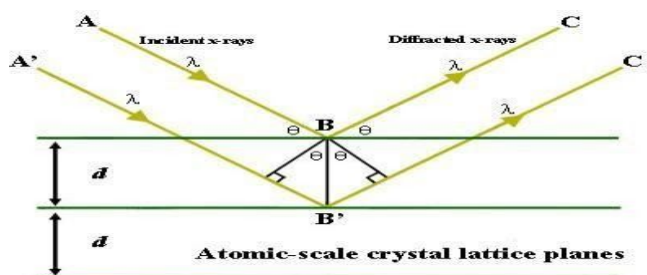
→ Intercepts: ∞ , 1, ∞

Fractional intercepts: $1/\infty$, $1/1$, $1/\infty$

Miller indices: (010)s

74. Define Bragg's law and give a diffraction pattern diagram.

The crystal diffract x- rays because the inter planar spacing in a crystal lattice is of the same order as that of the wavelength of the x-rays



75. Define the terms i. Critical temperature ii. Critical volume iii. Critical pressure.

- i. **Critical temperature (T_c).** It is defined as the temperature above which the gas cannot be liquefied.
- ii. **Critical volume (V_c).** The volume occupied by one mole of gas at critical temperature and pressure is called the critical volume (V_c).
- iii. **Critical pressure (P_c).** The minimum pressure required to liquefy the gas at the critical temperature is called Critical Pressure (P_c).

76. Write a short note on ion-ion interactions.

Ion-ion interactions are an attractive force between ions with opposite charges. They are also referred to as ionic bonds and are the forces that hold together ionic compounds. Like charges repel each other and opposite charges attract. These Coulombic forces operate over relatively long distances in the gas phase.

77. What is Dipole-dipole interaction? Give an example.

Dipole-Dipole interactions result when two **dipolar** molecules **interact** with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule.

Examples: NH_3 , SO_2 , HF , HCl

78. What are London forces of interactions? Give examples.

The **London dispersion force** is a temporary attractive **force** that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. The unequal distribution of electrons about the nucleus in an atom can induce some dipole in the atom. When another atom or molecule comes in contact with this induced dipole, it can be distorted that leads to an electrostatic attraction between either atoms or molecules. For example, consider London dispersion forces between two chlorine molecules. Here both

chlorine atoms are bonded through a covalent bond which forms by equal sharing of valence electrons between two chlorine atoms. The force of attraction between two chlorine molecules is the London dispersion force here which is due to unequal distribution of electron density in the molecule.

76. Write a note on ion-dipole interactions.

An ion-dipole interaction is an attractive force that results from the electrostatic attraction between anions and a neutral molecule that has a dipole. Most commonly found in solutions. A positive ion (cation) attracts the partially negative end of a neutral polar molecule. A negative ion (anion) attracts the partially positive end of a neutral polar molecule.

77. What is the modified form of VanderWaals equation?

Vander waals proposed his famous equation of state for a nonideal gas. He modified the ideal gas equation by suggesting that the gas molecules were not mass points but behave like rigid spheres having a certain diameter and that there exist intermolecular forces of attraction between them. The two correction terms introduced by Vander waals are

Correction for attractive forces
between molecules

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

Correction for volume
of molecules

For 1 mole of gas, $n = 1$, and the above equation becomes:

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

78. Give the Clausius equation for real gases.

10. (20 points) Clausius model for real gases is a three parameter equation:

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

where a , b , and c are the three parameters for this equation of state.

(a) Rearrange the state variables so that pressure is dependent variable and a temperature and volume are independent variables.

79. What are the postulates of Fajan's rule for ionic and covalent bonds? Give an example for the bonds mentioned.

The molecules containing high positive charge on cation, high negative charge on anion, smaller cation or large anion are covalent in character. The molecules containing low positive charge on cation, low negative charge on anion, large cation or small anion are ionic in character.

In anhydrous chlorides like NaCl, MgCl₂ and AlCl₃, the polarizing power of the cations Na⁺, Mg²⁺, Al³⁺ increases in order Na⁺ < Mg²⁺ < Al³⁺, since the positive charges on the cations also increases in the same order. With the increase of polarization of Cl⁻ anion by the cation (Na⁺, Mg²⁺, Al³⁺), the covalent character between the cation and anion of these chlorides also increases as we move from NaCl to AlCl₃.

82. First ionization energy of Al is lower than that of Mg. Comment on the statement.

Reason:-

Electronic configuration of Al = 1s²2s²2p⁶3s²3p¹

Electronic configuration of Mg = 1s²2s²2p⁶3s²

Al has one unpaired electron in its highest energy orbital (3p), and Mg's highest energy orbital (3s) has the paired electrons. It is easier to remove electrons from unpaired 3p¹ than from paired 3s².

It is energetically favorable for all the electrons in an orbital to be paired, which means that breaking up this pair would require more energy.

84. How many numbers of geometries are possible in C.N4? Give an example.

Two different geometries are possible.

The **tetrahedron** is the most common. e.g tetrahedral Cobalt(II) complexes while the **square planar** is found almost exclusively with metal ions having a d⁸ electronic configuration. e.g cis-PtCl₂(NH₃)₂

85. How many numbers of geometries are possible in C.N6? Give an example.

Three different geometries are possible.

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.

86. Define the terms i. Ionization energy, ii. Electron affinity and iii.

Electronegativity

- i. **Ionization energy**- The amount of **energy** required to remove an electron from an isolated atom or molecule.
- ii. **Electron affinity**- The amount of energy released when an electron is added to a neutral atom to form an anion.
- iii. **Electronegativity**- The tendency of an atom in a molecule to attract the shared pair of electrons towards itself.

87. What is effective nuclear charge and Shielding constant? Give their relationship.

The **effective nuclear charge** (often symbolized as Z_{eff} or Z^*) is the net positive **charge** experienced by an electron in a multi-electron atom. The term “**effective**” is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full **nuclear charge**.

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons in so far as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{\text{eff}} = Z - S$$

88. Give the formula to calculate Shielding constant[σ]for an electron residing in n [s]subshell and also in “d”subshell.

The value of σ for an electron residing in $(n - 1)d$ orbitals of $(n - 1)^{\text{th}}$ shell of an atom or an ion

- (a) There will be no contribution to the value of s by the electrons residing in ns orbitals in ns orbital.

- (b) Each of the remaining electrons present in $(n - 1)$ d orbitals, makes a contribution of 0.35
Each of the electrons present in the $(n - 1)s$, $(n - 1)p$ orbitals and inner shells [i.e. 1st 2nd, 3rd, ..., $(n - 2)$ th shells] makes a contribution of 1.0

σ for a $(n - 1)d$ electron = $0.35 \times [\text{No. of the electrons in } (n - 1)d \text{ orbitals}] + 1.0 \times [\text{No. of electrons in } (n - 1)s, (n - 1)p \text{ orbitals and inner shells}]$

88. List out elements from the following the most electropositive and electronegative element and give reasons. Li, Be, B, C, K and Fluorine.

Most electropositive element is K and most electronegative element is F

In the above list except K other elements belong to the same period (2nd). On moving from left to right the electronegativity increases with increase in the number of outer electrons.

Since F is the having more number of electrons in the outermost orbital, it is the most electronegative element. (present in the top right hand corner of the periodic table)

K is present in the first group. In groups from top to bottom the electronegativity decreases because of electron shielding effects. So compared with Li on the same group K is less electronegative. So the K is the most electro -positive element in the given list.

89. Arrange Br, F, I and Cl in the order of increasing electron affinity and give reasons.

$F > Cl > Br > I$

On moving down the group the electron affinity decreases. Because of the steady increase in atomic radius of the elements

90. Give the increasing order for Na, Al, Mg and Si atoms based on effective nuclear Charge and give reasons.

$Na < Mg < Al < Si$

All these elements belong to the 3rd period. We know that as we proceed from left to right in a period, the electrons are added to the orbital of the same main energy level. The addition of each electron increases the nuclear charge by one, so from Na to Si nuclear charge increases.

91. Give the increasing order for Na, Al, Mg and Si atoms based on effective nuclear charge and give reasons.

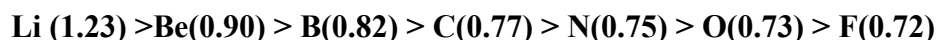
The order of increasing effective nuclear charge is $\text{Na} < \text{Mg} < \text{Al} < \text{Si}$ because, in a period, on moving from left to right, the electrons are added to the same principal shell. The added electrons shield each other poorly from the nucleus therefore the effective nuclear charge increases.

92. What are atomic radii? Give its variation along the period and down the group taking examples.

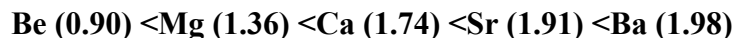
The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together.

In a period, from left to right, with increase in the atomic number, the atomic radius decreases due to increase in the nuclear charge which increases the attraction of the nucleus for the valence electrons.

For example, in the elements of the second period, the covalent radii decrease as we move from Li to F as shown below.



In a group, on moving from top to bottom, the atomic radius increases as a new energy level is added at each succeeding element but the number of valence electrons remains the same.



93. Arrange the following in the increasing order of atomic radii and give reasons: N, S, P and O.

The correct order of atomic radii of N, S, P, and O follows the order $\text{O} < \text{N} < \text{S} < \text{P}$. On going from N to O, the nuclear charge increases. But the additional electron is added in the same energy level. Hence, due to shielding effect, the effective nuclear charge increases. The attraction of the nucleus for the valence electrons increases. Hence, the atomic size decreases. The atomic size of N is larger than that of O. For the same, reason, the atomic size of P is larger than that of S.

94. Give reasons for: on-going from C to N in the second period, the values of electron affinity decrease instead of increasing.

On moving across the periodic table, the electron affinity increases. But, the period from Carbon to Nitrogen experiences an adverse reaction.

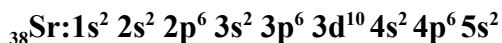
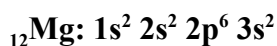
Reason:

- The electron affinity decreases because the atomic size increases.
- The nuclear force of attraction decreases
- The attraction for an electron becomes less.

Hence, ongoing from C to N in the second period, the values of electron affinity decrease instead of increasing.

95. Sr has larger atomic size when compared to Mg. Justify.

In general, the atomic size increases from the top to the bottom in any group as the number of energy levels increases. The electronic configuration of Mg and Sr is



Looking at the electron configuration we conclude that:

- Magnesium atoms are smaller than Strontium atoms because Strontium has more electrons (38e⁻) which will occupy more energy levels (n=5 for Strontium versus n=3 for Magnesium). As the energy level increases atomic size increases. Therefore Sr has larger atomic size when compared to Mg.

96. Ca²⁺ has a smaller ionic radius than K⁺. Give reasons.

Ca²⁺ has a smaller ionic radius than K⁺ because it has more nuclear charge. In a given period, on moving from left to right, the nuclear charge increases without addition of shell. The increased nuclear charge attracts the electrons more strongly towards the nucleus. This decreases the ionic size.

97. Define Polarizability and Polarizing power for an ion.

Polarizability :

- It is the tendency of an anion to undergo polarization. It indicates the easiness with which an anion undergoes distortion in presence of a cation.
- It is directly proportional to the size as well as the negative charge on the anion.
- The larger anions can undergo distortion very easily than the smaller ones.
- It is also important to note that the anions with greater negative charge also undergo polarization easily.

Polarizing Power :

- The ability of a cation to polarize the anion is referred to as polarizing power.
- It is directly proportional to the charge density, which in turn is directly related to the charge on cation, while inversely related to the size of anion.
- The polarizing power increases with increase in the size of cation i.e. smaller cations are very effective in the polarization of anion.
- However, the polarizing power increases with increase in the charge on cation.

- Greater the polarizing power of cation and greater the polarizability of anion, greater is the polarization and hence greater will be the covalent nature.

98. CuCl is more covalent than NaCl. Why?

According to Fajan Rule, Effective nuclear charge in cation having s^2, p^6, d^{10} configuration is greater than s^2p^6 configuration therefore cation having s^2, p^6, d^{10} configuration is more covalent. Hence CuCl (configuration s^2, p^6, d^{10}) is more covalent than NaCl.

Module-4

99. Give the differences between hard and soft acids.

Hard acid	Soft acid
Small ionic radii,	Large ionic radii,
High positive charge,	Low positive charge,
Empty orbitals in the valence shell	Completely filled atomic orbitals
High energy LUMOs.	Low energy LUMOs
H ⁺ , Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Sn ²⁺ , Al ³⁺ , Ga ³⁺ , In ³⁺ , Cr ³⁺ , Co ³⁺ , Fe ³⁺ , La ³⁺ , Si ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺ ,	Cu ⁺ , Ag ⁺ , Au ⁺ , Hg ⁺ , Cs ⁺ , Tl ⁺ , Hg ²⁺ , Pd ²⁺ , Cd ²⁺ , Pt ²⁺

100. What are hard acids and bases? Give examples.

- Hard acids consist of small highly charged cations and molecules in which a high positive charge can be induced on the central atom.
- Examples of Hard Acids: H⁺, Li⁺, K⁺, Ca²⁺, Al³⁺, Sn⁴⁺, BF₃, BCl₃, CO₂, RCO⁺, SO₃, RMgX, VO₂⁺, AlCl₃
- Hard bases are highly electronegative and of low polarizability.
- Examples of Hard Bases: F⁻, OH⁻, NH₃, N₂H₄, ROH, H₂O, SO₄²⁻, PO₄³⁻
- Hard bases react more readily to form stable compounds and complexes with hard acids.

101. What are soft acids and bases? Give examples.

- Soft acids consist of large low charge cations and molecules with relatively high energy occupied molecular orbitals. Soft acids are readily polarizable.
- Examples of Soft Acids: Cs⁺, Cu⁺, Au⁺, Pt²⁺, Hg⁺, BH₃, Br₂, I₂, RO⁺, quinones
- Soft bases contain larger, relatively polarizable donor atoms.
- Examples of Soft Bases: H⁻, R⁻, CO, PR₃, C₆H₆, SCN⁻
- Soft bases react more readily and form stable compounds and complexes with soft acids.

102. Define the terms i. Entropy ii. Enthalpy and iii. Internal energy.

i. Entropy

- Generally, entropy is defined as a measure of randomness or disorder of a system. Entropy is an extensive property which means that it scales with the size or extent of a system.
- It is a thermodynamic state function. It depends on the state of the system and not the path that is followed.
- It is represented by S but in the standard state, it is represented by S° .
- It's SI unit is J/Kmol.
- It's CGS unit is called/Kmol.

ii. Enthalpy

- Enthalpy is the measurement of energy in a thermodynamic system.
- The quantity of enthalpy equals the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.
- When a process begins at constant pressure, the evolved heat either absorbed or released equals the change in enthalpy.
- Enthalpy change is the sum of internal energy denoted by U and product of volume and Pressure, denoted by PV, expressed in the following manner.

$$H=U+PV$$

iii. Internal Energy

- Internal energy U of a system or a body with well defined boundaries is the total of the kinetic energy due to the motion of molecules and the potential energy associated with the vibration motion and electric energy of atoms within molecules.
- Internal energy also includes the energy in all the chemical bonds.
- Internal energy is a state function of a system and is an extensive quantity.
- The SI unit of specific internal energy would be the J/g.
- For a closed system the internal energy is essentially defined by

$$\Delta U = q + W$$

Where

- U is the change in internal energy of a system during a process

- q is the heat
- W is the mechanical work.

103. What is the relation between enthalpy and Internal energy?

The relation between enthalpy and Internal energy:

At a constant pressure, the equation for change in internal energy, $\Delta U = q + w$ can be written as

$$\Delta U = q_p - p\Delta V$$

Where q_p represents the heat absorbed by the system at a constant pressure and $-p\Delta V$ is the expansion work done due to the heat absorbed by the system.

We can write the above equation in terms of initial and final states of the system as:

$$U_F - U_I = q_p - p(V_F - V_I)$$

$$\text{Or} \quad q_p = (U_F + pV_F) - (U_I + pV_I)$$

Enthalpy H can be given by $H = U + PV$. Substituting it in the above equation, we get:

$$q_p = H_F - H_I = \Delta H$$

Hence, change in enthalpy $\Delta H = q_p$, which is the heat absorbed by the system at a constant pressure.

At constant pressure, we can also write,

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

- In exothermic reactions, heat from the system is lost to the surrounding. For such reactions, ΔH is negative.
- In endothermic reactions, heat is absorbed by the system from the surroundings. For such reactions, ΔH is positive.

104. What is entropy? Explain its significance.

Entropy is the measure of the disorder or randomness in a system. Entropy is very significant in thermodynamics. The significances are mentioned below:

- Entropy is a physical quantity. It is equal to the ratio of heat absorbed or rejected to the temperature.
- It indicates the direction of heat flow.

- It helps in determining the thermodynamic state of an object.
- Like temperature, pressure, volume, internal energy, magnetic behavior it expresses the state of a body.
- The orderliness of an object decreases with the increase of entropy. Hence spontaneous processes are accompanied by an increase in entropy as well as an increase in the disorder of the system.

105. Give only the Nernst and Gibbs-Helmholtz equations.

The Nernst equation for the electrode potential at 25° is given by

$$E = E^{\circ}_{\text{Red}} + \frac{0.0591}{n} \log[M^{n+}]$$

$$E = E^{\circ}_{\text{Oxi}} - \frac{0.0591}{n} \log[M^{n+}]$$

The Gibbs-Helmholtz equation in terms of Free energy (ΔG) and enthalpy (ΔH) is given by

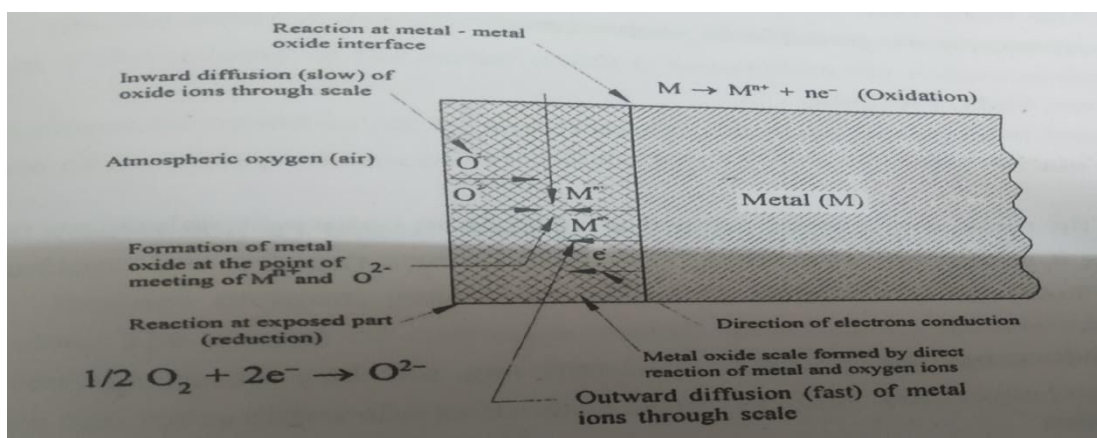
$$\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$$

106. Define Chemical corrosion. Give the schematic diagram for depicting the mechanism of oxidation corrosion.

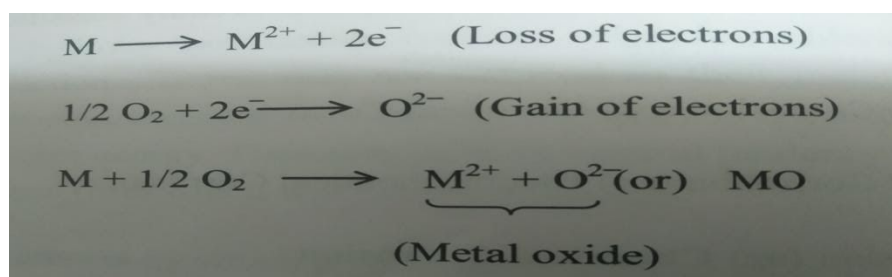
Chemical corrosion takes place due to the direct chemical action of atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulfur dioxide, nitrogen or anhydrous Inorganic liquid with metal surfaces.

When oxygen directly attacks the metal surface at low or high temperature oxidation corrosion takes place this type of corrosion usually occurs in the absence of moisture.

Schematic diagram for depicting the mechanism of oxidation corrosion:



The following reactions take place during oxidation corrosion:



Mechanism:

- Oxygen attacks the surface of the metal under oxidation and this results in the formation of metal oxide scale.
- The metal oxide scale formed on the metal surface acts as a barrier and prevents further oxidation.
- If oxidation has to continue either the metal ion must diffuse outwards through the metal oxide barrier or the oxide ions must diffuse inwards through the barrier.
- Though both transfers occur the outward diffusion of the metal ion is more rapidly than the inward diffusion of oxide ions.
- This may be accounted for by the higher mobility of the smaller size of the metal ions when compared to oxide ions.

107. Define Electrochemical corrosion. Give a neat sketch for depicting the mechanism of oxygen absorption and Hydrogen evolution corrosion.

Electrochemical corrosion

This type of corrosion takes place

- * When a conducting liquid is in contact with the metal or
- * When two dissimilar metals are either immersed partially or dipped in a solution.
- * When a metal is exposed to varying a concentration of oxygen or electrolyte.

Mechanism of oxygen absorption

If electrolyte is neutral or alkaline aqueous solution, corrosion takes place by absorption of O_2 .

Example: Rusting of iron in water containing dissolved oxygen occurs by oxygen absorption mechanism.

At anodic area iron will dissolve by oxidation. The surface of iron is usually coated with the thin film of iron oxide. But if this iron oxide film develops some cracks, anodic areas are created on the surface; while the metal (iron) acts as cathodes.

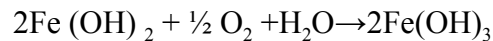
Here the anodic areas are small surfaces while the rest of the surface of the metal forms large cathodes.

At anode, $Fe \rightarrow Fe^{2+} + 2e^-$

The electrons flow to the cathodic area through and will be accepted by O_2 .

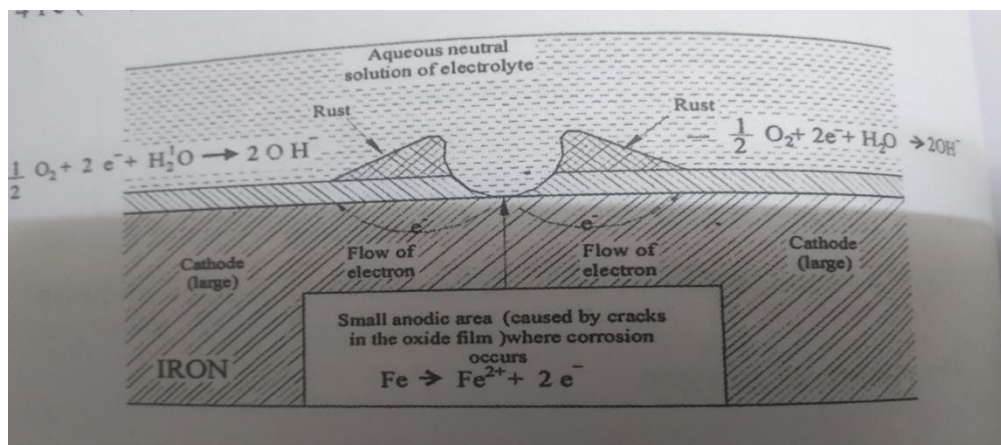
At Cathode $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

If enough O_2 is present, ferrous hydroxide easily oxidized to ferric hydroxide



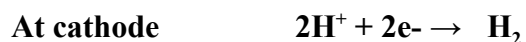
Ferric hydroxide rust. This product is called yellow rust, which is nothing but $Fe_2O_3 \cdot H_2O$.

If O_2 is limited, the corrosion product will be black anhydrous magnetite, Fe_3O_4 .



Mechanism of Hydrogen evolution:

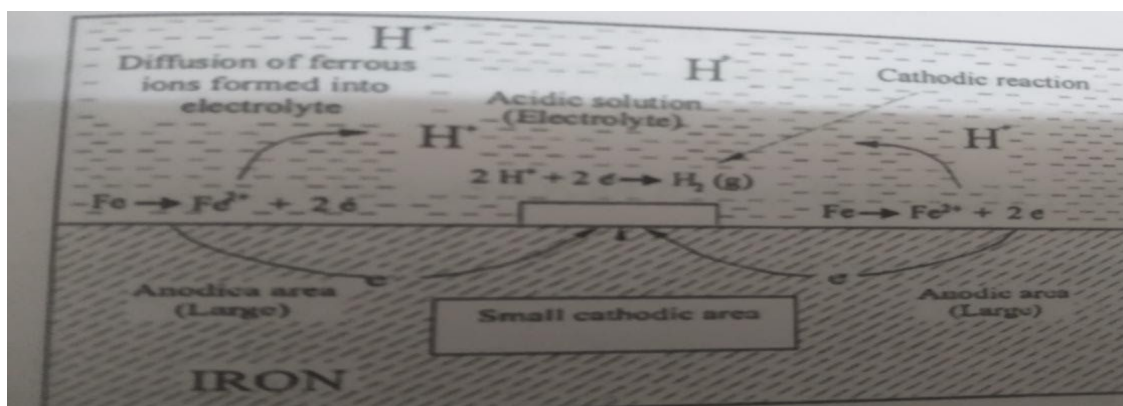
Evolution of Hydrogen Electrochemical corrosion with evolution of H_2 occurs in an acidic environment.



Iron tank which acts as an anode undergoes corrosion as Fe atoms from the tank pass into the acidic solution as Fe^{2+} ions as shown in reaction above.

Free electrons accumulate at cathode Hydrogen ions present in acidic solution take up these electrons forming H_2 gas as shown in the reaction above. H_2 gas liberates in the form of bubbles near the cathode.

Thus, hydrogen evolution type of corrosion is nothing but displacement of H^+ from acidic solution by metal ions.



108. Write a note on free energy for corrosion reaction.

In electrical and electrochemical processes electrical work is defined as the product of charges moved (Q) times the potential (E) through which it is moved. If this work is done in an electrochemical cell in which the potential difference between its two half-cells is E , and the charge is that of one mole of reaction in which n moles of electrons are transferred, then the electrical work ($-w$) done by the cell must be nE .

In this relationship, the Faraday constant F is required to obtain coulombs from moles of electrons. In an electrochemical cell at equilibrium, no current flows and the energy change occurring in a reaction is expressed in equation:

$$W = \Delta G = -nFE$$

Under standard conditions, the standard free energy of the cell reaction ΔG° is directly related to standard potential difference across the cell, E° .

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

Electrode potentials can be combined algebraically to give cell potential. For a galvanic cell, such as in the case of corrosion, reaction of positive cell voltage will be obtained if the difference is taken according to the equation.

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

The free energy change in a galvanic cell, or in a spontaneous cell region, is negative and the cell voltage is positive.

109. What is solubility product, K_{sp} and give the expression for the solubility product constant of common salt.

The solubility product constant, K_{sp} , is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher the K_{sp} value it has.

Consider, in general, a salt of the type A_xB_y which dissociates as



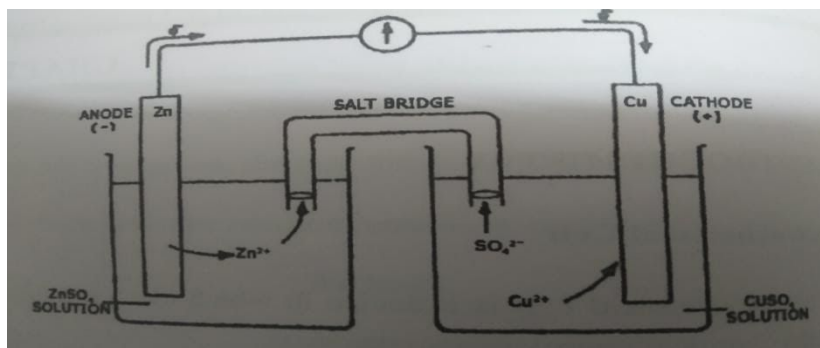
The solubility product of the salt is now given by

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Thus, the solubility product of a sparingly soluble salt forming a saturated solution in water given by the product of the concentrations of the ions raised to a power equal to the number of the ions occurs in the equation representing the dissociation of electrolyte.

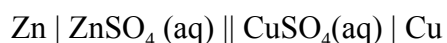
110. What is an Electrochemical cell or Galvanic cell? Give its representation.

Electrochemical cell or Galvanic cell is a device in which the free energy of chemical reaction is converted into electrical energy i.e. electricity is produced from a spontaneous chemical reaction.



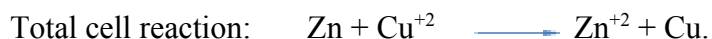
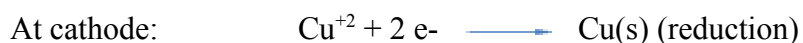
Cell representation:

Daniel cell is an example of a Galvanic cell obtained by coupling Zn half-cell and copper half-cell through a salt bridge.



Cell reactions:

The electrode reactions of Daniel Cell are:



111. Define Single electrode potential and standard electrode potential. Write the mathematical expression for the Nernst equation for $\text{Zn}(\text{s})/\text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$.

Single electrode potential:

It is the measure of tendency of metallic electrodes to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard electrode potential:

It is the measure of tendency of metallic electrodes to lose or gain electrons, when it is in contact with a solution of its own salt of 1molar concentration at 25°c.

Nernst equation for $\text{Zn}(\text{s})/\text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$

In Daniell cell, the electrode potentials of the half cells are written as:

$$E_{(Cu^{2+}|Cu)} = E_{(Cu^{2+}|Cu)}^0 - \frac{RT}{nF} \ln \frac{1}{[Cu^{2+}]}$$

$$E_{(Zn^{2+}|Zn)} = E_{(Zn^{2+}|Zn)}^0 - \frac{RT}{nF} \ln \frac{1}{[Zn^{2+}]}$$

$$E_{cell} = E_{(Cu^{2+}|Cu)} - E_{(Zn^{2+}|Zn)}$$

$$E_{cell} = E_{(Cu^{2+}|Cu)}^0 - \frac{RT}{nF} \ln \frac{1}{[Cu^{2+}]} - E_{(Zn^{2+}|Zn)}^0 + \frac{RT}{nF} \ln \frac{1}{[Zn^{2+}]}$$

$$= \left\{ E_{(Cu^{2+}|Cu)}^0 - E_{(Zn^{2+}|Zn)}^0 \right\} - \frac{RT}{nF} \left\{ \ln \frac{1}{[Cu^{2+}]} - \ln \frac{1}{[Zn^{2+}]} \right\}$$

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

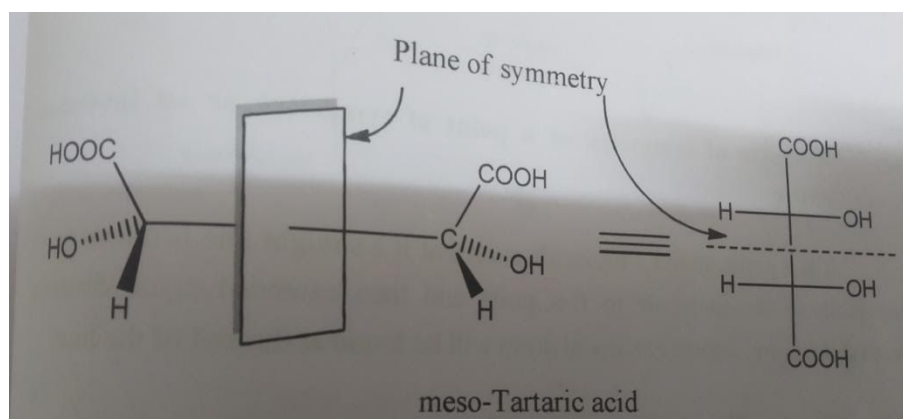
$$\text{At } 298 \text{ K, } E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

This is the Nernst equation for the Daniel cell.

112. Define Plane of symmetry with an example.

It is defined as an imaginary plane that bisects a molecule in such a way that one half of the molecule is the mirror image of the other half. The plane of symmetry (σ) is also called a mirror plane.

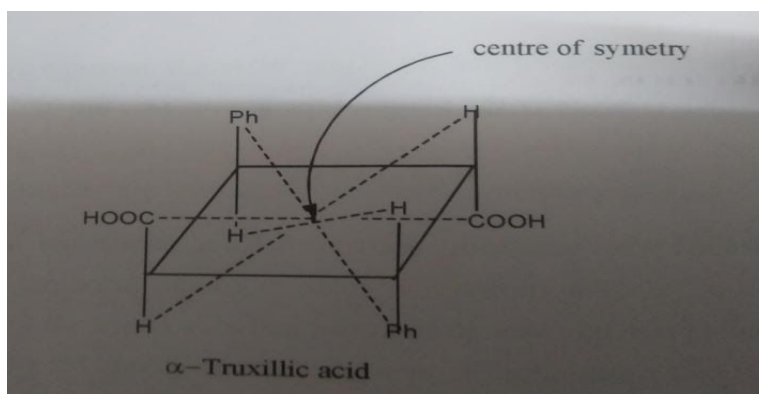
Example: The eclipsed conformation of meso-tartaric acid has a plane of symmetry.



113. Define Centre of symmetry with an example.

A centre of symmetry is a point within a molecule such that if a straight line is drawn from any atom of the molecule to this point and then extended equal distance beyond the point, another identical atom will be found at the end of the line.

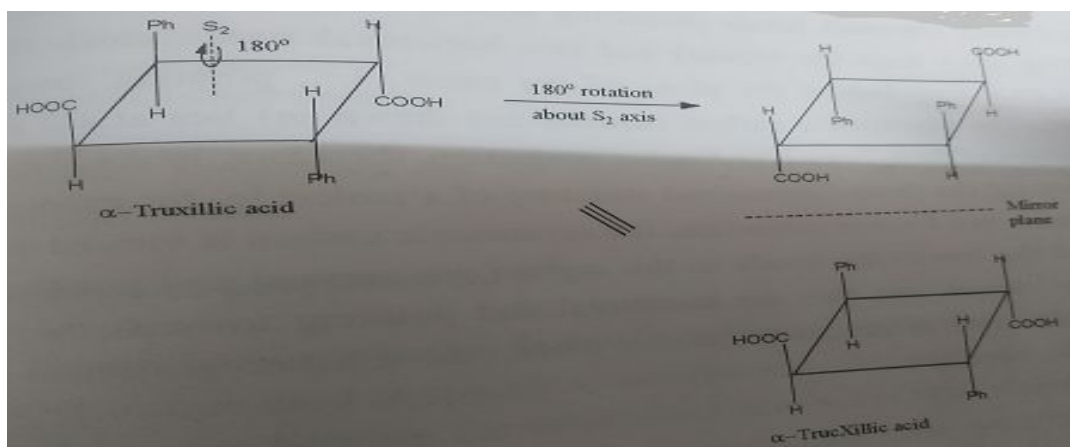
Example: α -truxillic acid has a Centre of symmetry.



114. Define Alternating axis of symmetry with examples.

An alternating axis of symmetry is an axis such that a rotation of the molecule about axis by $360^\circ/n$ followed by reflection in a plane perpendicular to this axis generates a structure indistinguishable from the original. The order of the two operations may be reversed without change in the result.

Example: α -truxillic acid has a two-fold alternating of symmetry.



115. Differentiate geometrical with optical isomerism.

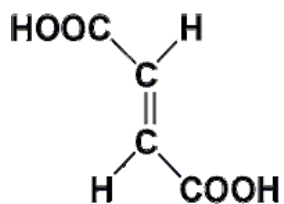
Optical isomers and geometrical isomers are two types of stereoisomers. The key difference between optical and geometrical isomerism is that optical isomers are pairs of compounds which appear as mirror images of each other, whereas geometrical isomers are pairs of compounds containing the same substituents attached to a carbon-carbon double bond differently. Thus, optical isomers are non-superimposable mirror images, whereas geometrical isomers have a difference in the connectivity of substituents to the double bond.

Moreover, another difference between optical and geometrical isomerism is that optical isomers have similar physical properties, but geometrical isomers have different physical properties.

116. Mention the types of isomerism exhibited by each of the following pairs:

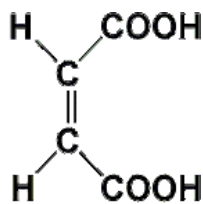
i. Maleic acid and Fumaric acid ii. n-Butyl alcohol and Diethyl ether and iii. Diethyl ether and Methyl propyl ether

- (i) Maleic acid and Fumaric acid exhibits Geometrical isomerism— fumaric acid trans form and maleic acid cis form



Fumaric Acid

Trans form



Maleic Acid

Cis form

- (ii) n-Butyl alcohol and Diethyl ether exhibits Functional isomerism –They have the same molecular formula but they differ in functional groups.

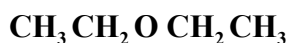


n-Butyl alcohol



Diethyl ether

- (iii) Diethyl ether and Methyl propyl ether exhibit Metamerism due to unequal distribution of carbon atoms on either side of the functional group.



Diethyl ether



Methyl propyl ether

117. Differentiate Chirality and Achirality with an example for each.

Chiral	Achiral
Chiral means asymmetric in such a way that the structure and its mirror image are not superimposable.	Chiral means asymmetric in such a way that the structure and its mirror image are superimposable.
Molecules are always asymmetric at one or more centres.	Molecules are always symmetric at every centre.
A molecule and its mirror image are two different compounds.	A molecule and its mirror image is the same.
The molecule and its mirror image are non-superimposable.	The molecule and its mirror image are superimposable
Molecules can rotate the plane-polarised light clockwise or anticlockwise.	Molecules cannot rotate the plane-polarised light in any direction.

Example: For chiral molecules- golf clubs, scissors, shoes and a corkscrew, our hands, Lactic acid $\text{CH}_3\text{--CH(OH)--COOH}$.

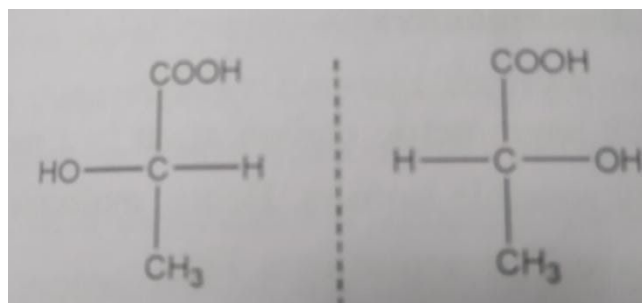
Example: For achiral molecules - two pieces of paper, A baseball bat, a hammer, most socks, Hexane-3-ol ($\text{C}_2\text{H}_5\text{--CH(OH)--C}_2\text{H}_5$).

118. What are Enantiomers and Diastereomers? Give examples.

Enantiomers:

- Optical isomers that are mirror images are called enantiomers. Enantiomers are stable isolable components that are differing from one another in three dimensional spatial arrangements.
- They have identical properties in all respects except in their interaction with planar polarized light.
- They have the same melting point density, solubility color and reactivity towards acids and bases.

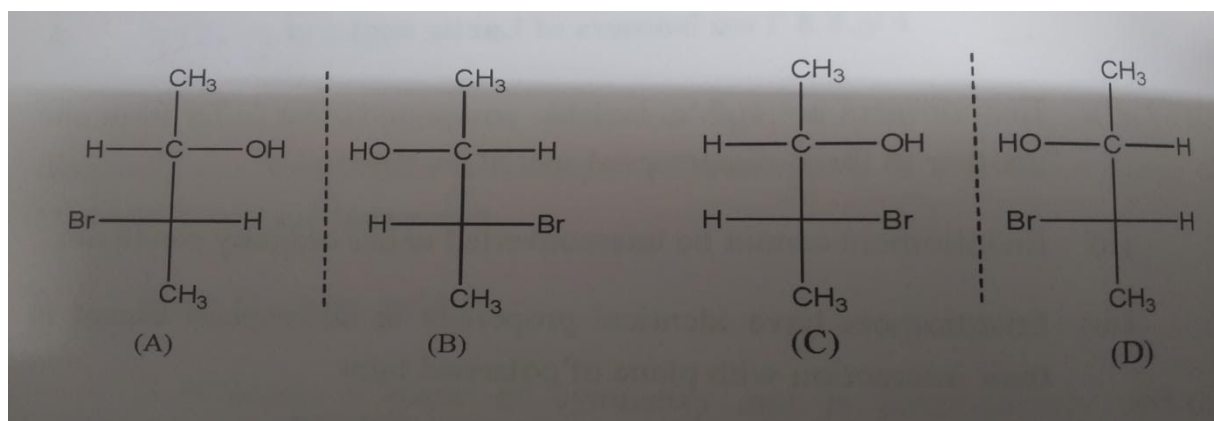
Example: Lactic acid.



Diastereomers:

- Stereoisomers that are not mirror images of each other are called diastereomers.
- They have different melting points, boiling points and solubility.
- They will have different chemical reactivity towards most reagents.

Eg: 3-bromo-2-butanol which has two asymmetric carbon atoms shows the four isomers.



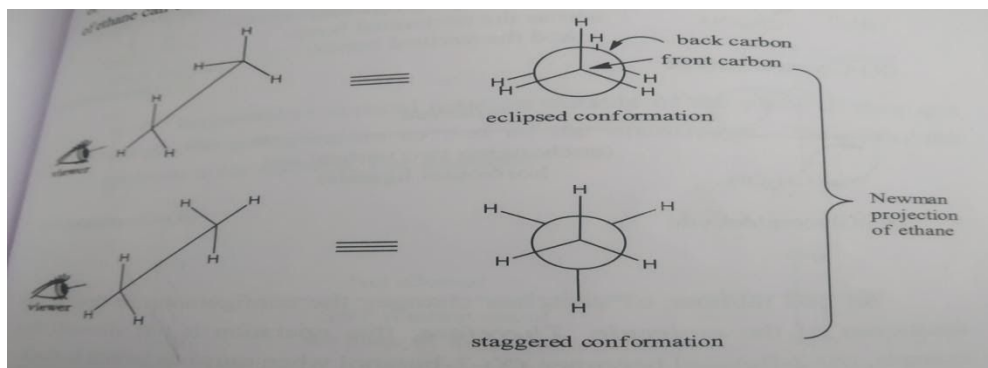
- It is known that (A) is the mirror image of (B) and (C) is the mirror image of (D). Thus the four isomers are two pairs of enantiomers.
- Now Comparing (A) with (C), (A) with (D), (B) with (C), and (B) with (D) they are neither superimposable nor mirror images. They are called diastereomers.

119. Write a note on Newman projection with an example.

- In the Newman projection the molecule is viewed along the bond joining the key carbon atoms.
- The front carbon atom is represented by a central point from which the remaining three bonds emerge.
- The rear carbon atom is depicted by a circle with the remaining three bonds pointing out from it.

- The angle between any two of these bonds on each carbon is 120° .

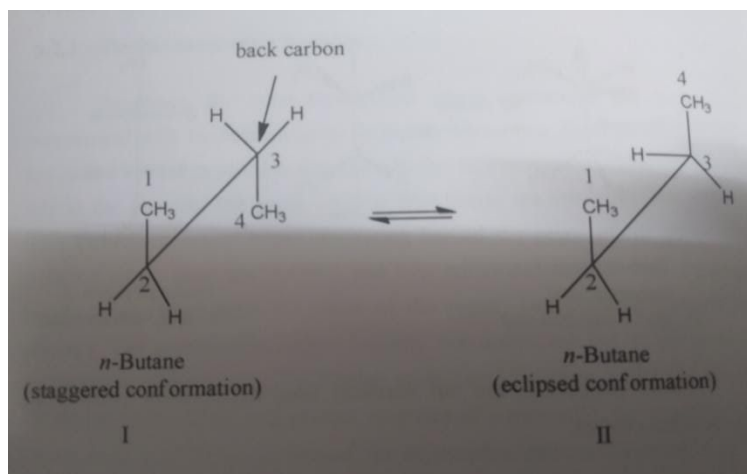
Example, the Newman projections of ethane is shown below:



120. What is Sawhorse projection? Give an example.

- Sawhorse projection shows the spatial relationship between the substituents attached to two adjacent carbon atoms.
- In this representation, the bond between the two carbon atoms is drawn diagonally and is slightly elongated.
- The remaining bonds are shown by small lines.
- The molecule is viewed from slightly above and to the right of the C-C bond.
- There is free rotation about the C-C bond and the three groups attached to one carbon may be rotated clockwise or anticlockwise in relation to the three groups attached to the other carbon atom.

Example: n-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$)

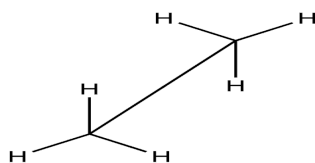


- The conformation I in which the groups on C2 and C3 are oriented as far away from each other as possible is known as **staggered** conformation
- The conformation II in which the groups on C2 and C3 are nearest is known as **eclipsed** conformation.

Module-5

121. What is Sawhorse projection? Give an example.

A **Sawhorse Projection** is a view of a molecule down a particular carbon-carbon bond, and groups connected to both the front and back carbons are drawn using *sticks* at 120 degree angles. **Sawhorse Projections** can also be drawn so that the groups on the front carbon are *staggered* (60 degrees apart) or *eclipsed* (directly overlapping) with the groups on the back carbon.



Staggered Conformation of Ethane

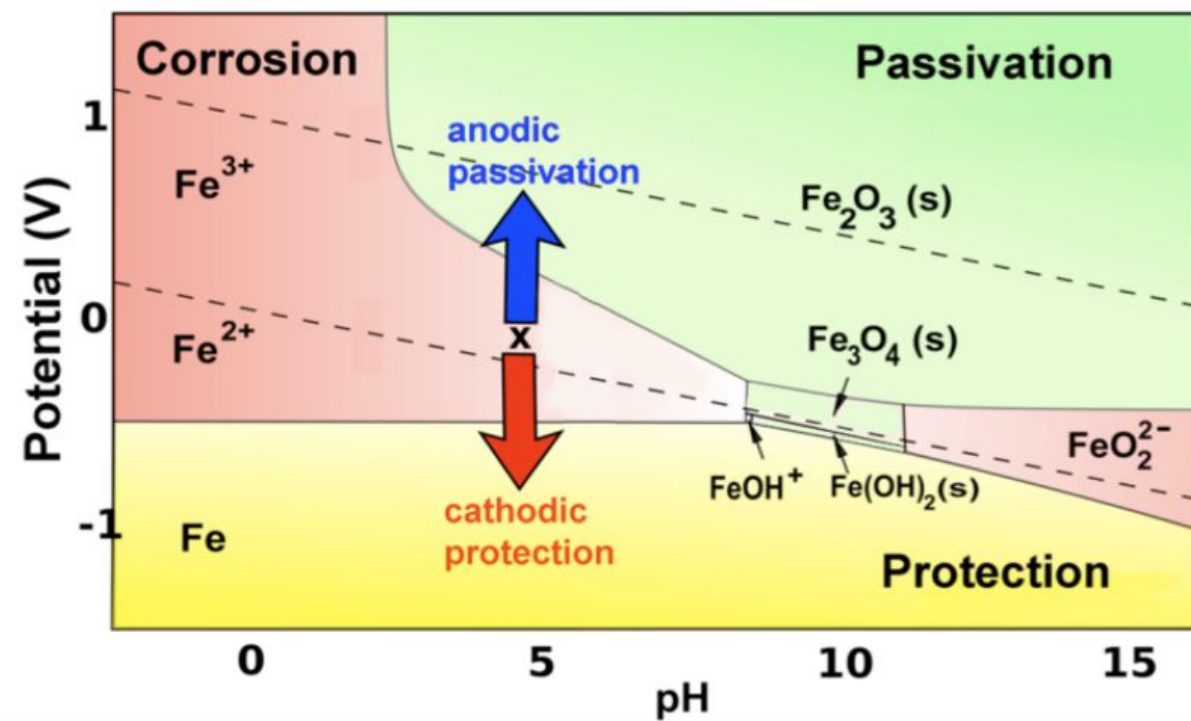
121. Based on Pourbaix diagram, define the terms passivity and immunity.

The zone in which Iron is present in the form of Iron Oxide is known as Passive zone.

The oxides act as a protective barrier and prevent further corrosion.

At negative potentials and acidic pH, Iron is in the stable form. It is known as Immunity.

122. Give a neat sketch on Pourbaix diagram.



123. What is Fischer Projection?

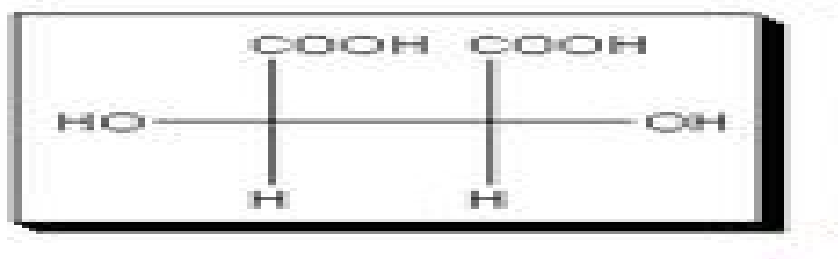
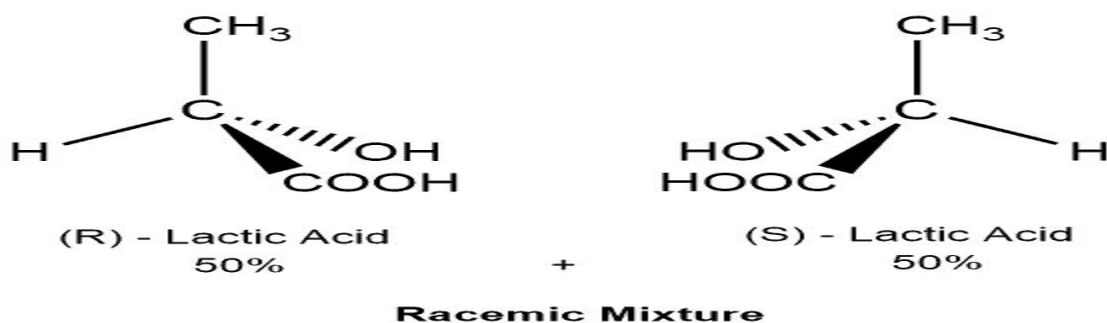
The Fischer Projections allow us to represent 3D molecular structures in a 2D environment without changing their properties and/or structural integrity. The Fischer Projection consists of both horizontal and vertical lines, where the horizontal lines represent the atoms that are pointed toward the viewer while the vertical line represents atoms that are pointed away from the viewer. The point of intersection between the horizontal and vertical lines represents the central carbon.

124. Give the steps to determine R/S configuration on a Fischer Projection
 Cahn-Ingold-Prelog priority rules to determine R/S configuration on a Fischer Projection.

125. Define the terms i. Racemic mixture and ii. Meso Isomers with suitable examples.

A racemic mixture is an equal (1:1) mixture of dextro and levo isomers known as enantiomers. It contains non-identical isomers. A racemic mixture contains chiral compounds.

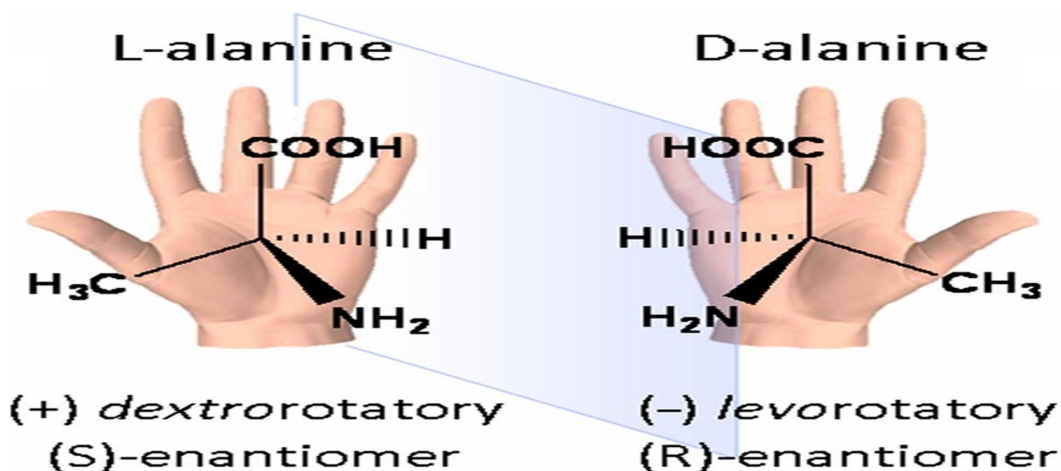
A meso compound is a molecule having more than one identical stereocenter and an identical or superimposable mirror image. It has identical mirror images. They are considered as achiral compounds.



Meso Tartaric acid

126. What are dextro and laevo rotatory isomers? Give examples.

A **dextrorotatory** compound is a compound that rotates the plane of polarized light clockwise as it approaches the observer. if a compound is dextrorotatory, its mirror image counterpart is **levorotatory**. That is, it rotates the plane of polarized light counterclockwise (to the left).

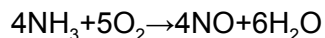


127. What is a reducing agent? Give an example with an equation.

A reducing agent is an element that loses electrons. The reducing agent means to lose electrons; it is said to have been oxidized.

The element which undergoes oxidation (gets oxidized) is called the reducing agent.

For example:



In the given reaction, nitrogen is oxidized to NO by gaining oxygen atom. Thus, NH_3 is reducing agent as it undergoes oxidation.

128. What is an oxidising agent? Give an example with an equation.

An oxidizing agent is an element that gains electrons. Since the oxidizing agent means to gain electrons; it is said to have been reduced.

The element which undergoes reduction (gets reduced) is called an oxidizing agent.

For example: $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$

In the given reaction, O_2 is reduced by losing oxygen atoms. Thus, O_2 is an oxidizing agent as it undergoes reduction.

129. What is the reaction of the following with Cyclopropane? i. Halogens. HI iii. Sulphuric acid and iv. Hydrogen

130. What is a medicinal drug? Give the use of Aspirin and Paracetamol.

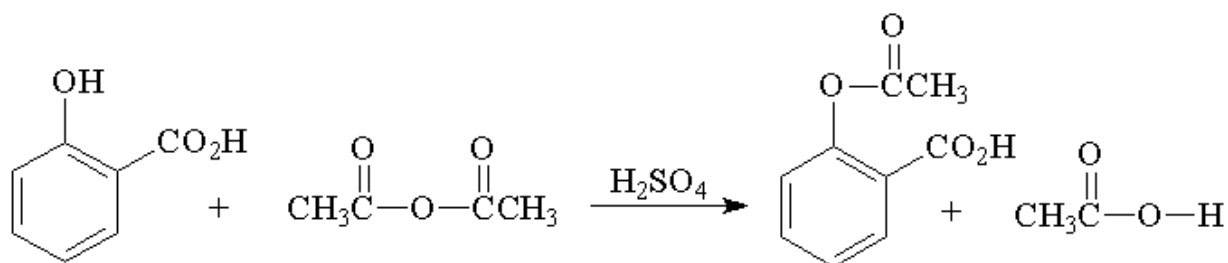
A medicinal drug is a medicine that treats or prevents or alleviates the symptoms of disease.

Aspirin can be used to relieve pain and inflammation caused by rheumatic and muscular pain, sprains, backache, **headache**, sore throat, toothache and period pain. It can also be used to treat flu-like symptoms and reduce fever in adults. In low doses, it can be used to thin the blood. **Aspirin given** shortly after a heart attack decreases **the** risk of death.

Paracetamol is used for reducing [fever](#) in people of all ages. It is used for the relief of mild to moderate pain. Paracetamol can relieve pain in mild arthritis, but has no effect on the underlying inflammation, redness, and swelling of the joint.

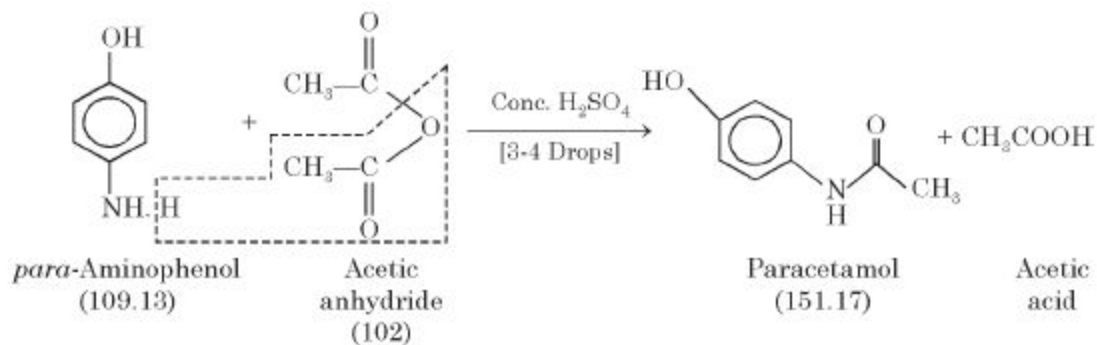
131. Write the synthesis of Aspirin and its uses.

Aspirin is prepared when **salicylic acid** is reacted with **an** excess of acetic anhydride and a small amount of a strong acid is used as a catalyst.



Aspirin, also known as **acetylsalicylic acid** (ASA), is a medication **used** to reduce pain, fever, or inflammation. Specific inflammatory conditions in which **aspirin** is **used** to treat Kawasaki disease, pericarditis, and rheumatic fever. **Aspirin given** shortly after a heart attack decreases **the** risk of death.

132. Give the synthesis and uses of Paracetamol.



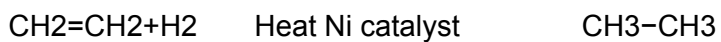
Paracetamol is made by reacting 4-aminophenol with acetic anhydride. This reaction forms an amide bond and ethanoic acid as a by- product. When the reaction is complete the **paracetamol** is then isolated and purified.

133.Explain the role of the following reagents in oxidation/ reduction reactions.a)NaBH₄b)K₂Cr₂O₇c)KMnO₄and d) LiAlH₄

134.What are addition reactions? Give an example.

The reaction in which an unsaturated hydrocarbon combines with another substance to give a single product is called an addition reaction.

Example: Ethene reacts with hydrogen when heated in the presence of nickel catalyst to form ethane:



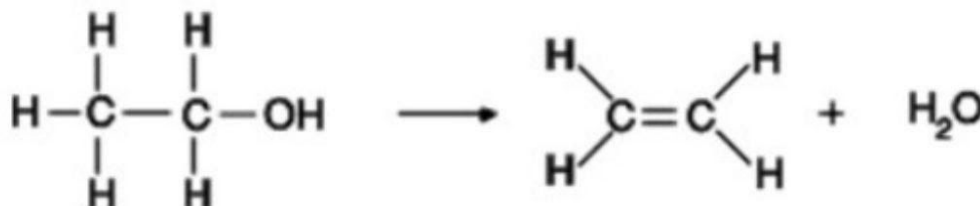
135.What are substitution reactions? Give an example

A substitution reaction is a single displacement or substitution of compounds reaction

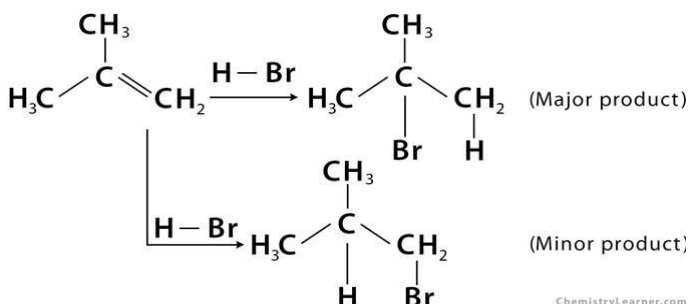
Eg: CH₃Cl on reaction with a hydroxyl ion (OH⁻) will produce CH₃OH.

136. What are elimination reactions? Give an example.

Elimination reactions are commonly known by the kind of atoms or groups of atoms leaving the molecule. The removal of a hydrogen atom and a halogen atom, for **example**, is known as dehydrohalogenation; when both leaving atoms are halogens, the **reaction** is known as dehalogenation.



137. What is Markovnikov's rule? Give an example to illustrate it.



Markonikoff's rule: When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the reagent is attached to the unsaturated C atom having less number of hydrogen atoms.

Thus, when HBr is added to propene, isopropyl bromide is obtained as a major product. Thus, bromide ion is added to the middle carbon atom (having less number of H atoms) and proton is attached to the terminal C atom.

138. Illustrate peroxide effect with an example.

The addition of HBr to unsymmetrical alkenes against the Markownikoff's rule is called peroxide effect or Anti Markovnikov's rule. According to this effect, the negative part of the unsymmetrical attacking reagent attached to that carbon atom of the double bond of unsymmetrical alkene which bears the higher number of hydrogen atoms." This reaction takes place in the presence of

peroxide.

Propene $\text{CH}_3\text{-CH=CH}_2$ + HBr

peroxide

n-propyl bromide $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$

139. Compare Nucleophilic with Electrophilic substitution reactions.

Electrophilic substitutions involve displacement of a functional group by an electrophile (generally a hydrogen atom). Electrophiles are species that are attracted to electrons.

Nucleophilic substitutions involve attack of a positively charged (or partially positively charged) atom or group by a nucleophile. Nucleophiles are species that can donate an electron pair.

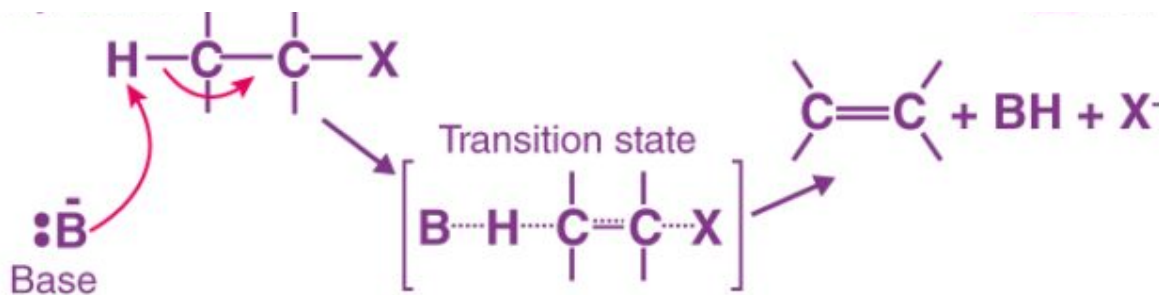
140. Give an example for bimolecular elimination[E2] and unimolecular nucleophilic substitution[SN1] reactions.

In an E2 mechanism which refers to *bimolecular elimination* is basically a one-step mechanism.

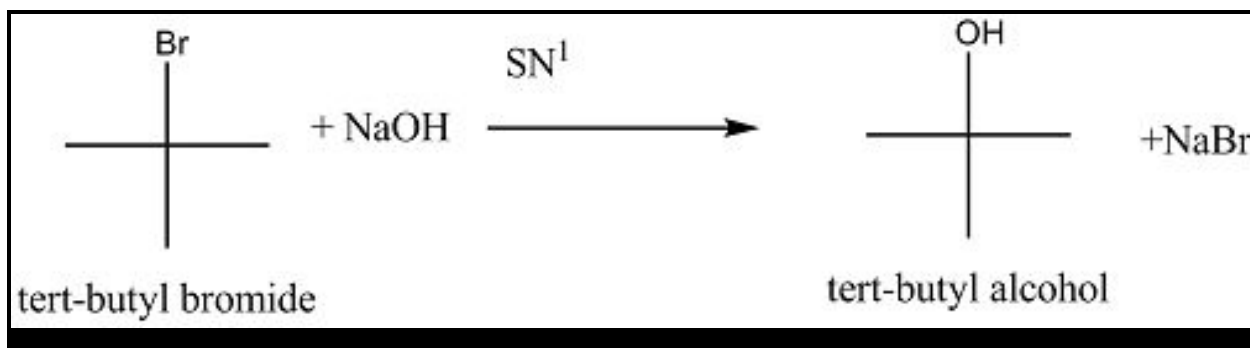
Here, the carbon-hydrogen and carbon-halogen bonds mostly break off to form a new double bond.

- 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 E2 mechanism can generally be represented as below. In the below-mentioned representation, B stands for base and X stands for the halogen.



SN1 reaction corresponds to unimolecular nucleophilic substitution reaction. The order of reaction is one. The hydrolysis of tert-butyl bromide with aqueous NaOH solution is an example of SN1 reaction. The rate of the reaction depends on the concentration of tert butyl bromide but it is independent of the concentration of NaOH. Hence, the rate determining step only involves tert-butyl bromide. In SN1 reaction, racemic mixture is obtained.



141. What is a free radical addition reaction? Give an example with an equation.

Free-radical addition is an [addition reaction](#) in [organic chemistry](#) which involves [free radicals](#).^[1] The addition may occur between a radical and a non-radical, or between two radicals.

Free Radical Addition Of HBr To Alkenes With ROOR (Peroxides)

142. What is Structural isomerism? Give examples

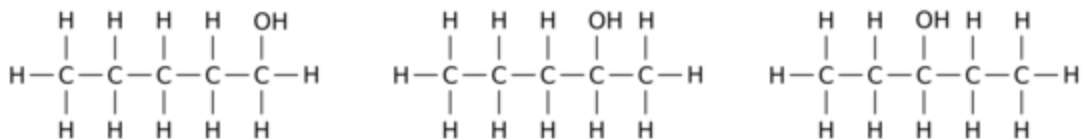
The isomers differing in the atomic arrangement of the molecules without any kind of reference to the spatial arrangement are known as the structural isomers. The phenomenon of these structural isomers is called structural isomerism.

Structural isomerism is also called constitutional isomerism as per the IUPAC. It is a kind of isomerism where the molecules have the same molecular formula with different orders and bondings, as opposed to that of the stereoisomerism.

1-pentanol

2-pentanol

3-pentanol



143. What is Coordination isomerism? Give examples.

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

When both positive and the negative ions of a salt are complex ions and the two isomers differ in the distribution of ligands in the cation and the anion; it is Coordination isomerism.

Example: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.

144. What are Hydrate isomers? Give examples

Hydrate isomerism or solvate isomers are a special case of ionisation isomerism in which compounds differ depending on the number of the solvent molecule directly bonded to the metal ion.

Examples:

- $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
- $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
- $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$

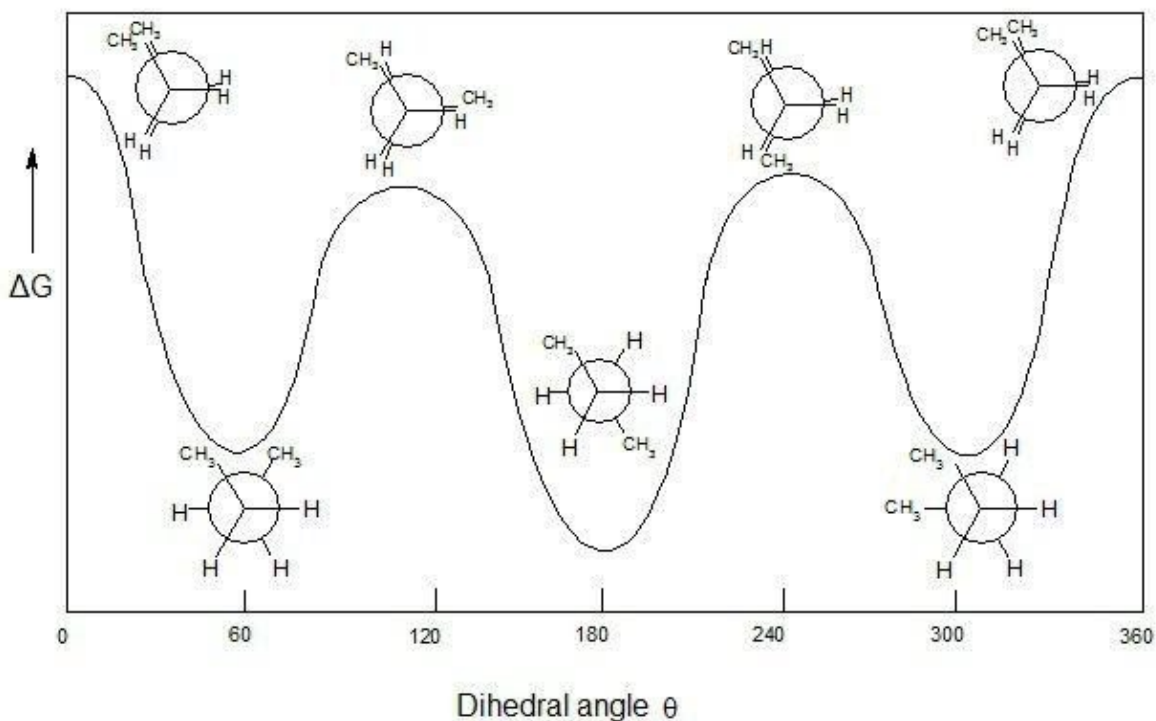
145. What are Linkage isomers? Give examples.

Linkage isomers are two or more coordination compounds in which the donor atom of at least one of the ligands is different. This type of isomerism can only exist when the compound contains a ligand that can bond to the metal atom in two (or more) different ways.

Linkage isomerism occurs with ambidentate ligands that are capable of coordinating in more than one way.

Another example of an ambidentate ligand is thiocyanate, SCN^- , which can attach to either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Typical ligands that give rise to linkage isomers are: thiocyanate, SCN^- and isothiocyanate, NCS^- selenocyanate, SeCN^- and isoselenocyanate, NCSe

146. How many conformations does n-butane have?



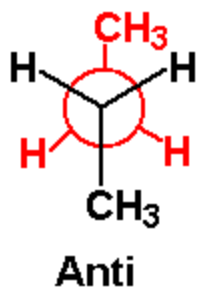
Conformation is a property of atoms in which rotation of groups about a carbon-carbon single bond takes place. The rotation usually results in different spatial arrangements of the atoms. Butane has

anti

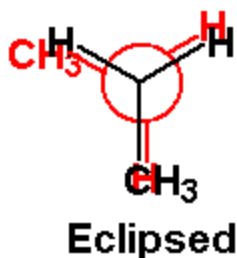
1. gauche
2. eclipsed
3. fully eclipsed

147. Which conformation is the most stable one in n-butane?

The **most stable conformation** of **butane** is the **one** in which the two terminal methyl groups are the farthest removed from each other, i.e. the anti **conformation**. Somewhat less favorable is the gauche **conformation** in which the methyl groups assume a dihedral angle of 60°.



148. Draw the least stable conformation for n-butane.



Eclipsed conformation is least stable because two methyl groups are closer to each other and the dihedral angle is 0°.

149. Illustrate the difference between gauche and staggered.

- In an anti conformer, the largest groups are 180° from each other.
- In a gauche conformer, the bonds are staggered but the largest groups are 60° from each other.

Because of different steric interactions, the most stable conformer is the anti conformer. The second-most stable conformer is the gauche conformer.
