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सर्वश्रेष्ठ परीक्षा पथ-प्रदर्शक

B.Sc.
First Year
(Certificate Course)
Semester-I

CHEMISTRY

Fundamentals of Chemistry

SYLLABUS

UNIT-I	Introduction to Indian ancient Chemistry and contribution of Indian Chemists, in context to the holistic development of modern science and technology, should be included under Continues Evaluation (CIE). **Molecular polarity and Weak Chemical Forces :** Resonance and resonance energy, formal charge, Van der Waals forces, ion-dipole forces, dipole dipole interactions, induced dipole interaction, dipole moment and molecular Structure (Diatomic and polyatomic molecules), Percentage ionic character from dipole moment, polarizing power and polarizability. Fajan's rules and consequences of polarization. Hydrogen bonding, van der Waals forces, ion-dipole forces, dipole-dipole interactions, induced dipole interaction.
UNIT-II	**Simple Bonding theories of Molecules :** Atomic orbitals, Aufbau principle, multiple bonding (s and p bond approach) and bond lengths, the valence bond theory (VBT), Concept of hybridization, hybrid orbitals and molecular geometry, Bent's rule, Valence shell electron pair repulsion theory (VSEPR), shapes of the following simple molecules and ions containing lone pairs and bond pairs of electrons: H_2O, NH_3, PCl_5, SF_6, SF_4 ClF_3, I_3^-, and H_3O^+. Molecular orbital theory (MOT). Molecular orbital diagrams bond orders of homonuclear and heteronuclear diatomic molecules and ions (N_2, O_2, C_2, B_2, F_2, CO, NO, and their ions).
UNIT-III	**Periodic properties of Atoms (with reference to s & p-block) :** Brief discussion, factors affecting and variation trends of following properties in groups and periods. Effective nuclear charge, shielding or screening effect, Slater rules, Atomic and ionic radii, Electronegativity, Pauling's/ Allred Rochow's scales, Ionization enthalpy, Electron gain enthalpy.
UNIT-IV	**Recapitulation of basics of Organic Chemistry :** Hybridization, bond lengths and bond angles, bond energy, localized and delocalized chemical bonding, Van der Waals interactions, inclusion compounds, Clatherates, Charge transfer complexes, hyperconjugation, Dipole moment; Electronic Displacements : Inductive, electromeric, resonance mesomeric effects and their applications.
UNIT-V	**Mechanism of Organic Reactions :** Curved arrow notation, drawing electron movements with allows, half-headed and double-headed arrows, homolytic and heterolytic bond fission, Types of reagents : electrophiles and nucleophiles, Types of organic reactions, Energy considerations. Reactive intermediates : Carbocations, carbanions, free radicals, carbenes, arynes and nitrenes (with examples).
UNIT-VI	**Stereochemistry (To be taught with demonstration of Molecular models in the classroom teaching) :** Concept of isomerism, Types of isomerism; Optical isomerism – elements of symmetry, molecular chirality, enantiomers, stereogenic center, optical activity, properties of enantiomers, chiral and achiral molecules with two stereogenic centers, disasteromers, threo and erythro diastereomers, meso compounds, resolution of enantionmer, inversion, retention and recemization. Relative and absolute configuration, sequence rules, D & L and R & S systems of nomenclature. Geometric isomerism – determination of configuration of geometric isomers, E & Z system of nomenclature, geometric isomerism in oximes and alicyclic compounds. Conformational isomerism – conformational analysis of ethane and n-butane; conformations of cyclohexane, axial and equatorial bonds, conformation of mono substituted cyclohexane derivatives, Newman projection and Sawhorse formulae, Fischer and flying wedge formulae, Difference between configuration and conformation.
UNIT-VII	**Basic Computer system (in brief) :** Hardware and Software; Input devices, Storage devices, Output devices, Central Processing Unit (Control Unit and Arithmetic Logic Unit); Number system (Binary, Octal and Hexadecimal Operating System); Computer Codes (BCD and ASCII); Numeric/String constants and variables. Operating Systems (DOS, WINDOWS, and Linux); Introduction of Software languages: Low level and High Level languages (Machine language, Assembly language; QBASIC, FORTRAN) Software Products (Office, chemsketch, scilab, matlab, hyperchem, etc.), internet application.
UNIT-VIII	**Mathematical Concepts for Chemistry :** Logarithmic relations, curve sketching, linear graphs and calculation of slopes, differentiation of functions like Kx, e^x, X^n, sin x, log x; maxima and minima, partial differentiation and reciprocity relations, Integration of some useful/relevant functions; permutations and combinations, Factorials, Probability.

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UNIT-I

Molecular Polarity and Weak Chemical Forces

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Explain why (i) H_2O is liquid but H_2S is a gas.
(ii) Acetone is more volatile then alcohol.

Ans. (i) Water is liquid because it is intermolecularily hydrogen-bonded with strong intermolecular attractions. H_2S is a gas because it is non-hydrogen bonded molecule and thus there are less intermolecular attractions.

(ii) Due to intermolecular hydrogen bonding, alcohol has the stronger intermolecular attractions. As a consequence, alcohol is less volatile than non-hydrogen bonded acetone.

Q.2. Arrange the following types of interactions in order of decreasing stability : Dipole attraction, Hydrogen bonding, Covalent bond, Van der Waals force.

Ans. Covalent > Hydrogen bonding > Dipole > Van der Waals force.

Q.3. Lithium salts are slightly covalent whereas sodium salts are ionic, explain.

Ans. Lithium salts are slightly covalent whereas sodium salts are ionic. This is because Li^+ ion has smaller size than Na^+ ion. Thus, Li^+ ion will polarize anion more than Na^+ ion. As a result, in the case of lithium salts, some sharing of electrons between two oppositely charged ions takes place, *i.e.* the bond becomes partly covalent.

Q.4. Which compound is more covalent and why?

Ans. NaCl will be more covalent than KCl. This is because in these compounds, anion (Cl^-) is the same but Na^+ ion has smaller size than K^+ ion. Thus, Na^+ ion will polarize Cl^- ions more than K^+ ions.

Q.5. Covalent character decreases from $BeCl_2$ to $RaCl_2$, explain.

Ans. The covalent character decreases from $BeCl_2$ to $RaCl_2$. This is because in all these compounds, anion (Cl^-) is the same and cationic size increase from Be^{2+} to Ra^{2+}. Thus Be^{2+} ion will polarize the Cl^- more than other cations of the IIA group. As a result, the covalent character decreases from $BeCl_2$ to $RaCl_2$.

Q.6. Which of the following compound is more covalent and why? $FeCl_2$ or $FeCl_3$.

Ans. $FeCl_3$ will be more covalent than $FeCl_2$. This is because in $FeCl_3$, the Fe^{3+} ion has smaller size and greater charge than Fe^{2+} ion in $FeCl_2$. As a result Fe^{3+} ion will polarize the Cl^- ions more strongly than Fe^{2+} ion.

Q.7. The dipole moment of HCl molecule is 1.03 D and its bond length is 1.275 Å. Calculate the percentage ionic character in this molecule.

Ans. Dipole moment expected for complete ionic character

$$\begin{aligned}\mu_{\text{exp}} &= e \times d \\ &= (4.8\times10^{-10})(1.275\times10^{-8}) \text{ e.s.u} \times \text{cm} \\ &= 6.12\times10^{-18} \text{ e.s.u.} \times \text{cm} = 6.12 \text{ D}\end{aligned}$$

$$\text{Percentage ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{exp}}}\times 100$$

$$= \frac{1.03}{6.12}\times 100 = 16.83\%$$

Q.8. Find the percentage ionic character of H—F bond. (Dipole moment of H—F is 1.92 D, bond length H—F = 0.92 Å).

Ans. Dipole moment expected for complete ionic character

$$\begin{aligned}\mu_{\text{exp}} &= e \times d \\ &= (4.8\times10^{-10})\times(0.92\times10^{-8}) \text{ e.s.u.} \times \text{cm} \\ &= 4.416\times10^{-10} \text{ e.s.u.} \times \text{cm} \\ &= 4.416 \text{ D}\end{aligned}$$

$$\text{Percentage ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{exp}}}\times 100$$

$$= \frac{1.92}{4.416}\times 100 = 43.47\%$$

Q.9. H_2O molecule has high dipole moment, explain.

Ans. H_2O molecule has high dipole moment due to its angular structure. It has been found that the dipole moment of each O—H bond is 1.60 D and the  bond angle is 104.5°. The resultant dipole moment μ comes out to be 1.84 D form :

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta$$

Q.10. The dipole moment of NaCl molecule is 8.5 D and its bond length is 2.36 Å. Calculate the percentage ionic character in this molecule.

Ans. Dipole moment expected for complete ionic character

$$\begin{aligned}\mu_{\text{exp}} &= e \times d \\ &= (4.8\times10^{-10})\times(2.36\times10^{-8}) \text{ e.s.u.} \times \text{cm} \\ &= 11.328\times10^{-18} \text{ e.s.u.} \times \text{cm} \\ &= 11.328 \text{ D}\end{aligned}$$

$$\text{Percentage ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{exp}}}\times 100$$

$$= \frac{8.5}{11.328}\times 100 = 75.03\%$$

Q.11. Arrange the following in the given order of their covalent character :

(i) NaCl, $AlCl_3$, $MgCl_2$ in the increasing order.

(ii) LiCl, LiBr, LiI in the increasing order.

(iii) AgF, AgBr, AgCl in the decreasing order.

Ans. (i) $NaCl < MgCl_2 < AlCl_3$

(ii) $LiCl < LiBr < LiI$

(iii) $AgBr > AgCl > AgF$

Q.12. $BeCl_2$ is more covalent than $MgCl_2$, explain.

Ans. $BeCl_2$ will be more covalent than $MgCl_2$. This is because in these compounds anion (Cl^-) is the same but Be^{2+} ion has smaller size than Mg^{2+} ion. Thus, Be^{2+} ion will polarize Cl^- ion more than Mg^{2+} ion.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Write a short note on Shanti Swarup Bhatnagar.

Ans.

Shanti Swarup Bhatnagar (1894-1955)

Bhatnagar was born on 21 February 1894 at Bhera, in the district of Shapur in Punjab (now in Pakistan). When he was barely eight months old, his father passed away. He spent his next 13 years under the care of his maternal grandfather in Bulandshahar in Uttar Pradesh. Under the influence of his grandfather, young Bhatnagar not only developed a taste for engineering and science but also became interested at a very early age in geometry and algebra and in making mechanical toys. In 1911, Shanti published a letter to the editor, in '*The Leader*', Allahabad, on how to make a substitute for carbon electrodes in a battery using molasses and carbonaceous matter under pressure and heat.

Matriculating the same year, he joined the Dayal Singh College, Lahore. After finishing his intermediate examination in first division, Shanti joined the Forman Christian College and after his B.Sc. and M.Sc. degrees, he spent the next two years at the University of London earning his D.Sc. degree on **the surface tension of oils**, under the supervision of Professor **F.G. Donnan.**

Returning to India in 1921, he joined the Banaras Hindu University as a Professor, remaining there till 1924. From 1924 to 1940 he served as the Director of the University Chemical Laboratories, Lahore, addressing problems in industrial and applied chemistry.

In August 1940, Bhatnagar took over as the Director of the newly created Directorate of Scientific and Industrial Research. This organisation became the Council of Scientific and Industrial Research, with Bhatnagar as its Director. Bhatnagar's tenure saw the setting up of 12 laboratories and the total number of CSIR laboratories today stands at 40.

The British Government conferred on him the Order of the British Empire and in 1941, he was made the Knight Bachelor. In 1943 he was elected a fellow of the Royal Society and received the Padma Vibhushan (1954) from the Government of India.

Shanti Swarup Bhatnagar played a significant part along with Homi Bhabha, Prasanta Chandra Mahalanobis, Vikram Sarabhai and others in building of post-independence Science & Technology infrastructure and in the formulation of India's science policies.

Q.2. Describe in brief about Prafulla Chandra Ray.

Ans.

Prafulla Chandra Ray (1861-1944)

Prafulla Chandra was born on 2 August 1861 in Raruli-Katipara, a village in the district of Khulna (in present day Bangladesh). His early education started in his village school. He often played truant and spent his time resting comfortably on the branch of a tree, hidden under its leaves. After attending the village school, he went to Calcutta (Kolkata), where he studied at Hare school and the Metropolitan college. The lectures of Alexander Pedler in the Presidency College, which he used to attend, attracted him to chemistry, although his first love was literature. He continued to take interest in literature, and taught himself Latin and French at home. After obtaining a F.A. diploma from the University of Calcutta, he proceeded to the University of Edinburgh on a Gilchrist scholarship where he obtained both his B.Sc. and D.Sc. degrees.

In 1888, Prafulla Chandra made his journey home to India. Initially he spent a year working with his famous friend Jagadish Chandra Bose in his laboratory. In 1889, Prafulla Chandra was appointed an Assistant Professor of Chemistry in the Presidency College, Calcutta. His publications on mercurous nitrite and its derivatives brought him recognition from all over the world. Equally important was his role as a teacher - he inspired a generation of young chemists in India thereby building up an Indian school of chemistry. Famous Indian scientists like Meghnad Saha and Shanti Swarup Bhatnagar were among his students.

Prafulla Chandra believed that the progress of India could be achieved only by industrialization. He set up the first chemical factory in India, with very minimal resources, working from his home. In 1901, this pioneering effort resulted in the formation of the Bengal Chemical and Pharmaceutical Works Ltd.

He retired from the Presidency College in 1916, and was appointed as Professor of Chemistry at the University Science College. In 1921 when Prafulla Chandra reached 60 years, he donated, in advance, all his salary for the rest of his service in the University to the development of the Department of Chemistry and to the creation of two research fellowships. The value of this endowinent was about two lakh rupees. He eventually retired at the age of 75. In Prafulla Chandra Ray, the qualities of both a scientist and an industrial entrepreneur were combined and he can be thought of as the father of the Indian Pharmaceutical industry.

Q.3. Describe in short note about :

(i) Animesh Chakravorty. **(ii) Venkatraman Ramakrishnan.**

Ans. (i) **Animesh Chakravorty :** The master brain in the subject Chemistry made significant contributions to the field. Mr. Chakravorty hold his Ph.D. in chemistry from the University of Calcutta. Earlier he started this career as a research professional at MIT and Harvard. He also worked as Research Professor at Hindustan Lever for a consistent period of time. He is the favorite professor for all his students for the reason of his guidance throughout their academics in the field of Chemistry.

(ii) **Venkatraman Ramakrishnan :** He born in Tamil Nadu hails from a family of scientist wherein both his parents were scientists. Mr. Ramakrishnan has recognition that is international for the reason of determining the atomic structure of 30S ribosomal subunit. He spouse Vera Rosenberry who is an author of Children books. From the year 2013, he used **cryo-EM** only to determine ribosome structures.

Q.4. What do you understand by formal charge? Discuss in brief.

Ans. Formal Charge (F.C.) on an Atom in a Polyatomic Molecule or Ion : The individual atoms present in a neutral molecule or a polyatomic ion do not possess any charge. In case of a polyatomic ion (*e.g.*, NH_4^+, NO_3^-, CO_3^{2-}, etc.), the charge present on the ion is actually the net charge possessed by the ion as a whole and not by any particular atom present in that ion. However, for some purposes, a formal charge is assigned to each individual atom.

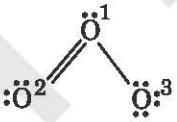
The formal charge on an atom in a polyatomic molecule or ion may be defined as equal to the difference between the number of valence electrons possessed by that atom in the free state and the number of electrons assigned to that atom in the Lewis structure of the molecule or ion. The formal charge may be calculated as given below :

Formal charge on an atom in a polyatomic molecule or ion

$$= [\text{Total number of valence electrons in the free atom}] - [\text{Total number of non-bonding (lone pair) electrons}] - \frac{1}{2}[\text{Total number of bonding (shared) electrons}]$$

The procedure of calculation of formal charge on a particular atom in a polyatomic molecule or ion can easily be understood by considering the example of ozone molecule, O_3 as discussed below.

On the basis of experimental data, the Lewis structure of ozone molecule (O_3) can be expressed as follows :



In the structure shown above, the three oxygen atoms present in O_3 molecule have been numbered as 1, 2 and 3. On the basis of the relationship given above, formal charges on the individual oxygen atoms can be calculated as follows :

O^1 atom : The oxygen atom marked 1 has 6 valence electrons, one lone pair (*i.e.*, 2 non-bonding electrons) and three bonds (*i.e.*, 6 bonding electrons). Hence,

$$\text{Formal charge on } O^1 \text{ atom} = 6 - 2 - \frac{1}{2} \times 6 = +1$$

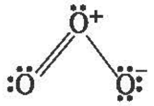
O^2 atom : The oxygen atom marked 2 has 6 valence electrons, two lone pairs (*i.e.*, 4 non-bonding electrons) and two bonds (*i.e.*, 4 bonding electrons). Hence,

$$\text{Formal charge on } O^2 \text{ atom} = 6 - 4 - \frac{1}{2} \times 4 = 0$$

O^3 atom : The oxygen atom marked 3 has 6 valence electrons, three lone pairs (*i.e.*, 6 non-bonding electrons) and one bond (*i.e.*, 2 bonding electrons). Hence,

$$\text{Formal charge on } O^3 \text{ atom} = 6 - 6 - \frac{1}{2} \times 2 = 1$$

Therefore, the Lewis structure of O_3 given above should be written as :



It is to be noted that formal charges do not indicate real charge separation within the molecule. However, the calculation of formal charges helps us in identifying the most stable structure if two or more structures can be assigned to a molecule. The most stable structure is the one which possesses the smallest formal charges on the atoms. A structure having the smallest formal charges on atoms possesses the least energy and is the most stable one.

Q.5. Write a short note on partial or percentage ionic character.

Ans. Partial Ionic Character in Covalent Compounds : There are some covalent compounds which dissolve in water and give ions. Such covalent compounds are said to have partial ionic character. The common most example is HCl. In such compounds the difference in electronegativity between the bonded atoms is sufficiently large but not as large as needed for ionic bonding. The dipole moment, i.e., the polarity in such compounds is quite high. On dissolving in water, the polarity is further increased and separate opposite ions are, thus, produced :

$$\overset{\delta+}{H}-\overset{\delta-}{Cl}\xrightarrow{\text{water}}\overset{+}{H}+\overset{-}{Cl}$$

Aqueous solution of HCl is, therefore, quite a strong acid (being capable of furnishing H+ ions). Because of the presence of ions, HCl solution is a good conductor of electricity as well.

In fact, such compounds have an intermediate character between ionic and covalent. Correctly speaking, the ionic or covalent nature of a bond is expressed in terms of the extent of percentage ionic character in it. This extent is decided by the difference in electro-negativities of the bonded atoms. To illustrate it, the percentage ionic character in halogen acids is being given below with reference to the difference in electro-negativities of the bonded atoms :

Table 1.1

Compound	$X_A - X_B(\Delta)$	Percentage ionic character
HF	1.9	45
HCl	0.9	19
HBr	0.7	11
HI	0.4	5

$X_A - X_B$ (X_A minus X_B) is the difference in electro-negativities of the bonded atoms.

Following table gives the nature of bond with respect to its percentage ionic character based upon the difference in electro-negativities of the bonded atoms :

Table 1.2

$X_A - X_B(\Delta)$	Percentage ionic character	Nature of bond
0.0	0	Pure covalent
> 0.0 – 0.8	1-15	Almost non-polar covalent
> 0.8 – 1.6	16-47	Polar covalent
1.7	50	Ionic
> 1.7 – 2.3	51-73	Ionic
> 2.3 – 3.3	74-93	pure ionic

Thus, the bond in CsF, having $\Delta = 4.0 - 0.7 = 3.3$, is more than 90% ionic in character. Such a bond is called as purely ionic. The tendency of forming the ionic or a covalent bond by different atoms in Periodic table can be determined using the term 'ionic potential', which is given by :

$$\text{Ionic potential } (\phi) = \frac{\text{Charge on cation}}{\text{Radius of cation}}$$

We have already seen that more covalent character is developed if the size of cation is small and charge over it is high (Fajans' rule). Thus ionic potential is a measure of the tendency to form covalent bond. Larger the value of ionic potential (ϕ), more is the tendency to form covalent bond.

In a period, on moving from left to right, the cationic charge increases whereas its size decreases. It results in the increase in ϕ and hence tendency to form covalent bond increases. In a group, on moving from top to bottom, the cationic charge remains same whereas its size increases. It results in the decrease in ϕ and hence tendency to form covalent bond decreases.

Q.6. What are Fajan's rules? Write in brief.

Ans. Fajan's Rules : When two oppositely charged ions approach each other closely, the positively charged cation attracts the outermost electrons of the anion and repels its positively charged nucleus. This results in the distortion or polarization of the anion followed by some sharing of electrons between the two ions, i.e., the bond becomes partly covalent in character. Given figure shows how a transition between ionic and covalent bonding occurs.

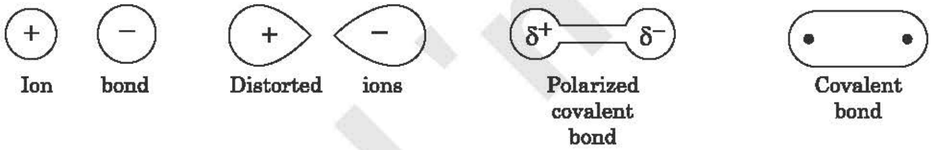


Fig. : Transition between ionic and covalent bonding

We may explain the same thing as follows :

The electron cloud of the anion is pulled towards the cation by electrostatic attraction. The electron density between the two ions in thus increased and the bond acquires some covalent character. The cation is generally small and brings about the polarization of comparatively bigger anion.

According to Fajan's rules, an increase in the degree of polarization of anion is favoured by :

1. Large charge on the ions;
2. Small cation and large anion;
3. **Nature of solvent :** Solvents of high dielectric constants, *e.g.*, water, decrease the tendency for the electrovalence to pass into covalence.
4. **Nature of the cation :** Cations with an 18-electron ($s^2p^6d^{10}$) outermost shell polarize an anion more strongly than cations of 8 electron (s^2p^6) type. The *d*-electrons of the 18-electron shell screen the nuclear charge of the cation less effectively than the *s* and *p* electrons of the 8-electron shell. Hence the 18-electron cations behave as if they had a greater charge. Copper (I) and Silver (I) halides are more covalent in nature compared with the corresponding sodium and potassium halides although charge on the ions is the same and the sizes of the corresponding ions are similar. This illustrates the effect of 18-electron configuration of Cu^+ ($3s^2, p^6, d^{10}$) and Ag^+ ($4s^2, p^6, d^{10}$) ions.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Describe the introduction to Indian ancient chemistry in detail.

Ans.

Introduction to Ancient Indian Chemistry

Chemistry is the study of elements present in the Universe which involves, the nature of the elements, their occurrence, their physical and chemical properties, their compounds, their reactivity, their uses and their applications. The word chemie was derived from Khem a synonym for Egypt, because the west believed that all the knowledge came from Egypt.

Chemistry known as Rasayana sastra or Rasa Sastra or Rasa Vada or Rasa Prakriya in Sanskrit, the Language of Ancient Indians used. This is evident from the literary works and archeological excavations of our nation, the India.

The basic principles of Chemistry emanated or revealed through the great works of our ancient rishis can be attributed to three major areas :

1. Intellectual thinking about the nature.
2. Development of professional skills for livelihood.
3. Welfare measures like health care of the Society.

Vaiseshika Darsana of Kanada propounded the concept of atom and its indivisibility and the law of cause and effect. Gautama, the propounder of Nyaya theory and school accepted the Vaiseshika doctrine thus came to know as Nyaya-Vaiseshika school of thought. Number of commentaries and treatises were written on Vaiseshika thought. The most important ones are Vatsayana's commentary on Nyaya, Prasastapada's Padartha dharma Samgraha, Sankara Mishra's Upaskara, Udayana's Kiranavali and Kanada Rahasya and Jayanarayana 's Vaiseshika Sutravritti.

Mahabharata mentions Pipilika gold which is a superior quality gold obtained from the ant hills or termite mounds. Ants dig the earth and makes hills. In these hills' gold is brought as particles and deposited in heaps. The kings of the area between Meru and Mandarachala hills mainly the tribal kings presented to Yudhishtira, Dronas of this pipilika gold saying that it is a very special gold. Drona is a measure in those days equivalent to a Kuncham or Tayva used earlier. This Pipilika gold is equivalent to the present day nano-gold which has enormous applications in chemistry as well as industry and in society.

Kautilya's Artha shastra is a treasure of the knowledge discussing about the mines, metals, precious articles like gems, rubys, pearls etc., A detailed description of the mines, factories that deals elaborately with the occurrence, nature and purification methods have been discussed in detail. It is stated that in all ores, heaviness of the ore is indication of the metal content, which can be stated in modern chemistry principles the greater the density of the ore, greater is the metal content'.

They have also characterized the ore based on the colour to which metal it belongs. For example, the ore from rocks or a region of the earth, which is heavy unctuous and soft tawny, greenish, reddish or red is copper ore. Crow black or of the colour of dove or yellow pigment studded with white lines smelling like raw flesh is lead ore. Grey like saline earth or of a baked lump of the earth is iron ore.

The director of mines known as Khanijadhyaksha was expected to be an expert in the science of metallic veins, exploration of ores, metallurgy and colouring of the Gems. Among the duties of the Khanijadhyaksha was that he should establish factories for copper, lead, tin, vaikranta, brass, steel, bronze, bell metal and iron and establish trade in metal ware.

Arthasastra also describes the qualities of gold and silver. Gold which is of the colour of lotus filament, soft, lustrous and not producing any type of sound is stated to be the best. The reddish yellow coloured metal is of medium quality and the red coloured one is the lowest quality. This indicates that the colour is taken as a measure of the purity or quality. As the red colour increases, the copper content increasing. Similarly, gold contaminated with lead gives brittleness to the metal and this material was used to mould on wooden anvils.

Similarly, silver was also characterized by its colour of white with smooth and soft property is the best silver metal. The impure one is purified using lead by melting and separation. The Khanitras or Artisans of that time not only skilled in Kshepana(setting), Guna (properties) and making solid or hollow articles of gold and silver , but also mixing the metals in the molten state of correct proportions. As regards minting the text says that silver coins should be made of four parts of copper, eleven parts of silver and one part of iron, tin or lead. Copper coins should be made of four parts of silver, eleven parts of copper and one part of iron or any other metal.

Intellectuals of the society tried to identify and use different plants and other materials as medicines for curing diseases and for longevity, of the society which they called as **Rasayana**. The word Rasayana has been used as a synonym for chemistry in Sanskrit and other Indian languages.

The medicinal treatise Charaka Samhita discussed 150 types of diseases with further subdivisions, 341 medicinal plants, 177 medicinal substances of animal origin, and 64 medicinal substances from Mineral origin. He also further categorized 102 types of pathological conditions and congenital defects, 109 anatomic and 42 physiological terms and 33 varieties of bones. He also differentiated the cereals and legumes, natural waters, sugar cane derivatives, types of honey, different milks and milk products, different vegetable oils, and alcoholic beverages. This classification was mostly based on the physical characteristics and their utilities.

Susruta (7) the great surgical specialist of that time, developed number of instruments for operations of the body and made very significant contributions for the modern anatomy of the human body. The contributions of Susruta are even today practiced and he is called as the **father of surgery**. During his time many fermentation products were developed for giving patients during operations, which act as modern anaesthesia drugs. He has designed number of surgical devices and equipments which are of use even today.

Vagbhatas (Both Vriddha and Laghu) presented Ashtanga Sangraha and Ashtanga Hridaya , the medical treatises constituting along with Charaka and Susruta the Brhatrayi. Metal and medicinal plant combinations and preparations started with Nagarjuna, the great alchemist of India and the founder of Rasasastra and wrote number of books. 8th – 16th century was the period where Rasasastra classics were written by many saints or alchemists. Among them Vagbhata, Nityanatha, Manthana Bhairava, SomaDeva, Yasodhara, Chakrapani, Basavaraju etc., were well known.

Professor Prafulla Chandra Ray of Calcutta, Father of Indian Chemistry, who has spent his life for establishing chemistry and chemical industries in India. Not only he established chemistry in India, he has written an authoritative book entitled *'The Hindu Chemistry.'* It gives the contributions of our ancient people to the chemistry and published the English translations of the great books on Rasasastra with Sanskrit texts with commentary so that the whole world can know the contributions of chemistry by Ancient Indians as annexures in 1919. He has translated the following books into english and also tried to explain in terms of Modern chemistry.

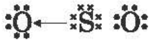
Great chemists of India like Prof. T.R. Seshadri, Dr. T.R. Govindachari, Dr. Sukhdev, Prof. Asima Chatterjee, etc., contributed significantly in natural products chemistry. Prof. T.R. Seshadri's work on Sandalwood, Prof. T.R. Govindachari's work on Neem are worldwide acknowledged. CSIR has started Traditional Knowledge Digital Library wherein 134 medicinal plants and about 500 formulations based on ancient texts were adopted in TKDL.

Q.2. What is resonance and resonance energy? Describe in detail. What is resonance hybrid? What are the applications of resonance?

Ans.

Resonance

There are many covalent compounds is which a single definite structure of the compound is not capable of explaining all of its properties. To explain all the properties of such a compound we need the help of two or more structures and actual compound is somewhat intermediate of these two or more structures, *i.e.,* actual compound is the hybrid of these two or more different structures. For example, SO_2, molecule is supposed to be having the following structure :



$:\ddot{\underset{\cdot\cdot}{O}} \leftarrow :\ddot{S}: \; :\ddot{O}:$

or $O \leftarrow S = O$

In this, S atom is linked with one O atom by double bond and with other O atom by coordinate bond. But, experiments (measurement of bond length, polarity, and bond energy etc.) indicate that the bonds between S and the two O atoms are identical. Neither the O← S bond has perfect co-ordinate character nor the S =O bond has a perfect double bond character, instead both are identical and have the intermediate character. It means a single structure, shown above, is not sufficient to express SO_2. Neither the structure

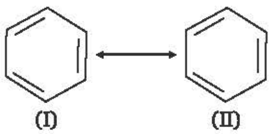
$$O = S \rightarrow O$$

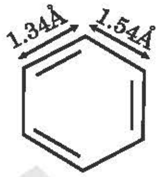
alone is sufficient to represent the true SO_2 molecule. Instead the true SO_2 molecule needs to be represented by both of these structures together, and actual molecule is intermediate between the two, *i.e.,* SO_2 is a hybrid of these two structures.

$$\underset{\text{(I)}}{O \leftarrow S = O} \quad \longleftrightarrow \quad \underset{\text{(II)}}{O = S \rightarrow O}$$

This phenomenon is called **resonance** and the actual molecule is said to be the resonance hybid of its different contributing structures. Thus, resonance may be defined as a phenomenon in which a single compound is supposed to be existing as a hybrid of two or more structures differing in distribution of electrons. These different structures of a molecule are known as contributing structures or canonical forms. No one of the contributing structures truly represents the molecule, but each one of them contributes to the final, *i.e.,* actual molecule is intermediate between all the contributing structures. Different canonical forms are written by putting a double head arrow (⟷) between them.

The phenomenon can be illustrated by taking the example of benzene (C_6H_6) also. Benzene molecule is resonance hybrid of following two main contributing structures :





If only a single structure, say (I), is considered for benzene, the (C—C) single bond lengths should be 1.54 Å each and double bond lengths should be 1.34 Å each. But, in benzene all the carbon-carbon bond lengths are found to be identical and each has a value of 1.39 Å, which is in between a single and a double bond length. It indicates an intermediate character of each bond which is possible only if benzene molecule is represented together by the two canonical forms.

Criteria of Resonance

Change in bond length is one of the important criteria of resonance, as clear from above examples. Another important criterion of resonance is the resonance energy. The actual energy of molecule (*i.e.,* energy of resonance hybrid), which can easily be determined experimentally, is always found to be less than the energy of any of its contributing structures (which can be determined theoretically). This difference in energy is called as **resonance energy** and can be defined as the difference in energy between the energy of a most stable of the contributing structures and the energy of actual molecule (resonance hybrid). Due to its low energy, the actual molecule is always more stable than any of its contributing structures. In other words it can be said that the resonance hybrid (*i.e.,* actual compound) is always more stable because of resonance energy. Larger the resonance energy, more is the stability of a compound.

Resonance Energy

Resonance energy of a molecule can be determined by calculating the theoretical heat of hydrogenation (or the heat of formation) by looking at the contributing structures and by measuring the actual heat of hydrogenation of molecule experimentally and finding the difference between the two. For example, resonance energy of benzene is 150.62 kJ mol^{-1}. It is because the heat of hydrogenation of a C═C is 119.66 kJ mol^{-1}, and since a contributing structure has three such bonds, the theoretical heat of hydrogenation of benzene is $3\times119.66=358.98$ kJ mol^{-1}. Experimental value of heat of hydrogenation of benzene is found to be 208.36 kJ mol^{-1}. Therefore, resonance energy is 358.98 – 208.36= 150.62 kJ mol^{-1}.

Another good example of resonance is that of CO_2 molecule. CO_2 molecule is the resonance hybrid of the following three structures :

$$\underset{\text{(I)}}{:\overset{+}{\ddot{O}}\equiv C-\underset{\cdot\cdot}{\ddot{O}}\overset{-}{:}} \longleftrightarrow \underset{\text{(II)}}{:\ddot{O}=C=\underset{\cdot\cdot}{\ddot{O}}:} \longleftrightarrow \underset{\text{(III)}}{:\underset{\cdot\cdot}{\ddot{O}}\overset{-}{}-C\equiv\overset{+}{\ddot{O}}:}$$

Measurement of carbon-oxygen bond lengths confirm it. If O = C = O is the correct formula of CO_2, then C═O distance should be the sum of the covalent radii of double bond carbon (C = 0.67 Å) and the covalent radii of double bond oxygen (O = 0.55 Å) *i.e.*, $0.67+0.55=1.22$ Å. But measured value of each C—O bond length in CO_2 is 1.15 Å only. Bond energy data too confirm the resonance in CO_2. Bond energy of a C═O bond is 723.8 kJ mol^{-1} and therefore, the heat of formation of CO_2 should be $2\times723.8=1447.6$ kJ mol^{-1}. But, the experiments indicate its heat of formation to be 1602.5 kJ mol^{-1}. Therefore, $1602.5-1447.6=154.9$ kJ mol^{-1} is the resonance energy of CO_2.

Resonance Hybrid

It is to be emphasised that the different contributing structures of a molecule differ only in the distribution of electrons and not in the arrangement of atoms. Most of the times these are the π-electrons involved in resonance, as evident from above examples. However, sometimes

σ-electrons are involved in resonance, *e.g.*, H_2 molecule is supposed to be the resonance hybrid of following structures :

$$\underset{\text{(Main)}}{H-H} \longleftrightarrow H^+ : H^- \underset{\text{(Negligible)}}{\longleftrightarrow} H^- : H^+$$

Applications of Resonance

The concept of resonance has a very wide range of applications in chemistry. Some of its important applications are as follows :

1. It is helpful in explaining the mechanism of several chemical reactions.
2. It explains the existence of odd electron bonds.
3. Several observed facts in organic chemistry can easily be explained on the basis of the concept of resonance.
4. It has been found very useful in calculating inter-ionic distance, partial ionic character of bonds and energy of the molecules.
5. Resonance alongwith hydrogen bond is helpful in various ways in biological systems.
6. With the help of resonance energy, the relative electro-negativity of the atoms can be determined.

$$\text{Relative electro-negativity} = 0.208\sqrt{\text{Resonance energy}}$$

Q.3. What are Van der Waal's forces? Give the types and origin of Van der Waal's forces. What are the factors on which the strength and magnitude of Van der Wall's forces depend?

Ans.

Van der Waal's Forces

J. Van der Waals a Dutch scientist, in 1873, pointed out that particles (atoms, molecules or ions) of substances exert attractive forces on each other when they are brought close to each other. These forces are electrostatic in nature and are much weaker than chemical forces. These forces were named as **Van der Waals' Forces**. These may be defined as follows :

Van der Waals forces are very short lived electrostatic attractive forces which exist between all kinds of atoms, molecules and ions when they are brought sufficiently close to each other.

Van der Waals' forces have no concern with the valence electrons of the species. They exist in neutral molecules, atoms and ions. Even the inert gas atoms may develop these forces when brought sufficiently close to each other.

Types and Origin of Van der Waals' Forces

Van der Waals' forces consist of following :

1. **Dipole-dipole interactions (Keesom forces) :** The forces which come into existence by dipole-dipole interactions are called **Keesom forces**. When polar molecules (molecules having permanent dipole moment) are brought closer, they orient themselves in such a way that the positive end of one dipole is opposite to the negative end of some other dipole or *vice-versa*. Thus the two dipoles attract each other by an electrostatic force (Fig. 1). The dipole-dipole interactions are more pronounced at low or moderate temperatures.

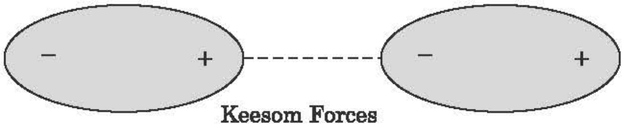


Fig. 1 : Dipole-dipole interaction

2. **Dipole-induced dipole interactions (Debye forces) :** Sometimes a polar molecule (having a permanent dipole moment) distorts a normal non-polar molecule and induces a dipole moment in it. The forces developed due to interaction between a dipole and an induced dipole are called **Debye forces**.

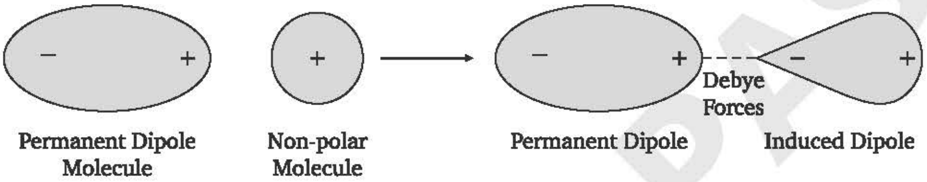


Fig. 2 : Dipole-induced dipole interaction

Debye forces come into existence when a polar molecule is brought closer to a non-polar molecule. The positive end of the polar molecule attracts the mobile electrons of the non-polar molecule, distorts it and changes it into an induced dipole (Fig. 2). The positive end of the permanent dipole molecule can now attract the displaced electron cloud of the induced dipole and the two may held together by an electrostatic attraction. Debye forces are not affected by temperature. However, they depend upon the distance between dipole and induced dipole.

3. **Temporary dipole-induced dipole interactions (London forces) :** As mentioned earlier, Van der Waals' forces also exist between neutral molecules and atoms, inspite of the fact that they are not polar in nature. The non-polar molecules like H_2, O_2, Cl_2, I_2, etc., and monoatomic inert gases like He, Ne, Ar, Xe, etc., also develop these forces when brought closer.

The existence of Van der Waals' forces in such molecules are due to the development of an instantaneous or temporary dipole moment in them. Atoms and molecules are electrically symmetrical and as such do not possess any dipole moment. However, any slight relative displacement of the nuclei or the electrons may develop an instantaneous or temporary dipole moment in them and for a moment they may act as dipoles. Such displacements are very common and constantly occur in atoms and molecules. These displacements are temporary and random. Therefore the molecule as a whole has no measurable dipole moment, The formation and decay of a temporary dipole is shown in Fig. 3.

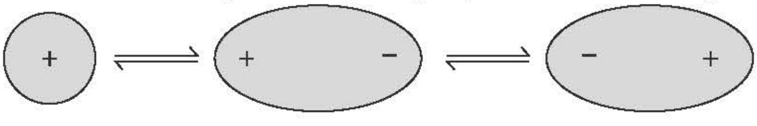


Fig. 3 : Instantaneous formation and decay of a dipole in a gas atom.

At the moment the molecule develops a temporary dipole moment, it can polarise a neighbouring non-polar molecule and may change it into an induced dipole. The two can thus be held together by electrostatic forces called **London forces**. These forces are very weak because the atoms and molecules are in ceaselessly rapid motion and are constantly departing from the sites of temporary dipoles.

Factors on Which the Strength and Magnitude of Van der Waal's Forces Depend

The strength and magnitude of Van der Waals' forces depend upon the following factors :

1. **Temperature :** The strength and the magnitude of these forces decrease with increase in temperature. At low temperature, there are less random movement of molecules and they can come closer to each other. Thus the chances of molecular interactions are more. When the temperature is high, the random movements are more and there are less chances of molecular interactions. Hence, a decrease in temperature increases the strength and magnitude of Van der Waals' forces.
2. **Pressure :** At high pressure, the molecules come closer and thus the chances of molecular interactions increase. Therefore, an increase in pressure increases the strength and magnitude of these forces.
3. **Number of electrons present in molecules :** When a molecule contains a large number of electrons, the chances of diffusion of electron clouds increase, This results in a greater polarisation and greater intermolecular interactions. Thus, the strength and magnitude of Van der Waals' forces increase.
4. **Molecular size :** Larger molecules are more easily polarisable because electron clouds are more diffused in them. This increases the chances of molecular interactions and consequently the magnitude and strength of these forces increase. Thus, larger molecules are held together by stronger Van der Waals' forces.

Q.4. What is dipole moment? Describe its applications.

Ans.

Dipole Moment

The polarity in a covalent bond can conveniently be measured in terms of a physical quantity called dipole moment. It is represented by a Greek letter μ (mu) and may be defined as follows :

Dipole moment of a covalent bond in a polar molecule may be defined as the product of the magnitude of the charges present on either of the two atoms and the distance by which the two atoms are separated in the molecule. It is a vector quantity and works in the direction of the line joining the positively charged atom to the negatively charged atom.

If in a polar molecule, two atoms A and B forming a polar covalent bond $A^{+q}—B^{-q}$ possess partial charges equal to $+q$ and $-q$ respectively and the distance between the two atoms is r, then the dipole moment μ of the bond is given by

$$\mu = q \times r$$

Chemical Bonding and Molecular Structure

The direction of the dipole moment is indicated by two crossed arrow (+→) pointing from positive end to the negative end as shown below :

$$\text{Polar molecule} \xrightarrow[\text{Direction of dipole moment}]{A^{+q}-B^{-q}}$$

The partial positive (+) and negative (–) charges present on the atoms in polar molecules are of the order of 10^{-10} e.s.u. while the distances between the atoms are usually of the order of 10^{-8} cm. Therefore, the dipole moment of a covalent bond will be of the order of 10^{-18} e.s.u cm ($\mu = q \times r$). Therefore, an unit called **Debye** (D) has been introduced to measure the dipole moment. It is equal to 10^{-18} e.s.u. cm and is represented by D.

Thus, $$1\text{ D} = 1 \times 10^{-18} \text{ e.s.u. cm}$$

Dipole moment of a particular covalent bond is referred to as bond dipole. The bond dipole and the net dipole moment of a molecule can be measured experimentally. The dipole moment not only indicates the degree of polarity of bonds but also provides important imformation regarding the structure of the molecule.

Applications of Dipole Moment

1. **Dipole moment and molecular structure :** Since dipole moment is a vector quantity, the net dipole moment of a molecule is the resultant of the dipole moments of all the polar bonds present in it. Therefore, the net dipole moment depends upon the geometry of the molecule. Hence, the dipole moment measurements of polar molecules are quite helpful in deciding their geometrical shapes. Following examples illustrate this fact.

   (a) **Diatomic molecules :** In a polar diatomic molecule two atoms are linked together by a polar covalent bond. In such a case, the dipole moment of the molecule is the same as that of the polar covalent bond. For example, the dipole moment of HF molecule is 1.91 D while that of HCl molecule is 1.03 D.

   $$\underset{\mu = 1.91\ \mathrm{D}}{\overset{H^{\delta+} - F^{\delta-}}{\longmapsto}} \qquad \underset{\mu = 1.03\ \mathrm{D}}{\overset{H^{\delta+} - Cl^{\delta-}}{\longmapsto}}$$

   Higher the difference in the electro-negativities of the two atoms, greater is the dipole moment of the diatomic molecule. This is why the dipole moment of HF is greater than that of HCl.

   (b) **Triatomic molecules :** The triatomic molecules are either linear or angular (bent). The net dipole moment of a triatomic molecule is the resultant of the dipole moments of two polar covalent bonds (bond dipoles) present in it.

   In a linear molecule of the type AB_2, the two polar covalent bonds are oriented in the opposite direction at an angle of 180°. Therefore, the two bond dipoles act in opposite direction and cancel each other. On account of this, the net dipole moment of the molecule is zero. Some examples of this type of molecules are BeF_2, $BeCl_2$, CO_2 etc. BeF_2 and CO_2 are shown in Fig.1. Although these molecules possess polar covalent bonds, yet they are regarded as non-polar molecules because the net values of their dipole moments are equal to zero.

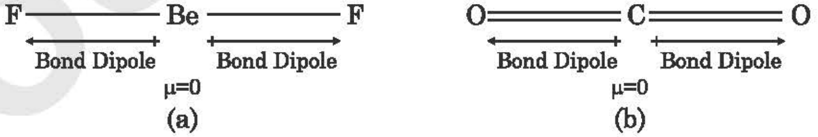


Fig. 1 : Dipole moment diagrams of (a) BeF_2, (b) CO_2 molecules

   In an angular triatomic molecule of the type AB_2, the net dipole moment is not equal to zero. Such molecules possess a definite value of dipole moment which depends upon the magnitudes of the bond dipoles and the bond angle. Knowing the dipole moment of the molecule and the magnitudes of the bond dipoles, the bond angle can be estimated. Some examples of this type of molecules are H_2O, SO_2, etc. H_2O has a dipole moment equal to 1.85 D. This immediately rules out a linear structure for H_2O. Had water moelcule possessed a linear structure, its dipole moment should have been equal to zero. Since H_2O has a definite dipole moment, it must be an angular molecule as shown in Fig. 2.

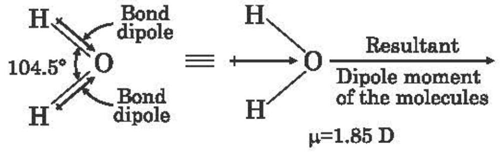


Fig. 2 : Dipole moment diagram of H_2O

(c) **Tetraatomic molecules :** Molecules of the types AB_3 may or may not possess a net dipole moment depending upon their geometries. For example, both BF_3 and NH_3 are tetraatomic molecules and are of the type AB_3 but the net dipole moment of BF_3 is zero while that of NH_3 is 1.47 D. This is due to a difference in their geometries and can be explained as follows.

In BF_3, each B—F bond has a bond dipole. The zero value of the dipole moment of BF_3 molecule suggests that the three fluroine atoms present in it must be at the vertices of an equilateral triangle with the boron atom at the centre. In this geometry, the resultant of the two B—F bond dipoles cancel the third B—F bond dipole leading to the zero value of the net dipole moment as shown in Fig. 3.

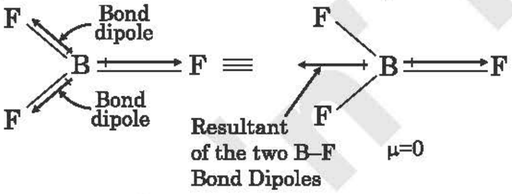


Fig. 3 : Dipole moment diagram of BF_3

A definite value of dipole moment of NH_3 suggests that its geometry is different from that of BF_3. Ammonia is found to have a pyramidal strucutre. In this geometry (Fig. 4) the vector addition of two bond dipoles does not cancel the third one. Moreover, in ammonia, the lone pair makes a large contribution to the net dipole moment. Therefore, the overall dipole moment of NH_3 molecule is the resultant of the bond moments of three N—H bonds and that due to the lone pair (Fig. 4). This is why NH_3 has a net value of the dipole moment.

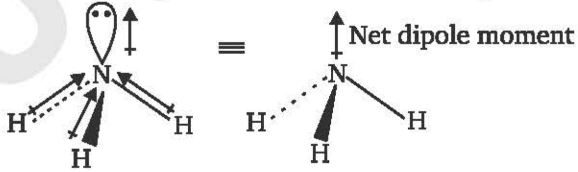


Fig. 4 : Dipole moment of diagram of NH_3
(..., and ◀ signify the different planes of the bonds)

Thus, dipole moment is an important tool to decide the geometry of a molecule possessing bond dipoles. It has been largely used to determine the shapes and bond angles of a large number of molecules.

Q.5. What do you understand by hydrogen bonding? What are the conditions necessary for hydrogen bonding? Describe the types and consequences of hydrogen bonding.

Ans.

Hydrogen Bonding

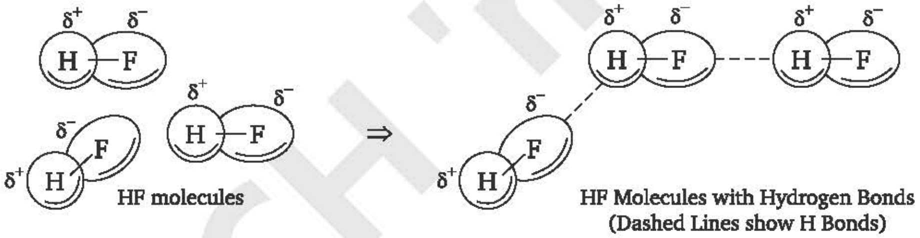
Hydrogen bonding is said to be formed, when slightly acidic hydrogen atom (*i.e.,* H-atom attached to a strongly electro-negative atom (F, O or N), is held with weak electrostatic forces by the non-bonded pair of electrons of another atom. The coordination number of H-atom in such cases is 2. It acts as a bridge between two atoms, to one of which it is covalently bonded, and to the other it is attached through electrostatic forces. 'The attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is known as **hydrogen bond.**'

Conditions Necessary for the Formation of a Hydrogen Bond

1. A hydrogen atom is covalently bonded to a small sized, electro-negative atom (F, O or N), so that due to the polarization of the bonded electron pair, hydrogen atom acquires a slightly positive charge, and
2. A lone pair of non-bonded electrons is available on one of the atoms so that it can be donated to the positive hydrogen atom. Again such atoms are F, O and N etc.

It is found that of all the electro-negative donors atoms, only F, O and N atoms enter into stable H-bond formation, other elements like Cl or S give extremely weak H-bonds which are of no consequence in isolation.

The weak electrostatic interaction leading to the hydrogen bond formation is shown by dotted lines. Thus X—H...Y represents H-bonding between H and Y atom.



HF molecules

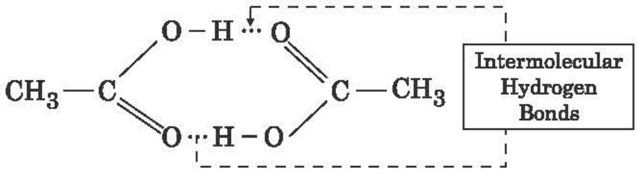
HF Molecules with Hydrogen Bonds (Dashed Lines show H Bonds)

Fig. : Illustrate of H-bonds

Types of Hydrogen Bonds

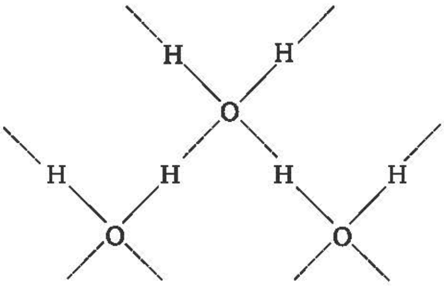
Two types of hydrogen bonds exist :

1. **Intermolecular H-bond :** When hydrogen atom acts as a bridge between two molecules as in water, ammonia, hydrogen fluoride, acetic acid, etc.

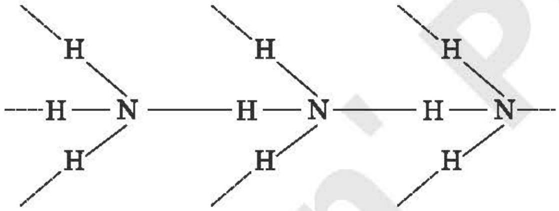


Other examples of intermolecular hydrogen bonding :

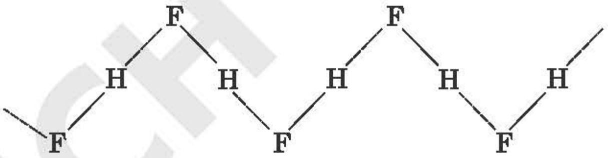
(i) **Water :** In H_2O molecule, the central oxygen atom is covalently linked to two H-atoms. Each H can form a hydrogen bond. In addition to these two hydrogen bonds, the central oxygen atom also forms two hydrogen bonds with the neighbouring molecules. Therefore four hydrogen H-bonds are formed by a single molecule of water as shown in the adjacent figure.



(ii) **Ammonia :** In NH_3 molecule, the more electro-negative nitrogen atom is covalently linked to three hydrogen atoms. In the liquid state, several molecules of ammonia get associated through hydrogen bonds as shown in the figure given below :



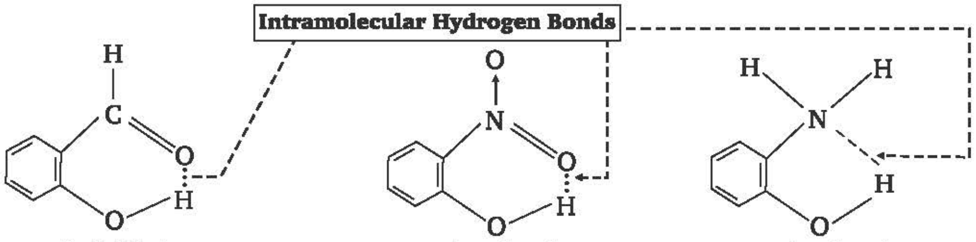
(iii) **Hydrogen fluoride :** In the solid state, hydrogen fluoride consists of long zig-zag chains of HF molecules linked together through hydrogen bonds as shown in the figure given below :



These chains persist to a large extent in the liquid and gaseous phases also. However, in the liquid and gaseous states, the length of the chain shortens.

(iv) **Hydrogen bonding between alcohol and water :** As mentioned above, intermolecular hydrogen bonding is also possible between the molecules of different substances. For example, when ethyl alcohol (C_2H_5OH) is dissolved in water, the molecules of the two substances get associated through intermolecular hydrogen bonding as shown in the figure given below :

2. **Intramolecular H-bond :** Where the hydrogen bond is formed within the molecule as in salicylaldehyde, *o*-nitrophenol, *o*-aminophenol etc.



Salicyladehyde *o*-nitro Phenol *o*-amino Phenol

Consequences of the Hydrogen Bonding

1. **Boiling points** of liquids increases because H-bonding leads to increase in intermolecular attractions which leads to increase in heat of vaporization.
   (i) Boiling point H_2O (373 K) > CH_3OH (336 K) > CH_3OCH_3 (268 K)

   Because extent of H-bonding $H_2O > CH_3 > OH > CH_3OCH_3$.

   (ii) Boiling point H_2O (373 K) > H_2S (212.9 K)

   Because H_2O is intermolecularily hydrogen-bonded while H_2S is non-hydrogen bonded molecule. Thus, water is liquid but H_2S is gas.

   (iii) Ammonia is H-bonded with a higher boiling point, melting point, heat of fusion and vaporization than the non-hydrogen bonded phosphine.

   (iv) Boiling point : $HF > CH_3F$

   (v) Boiling point : NH_3 (hydrazoic acid) > CH_3N_3 (methylazide).

   (vi) Boiling point : $H_2SO_4 > (CH_3)_2SO_4$

   (vii) Boiling point : $H_3PO_4 > (CH_3)_3PO_4$

2. **Solubility :** The solubility of organic compounds in water is attributed to hydrogen bond formation. For example :
   (i) CH_3OCH_3, (Dimethyl ether) is completely miscible with water whereas CH_3SCH_3 (dimethyl sulphide) is partially miscible.

   ∵ Dimethyl ether is capable of forming H-bond with H_2O molecule.

   (ii) Pyridine; Sugars and Dioxane are completely miscible with H_2O.

   (iii) In non-aqueous polar solvents also, the H-bonding plays an important role.

   For examples, (a) chloroform with its polar C—H bond is a good solvent for organic fatty acids due to the H-bonding between the polar hydrogen atom of chloroform and oxygen atom of the COOH. (b) HCl dissolves in ether due to ($Cl—H...OR_2$) hydrogen bond formation; (c) Acetylene dissolves in acetone due to [$H—C\equiv C—H ...O=(CH_3)_2$] hydrogen bond formation.

   However acetylene does not dissolve in water as the hydrogen bonds present in water are stronger than those formed between the acetylenic H-atoms and oxygen atoms of water.

3. **Viscosity :** Intermolecular H-bonding increases attractions between the molecules in the different layers of the H-bonded liquids. This results in the increase in viscosity (η) due to hindrance in the smooth flow of liquid layers over one another.

$$\eta(H_2O) = 10.05 \text{ millipoise,}$$

$$\eta(CH_3OH) = 5.97 \text{ millipoise}$$

$$\eta(CH_3OCH_3) = 2.33 \text{ millipoise,}$$

$$\eta(\text{glycerol}) = 10^4 \text{ millipoise}$$

4. **Azeotropic behaviour :** According to **Raoult's law** vapour pressure of ideal mixture of two liquids is given by $P = p_1 n_1 + p_2 n_2$, where p_1 and p_2 are vapour pressures of component liquids and n_1 and n_2 are their mole fractions.

   High boiling azeotropic mixture *e.g.,* Acetone-chloroform, pyridine-chloroform, cyclohexanone-bromoform and 1, 2, 3-trichlorohexane-butyl acetate show negative deviation from Raoult's law due to intermolecular H-bonding.

   Low boiling azeotropic mixture results when a liquid having a strong H-bonding is mixed with a non-polar liquid (hydrocarbon or carbon disulphide), *e.g.,* carbon disulphide and amine alcohol mixture. Such solutions show positive deviations from Raoult's law. If deviation is too much, separation into two phase results, *e.g.,*H_2O and hydrocarbon mixtures.

5. **Intramolecular H-bonding and its effects :**

   (i) Melting and boiling points of para isomer > Ortho-isomer because of reduced intermolecular attractions in ortho-isomer.

   (ii) Melting points of hydroxy benzeldehyde : para-isomer (389K) > Meta-isomer (380 K) > Ortho-isomer (280 K).

   (iii) Solubility of nitrophenols in polar solvents like H_2O.

   Para-isomer > Ortho-isomer because in ortho-isomers there is no possibility of H-bond formation with H_2O molecules. However, para-isomer can form intermolecular hydrogen bond with water so they are soluble in water.

   (iv) Solubility in organic solvents like ether : Ortho-isomer > para-isomer ; due to reduced intermolecular attractions in ortho isomer thus solvation by organic solvents is easier.

   (v) Steam distillation depends upon a substance having an appreciable vapour pressure at the boiling point of water ; by lowering the vapour pressure, intermolecular H-bonding inhibits steam distillation of *m*- and *p*-nitrophenol. Only O-nitrophenol is readily steam-distillable, because —NO_2 and —OH groups are located exactly right for the formation of a H-bond within a single molecule. Therefore, o-isomer does not have the low volatility of an associated liquid and is steam-distillable.

❑

UNIT-II

Simple Bonding Theories of Molecules

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Why is σ bond stronger than π bond?

Ans. The strength of a bond depends on the overlap of atomic orbitals. Greater the overlap, greater will be the strength of the bond formed. Sigma bond is formed by the linear overlap of atomic orbitals which is very effective, whereas a pi (π) bond is formed by the lateral overlap of atomic orbitals where in the overlap is not very effective. Since the overlap is large in the σ-bond formation than in the π-bond formation, σ-bond is stronger than π-bond.

Q.2. Explain molecular orbital.

Ans. Molecular orbitals are formed by the linear combination of atomic orbitals (LCAO). Out of the two newly formed molecular orbitals, one has a lower energy (called bonding molecular orbital) and other has a higher energy (called antibonding molecular orbital) than the combining atomic orbitals. The electrons in the antibonding molecular orbital tend to increase the energy of the molecule, thus decrease its stability, while the electrons in the bonding molecular orbital tend to decrease the energy and hence increase its stability. The atomic orbitals forming molecular orbitals lose their individual identity.

Different atomic orbitals which on combination give different molecular orbitals are :

AO	AO	MO	AO	AO	MO
s	s	σ and σ^*	p_x	p_x	σ and σ^*
s	p_x	σ and σ^*	p_y	p_y	π and π^*
p_x	s	σ and σ^*	p_z	p_z	π and π^*

Q.3. The correct outer electronic configuration of Cu is $3d^{10}4s^1$ and not $3d^9 4s^2$, explain.

Ans. The correct outer electronic configuration of Cu is $3d^{10}4s^1$ and not $3d^9 4s^2$. This is due to the stability associated with completed subshells which is due to the symmetrical distribution of electrons and large exchange energy.

Q.4. 4*s* orbital is lower in energy than 3*d* orbital, explain.

Ans. According to Aufbau principle, an orbital having lesser value of $(n+l)$ is lower in energy. For 4*s* orbital, $n=4, l=0$.

$$\therefore \quad n+l=4+0=4$$

For 3*d* orbital, $n = 3, l = 2$

$$\therefore \qquad n + l = 3 + 2 = 5$$

Since the value of $(n + l)$ is lesser for 4*s* orbital as compared to 3*d* orbital, 4*s* orbital has lower energy than that of 3*d* orbital.

Q.5. Arrange the following as directed :

(i) $O_2^+, O_2, O_2^-, O_2^{2-}$ in the decreasing order of bond length.

(ii) O_2, N_2, NO in the increasing order of bond order.

(iii) H_2^+, H_2^- and H_2 in the decreasing order of bond energy.

(iv) $O_2^+, O_2, O_2^-, O_2^{2-}$ in the decreasing order of bond dissociation energy.

(v) O_2, N_2, F_2, Cl_2 in the increasing order of bond length.

(vi) N_2, N_2^-, N_2^{2-} in the decreasing order of bond order.

Ans. (i) $O_2^{2-} > O_2^- > O_2 > O_2^+$, (ii) $O_2 < NO < N_2$, (iii) $H_2 > H_2^+ > H_2^-$, (iv) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(v) $N_2 < O_2 < F_2 < Cl_2$, (vi) $N_2 > N_2^- > N_2^{2-}$

Q.6. Can a π-bond be formed without the formation of a σ-bond?
Ans. No.

Q.7. What type of orbitals can overlap to form a covalent bond?
Ans. Half filled orbitals.

Q.8. Is hybridisation between the orbitals of two atoms possible?
Ans. No.

Q.9. What type of bond is formed when two *p*-orbitals overlap axially?
Ans. σ-bond.

Q.10. How many σ and π-bonds are present in $CH_3—CH=CH_2$?
Ans. Eight σ and one π-bonds.

Q.11. How much *s* and *p* characters are present in sp^3 hybrid orbitals?
Ans. 25% *s* and 75% *p* character.

Q.12. What type of hybridisation do you expect in the following molecules?

$$BF_3, CH_4, C_6H_6, BeF_2$$

Ans. $BF_3—sp^2, CH_4—sp^3, C_6H_6—sp^2, BeF_2—sp.$

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. Discuss in brief the concept of atomic orbitals.

Ans.

Concept of Atomic Orbitals (Probability Picture of Electrons)

When Schrodinger wave equation is solved for hydrogen atom, the wave function ψ associated with the electron having energy equal to -2.18×10^{-18} J (the energy of the electron in first Bohr's orbit) situated at the distance *r* from the nucleus, is given by

$$\psi = c_1 e - c_2 r \qquad \ldots(i)$$

where c_1 and c_2 are constants. As mentioned above, ψ^2 gives the probability of finding an electron in a given region. The distribution of electron in space is generally described in terms of function *D*, known as distribution function and is given by

$$D = 4\pi r^2 \psi^2 \qquad \text{...(ii)}$$

The distribution function *D* can be regarded as a measure of probability of finding an electron in a spherical shell of thickness *dr* at various distances *r* from the nucleus.

Bohr assumed that an electron moves in a well defined orbit. The quantum mechanical picture of atom is quite different from it. This picture implies that electronic cannot be supposed to be confined in well defined orbits and nothing can be said with certainty about their exact position in an atom.

From the above discussion, it is clear that a precise description of the position of an electron in an atom is not possible. Hence, we adopt the probabilistic description. We talk in terms of the probability of finding electron at different points in the space around nucleus. This gives birth to the concept of orbitals. When Schrodinger wave equation is solved for a particular electron having a particular energy, a three dimensional arrangement of points is obtained. The given electron can be found at these points. These are the points of negative-charge. If these points are seen as a whole, a cloud of negative charge appears to exist around the nucleus. This cloud of negative charge is termed as **electron cloud**. The density of electron cloud is not uniform every where around the nucleus. There is a particular region in which electron cloud is most dense. For example, in hydrogen atom, the electron cloud is most dense at a distance of 0.53 Å from the nucleus. In this region, the probability of finding electron is maximum. Such a region is referred to as an orbital. Thus, an orbital can be defined as follows.

The three dimensional region in the space around the nucleus in which the probability of finding an electron is maximum is called an **orbital**.

Q.2. What do you understand by Aufbau principle?

Ans.

Aufbau Principle

'Aufbau' is a German word meaning 'building up', *i.e.*, Aufbau principle deals with the building up of an atom; it tells how the electrons are filled up in different orbitals of an atom. Broadly, this principle states that in the ground state of an atom the successive electrons occupy the lowest available energy state. In other words it can be said that electron tries to occupy the most stable available state, *i.e.*, in an atom electrons are filled up in different orbitals in the order of increasing energy.

In fact, the electrons are filled up in different orbitals in an atom by obeying the following rules which collectively constitute the Aufbau process :

1. In an atom, the incoming electron enters the vacant orbital of lowest possible energy, *i.e.*, the orbitals are filled up in the **increasing order of energy**.
2. **Pauli's exclusion principle** is obeyed, *i.e.*, in an atom, no two electrons can have same set of values for all the four quantum numbers.
3. **Hund's rule** is also obeyed, *i.e.*, in an atom, the orbitals with equal energies are filled up at the first singly. When all such orbitals become singly occupied then only the pairing starts in them.

$(n+1)$ rule : Increasing order of energy of different orbitals in an atom can be known by the $(n+1)$ rule. The orbital with minimum value of $(n+1)$ has the lowest energy and the increasing value of $(n+1)$ gives the increasing order of energy. However, if there are two or more orbitals with same $(n+1)$ value then the orbital with lower value of n has lower energy.

It is being illustrated below:

For 1*s*-orbital $(n=1, l=0)$, the $(n+1)$ value is 1 and for 2*s*-orbital $(n=2, l=0)$, the $(n+l)$ value is 2. Thus, energy of 1*s* is lower than 2*s*, so 1*s* is filled first and then 2*s*. For 2*p*-orbital $(n=2, l=1)$, the $(n+l)$ value is 3, and also for 3*s*-orbital $(n=3, l=0)$, the $(n+l)$ value is 3. In such a case the orbital with lower value of *n* has lower energy. So out of these, 2*p* is filled first. Thus, the order is 1*s*, 2*s*, 2*p*, 3*s* etc. Going in this manner, the complete order of different orbitals comes to be :

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s.$$

It is to be noted that energy of 4*s* is lower than energy of 3*d* although the principal quantum number (main energy level) is higher for 4*s*. It is because the energy of an orbital is not governed by only the principal quantum number, some other factors also play a role. For instance, *s*-orbitals are spherically symmetrical, thus being less shielded, they are closer to nucleus in comparison to *d*-orbitals which are double dumb-bell in shape and remain farther from nucleus. It can be said that the penetrating power of *s*-orbitals is more. It makes them closer to nucleus and is responsible for their lower energy. Thus, the penetrating power of 4*s*-orbital is more in comparison to 3*d*-orbitals, resulting in lower energy of 4*s* in comparison to 3*d*. Similar is the case with 5*s* and 4*d* etc.

The sequence of filling the orbitals may also be known by **Simmon's scheme** (Fig. 1). In it the *s, p, d, f* are written and eight circles are drawn below *s*, six below *p* (leaving one above and one below), four below *d* in the same manner, and two below *f*. 1, 2, 3,......8 are marked in *s*-circles, each representing an orbital. Then same numbers are written horizontally in each circle of *p*, *d*, and *f*-orbitals. A diagonal arrow is drawn on 1*s* and parallel arrows to it are made as shown in the given figure :

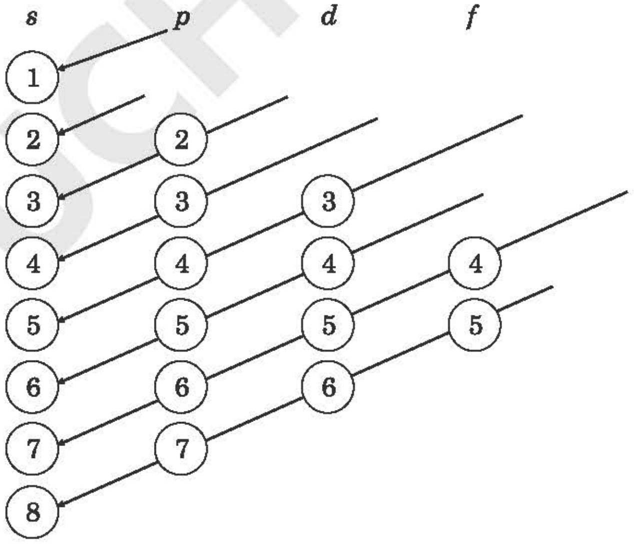


Fig. : Simmon's array

The order of cutting the circles by arrows comes to be as under :

First arrow is cutting 1*s*, second arrow is cutting 2*s*, third arrow is cutting at the first 2*p* and then 3*s*, and so on. So, the order is

$$1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s\ 4f\ 5d\ 6p\ 7s\ 5f\ 6d\ 7p\ 8s.$$

Q.3. Give the comparison between sigma (σ) and pi (π) bonds.

Ans.

Comparison of Sigma and Pi Bonds

S.No.	Sigma (σ) bond	Pi (π) bond
1.	This bond is formed by the axial overlapping of half filled atomic orbitals.	This is formed by the size wise or lateral overlapping of half filled atomic orbitals.
2.	The σ-molecular orbital is symmetric about the internuclear axis.	The π-molecular orbital consists of two charge clouds one above and the other below the plane of the atoms.
3.	The σ-molecular orbital does not contain a nodal plane which contains the internuclear axis.	The π-molecular orbital contains a nodal plane which contains the internuclear axis and divides the orbital into two halves.
4.	This bond is stronger due to a large overlapping of atomic orbitals.	This bond is weaker due to relatively lesser overlapping of atomic orbitals.
5.	The atoms forming a σ bond can be rotated along the bond axis.	The atoms forming a π-bond cannot be rotated relative to one another along the bond axis. An attempt to rotate the atoms makes the bond further weaker.

Q.4. Write a short note on Bent rule.

Ans.

Bent's Rule

This rule describes and explains the relationship between the orbital hybridization of central atoms in molecules and electro-negativities of substituents. This rule was given by American chemist A. Bent in 1926. The rule states that more electro-negative substituents prefer hybrid orbitals having less *s*-character and more electropositive substituents prefer hybrid orbitals having more *s*-character. For example, in the case of CH_2F_2 the F—C—F bond angle is less than that in H—C—H. This is because F is more electro- negative than H. Hence F—C—F *s*-character is less than 25% whereas it is more than 25% in H—C—H. Due to less *s*-character bond angle is less in CH_2F_2.

This law is particularly useful for trigonal bipyramidal geometry to decide the positions of atoms of different electro-negativities and also the positions of lone pairs and electronegative atoms. In sp^3d hybridization one *s* three *p* and one *d* orbitals mix and form five sp^3d hybridised orbitals. These five hybrid orbitals are not equivalent because of group hybridization. Hence, these can be divided into two non-equivalent sets. The first set is known as equatorial set of orbitals. It is formed from one *s* and two *p* orbitals. The second set is known as axial set. It is formed from one *p* and one *d* orbitals.

$$sp^3d = \underset{\substack{\text{Equatorial orbitals} \\ (33.3\%\ s\text{-character})}}{sp^2} + \underset{\substack{\text{Axial orbitals} \\ (0.0\%\ s\text{-character})}}{pd}$$

It is experimentally observed that less electronegative substituent occupies equatorial positions (more *s*-character) and high electronegative substituent occupies axial positions (less *s*-character). For example, PCl_3F_2 can be represented by the adjacent structure.

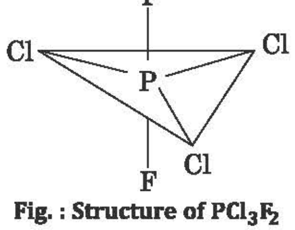


Fig. : Structure of PCl_3F_2

This is because more is the *s*-character of hybridized orbital, more it is closer to the nucleus. Moreover it is more electronegative and will occupy more space. On the other hand, more is *p*-character of hybridized orbital, it will be longer and more thin. As a result, the bond formed by hybridized orbital will be comparatively weak. For this reason PCl_3F_2 on heating decomposes as :

$$PCl_3F_2 \longrightarrow PCl_3 + F_2$$

Q.5. Write the comparison between valence bond theory and molecular orbital theory.

Ans.

Comparison of Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT)

Differences in Valence bond and Molecular Orbital Theories are given as follows :

S.No.	Valence Bond Theory (VBT)	Molecular Orbital Theory (MOT)
1.	After the bond formation, the combining atoms in a molecule retain their dentity. Bonding is explained with the help of atomic orbitals.	After the bond formation, the combining atoms in a molecule lose their identity. Bonding in explained with the help of molecular orbitals.
2.	Only the half filled atomic orbitals of the valency shell take part in bond formation.	It considers all the electrons in the given atoms for the prediction of number of bonds per atom.
3.	The concept of resonance is applicable only to valence bond theory.	Resonance has no role in molecular orbital.
4.	If fails to explain the paramagnetic character of O_2 molecule.	It explains the paramagnetic character of O_2 molecule.
5.	This theory finds difficulty in explaining the stability of one-and-three electron bonds having unpaired electrons.	The formation of one-electron bond and three-electron bonds can be easily explained by MOT.
6.	VBT fails to explain the formation of O_2^+ and O_2^- ions from O_2, if O_2 has the stable octet.	MOT can explain the formation of O_2^+ and O_2^- ions from O_2^-.

Q.6. Bond angle in NH_3 is more than that in H_2O, explain.

Ans. In NH_3 molecule one lone pair of electron on nitrogen is present whereas in H_2O molecule two lone pair of electrons on oxygen are present. According to VSEPR theory we know that

lone pair – lone pair repulsion > lone pair – bond pair repulsion
> bond pair – bond pair repulsion

As the number of lone pairs is more in oxygen, the O—H bond pairs come close in H_2O than N—H bond pairs in NH_3. Hence, bond angle in NH_3 (106° 45') is more in NH_3 than that in H_2O (104° 27').

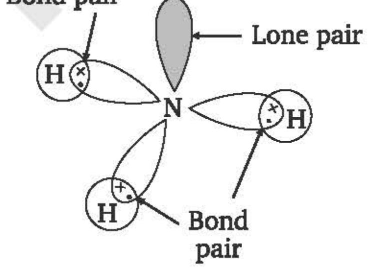


Fig. 1 : Pyramidal structure of NH_3

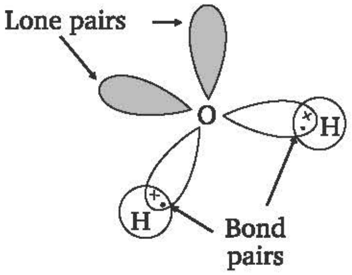
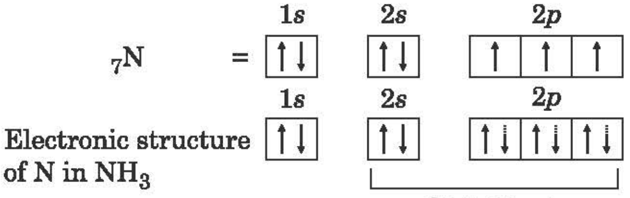


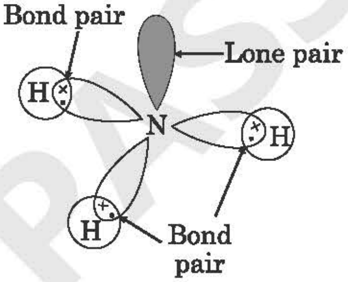
Fig. 2 : V-shaped structure of H_2O

Q.7. NH_3 has pyramidal structure, explain.

Ans. The nitrogen atom in NH_3 molecule is sp^3 hybridized. The three hybrid orbitals of nitrogen are used for bond formation with three hydrogen atoms and contain shared pair of electrons whereas the fourth hybrid orbital contains a lone pair of electrons. Due to greater repulsion between lone pair and bond pair of electrons, the bond angle in NH_3 is reduced from 109° 28′ to 106° 45′. Due to this distortion in the bond angle, the resulting structure of NH_3 is pyramidal.



Dotted arrows indicate the electrons shared with hydrogen atom



Q.8. What are bonding and antibonding molecular orbitals?

Ans.

Bonding Molecular Orbital

A bonding molecular orbital is formed when the electron waves of the combining atoms are in phase, *i.e.,* both have positive (+) amplitude. In this molecular orbital, the electron density is centred between the nuclei of the combining atoms. It shields the two nuclei from mutual repulsion and holds them at a definite distance which is equal to the bond length. Due to increased attraction between the two atoms, the energy of the system decreases. This is why a bonding molecular orbital is a low energy orbital.

Antibonding Molecular Orbital

An antibonding molecular orbital is formed when the electron waves of the combining atoms are not in phase, *i.e.,* one possesses a positive (+) amplitude while the other possesses a negative (–) amplitude. In this case, the wave functions of the component atoms cancel each other and form a node between the nuclei. In such an orbital, electrons are in those regions of space where they are not under the attraction of both the nuclei. The probability of finding the electron between the nuclei is negligible. Thus the two nuclei repel each other and make the molecule unstable. Each electron in an antibonding molecular orbital contributes to the repulsion and increases the energy of the system. Thus, an antibonding molecular orbital is a repulsive orbital of higher energy.

Q.9. Differentiate between bonding and antibonding molecular orbitals.

Ans.

Differences between Bonding and Antibonding Molecular Orbitals

S.No.	Bonding	Antibonding
1.	It is formed by additive overlap of atomic orbitals.	It is formed by substractive overlap of atomic orbitals.
2.	Its formation takes place when lobes of atomic orbitals have same signs.	Its formation takes place when lobes of atomic orbitals have different signs.
3.	The energy of bonding molecular orbital is lower than that of atomic orbitals from which it is formed.	The energy of antibonding molecular orbital is higher than that of atomic orbitals from which it is formed.

4.	The electron density is high in the region between the nuclei of bonded atoms.	The electron density is low in the region between the nuclei of bonded atoms.
5.	Every electron in bonding molecular orbital contributes toward stability of the molecule.	Every electron in antibonding molecular orbital contributes toward unstability of the molecule.

Q.10. (i) On the basis of MOT, prove that the molecular of oxygen is paramagnetic in nature.

(ii) Calculate the bond order of O_2, O_2^+, O_2^- and O_2^{2-} also show their magnetic behaviour.

(iii) Arrange O_2, O_2^+, O_2^- and O_2^{2-} in the increasing order of their bond lengths.

Ans.

Molecules	Electronic configuration	Bond order	Magnetic behaviour
O_2^+	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\sigma_{2px})^2\begin{bmatrix}(\pi_{2py})^2\\(\pi_{2pz})^2\end{bmatrix}\begin{bmatrix}(\overset{*}{\pi}_{2py})^1\\(\overset{*}{\pi}_{2pz})^0\end{bmatrix}$	$\frac{1}{2}(8-3)=2.5$	Paramagnetic
O_2	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\sigma_{2px})^2\begin{bmatrix}(\pi_{2py})^2\\(\pi_{2pz})^2\end{bmatrix}\begin{bmatrix}(\overset{*}{\pi}_{2py})^1\\(\overset{*}{\pi}_{2pz})^1\end{bmatrix}$	$\frac{1}{2}(8-4)=2$	Paramagnetic
O_2^-	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\sigma_{2px})^2\begin{bmatrix}(\pi_{2py})^2\\(\pi_{2pz})^2\end{bmatrix}\begin{bmatrix}(\overset{*}{\pi}_{2py})^2\\(\overset{*}{\pi}_{2pz})^1\end{bmatrix}$	$\frac{1}{2}(8-5)=1.5$	Paramagnetic
O_2^{2-}	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2(\sigma_{2px})^2\begin{bmatrix}(\pi_{2py})^2\\(\pi_{2pz})^2\end{bmatrix}\begin{bmatrix}(\overset{*}{\pi}_{2py})^2\\(\overset{*}{\pi}_{2pz})^2\end{bmatrix}$	$\frac{1}{2}(8-6)=1$	Diamagnetic

As the bond length is inversely proportional to bond order, so we can easily explain the gradation of the internuclear distances in the given series.

Since bond order varies as $O_2^+ > O_2 > O_2^- > O_2^{2-}$

Hence the bond length is in the order $O_2^+ < O_2 < O_2^- < O_2^{2-}$.

Q.11. Write the electronic configuration of N_2, N_2^+, N_2^- and N_2^{2-}. Establish their stability order based on calculation of bond order.

Ans.

Molecule (or Ion)	Electronic configuration	Bond order $=\frac{1}{2}(N_b-N_a)$	Magnetic behaviour
N_2	$KK(\sigma_{2s})^2\ (\overset{*}{\sigma}_{2s})^2\begin{bmatrix}(\pi_{2py})^2\\(\pi_{2pz})^2\end{bmatrix}(\sigma_{2px})^2$	$\frac{1}{2}(8-2)=3.0$	Diamagnetic

N_2^+	$KK(\sigma_{2s})^2\,(\overset{*}{\sigma}_{2s})^2 \begin{bmatrix}(\pi_{2py})^2 \\ (\pi_{2pz})^2\end{bmatrix} (\sigma_{2px})^1$	$\frac{1}{2}(7-2)=2.5$	Paramagnetic
N_2^-	$KK(\sigma_{2s})^2(\overset{*}{\sigma}_{2s})^2 \begin{bmatrix}(\pi_{2py})^2 \\ (\pi_{2pz})^2\end{bmatrix} (\sigma_{2px})^2\,[(\overset{*}{\pi}_{2py})^1]$	$\frac{1}{2}(8-3)=2.5$	Paramagnetic
N_2^{2-}	$KK(\sigma 2s)^2\,(\overset{*}{\sigma}_{2s})^2 \begin{bmatrix}(\pi_{2py})^2 \\ (\pi_{2px})^2\end{bmatrix} (\sigma_{2px})^2 \begin{bmatrix}(\overset{*}{\pi}_{2py})^1 \\ (\overset{*}{\pi}_{2pz})^1\end{bmatrix}$	$\frac{1}{2}(8-4)=2.0$	Paramagnetic

Now, stability order based on calculation of bond order is : $N_2 > (N_2^+ = N_2^-) > N_2^{2-}$.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What are sigma (σ) and pi (π) bonds? How they are formed?

Ans.

Sigma (σ) Bond

When the overlapping of atomic orbitals takes place in the direction of the axis of two nucleus of the combining atoms, Sigma (σ) bond is formed. There is maximum overlapping of orbitals in sigma bond formation. Sigma bond is a very strong bond. The electrons of a bond are not mobile. Sigma bond results by the maximum ovelap of *s-s*, *s-p* and p_x-p_x orbitals along their axis as shown below :

The linear overlapping of atomic orbitals results in the decrease of energy and the new orbitals become more stable compared to the other orbitals. These new orbitals are symmetrically oriented around the nuclear axis and are called **sigma orbitals**. The bonds formed by these orbitals are therefore called sigma bonds. In fact, the single bond between two atoms is always a sigma bond.

Water (H_2O), ammonia (NH_3), methane (CH_4), carbon tetrachloride (CCl_4) etc. all contain σ bonds.

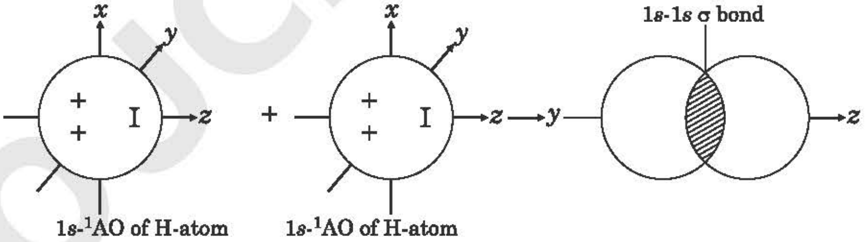


Fig. 1

Pi (π) Bond

π-bonds are formed by the lateral overlap of atomic orbitals. Since the lateral overlapping is always small, the π-bond is always weak. It is so weak that a π-bond alone is incapable of holding atoms together. This is why a π-bond is always present along with a σ-bond. The electrons of π-bond are mobile and are said to be delocalized electrons.

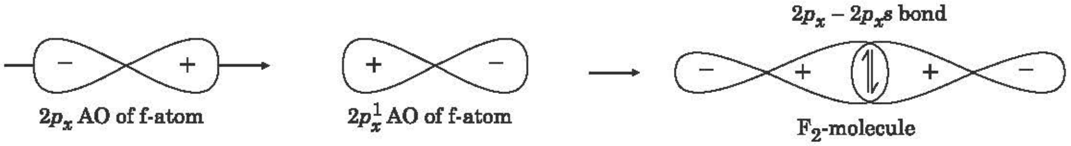


Fig. 2 : Sigma bond formation by overlapping of p_x-p_x orbitals.

Atomic orbitals formed by the overlapping of $p_y - p_y$ or $p_z - p_z$ atomic orbitals are called **π-orbitals** and the resulting bond is therefore known as **π-bond.** A pi-bond has a nuclear axis along with a nodal plane. The electron cloud is distributed above and below the nodal plane but the electron cloud is zero at the modal plane. The formation of a π-bond is shown below :

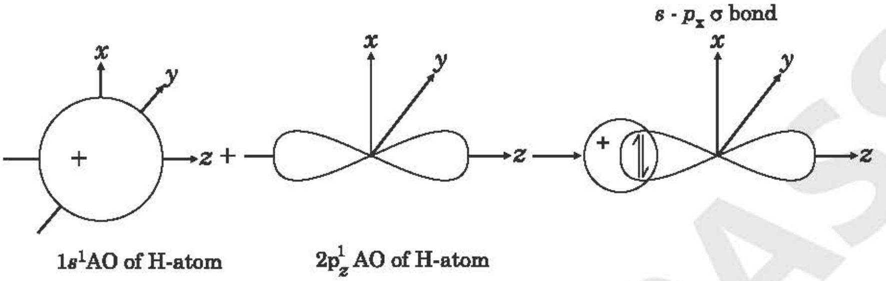


Fig. 3 : Formation of a σ bond by the overlap of *s-p* orbitals.

The union of two oxygen atoms produces a molecule of oxygen. Oxygen atom ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) with two unpaired electrons form a double covalent bond in oxygen molecule. The p_y and p_z orbitals of one atom overlap the same orbital of the second atom forming two pi bond and one sigma bond.

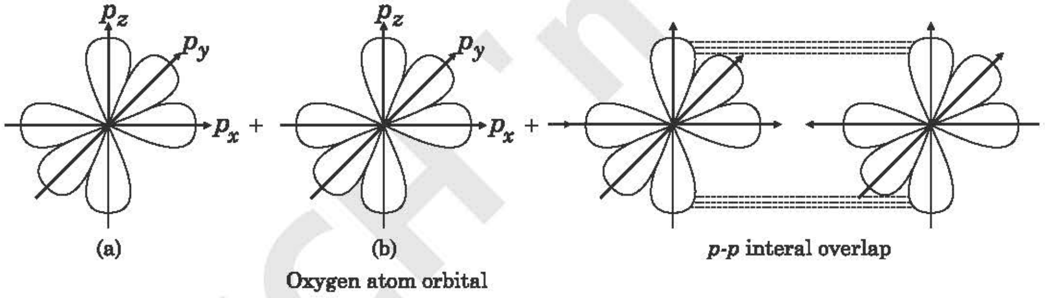


Fig. 4 : Lateral overlapping of *p-p* orbitals in the formation of π bonds in oxygen molecule.

Pi bonds also occur in ethylene, acetylene and benzene. In ethylene hybridization of one 2*s* and two 2*p* orbitals (p_x and p_y) occurs in each carbon with its third 2*p* orbital ($2p_z$) being left in its natural state. The sp^2 hybridization gives three coplanar bonds mutually directed at angles of 120°. One of such hybridized orbitals overlaps with a similar orbital of an the other carbon atom to form a sigma bond between the carbon atoms. The remaining two hybrid orbitals on each carbon atom overlaps with 1*s* orbital of hydrogen atoms to give four sigma type C—H bonds as shown in figure 5.

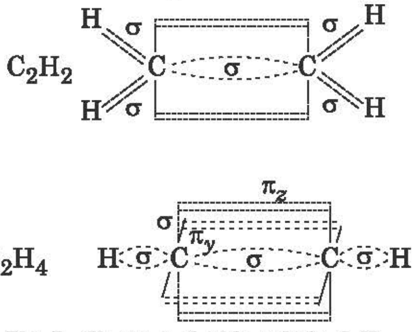


Fig. 5 : Sigma and pi bonds in C_2H_2 and C_2H_4.

The two p_z unhybridized orbitals one on each carbon atom over laps side ways (*i.e.*, laterally) to form a pi bond. The electron cloud of this bond is unsymmetrical and concentrated above and below the plane of carbon and hydrogen atoms. Thus the double bond between carbon atoms in C_2H_4 is a combination of a sigma and a pi bonds. Since π bonds are formed by horizontal overlap, π bonds are much weaker than σ bonds.

This accounts for the reactivity of ethylene and other compounds containing similar double bonds.

The formation of acetylene molecule can similarily be explained. The triple bond between carbon atoms consists of one sigma and two pi bonds (see figure 5 above).

Q.2. What do you understand by valence bond theory?

Ans.

Valence Bond Theory (VBT)

The classical idea of **Lewis** and others that electron pairing takes place during the formation of a covalent bond, lead to the development of an important theory known as **valence bond theory**. This theory was suggested by **Heitler** and **London** in 1927. **W. Heitler** and **E. London** basically proposed a quantum mechanical treatment of hydrogen molecule. Their method has come to be known as the valence bond approach. This approach was later on developed extensively by **Linus Pauling** and **J.C. Slater**. The modified valence bond theory commonly known as Pauling Slater theory is briefly discussed below.

Heitler-London Theory

According to **Heitler** and **London**, atoms having unpaired electrons enter into chemical combination and form a covalent bond. A covalent bond basically arises from the exchange forces between a pair of electrons of opposite spin. The main features of the theory are as follows :

1. Atoms having one or more unpaired electrons can only form covalent bonds.
2. The maximum number of covalency formed by an atom is equal to the number of its unpaired electrons.
3. A covalent bond is formed only when the electrons of combining atoms get paired up by the mutual neutralisation of their spin. Therefore, the unpaired electrons of the combining atoms must be of opposite spins.
4. The pair of electrons is localised between two bonded atoms.
5. After bond formation electrons are indistinguishable, *i.e.*, it is not possible to ascertain which electron belongs to which atom.
6. Each atom in a molecule tends to acquire a closed shell structure.

For example, the formation of the H_2 molecule by the combination of two hydrogen atoms can be explained as follows :

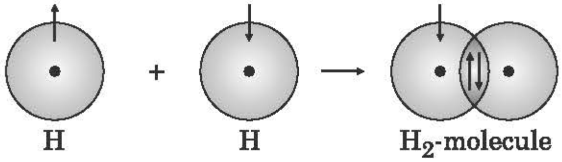


Fig. 1 : Formation of H_2 molecule

When two hydrogen atoms approach each other, then at a certain internuclear distance there may be two possibilities. If the two atoms possess electrons of opposite spin, they attract each other and fuse together to form H_2 molecule (Fig. 1). In this case, potential energy (PE) of the system decreases and a minimum in PE. diagram is obtained (Fig. 2a). However, if the electrons of the combining atoms are of parallel spin , the two atoms repel each other and the potential energy of the system increases (Fig. 2b). In this case no bond is formed.

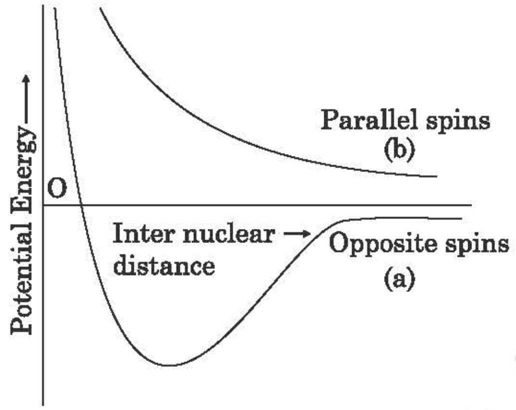


Fig. 2 : Potential energy diagram for the H_2 molecule

Pauling-Slater Theory

The main postulates of this theory are as follows :

1. A covalent bond is formed when the atomic orbitals of the two combining atoms, possessing unpaired electrons of opposite spin, mutually overlap together. During the formation of bond, spins of the two electrons get mutually neutralised. If atomic orbitals have parallel spins, repulsion takes place and no bond is formed.
2. The strength of covalent bond thus formed depends upon the extent of overlapping of the two atomic orbitals. Higher the overlapping, greater is the strength of covalent bond formed. The extent of overlapping between two orbitals having wave functions ψ_A and ψ_B is given by the following integral S, known as overlap integral.

   $$S = \int \psi_A \psi_B d\tau$$

   When S is positive, there is an increase in the electron density between the two nuclei, resulting in the formation of a covalent bond. If S is negative, electron density decreases, between the two nuclei. The nuclei thus repel each other and no bond is formed. When S is zero, no overlapping takes place and there is neither attraction not repulsion between the two nuclei.
3. The atomic orbitals of only unpaired electrons (bonding electrons) take part in overlapping. The atomic orbitals of other electrons (non-bonding electrons) do not overlap.
4. If an atom possesses more than one atomic orbita containing unpaired electrons, multiple bonds may be formed.
5. Combining atoms retain their identity in the molecule formed by their combination.
6. The bond formed by a given set of orbitals lies in the direction of their maximum overlapping. The covalent bonds are thus directional in nature.

   When two atomic orbitals come closer and overlap, the maximum electron density lies in the region of overlap. This subsequently develops an attraction between the two nuclei and accounts for the bond formation.
7. An axial overlap between the two orbitals of same energy content always forms a stronger bond.

8. A spherically symmetric orbital does not show any directional preference but non-spherical orbitals have a tendency to form a bond in the direction of maximum electron density, *i.e.,* along their axes.

   s-orbitals being spherically symmetric overlap to the same extent in all directions whereas *p*-, *d*- and *f*-orbitals have a tendency to overlap along their axes where electron density is maximum.

Overlapping of Atomic Orbitals

Overlapping of different atomic orbitals takes place in white following ways :

1. ***s-s* overlapping :** *s*-orbitals are spherically symmetric and can overlap to the same extent in all directions. Formation of a H_2 molecule involves *s-s* overlapping. A hydrogen atom contains 1st atomic orbital with one unpaired electron. When two hydrogen atoms approach each other along any axis, their *s*-orbitals overlap together and form a stable H-H sigma bond as shown in Fig. 3.

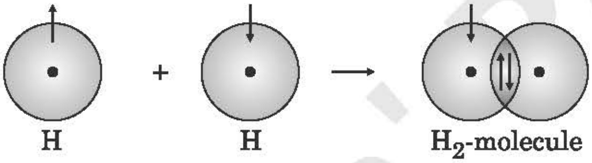


Fig. 3 : Formation of H_2 molecule by *s-s* overlapping

2. ***s-p* overlapping :** This type of overlapping takes place when one of the combining atoms possesses an *s*-orbital while the other a *p*-orbital. In this case, *s*-orbital will have to approach in the axial direction of orbitals for maximum overlapping. For example, overlapping between *p* and p_x orbital occurs as shown in Fig. 4.

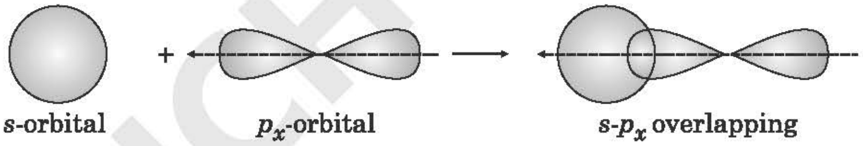


Fig. 4 : *s-p* overlapping

3. ***p-p* overlapping :** A *p*-orbital possesses electron density along a particular axis. For example, in a p_x-orbital, due electron density is distributed along *X*-axis. Therefore, two *p*-orbitals can overlap in the following two ways depending upon their mode of approach.

   (i) **Head on or Axial overlapping :** This type of overlapping occurs when two *p*-orbitals approach each other along their axes. For example, if two p_x-orbitals approach along *X*-axis, head on overlapping occurs as shown in Fig. 5.

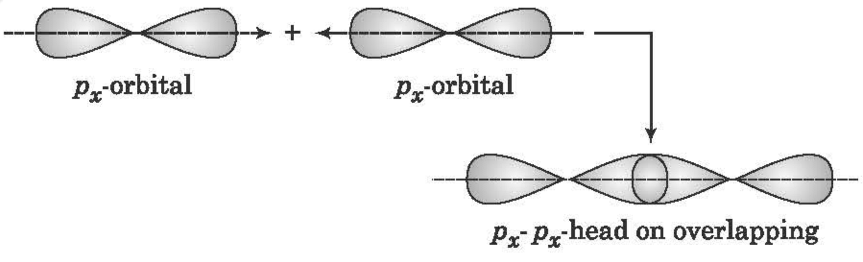


Fig. 5 : *p-p* head on overlapping

(ii) **Side wise or Lateral overlapping :** When the axes of the two *p*-orbitals and their axis of joining are perpendicular, the overlapping is said to be side wise or lateral. For example, when two p_y orbitals Y-axis approach each other along X-axis (perpendicular to Y-axis), the side wise overlapping takes place as shown in Fig. 6.

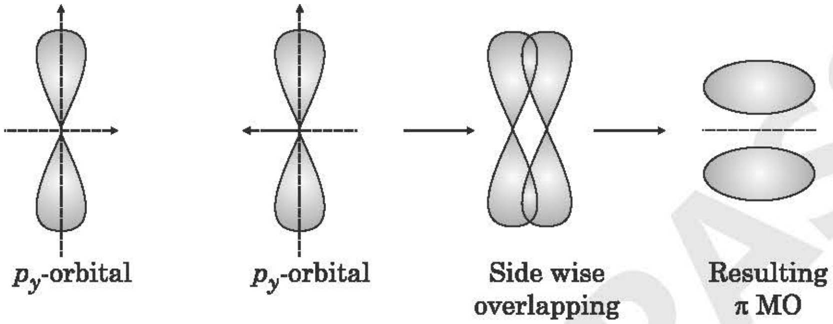


Fig. 6 : *p-p* sidewise overlapping

Limitations of Valency Bond Theory

This theory is unable to explain :

1. The formation of co-ordinate bond in which shared pair of electrons is contributed by only one of the combining atoms.
2. The paramagnetic nature of oxygen molecule.
3. The structures of odd electron molecules or ions where no pairing of electrons takes place.
4. The directional nature of covalent bond.
5. The formation and structures of several compounds involving resonance and hybridization.

Q.3. Explain the concept of hybridisation. What are the necessary conditions for hybridisation? Describe *sp*, *sp*^{2} and *sp*^{3} hybridisation with examples.

Ans.

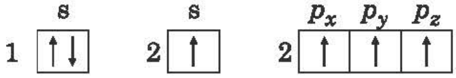
Concept of Hybridisation

The term 'hybridisation' has been suggested to explain the geometry (shape and bond angles) of some molecules and the nature of valency of their central atom. It is a phenomenon in which two or more orbitals of almost equal energy in an atom combine and then reseparate into the same number of new but exactly identical orbitals. New orbitals are identical in shape, size as well as energy. Each of the new orbitals is known as 'hybridised orbital'.

Consider the example of methane (CH_4) molecule in which all four valencies of carbon are identical, the shape of molecule is tetrahedral, and the bond angles are 109°28' each. It can be explained on the basis of hybridisation. The electron configuration of carbon in ground state is

			1s		2s		p_x	p_y	p_z
C_6	$1s^2 2s^2 2p^2$	1	↑↓	2	↑↓	2	↑	↑	

Looking to this configuration, the valency of carbon should be two due to the presence of two unpaired electrons. But it is found to be four in almost all the carbon compounds. To explain this, it is assumed that promotion of one 2*s* electron to 2*p* takes place in excited state so that electron configuration in excited state is



It makes the valency of carbon to be four due to the presence of four unpaired electrons. However, looking to this configuration, out of the four valencies of carbon, three (due to *p*) should be identical and fourth (due to *s*) should be different. But in CH_4 all the four valencies of carbon are found to be identical and the answer is given by the phenomenon of hybridisation. Promotion of 2*s* electron to 2*p* is accompanied by process of hybridisation, *i.e.*, the 2*s* and three 2*p*-orbitals merge together (since the difference in their energy is very low) and then reseparate into four new orbitals which are now equivalent, *i.e.*, identical in shape, size, and energy. It leads to four identical valencies in CH_4. Such a type of hybridisation, in which one *s* and three *p*-orbitals merge together, is termed as sp^3 hybridisation and each of the new orbitals is known as sp^3 hybridised orbital.

Correctly speaking, the hybridised orbital has got entirely a new shape which is neither of *s* nor of *p*. Shape is being illustrated below. It has two lobes, but one lob is very much larger than the other :

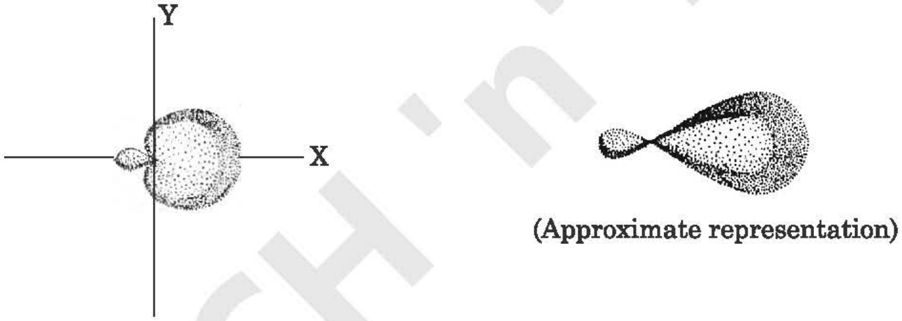


Fig. 1 : sp^3 hybrid orbital

Hybridisation of orbitals leads to a definite geometry. The shape after sp^3 hybridisation is tetrahedral (each of the new orbitals is directed towards the corner of a regular tetrahedron with the nucleus of the atom at the centre) and angle between every two orbitals is 109°28' (because in a tetrahedral shape with the angle of 109°28' each, the four orbitals feel minimum repulsion).

Each hybrid orbital is directional and extends out farther in space in comparison to a pure (unhybridised) orbital. Because of greater extension in space, hybrid orbital can overlap more effectively than a pure orbital. This increased overlap results in a more stable bond.

Promotion of the electron from 2*s* to 2*p* level requires energy, but the increase in stability gained by the formation of stronger covalent bonds by hybrid orbitals results in the liberation of energy which more than compensates for the energy needed to promote electron.

Conditions for Hybridisation

Following are the main requirements of hybridisation :

1. All the orbitals participating in hybridisation should be of the same atom.
2. All the orbitals participating in hybridisation should be of nearly equal energy but not of exactly identical energy.

Note : It is not necessary that all the orbitals participating in hybridisation be with unpaired electron. Orbitals with paired electrons also sometimes participate in hybridisation, *e.g.,* in NH_3 and H_2O molecules.

Types of Hybridisation

Hybridisation between *s* and *p* orbitals is mainly of three types :

(i) *sp* hybridisation
(ii) sp^2 hybridisation
(iii) sp^3 hybridisation

sp hybridisation

In this, one *s* and one *p*-orbital of an atom mix and then reseparate to produce two new equivalent orbitals (identical in shape, size, and energy). Each of the new orbitals is known as *sp* hybridised orbital or simply the ***sp* orbital**.

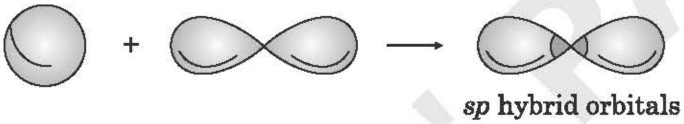


Fig. 2

The two *sp* hybridised orbitals are **linearly opposite** with an angle of **180°** so that they experience minimum repulsion. *sp* hybridisation can be illustrated by taking the example of beryllium in its compounds like $BeCl_2$, BeF_2 etc. Electron configuration of Be in ground state is

$$\text{Be}_4 \quad 1s^2 2s^2 \quad \overset{s}{\boxed{\uparrow\downarrow}} \quad \overset{s}{\boxed{\uparrow\downarrow}}$$

In excited state one electron from 2*s* is promoted to 2*p* and the valency of Be is found to be two :

$$1 \quad \overset{s}{\boxed{\uparrow\downarrow}} \quad \overset{s}{\boxed{\uparrow}} \quad \overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{}}\overset{p_z}{\boxed{}}$$

This promotion is accompanied by hybridisation resulting in two identical valencies. In $BeCl_2$, the *sp* hybrid orbitals of Be overlap with unpaired electron 3*p*-orbital of each of the two chlorine atoms as shown below :

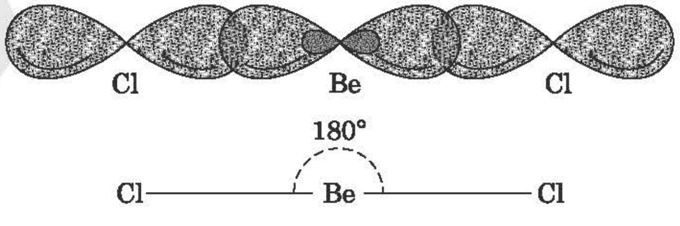
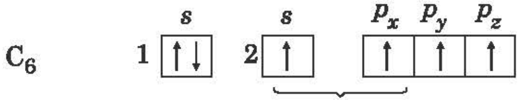


Fig. 3 : Orbital structure of $BeCl_2$

Thus, the shape of BeCl, molecule is linear with a bond angle of 180°. *sp* hybridisation may be called as **linear** or **diagonal hybridisation** also.

Hybridisation at each carbon atom in acetylene(CH≡CH) is also *sp*. In acetylene, out of the four valencies of each carbon, only two are identical, indicating *sp* hybridised state at each carbon atom.



At each carbon atom two identical *sp* hybrid orbitals are formed in a linear geometry at an angle of 180°. Remaining two 2*p*-orbitals (say $2p_y$ and $2p_z$) of each carbon are unhybridised and perpendicular to plane of hybridisation and mutually perpendicular as well (Fig. 4). The two *sp* hybridised carbon atoms in acetylene have the overlappings as shown in fig.5. Unpaired 1*s*-orbital of each hydrogen atom overlaps with one *sp* hybrid orbital of each of the two carbon atoms so that two *s*-*sp* overlappings are formed (σ-bonds). Unhybridised *p*-orbitals of the two carbon atoms are parallel and, therefore, overlap collaterally to give two π-bonds :

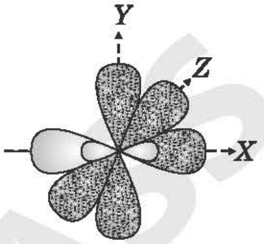
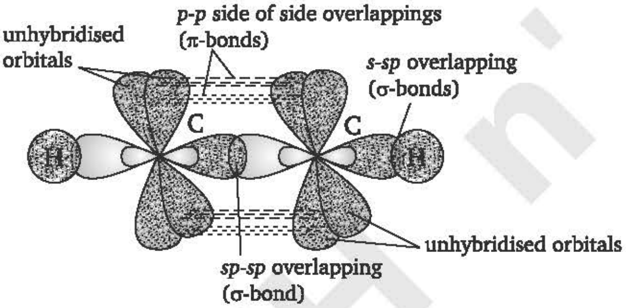


Fig. 4 : Carbon atom in *sp* hybridised state (Unhybridised orbitals shown with broken lines)



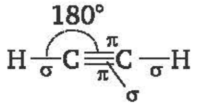


Fig. 5 : Orbital structure of C_2H_2 molecule

Thus, the shape of acetylene molecule is linear with the bond angles of 180° each. Hybridisation at carbon atom in CO_2 is also *sp*.

sp^2 hybridisation

It is the type of hybridisation in which one *s* and two *p*-orbitals of an atom mix to reproduce three new equivalent orbitals. Each of the new orbitals is known as sp^2 orbital.

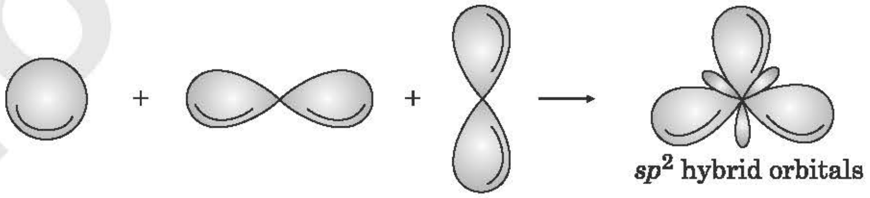


Fig. 6

Shape after sp^2 hybridisation is trigonal planar, *i.e.*, each of the three sp^2-orbitals is directed towards the corner of a regular triangle with nucleus of the atom at the centre. In a triangular geometry the angle between every two orbitals is **120°** so to have a minimum of repulsion. sp^2 hybridisation can be illustrated by taking the example of boron in its compounds like BF_3, BCl_3 etc. Electron configuration of B in ground state is

$$B_5 \qquad 1s^22s^22p^1 \quad 1\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{}}\overset{p_z}{\boxed{}}$$

In excited state, one electron from $2s$ is promoted to $2p$ resulting in the valency of B to be three :

$$1\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\overset{s}{\boxed{\uparrow}} \quad 2\overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{\uparrow}}\overset{p_z}{\boxed{}}$$

This promotion is accompanied by hybridisation resulting in three identical valencies of B. In BF_3, the sp^2 hybrid orbitals of B overlap with the unpaired electron $2p$-orbital of each of the three F atoms as shown in fig. 7 :

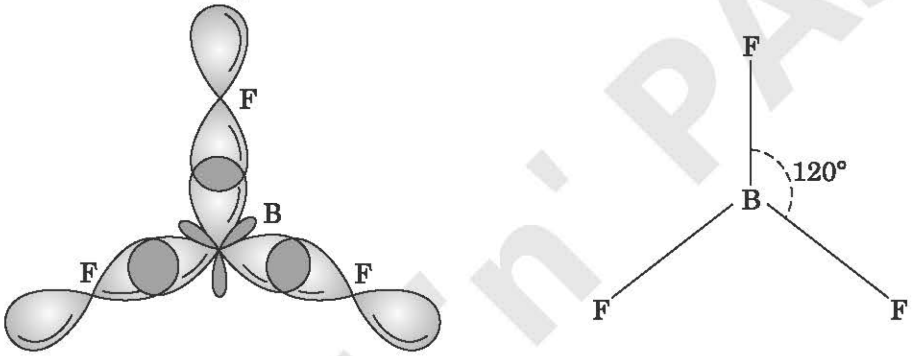


Fig. 7 : Orbital structure of BF_3

Thus, the shape of BF_3 molecule is trigonal planar with the bond angles of 120° each. sp^2 hybridisation may be called as **trigonal hybridisation** also.

Hybridisation at each carbon atom in ethylene ($CH_2 = CH_2$) is also sp^2. In ethylene, out of the four valencies of each carbon, only three are identical, indicating sp^2 hybridised state.

$$C_6 \qquad 1\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\underbrace{\overset{s}{\boxed{\uparrow}} \quad \overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{\uparrow}}}\overset{p_z}{\boxed{\uparrow}}$$

At each carbon atom three identical sp^2 hybrid orbitals are formed in a triangulur geometry at an angle of 120°. Remaining p-orbital (say p_z) of each carbon is unhybridised and perpendicular to plane of hybridisation (shown with broken lines in fig. 8). The two sp^2 hybridised carbon atoms in ethylene have the overlappings shown in fig. 9.

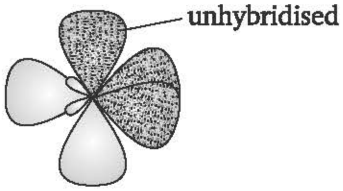


Fig. 8 : Carbon atom in sp^2 hybridised state

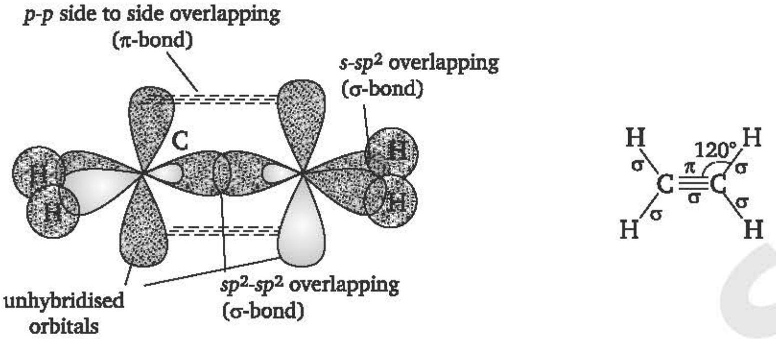


Fig. 9 : Orbital structure of C_2H_4 molecule

Hybridisation at each carbon atom in graphite is also sp^2.

sp^3 hybridisation

It is the type of hybridisation in which ones and three *p*-orbitals of an atom mix to reproduce four new equivalent orbitals. Each of the new orbitals is known as sp^3 orbital.

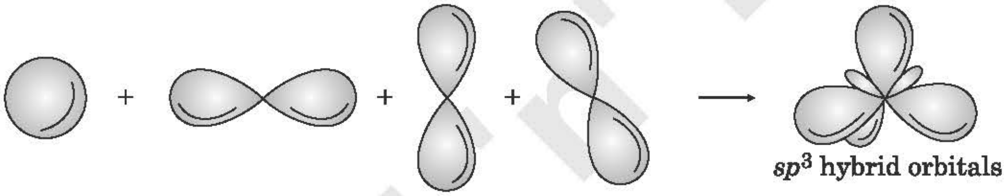


Fig. 10

Shape after sp^3 hybridisation is tetrahedral, *i.e.*, the four sp^3-orbitals are directed towards the corner of a regular tetrahedron with the nucleus of the atom at the centre. In a tetrahedral shape the angle between every two orbitals is 109°28′ so that they feel a minimum of repulsion. sp^3 hybridisation (as discussed earlier) can be illustrated by taking the example of carbon in its compounds like CH_4, CCl_4 etc. Electron configuration of carbon in ground state is

$$C_6 \qquad 1s^2\,2s^2\,2p^2 \qquad 1\,\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\,\overset{s}{\boxed{\uparrow\downarrow}} \quad 2\,\overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{\uparrow}}\overset{p_z}{\boxed{}}$$

In excited state, one electron from 2*s* is promoted to 2*p* resulting in the valency of carbon to be four :

$$1\,\overset{s}{\boxed{\uparrow\downarrow}} \quad \underbrace{2\,\overset{s}{\boxed{\uparrow}} \quad 2\,\overset{p_x}{\boxed{\uparrow}}\overset{p_y}{\boxed{\uparrow}}\overset{p_z}{\boxed{\uparrow}}}$$

This promotion is accompanied by hybridisation resulting in four identical valencies of carbon. In CH_4, the four sp^3 hybrid orbitals overlap with 1*s*-orbital of each hydrogen atom as shown below :

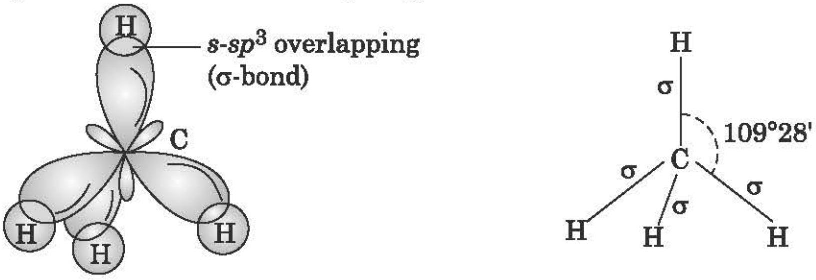


Fig. 11 : Orbital structure of CH_4

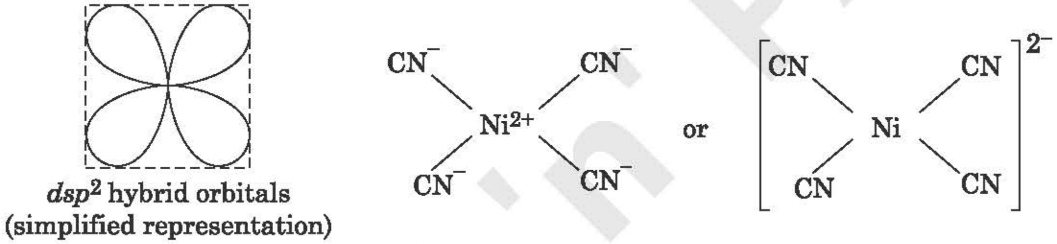
Thus, the shape of CH_4 molecule is tetrahedral with a bond angle of 109°28′ each. sp^3 hybridisation may be called as **tetrahedral hybridisation** also. Hybridisation at each carbon atom in ethane ($CH_3—CH_3$) is also sp^3. Hybridisation at Si in SiH_4 and $SiCl_4$ is also sp^3. Hybridisation at each carbon in diamond is also sp^3. Hybridisation at N-atom in NH_3 and O atom in H_2O is also sp^3.

Q.4. Describe dsp^2, dsp^3, d^2sp^3 and d^3sp^3 with examples.

Ans. Elements in the third period and beyond possess *d*-orbitals also, hence, in them the *d*-orbitals may also participate in bonding. In such elements the hybridisation involving *d*-orbitals may take place. Such hybridisations, in brief, are being discussed below :

dsp^2 hybridisation

In this, one *d*, one *s*, and two *p*-orbitals of an atom mix and reproduce four new equivalent dsp^2-orbitals in a square planar shape with an angle of 90°. Hybridisation at nickel in $Ni(CN)_4^{2-}$ is dsp^2.



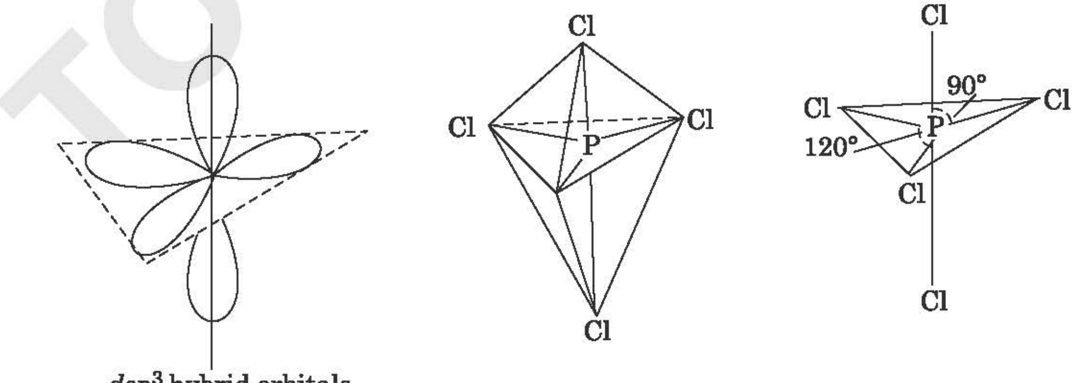
*dsp*² hybrid orbitals
(simplified representation)

Fig. 1

Thus, dsp^2 hybridisation also leads to the four identical valencies of an atom. But the valencies here are in a square planar shape and not in a tetrahedral shape.

dsp^3 hybridisation

One *d*, one *s*, and three *p*-orbitals of an atom mix to reproduce five new orbitals known as dsp^3 (or sp^3d)-orbitals. These five hybridised orbitals form a trigonal bi-pyramidal geometry with three bond angles of 120° each and two bond angles of 90° each. Out of these five orbitals, three are in a trigonal plane (120°) and remaining two are perpendi cular to this plane (one above and one below the trigonal plane). Hybridisation at P atom in PCl_5 is considered to be dsp^3.



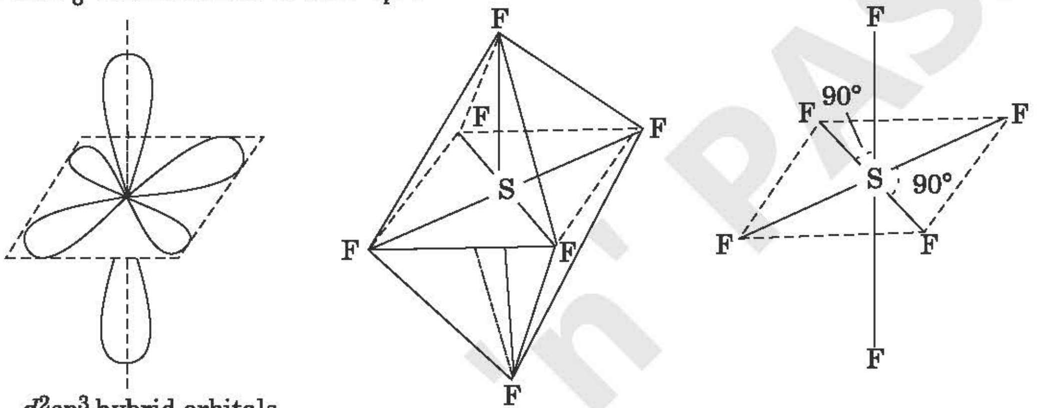
*dsp*³ hybrid orbitals

Fig. 2

Trigonal bipyramidal shape leads to dissymmetry in the molecule, therefore such com pounds are less stable and more reactive. For the same reason PCI_5 is very reactive and readily dissociates into PCl_3 and Cl_2.

d^2sp^3 hybridisation

Two *d*, one *s*, and three *p*-orbitals of all atom mix and reproduce six new equivalent d^2sp^3 (or sp^3d^2)-orbitals. These six orbitals form a regular octahedral geometry with the bond angles of 90° each. Out of the six orbitals, four are in square planar level and remaining two are perpendicular to this plane (one above and one below the square plane). Hybridisation at S atom in SF_6 is considered to be d^2sp^3.



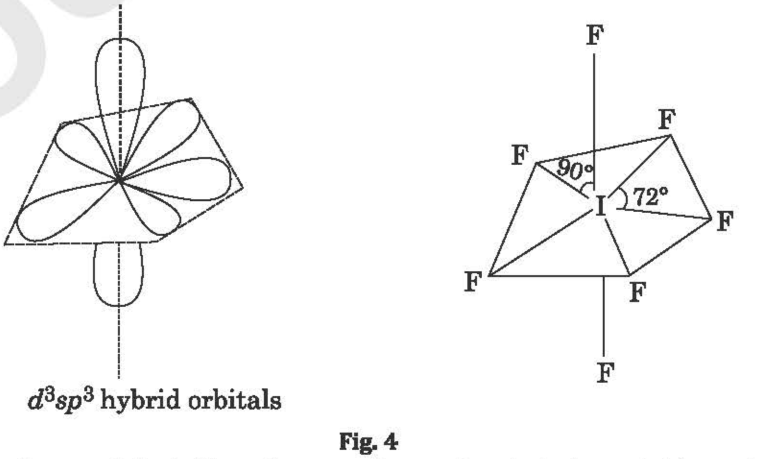
d^2sp^3 hybrid orbitals

Fig. 3

Octahedral geometry, being symmetrical, is quite stable. It is the reason why SF_6 is quite stable and a less reactive compound.

d^3sp^3 hybridisation

Three *d*, one *s*, and three *p*-orbitals of an atom mix and reproduce seven d^3sp^3 (or sp^3d^3) hybridised orbitals. They form a pentagonal bipyramidal geometry with five bond angles of 72° each and two bond angles of 90° each. Out of the seven orbitals, five are in a regular pentagonal plane and remaining two are perpendicular to this plane (one above and one below the pentagonal plane). Hybridisation at I atom in IF_7 is considered to be d^3sp^3.



d^3sp^3 hybrid orbitals

Fig. 4

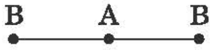
This geometry is dissymetrical. Therefore, such a molecule is less stable and more reactive.

Q.5. Describe VSEPR theory in detail. Discuss the shapes of NH_3 and H_2O molecule.

Ans. Valence Shell Electron Pair Repulsion (VSEPR) Theory

Shapes of a variety of polyatomic molecules are easily predicted with the help of the VSEPR model. According to this model the arrangement of bonds around the central atom depends upon the number of valence shell electron pairs and on the relative sizes and shapes of these orbitals. Two important postulates of this model are :

1. **Electron pairs around the central atom in a molecule must stay as far apart as possible :** Each electron pair occupies a well-defined region of space and other electrons are excluded from this space. Thus an electron pair orbitals behave as if they repel each other and, therefore, stay at maximum possible distance apart.
2. **A non-bonding pair of electrons takes up more room on the surface of atom than a bonding pair :** A molecule with two valence electron pairs around the central among, *e.g.*, $BeCl_2$, $HgCl_2$, CO_2 will have linear arrangement since this places the electron pairs at maximum possible distance.



Cl — Be — Cl

O=C=O

Fig. 1 : Linear molecules of AB_2 type (*e.g.*, $BeCl_2$ and CO_2)

Another molecule with three valence electron pairs available around the central atom (*e.g.*, BF_3) the most favourable configuration is when three B—F bonds are inclined at 120° (maximum distance apart), *i.e.*, the three electron pairs at the vertices of an equilateral triangle and the central atom is situated at the centre of this triangle.

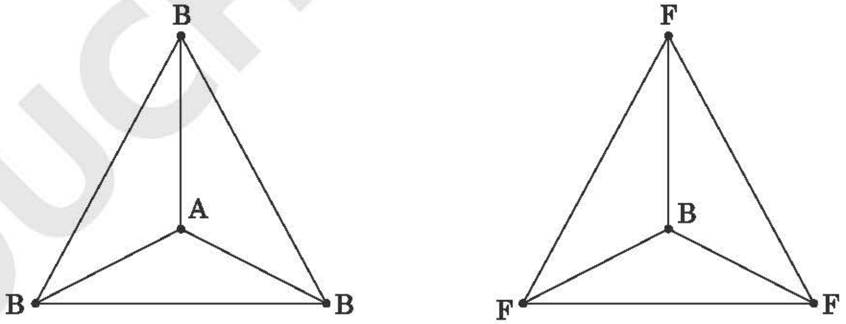


Fig. 2 : Shapes of molecules of AB_3 type (*e.g.*, BF_3)

Similarly, molecules of the AB_4 type (*e.g.*, CH_4) are tetrahedral, those of AB_5 type (*e.g.*, PF_3) have trigonal bipyramid geometry and others of AB_6 type (*e g.*, SF_6) are octahedral in shape.

Shapes of Polyatomic Molecules

Shapes of a number of simple molecules like $BeCl_2$, CO_2, BF_3, CH_4, NH_3, H_2O and SO_2 have been discussed in the previous sections. Their molecular shapes were predicted with the help of the VSEPR model. These arguments can now be generalized. Shapes of different molecules containing central atoms with two, three, four, five and six electron pairs are given in Fig. 3.

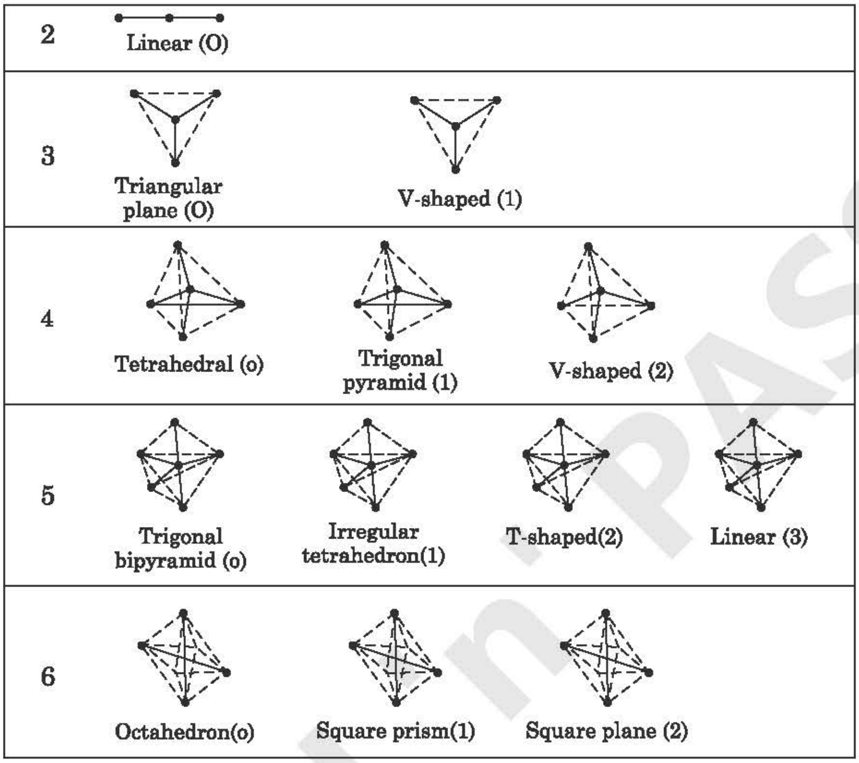


Fig. 3 : Shape of polyatomic molecules. Number of ione pairs with central atom are shown with digits within brackets

Molecular shape depends not only on the number of pairs of electrons with the central atom but also on the fact as to how many of these are bond pairs and how many lone pairs. For example, a molecule with three pairs of electrons with the central atom and all of these being bond pairs is triangular plane, *e.g.,* BCl_3. Another molecule with the same number of pairs of electrons with the central atom but one of these being a lone pair, will be V-shaped, *e.g.,* $SnCl_2, SO_2$. Similarly, a molecule with four pairs of electrons with its central atom may be tetrahedral, trigonal pyramid or V-shaped according to the number of lone pairs being 0, 1 or 2 respectively.

The arrangement of electron pairs in valence shells and shapes of some common molecules or ions based in the number of bonding pairs of electrons and the ione (non-bonding) pairs of electrons are given in table.

Electron pairs available with the central atom		**No. of bonding pairs**	**No. of lone pairs**	**Shape of the molecule**	**Typical examples**
Total No.	**Their arrangement**				
2	Linear	2	0	Linear	$BeCl_3, HgCl_2$
2	Triangular plane	3	0	Triangular plane	BCl_2
		2	1	V-shape	$SnCl_2$

4	Tetrahedraon	4	0	Tetrahedron	CH_4, PCl_4^+
		3	1	Trigonal pyramid	NH_2
		2	2	V-shape	H_2O, F_2O
5	Trigonal pyramid	5	0	Trigonal bipyramid	PCl_5 (gas)
		4	1	Irregular tetrahedron	$TeCl_4$
		3	2	T-shape	CiF_3
6	Octahedron	6	0	Octahedron	SF_6, PCl_4^-
		5	1	Square pyramid	IF_5
		4	2	Square	ICl_4^-

1. Shape of NH_3 Molecule

In ammonia (NH_3) molecule, the central nitrogen atom ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) possesses five valence electrons. It shares its $2p_x^1$, $2p_y^1$ and $2p_z^1$ electrons with three hydrogen atoms and forms three N—H bonds. After bond formation the central nitrogen atom is left with a lone pair ($2s^2$). Thus in all, the nitrogen atom possesses one lone pair and three bond pairs of electrons in ammonia molecule as shown in Fig. 4. These four pairs of valence electrons (one lone pair and three bond pairs) repel each other and acquire a tetrahedral geometry (Fig. 4) in space. Thus, ammonia molecule acquires a tetrahedral geometry. The nitrogen atom lies at the centre while the three hydrogen atoms lie at the three corners of a regular tetrahedron. The fourth corner of the tetrahedron is occupied by the lone pair of electrons.

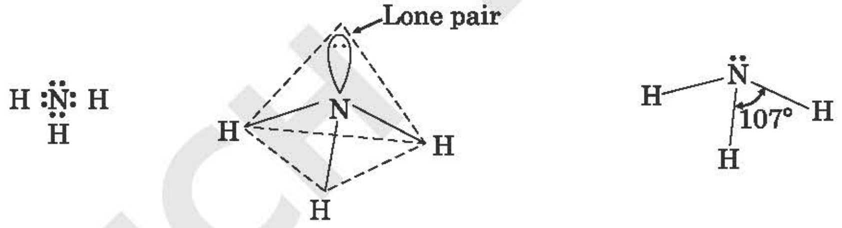


Fig. 4 : Shape of NH_3 molecule

Due to the presence of a lone pair of electrons on the central nitrogen atom, the tetrahedral geometry of the ammonia molecule gets slightly distorted. In a tetrahedral geometry, the usual bond angle is 109°28′ but in ammonia molecule the H—N—H bond angle is found to be equal to 107°. This can very well be explained on the basis of VSEPR theory. According to this theory, the lone pair-bond pair repulsion is more than the bond pair-bond pair repulsion. The lone pair present on the nitrogen atom repels all the N—H bond pairs strongly resulting in the shrinking of the bond angle. Thus, the expected H—N—H bond angle of 109°28′ decreases to 107°. The shrinking in bond angle distorts the tetrahedral geometry. Therefore, ammonia molecule is said to possess a distorted tetrahedral geometry.

Some other molecules, *e.g.*, PCl_3, NF_3, H_3O^+, etc., also possess geometries similar to that of NH_3.

2. Shape of H_2O Molecule

In water (H_2O) molecule, the central atom oxygen ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) possesses 6 valence electrons. Among these, the two unpaired electrons get shared with the valence electrons of the two hydrogen atoms resulting in the formation of two O—H covalent bonds. Thus, oxygen atom possesses two bond pairs and two lone pairs. Due to mutual repulsion, these valence shell electron pairs get orient themselves in a tetrahedral geometry around the central oxygen atom. The oxygen atom occupies the centre and the two hydrogen atoms occupy the two corners of a regular tetrahedron. The remaining two corners of the tetrahedron are occupied by the two lone pairs as shown in Fig. 5.

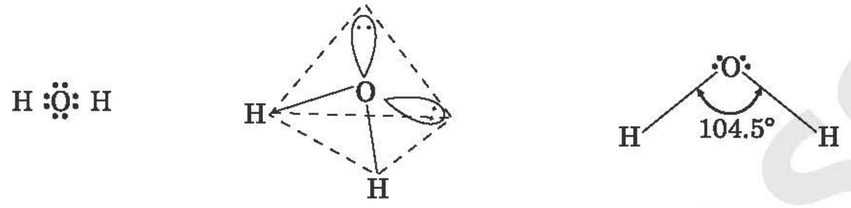


Fig. 5 : Shape of H_2O molecule

The two lone pairs of electrons present on the central atom strongly repel the O—H bond pairs. Since lone pair bond pair repulsion is more than the bond pair-bond pair repulsion, the normal angle of 109° 28' in a tetrahedral geometry decreases to 104.5° and the tetrahedral geometry gets distorted. The resulting geometry is regarded as bent or angular. These predictions of VSEPR theory agree well with the observed facts. Water molecule is really found to be bent or angular with H—O—H bond angle equal to 104.5°. The molecules like H_2S, OF_2, SCl_2 etc., also possess shapes similar to that of H_2O molecule.

Limitations of VSEPR Theory

Important limitations of VSEPR theory are :

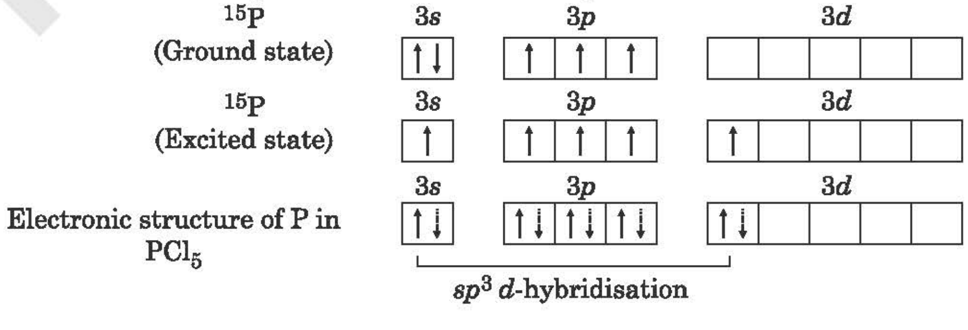
1. The theory is applicable to covalent compounds only and cannot be applied to ionic compounds.
2. The theory does not make any distinction between *s, p, d* and *f* orbitals.
3. The theory does not help in the prediction of shapes of coordination compounds.
4. The theory simply predicts that molecules such as NH_3, H_2O, $CHCl_3$, etc. have distinction from the regular geometrical shapes but does not quantify the extent of distortion.

Q.6. Explain the shapes of following compounds and ions on the basis of VSEPR theory :

(i) PCl_5 **(ii) SF_6** **(iii) SF_3** **(iv) ClF_3**

(v) I_3^- **(vi) H_3O^+**

Ans. **(i) Shape of PCl_5 :** In PCl_5 molecule phosphorus atom is sp^3d hybridized. These five hybrid orbitals containing one electron each form bond with five chlorine atoms and contain shared pair (bond pair) of electrons. In this molecule no hybrid orbital contains lone pair of electron. In this case the repulsion between the five hybrid orbitals is minimum.



(Dotted arrows indicate the electrons shared with chlorine atoms)
This molecule is trigonal bipyramidal in shape having bond angle 120° and 90°.

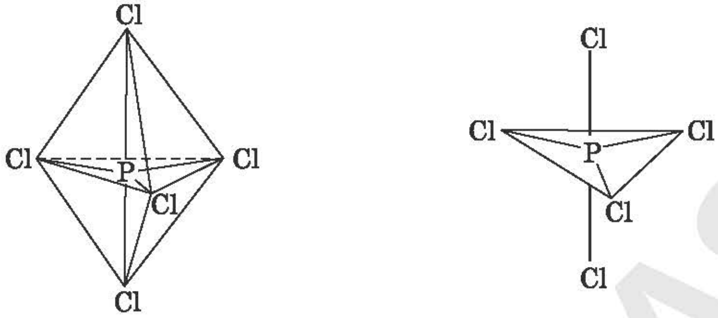
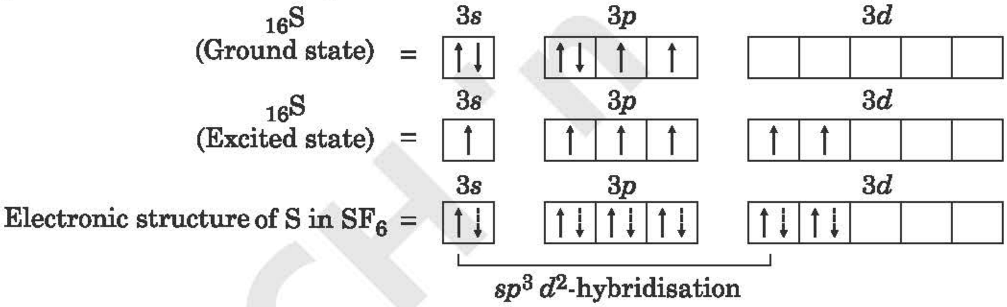


Fig. 1 : Structure of PCl_5

(ii) Shape of SF_6 : In SF_6 molecule sulphur atom is sp^3d^2 hybridized. These six hybrid orbitals containing one electron each form bond with six fluorine atoms and contain shared (bond) pair of electrons. In this molecule no hybrid orbital contains lone pair of electron. In this case the repulsion between the six hybrid orbitals is minimum.



(Dotted arrows indicate the electrons shared with fluorine atoms).

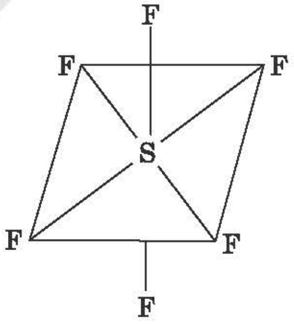
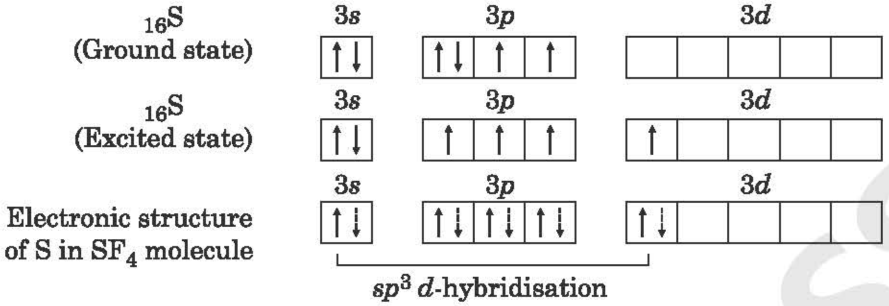


Fig. 2

This molecule is octahedral in shape having a bond angle of 90°.

(iii) Shape of SF_4 : In SF_4 molecule sulphur atom is sp^3d hybridized. Out of these four hybrid orbitals containing one electron each form bond with four fluorine atoms and contain shared (bond) pair of electrons whereas one hybrid orbital contains lone pair of electrons are shown as follows :



The molecule should have trigonal bipyramidal structure. Due to greater repulsion between lone pair and bond pair of electrons than between two bond pair of electrons, its shape is distorted. According to Bent rule two fluorine atoms occupy axial positions whereas one lone pair and two fluorine atoms occupy equilateral positions are shown as follows :

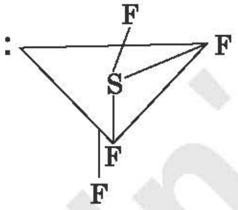
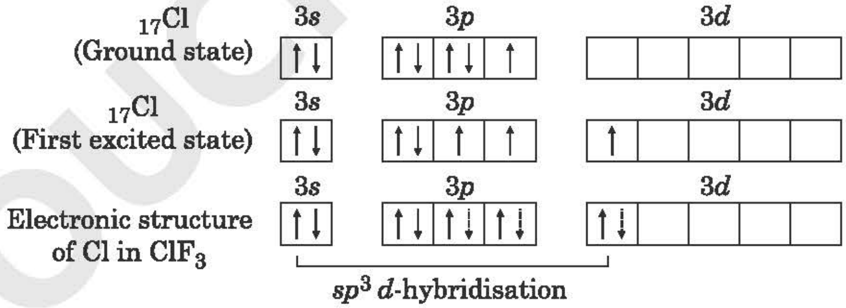


Fig. 3 : Structure of SF_4

(iv) Shape of ClF_3 : In ClF_3 molecule chlorine atom is sp^3d hybridized. Out of these three hybrid orbitals containing one electron each form bond with three fluorine atoms and contain shared (bond) pair of electrons whereas two hybrid orbitals contain lone pair of electrons are shown as follows :



This gives the molecule a trigonal bipyramidal structure but due to the presence of two lone pairs of electrons, the shape of the molecule is distorted and becomes slightly T-shaped with bond angle 87.5°.

According to Bent's rule two fluorine atoms in ClF_3 occupy axial positions and two lone pair of electrons and remaining fluorine atom occupy equilateral positions are shown as follows :

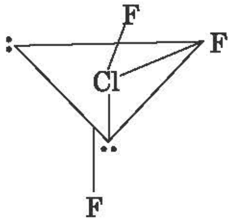
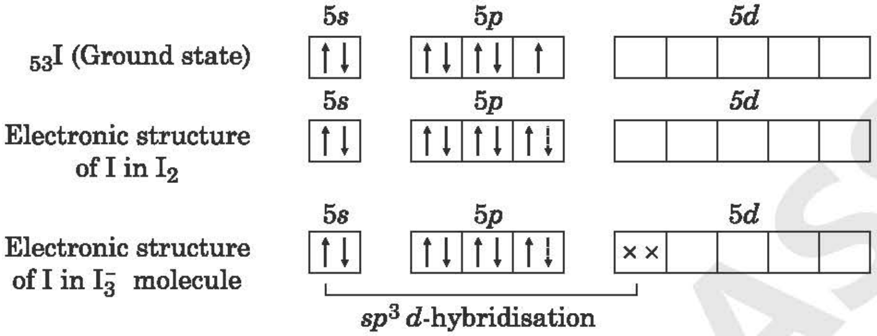


Fig. 4 : Structure of ClF_3

(v) Shape of I_3^- : In I_3^- ion iodine atom is sp^3d hybridized. Out of these one hybrid orbital contains one electron. It forms bond with one iodine atom and contains shared (bond) pair of electron. One hybridized orbital accepts lone pair of electron atom I^- ion. The remaining three hybrid orbitals contain lone pair of electrons are shown as follows :



(crosses indicate the line pair of electrons donated by I^-)

This gives the molecule a trigonal bipyramidal structure but due to the presence of three lone pairs of electrons, the shape of the molecule is distorted and the molecule assumes a linear structure. According to Bent's rule two iodine atoms in I_3^- ion occupy axial positions and three lone pair of electrons occupy equilateral positions are shown as follows :

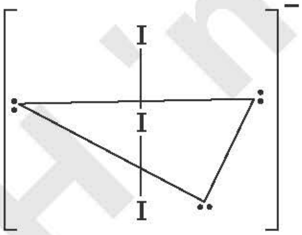


Fig. 5 : Structure of I_3^-

(vi) Shape of Hydronium Ion $[H_3O]^+$: In the formation of hydronium ion, coordinate, bond is involved. Here, oxygen atom in the water molecule is the donour while hydrogen ion is the acceptor. The formation of coordinate bond in H_3O^+ may be represented as below pointing from the donor to the acceptor, as shown below in the formation of hydronium ion.

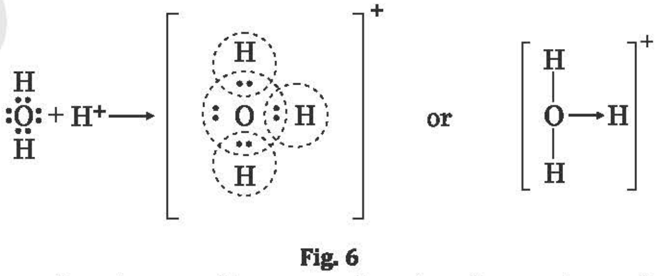


Fig. 6

It is important to note that the coordinate covalent bond once formed is indistinguishable from a covalent bond. According to the atomic orbital overlap concept of covalency, a coordinate covalent bond results when an empty orbital present in the other atom. The central atom, oxygen, in water molecule has four orbitals. Two of these orbitals contain bond pairs of electrons while the other two (shaded ones) contain lone pairs of electrons, as shown in Fig. 7. The H^+ ion has an empty *s* orbital which overlaps with one of the orbitals of oxygen atom containing a lone pair of electrons forming hydronium ion, H_3O^+, as illustrated in Fig. 7.

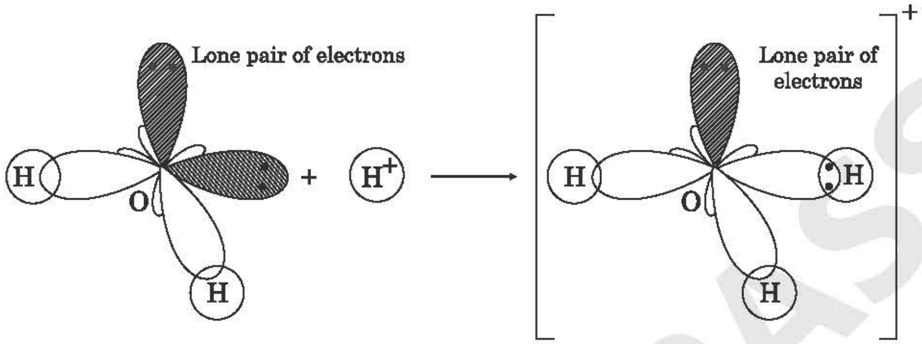


Fig. 7 : Formation of hydronium ion

It may be noted that the shape of $[H_3O]^+$ will continue to remain tetrahedral because the hybridisation involved remains sp^3. The difference between H_2O and H_3O^+ is : while in H_2O, two tetrahedral positions are occupied by lone pairs of electrons, it is only one tetrahedral position that is occupied by loans pair of electrons in H_3O^+.

Q.7. What is molecular orbital theory? Describe the linear combination of atomic orbitals (LCAO) method.

Ans.

Molecular Orbital Theory (MOT)

Molecular orbital theory was developed by **Robert Mulliken** in 1932. This is supposed to be the most versatile theory to explain the nature of covalent bond. The salient features of this theory are as follows :

1. When two atoms approach each other, their atomic orbitals lose their identity and mutually overlap to form new orbitals called **molecular orbitals.**
2. Molecular orbitals are associated with the molecule as a whole and are quantised.
3. The molecular orbitals are polycentric. They surround the nuclei of the combining atoms and the electrons are considered moving over the whole nuclear system instead of moving around a particular nucleus.
4. Molecular orbitals are formed only by those atomic orbitals which are of comparable energies and possess proper orientation.
5. The number of molecular orbitals formed is the same as the number of combining atomic orbitals.
6. A molecular orbital can accommodate a maximum of two electrons.
7. The molecular orbitals are filled within the framework of the same rules as applied for the filling of atomic orbitals, *i.e.,* Pauli's exclusion principle, Hund's rule and Aufbau principle.
8. The shape of a molecular orbital depends upon the shapes of combining atomic orbitals.

Linear Combination of Atomic Orbitals (LCAO) Method

Consider two atoms *A* and *B* which have atomic orbitals described by the wave functions $\Psi_{(A)}$ and $\Psi_{(B)}$. If the electron clouds of these two atoms overlap when the atoms approach, then the wave function for the molecule (molecular orbital $\Psi_{(AB)}$) can be obtained by a linear combination of the atomic orbitals $\Psi_{(A)}$ and $\Psi_{(B)}$:

$$\Psi_{(AB)} = N\,(C_1\Psi_{(A)} + C_2\Psi_{(B)})$$

where N = is a normalizing constant chosen to ensure that the probability of finding an electron in the whole of the space is unity, and C_1 and C_2 are constants chosen to give a minimum energy for $\Psi_{(AB)}$.

The probability of finding an electron in a volume of space dV is $\Psi^2 dV$ so the probability density for the combination of two atoms as above is related to the wave function squared :

$$\therefore \qquad \Psi^2_{(AB)} = (C_1^2\Psi^2_{(A)} + 2C_1C_2\Psi_{(A)}\Psi_{(B)} + C_2^2\Psi^2_{(B)})$$

where $C_1^2\ \Psi^2_{(A)}$ = is related to the probability of finding an electron on atom A if A is an isolated atom, and $C_2^2\Psi^2_{(B)}$ = is related to the probability of finding an electron on atom B if B is an isolated atom.

The term $2C_1C_2\ \Psi_{(A)}\Psi_{(B)}$ becomes increasingly important as the overlap between the two atomic orbitals increases, and this term is called **overlap integral**.

This term represents the main difference between the electron clouds in individual atoms and in the molecule. The larger this term, the stronger the bond.

Rules for Linear Combination of Atomic Orbitals

In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be considered :

1. The atomic orbitals must be roughly of the same energy. This is important when considering overlap between two different types of atoms.
2. The orbitals must overlap one another as much as possible. This implies that the atoms must be close enough for effective overlap.
3. In order to produce bonding and antibonding molecular orbitals, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line; or both atomic orbitals change symmetry in an identical manner.

Q.8. Explain the molecular orbital diagrams of (i) B_2, (ii) N_2, (iii) O_2 and find their bond order and magnetic behaviour.

Ans.

(i) Boron Molecule (B_2)

For the formation of B_2 molecule, two B atoms are required. We know that atomic number of B is 5 and its electronic configuration is $1s^2\,2s^2\,2p^1$. And the total of 10 electrons in B_2 molecule can be filled by following the rules : Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity. The filled molecular orbitals in B_2 molecule are shown in Fig. 1. It is to be noted that since the molecular orbitals $\pi_{2_{p_y}}$ and $\pi_{2_{p_z}}$ have identical energies, these orbitals are degenerate, hence Hund's rule is applicable in this case and accordingly both the molecular orbitals have one electron each. Stabilization occurs by the filling of two electrons in these orbitals. The effects of bonding and antibonding σ_{2s} orbitals cancel and the inner shell (K-shell) does not participate in bonding.

Hence, molecular orbital electronic configuration of B_2 molecule

$$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2 \begin{bmatrix} (\pi_{2p_y})^1 \\ (\pi_{2p_z})^1 \end{bmatrix}$$

—— Increasing Energy →

$$\text{Bond order : }(B_2) = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(4-2) = 1$$

As the bond order is one hence B_2 molecule exists and there is single bond between two boron atoms. Magnetic behaviour of B_2. As there are two unpaired electrons hence B_2 molecule is paramagnetic.

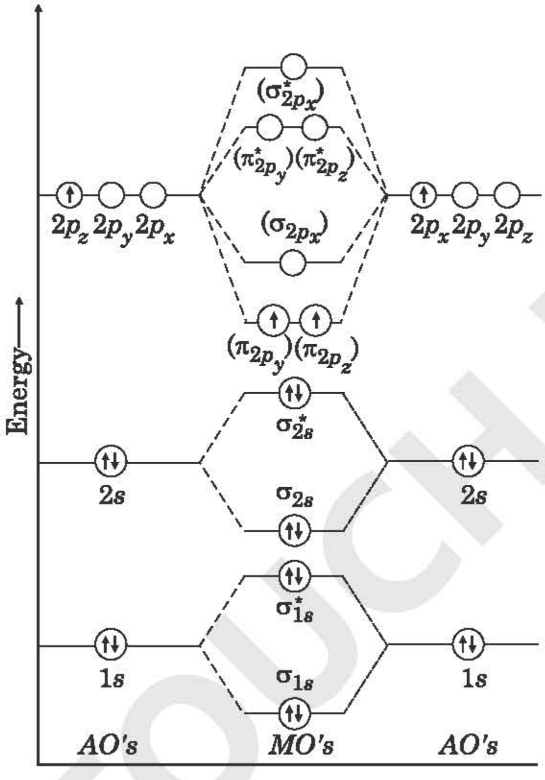


Fig. 1 : Molecular orbital energy level diagram for B_2 molecule

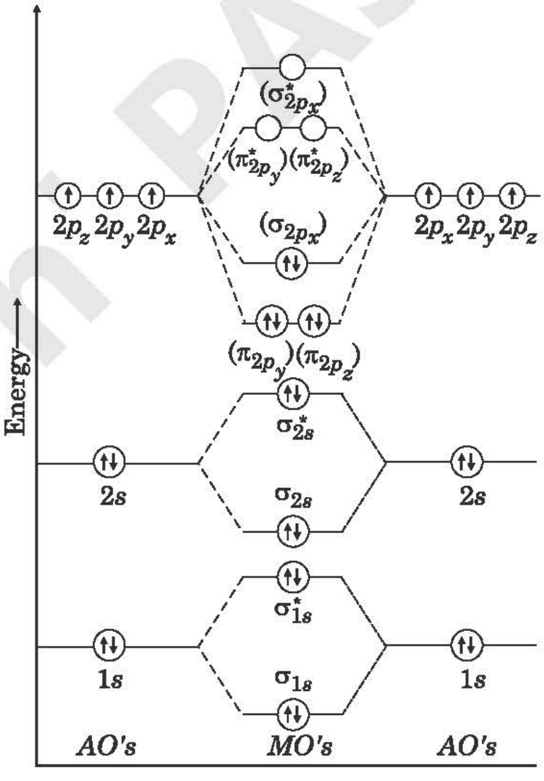


Fig. 2 : Molecular orbital energy level diagram for N_2 molecule

(ii) Nitrogen Molecule, (N_2)

Atomic number of nitrogen is 7 and its electronic configuration is $1s^2 2s^2 2p^3$. Two nitrogen atoms overlap to form N_2 molecule and total of 14 electrons are then filled in molecular orbitals of N_2 molecule (Fig. 2).

There are ten electrons in bonding molecular orbitals and only four in antibonding molecular orbitals. This gives $\frac{(10-4)}{2} = 3$ bonds between two nitrogen atoms in N_2 molecule.

$\Rightarrow$ $N \equiv N$

Hence, the bond order of N_2 is 3. Since no unpaired electron in N_2, therefore it is magnetic.

(iii) Oxygen Molecule, (O_2)

Atomic number of oxygen is 8 and its electronic configuration is $1s^2\,2s\,2p^4$. Two oxygen atoms overlap to form O_2 molecule. Total of 16 electrons are then filleds in molecular orbitals of O_2 molecule (Fig. 3).

This is to be noted that the order of the π_{2p} and π_{2p} orbitals in the dioxygen molecule differs from that for B_2, C_2 and N_2 : the σ_{2p} orbital in oxygen is at a lower energy than the π_{2p} orbitals. This was explained by mixing of *s* and *p*σ-orbitals.

$$\text{The electron configuration for } O_2 : \left[KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_x})^2 \begin{bmatrix}(\pi_{2p_y})^2\\(\pi_{2p_z})^2\end{bmatrix}\begin{bmatrix}(\pi^*_{2p_y})^1\\(\pi^*_{2p_z})^1\end{bmatrix}\right]$$

———————— Increasing Energy →

is consistent with the fact that an oxygen molecule has two unpaired electrons. This was difficult to explain on the basis of valence electron theory, but molecular orbital theory explains it quite simply. In fact, the unpaired electrons of the oxygen molecule provide one of the strong pieces of evidence for supporting the molecular orbitals theory.

There are ten electrons in bonding molecular orbitals and six electrons in antibonding molecular orbitals.

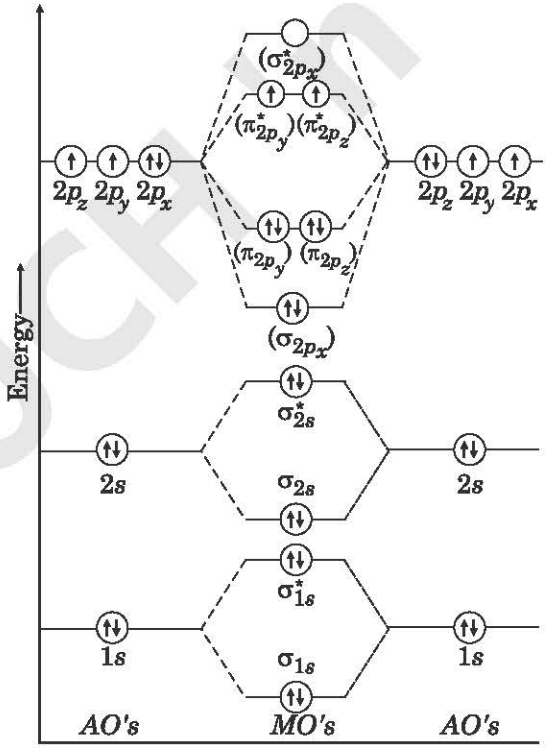


Fig. 3 : Molecular orbital energy level diagram for O_2 molecule

$$\therefore \text{ Number of bonds in } O_2 \text{ molecule} = \frac{(10-6)}{2} = 2.$$

Thus, there is a double bond between two oxygen atoms in O_2 molecule.

$\Rightarrow$ $O=O$

Hence bond order of O_2 is 2. Since, there are two unpaired electrons in O_2, therefore, it is paramagnetic.

Q.9. Describe the molecular orbital treatment for heteronuclear diatomic molecules. Explain the molecular orbital diagram for NO and CO.

Ans.

Molecular Orbital Treatment for Heteronuclear Diatomic Molecules

The wave function describing a molecular orbital (Ψ_{AB}) for a heteronuclear diatomic molecule can be obtained from linear combination of the atomic orbitals Ψ_A and Ψ_B.

$$\Psi_{AB} = N[C_A\Psi_A + C_B\Psi_B]$$

Here $C_A \neq C_B$ because the electron distribution in the internuclear region is not symmetrical.

Let us assume that electronegativity of atom A is greater than the electronegativity of atom B. In this case, energy of $\Psi_B > \Psi_A$ and atom A with wave function Ψ_A makes greater contribution to the bonding molecular orbital (Ψ_{AB}) because it is having a lower energy and it lies close to the Ψ_{AB}. Similarly atom B with wave function Ψ_B makes greater contribution to the antibonding molecular orbital (Ψ^*_{AB}) because Ψ_B has higher energy and it lies close to Ψ^*_{AB}.

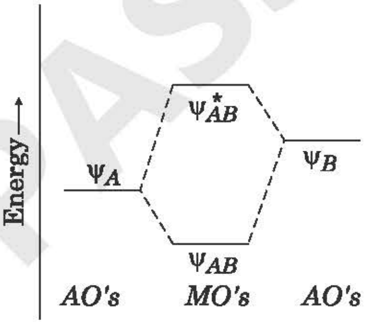


Fig. 1 : Molecular orbital energy level diagram for heteronuclear diatomic molecule *AB*

Nitric Oxide (NO) Molecule

The nitrogen atom (atomic number = 7) and oxygen atom (atomic number = 8) have 7 and 8 electrons respectively. Their electronic configurations are :

Atom	Electronic configuration
N	$1s^2 \quad 2s^2 \quad \begin{bmatrix} 2p_x^1 \\ 2p_y^1 \\ 2p_z^1 \end{bmatrix}$ ——— Increasing Energy →
O	$1s^2 \quad 2s^2 \quad \begin{bmatrix} 2p_x^2 \\ 2p_y^1 \\ 2p_z^1 \end{bmatrix}$ ——— Increasing Energy →

Thus, in nitric oxide molecule, there are 15 electrons. These 15 electrons need to be accommodated in the molecular orbitals of NO molecule. The order of energy levels of the various molecular orbitals are the same as for homonuclear diatomic molecules heavier than C_2. Hence, the MO diagram for NO molecule can be shown as given in Fig. 2.

It is obvious from the molecular orbital energy level diagram that the bonding molecular orbitals are closer to oxygen atom and antibonding molecular orbitals are closer to nitrogen atom because nitrogen is less electronegative than oxygen.

(i) The molecular orbital electronic configuration of NO molecule is :

$$\sigma_{1s}^2 \quad \sigma_{1s}^{*2} \quad \sigma_{2s}^2 \quad \sigma_{2s}^{*2} \quad \sigma_{2p_x}^2 \quad \begin{bmatrix} \pi_{2p_y}^2 \\ \pi_{2p_z}^2 \end{bmatrix} \begin{bmatrix} \pi_{2p_y}^{*1} \\ \pi_{2p_z}^{*0} \end{bmatrix}$$

$$\xrightarrow{\hspace{4cm}} \text{Increasing Energy} \rightarrow$$

(ii)

$$\text{Bond order of NO} = \frac{\begin{pmatrix}\text{Number of electrons in bonding orbitals} \\ - \text{Number of electrons in antibonding orbitals}\end{pmatrix}}{2}$$

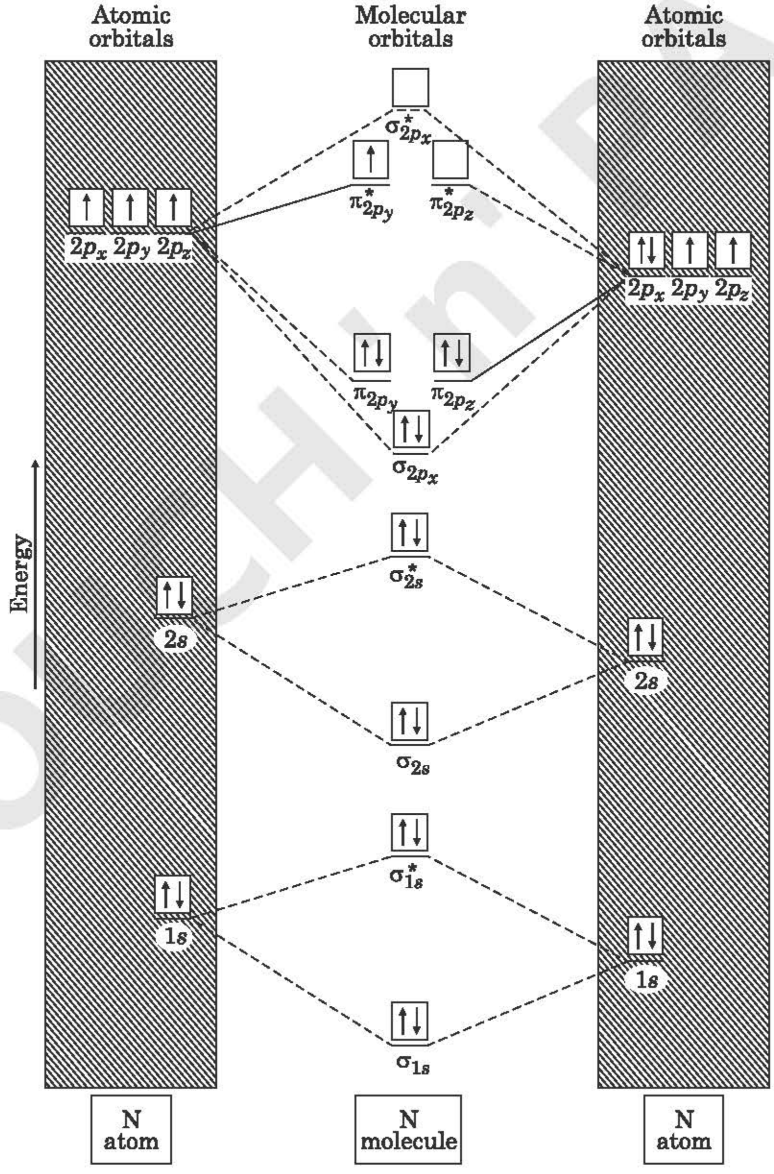


Fig. 2 : Molecular orbital energy level diagram for nitric oxide molecule

$$\Rightarrow \qquad \text{Bond order} = \frac{1}{2}(N_b - N_a)$$

$$\Rightarrow \qquad \text{Bond order of NO} = \frac{1}{2}(10-5) = 2.5 \qquad \ldots(1)$$

Since NO molecule contain one unpaired electron so, it is paramagnetic.

Carbon Monoxide (CO) Molecule

The carbon atom (atomic number 6) and oxygen atom (atomic number 8) have 6 and 8 electrons respectively. Their electronic configurations are :

Atom	Electronic configuration
C	$1s^2 \quad 2s^2 \quad \left[\begin{array}{l} 2p_x^1 \\ 2p_y^1 \\ 2p_z^0 \end{array}\right.$ Increasing Energy →
O	$1s^2 \quad 2s^2 \quad \left[\begin{array}{l} 2p_x^2 \\ 2p_y^1 \\ 2p_z^1 \end{array}\right.$ Increasing Energy →

Thus, in carbon monoxide molecule, there are 14 electrons. These 14 electrons need to be accommodated in the molecular orbitals of CO molecule. The energy levels of the atomic orbitals of oxygen and carbon atoms are not identical. Bonding molecular orbitals in CO molecule will contain bigger contribution from the more electronegative oxygen atom. Moreover, experimentally, it is found that the bond length in CO is 1.128 Å and in CO^+ it is 1.115 Å. The decrease in bond length in going from CO to CO^+ indicates that the electron must have been removed from an antibonding orbital. The most likely explanation of the bond shortening is that the σ_{2s} and $\overset{*}{\sigma}_{2s}$ molecular orbitals differ in energy more than was expected. It means they are wider apart, and the $\overset{*}{\sigma}_{2s}$ molecular orbital is higher in energy than the σ_{2p_x}, π_{2p_y} and π_{2p_z} molecular orbitals. This is shown in Fig. 3.

(i) The molecular obrital electronic configuration of CO molecule is :

$$\sigma_{1s}^2 \quad \overset{*}{\sigma}{}_{1s}^2 \quad \sigma_{2s}^2 \quad \begin{matrix} \pi_{2p_y}^2 \\ \pi_{2p_z}^2 \end{matrix} \quad \sigma_{2p_x}^2 \quad \overset{*}{\sigma}{}_{2s}^2$$

Increasing Energy →

(ii) Bond order of CO molecule :

$$= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-4) = 3$$

This bond order is in accord with experimental bond energy of 1073 kJ/mol.

(iii) **Magnetic character**, because in the CO molecule, all the electrons are paired so it is diamagnetic molecule.

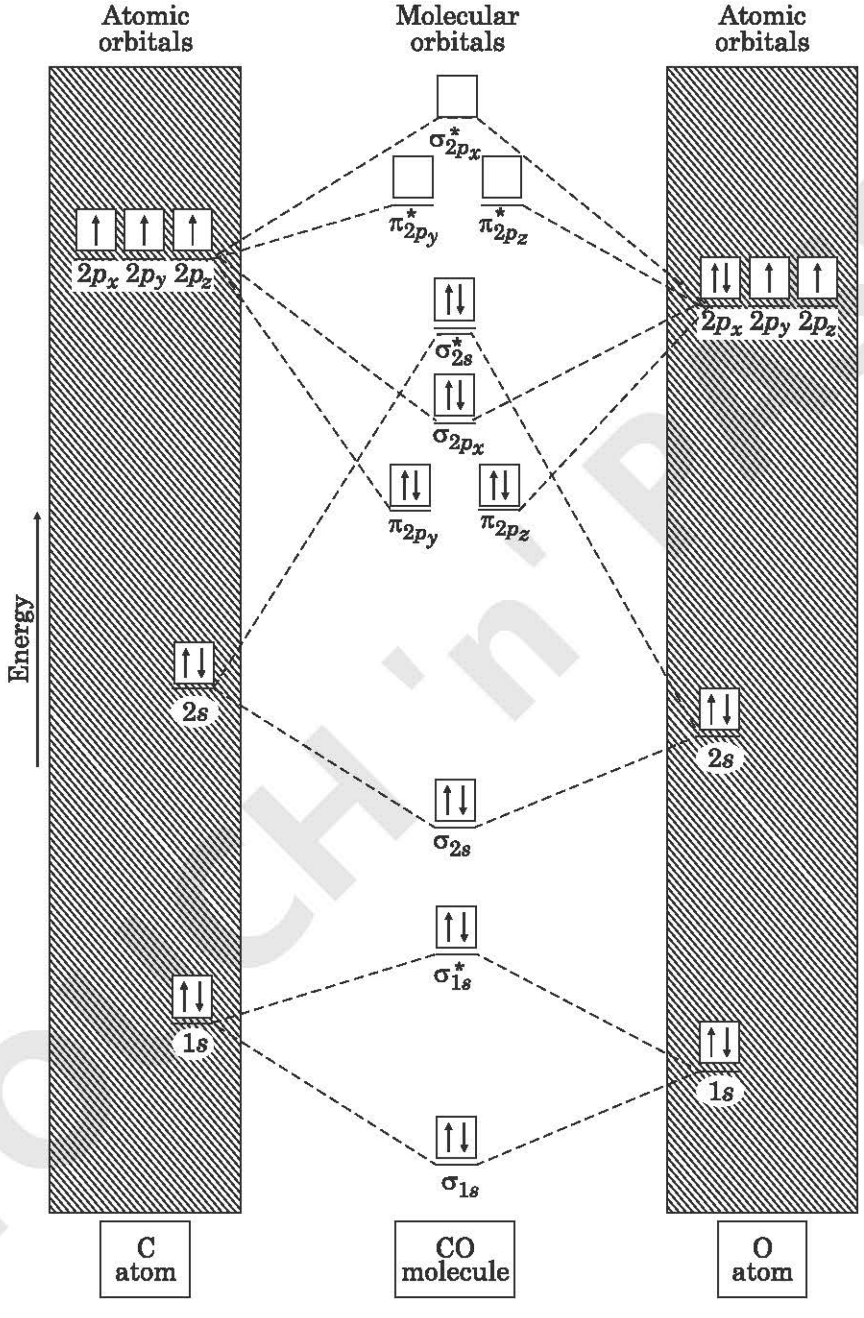


Fig. 3 : Molecular orbital energy level diagram for carbon monoxide molecule

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UNIT-III

Periodic Properties of Atoms

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Out of the following which has largest atomic size and which has the smallest : Na, Be, Mg, Li.

Ans. The elements Na, Be, Mg, Li may be arranged in the groups and periods as :

Li	Be
Na	Mg

The size of Na atom will be maximum and that of Be atom will be minimum because in the group, atomic size increases, whereas in the period it decreases with the increase of atomic number.

Q.2. Arrange the following as directed :

(i) I, I^+ and I^- in the increasing order of size.

(ii) Na^+, Mg^{2+} and Al^{3+} in order of increasing ionic radius.

(iii) Ca^{2+}, K^+, Cl^- and S^{2-} in order of increasing size.

(iv) $Mg^{2+}, Li^+, Ca^{2+}, Cl^-$ and O^{2-} in order of increasing ionic size.

(v) $Ra^{2+}, Sr^{2+}, Ca^{2+}, Ba^{2+}$ in the order of increasing size.

(vi) Ne, $O^{2-}, Na^+, F^-, Mg^{2+}$ in the order of increasing size.

Ans. (i) $I^+ < I < I^-$

(ii) $Al^{3+} < Mg^{2+} < Na^+$

(iii) $Ca^{2+} < K^+ < Cl^- < S^{2-}$

(iv) $Li^+ < Mg^{2+} < Ca^{2+} < O^{2-} < Cl^-$

(v) $Ca^{2+} < Sr^{2+} < Ba^{2+} < Ra^{2+}$

(vi) $Mg^{2+} < Na^+ < Ne < F^- < O^{2-}$

Q.3. What are the limitations of slater rules?

Ans. Limitations of Slater's rule are as follows :

1. Both *s*- and *p*-electrons in the $(n-1)$ shell have been given the same value of screening constant (0.85 unit) for calculating effective nuclear charge although *s*-electrons screen the nuclear charge more than *p*-electrons.
2. All the electrons present in *s, p, d* or *f*-orbitals at positions lower than $(n-1)$ shell have been given the same value of screening constant (1.00 unit). This is not justified because electrons present in different orbitals can not screen the nuclear charge to the same extent.

Q.4. Arrange the following as directed :

(i) Ba, Sr, Ca in the order of increasing size.

(ii) I, Br, CI, F in decreasing order of their atomic radii.

(iii) Al, P, Si, Cl, S, Ar in the decreasing order of their atomic radii.

(iv) Li, Na, K in order of increasing atomic volume.

Ans. (i) $Ca < Sr < Ba$ (ii) $I > Br > Cl > F$

(iii) $Ar > Al > Si > P > S > Cl$ (iv) $Li < Na < K$

Q.5. Out of nitrogen and oxygen which has larger size and why?

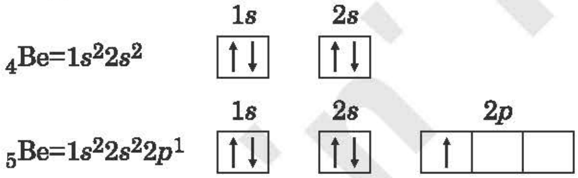
Ans. Out of nitrogen and oxygen, nitrogen has larger size. This is because both nitrogen and oxygen are the elements of the same period.

$$_7N = 2, 5; \quad _8O = 2, 6$$

The number of shells are same in both the cases but the nuclear charge of oxygen is more than that of nitrogen. Thus, the shells are attracted more strongly towards the nucleus in the case of oxygen than nitrogen. As a result the size of nitrogen is more than that of oxygen.

Q.6. The first ionization potential of beryllium is higher than that of boron, explain.

Ans. The electronic configuration of beryllium and boron are :



The electronic configurations of these elements indicate that in the case of beryllium, there is a completed *s* subshell in the outermost shell, which is relatively more stable and the amount of energy required to remove the electron from the stable system will be high. This is not the case with boron. Therefore, the first ionization potential of Be is higher than that of B.

Q.7. The ionization energy of Na^+ is more than that of Ne although both have the same electronic configuration. Explain.

Ans. The ionization energy of Na^+ is more than that of Ne although both have the same electronic configuration. This is because in Na^+, the charge on the nucleus (11 protons) is more than that in Ne (10 protons). Therefore, the electrons are attracted more strongly in Na^+ than in Ne. Hence, in Na^+ greater amount of energy will be required to remove the electron than in Ne. As a result, ionization energy of Na^+ is more than that of Ne.

Q.8. The second and higher electron affinities are always negative, explain.

Ans. The second and higher order electron affinities are always negative because there occurs a repulsion between negatively charged ion and electron being added and energy has to be given for this addition of electron.

Q.9. The electron affinity of fluorine is lower than that of chlorine, explain.

Ans. The electron affinity of fluorine is lower than that of chlorine. This is due to the fact that in fluorine, the added electron will go to the second shell which is comparatively small. Thus, there is a large repulsion between the electrons already present and the electron being added to the atom. In this case, a small amount of energy released is utilized in overcoming these forces of repulsion.

Q.10. Why are electron affinities of noble gases zero?

Ans. The electron affinities of noble gases are zero. This is because the noble gases have completed shells and the added electron will have to go to the next shell of considerably higher energy. This accounts for their electron affinites being zero.

$$\left.\begin{array}{l} {}_{2}\mathrm{He} = 1s^2 \\ {}_{10}\mathrm{Ne} = 1s^2\,2s^2\,2p^6 \end{array}\right\} \text{completed shell electronic configuration.}$$

Q.11. Arrange the following elements in the given order of ionization potentials :

(i) Li, Na, K and Rb in the increasing order.

(ii) Na, Mg and Al in the decreasing order.

(iii) P, S and Cl in the increasing order.

(iv) Mg, Al and Ar in the increasing order.

Ans. (i) Rb < K < Na < Li (ii) Mg > Al > Na

(iii) S < P < Cl (iv) Al < Mg < Ar

Q.12. Arrange the following elements in the increasing order of their electron affinities :

(i) F, CI, Br and I **(ii) Be, B, N, O and F**

Ans. (i) I < Br < F < Cl (ii) Be < N < B < O < F.

Q.13. Which has largest electronegativity and why (F or CI)?

Ans. Electronegativity is the tendency of an atom in a compound to attract shared electrons towards itself. Fluorine has larger electronegativity than chlorine. This is because fluorine has lesser atomic size than chlorine. Fluorine, therefore, attracts the shared electrons more strongly.

Q.14. Arrange the following elements in the given order of electronegativity :

(i) F, Cl, Br and I in the increasing order.

(ii) N, O, F in the decreasing order.

Ans. (i) I < Br < Cl < F (ii) F > O > N.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you mean by periodicity in properties?

Ans.

Periodicity in Properties

In periodic table, as we approach from left to right in a period (with a rise in atomic number) the atomic properties show a regular gradation, i.e., the properties show either a regular increase or a regular decrease. Altogether, after a definite interval the properties are repeated. Similar is the case in a group. A regular gradation in properties is observed from top to bottom in a group. This regular graddtion in properties from left to right in a period and the repetition of properties after a definite interval is known as periodicity in properties. In a group the gradation is found from top to bottom.

Q.2. Discuss in brief the cause of periodicity.

Ans.

Cause of Periodicity

Properties of an atom depend mainly upon two factors. One upon the number of valence electrons (electrons present in outermost shell of the atom) and other upon the distance of valence shell from nucleus (depending mainly upon the number of shells in the atom and the nuclear charge). In periodic table, as we move from left to right in a period, one electron and one proton are successively added. The electron is added in the same outermost shell due to which in a period, though the number of shells remains same, the number of valence electrons goes on increasing, along with a gradual increase in nuclear charge. It results in gradual change in properties. After a definite interval, *i.e.*, at extreme right of a period, the outermost shell becomes complete and a new shell starts for the next atom, *i.e.*, similar electronic structure (as that of first element) is now repeated. Due to this recurrence of structure in a period the properties are repeated, *i.e.*, the periodicity in proper ties is observed.

In a group from top to bottom, the number of shells increases one by one whereas the number of valence electrons remains same. It results in the regular gradation of properties from top to bottom also. However, due to the same number of valence electrons in all the atoms of a group, the properties are similar and only a gradation is observed.

Q.3. What is effective nuclear charge? Write Slater rules for determining or calculating effective nuclear charge.

Ans.

Effective Nuclear Charge

The valency electron experience less force of attraction from the nucleus due to screening effect of inner and outer electrons. The decrease in the attractive force reduces the effect of nuclear charge, Z. The resulting nuclear charge is known as effective nuclear charge, Z_{eff}. Thus, effective nuclear charge is defined as the actual nuclear charge minus the screening effect of the outer and other electrons present in the atom.

It is given by the relation

$$Z_{eff} = Z - \sigma$$

where Z is the atomic number and σ is the screening constant. The magnitude of screening constant determines the extent to which the valency electron is screened or shielded by other electrons in the atom from the nuclear charge.

Slater Rules for determining Effective Nuclear Charge

Slater gave a set of empirical rules for calculating the effective nuclear charge (Z_{eff}) experienced by electrons in different orbitals. As stated above, the Z_{eff} acting on a given electron is calculated by subtracting the screening constant (S) from the atomic number Z (nuclear charge). That is :

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

The 'Slater rules' for calculating screening on shielding constant (S) are as follows :

1. The electronic configuration of the element is first written in the following order and groupings : ($1s$); ($2s, 2p$); ($3s, 3p$); ($3d$); ($4s, 4p$); ($4d$); ($4f$); ($5s, 5p$); ($5d$); ($5f$) and so on.
2. For an electron considered in a group of *s*, *p* electrons the shielding constant (S) is the sum of the following contributions :
   (i) No contribution for electrons in groups beyond the one considered.
   (ii) An amount of 0.35 for each electron in the group considered (except in 1s group where 0.30 is used instead of 0.35).
   (iii) An amount of 0.85 for each electron in the next inner shell ($n-1$).
   (iv) An amount of 1.00 for each of all other inner shell electrons.

3. For an electron considered in *d* or *f* group, rules 2*a* and 2*b* apply as such; however rules 2*c* and 2*d* are replaced with the rule that all other electrons lying to the left of *d* or *f* group contribute 1.00 each.

Q.4. What is screening effect?

Ans.

Screening Effect (Shielding Effect)

In an atom containing number of electrons in the different energy levels, the valency electrons are attracted by the nucleus and are also repelled by the electrons present in the inner shells. As a result, the attractive force of the nucleus on the valency electrons is partially counter balanced by the repulsive force operated by the electrons present in the inner shells and therefore the valency electrons are attracted with the lesser force as they were attracted in the absence of these inner shells. In other words, the electrons of the inner shells screen or shield the valency electrons from the nucleus. This is known as screening effect or shielding effect.

Thus, larger the number of electrons in the inner shells more will be the screening effect. The value of ionization potential of the elements depend upon the screening effect, the greater the screening effect, the lesser will be the force with which the valency electron is attracted by the nucleus and consequently lower will be the value of ionization potential.

The magnitude of screening effect, not only depends upon the number of electrons present in the inner shells, but also depends upon the type of orbital occupied by the electrons. In general, It is the order $s > p > d > f$ *i.e.*, an *s*-electron screens the nucleus more effectively than a *d*-electron and so on.

Q.5. Differentiate between electronegativity and electron affinity. Write your answer in about 120-150 words.

Ans.

Electronegativity and Electron Affinity

1. Electron affinity is defined as the energy released when an electron is added to a gaseous atom in its lowest energy state to form an anion. On the other hand, electronegativity is merely a measure of the tendency of an atom to attract electrons towards itself in a molecule.
2. There is no experimental method by which electronegativity of an atom can be estimated. It has been obtained by Pauling by assigning an arbitrary value of one particular atom (for example fluorine = 4) and then estimating the electronegativity of the other element. Although direct experimental determination of electron affinity can be made, but it is more common to determine it indirectly by **Born-Haber cycle**.
3. The unit in which electron affinity is expressed is either-electron volt (eV) or calories per mole (cal/mole). Since electronegativity of an atom is expressed as relative to fluorine, it has no unit.
4. The magnitude of electron affinity mainly depends on the atomic size and effective nuclear charge. On the other hand the numerical value of the electronegativity depends upon the ionization potential and the electron affinity of the atom concerned.

Q.6. Why second ionization potential of lithium is very high as compared to its first ionisation potential?

Ans. Lithium has electronic configuration $1s^2 2s^1$.

First ionization potential is the energy required to convert.

$$\text{Li} \longrightarrow \text{Li}^{2+} \qquad i.e., \qquad 1s^2 2s^1 \longrightarrow 1s^2$$

Second ionization potential is the energy required to convert.

$$\mathrm{Li^+} \longrightarrow \mathrm{Li^{2+}} \qquad i.e., \qquad 1s^2 \longrightarrow 1s^1$$

The second ionization potential of lithium is very high as compared to its first ionization potential, because after the removal of outer electron the effective nuclear charge is increased and the removal of the second electron will have to be done against greater nuclear attractions. Secondly, the second electron is to be removed from the completed shell or from the stable system. Therefore, the amount of energy required for the said removal will be very high.

Q.7. Why noble gases have comparatively large atomic radii?

Ans. The noble gases have stable electronic configurations. So they have no tendency to lose, gain or share electrons and thus, they ordinarily do not form any bonds. Being bendless, they exist as single atoms. The only forces which keep the atoms together one weak Van der Waal's forces. Hence, the atomic radii of noble gas atoms are only the Van der Waal's radii which are comparatively larger as compared to covalent radii.

Q.8. Van der Waals radius of chlorine is more than covalent radius of chlorine. Explain.

Ans. Van der Waal's radius of chlorine is one-half of the distance between the nuclei of two nearest atoms of two adjacent molecules of chlorine in the solid state which are non-bonded together whereas covalent radius of chlorine is one-half of the distance between the nuclei of two atoms which are bonded together in a single chlorine molecule by a covalent bond.

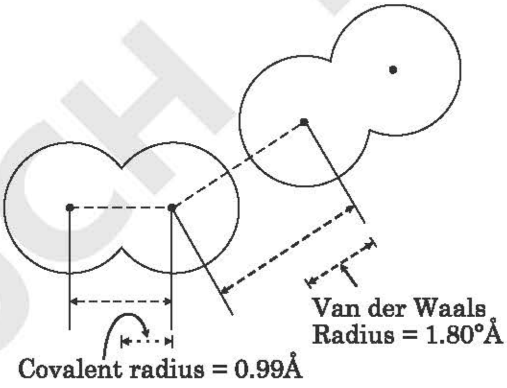


Fig. 1 : Covalent and Van der Walls' radii of chlorine atoms.

The Van der Waals' radius of chorine is more than covalent radius of chlorine is also evident from the figure given above.

Q.9. On moving along a period the ionization potential of elements increases, then why the first ionization potential of nitrogen is more than first ionization potential of oxygen but the second ionization potential of oxygen is more than second ionization potential of nitrogen?

Ans. The electronic configurations of nitrogen and oxygen are :

$$_7\mathrm{N} = 2, (2, 3) \qquad\qquad _8\mathrm{O} = 2, (2, 4)$$
$$= 1s^2 2s^2 2p^3 \qquad\qquad = 1s^2 2s^2 2p^4$$
$$= 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1 \qquad\qquad = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$

The first ionization potential of nitrogen is higher than that of oxygen because in the case of nitrogen, $2p$ sub-shell is exactly half completed and hence, is relatively more stable. Therefore, the amount of energy required to remove electron from the stable system will be high.

After the removal of one electron, the $2p$ subshell of oxygen is exactly half completed and hence is relatively more stable. Therefore, the amount of energy required to remove the second electron from the outermost shell of oxygen will be higher than required for the removal of second electron from the outermost shell of nitrogen. Thus, the second ionization potential of oxygen is more than the second ionization potential of nitrogen.

Q.10. Why is ionization potential in transition metals reasonably constant? Explain it.

Ans.

Ionization Potential in Transition Elements

A very little change in ionization potential occurs in a given transition series. In fact, the first ionization potential of transition elements are said to be reasonably constant. This would appear as a result of the interplay of the several factors. The ionization potential depends on the effective nuclear charge (Z^*)

$$Z^* = \text{Nuclear charge } (Z) - \text{Screening effect } (\sigma)$$

In transition elements, the addition of an electron to an inner quantum shell (d) gives a high shielding effect which virtually compensates the increased nuclear charge. This makes effective nuclear charge almost constant across the series and thus the values of first ionization potential become reasonably constant.

Q.11. What are the applications of slater rules?

Ans.

Important Applications of Slater Rules

1. It justifies the filling of $4s$ orbitals in preference to $(n-1)d$ orbitals. For example, potassium has electronic configuration,

   $$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

   Here Z_{eff} for $3d = 19 - (10 \times 1.00) + (8 \times 0.85) = 2.20$

   If the electronic configuration were

   $$1s^2 2s^2 2p^6 3p^6 3d^1$$

   Then Z_{eff} for $3d = 19 - [(18 \times 1.00) + 0 \times 0.35)] = 1.00$

   This shows that a $4s$ electron experiences a higher Z_{eff} and hence a configuration in which $4s$ is occupied in preference to $3d$ would be more stable.

2. Although Slater rules do not allow the exact calculations of the energies of electron, yet these are useful in understanding variation in size, ionization potential and electronegativity. For example, for an outer electron in elements along the 3rd-period, we notice the following trend in Z_{eff} value :

Element	P	S	Cl	Ar	H
Z_{eff}	4.80	5.45	6.10	6.75	(2.2)

   This shows that Z_{eff} increases along the period and attains maximum value at the noble gas which accounts for increasing ionization potential along the period with maximum at the noble gas. Ionization potential shows sudden drop after that as evidenced in Z_{eff} value of H.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What do you understand by atomic radii? What are the factors that affects atomic radii? How does the atomic radii change with in a group and in a period of the periodic table?

Ans.

Atomic Radius or Size of Atom

The term size of atom actually means to the size of an isolated atom which is, in fact, the distance between nucleus and outermost shell of an atom. But the size of an isolated atom is difficult to determine as it has no sharp boundaries and altogether its isolation is difficult. A convenient method of determining the size of an atom seems to be the measurement of distance between the nuclei of two neighbouring atoms in its molecule and to divide it by two. This half of the interatomic distance gives idea of the size of an atom, but it is not the true size as discussed in the following paragraphs. However, for all practical purposes it is taken to be the size of an atom and termed as 'atomic radius'. Thus, in general, the radius of an atom may be defined as half of the distance between the nuclei of two adjacent atoms in its molecule.

However, in the true sense above is to be called as **covalent radius** because it is, in fact, half the covalent bond length of the two bonded atoms as shown in fig. 1 by taking the example of Cl_2 molecule.

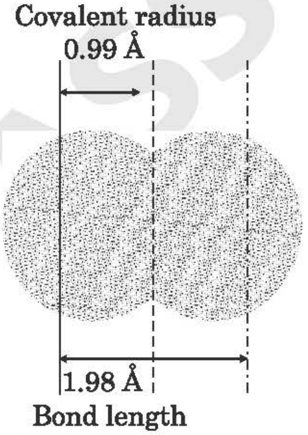


Fig. 1 : Chlorine molecule

From the figure it is clear that in a molecule the bonded atoms are not perfect spheres but they are a bit overlapped with each other (fused). The distance between their nuclei gives the covalent bond length and its half can not give the true radius of atom, instead it gives the covalent radius. But as mentioned earlier it is to be called as **atomic radius**.

In metals, the atomic radius is half of the interatomic distance in a metallic crystal.

Unit of atomic radius is Å (1 Å $=10^{-10}$ m).

Measurement of Atomic Radii

Atomic radii (covalent radii) are measured by measuring the bond lengths (interatomic distances) by *X*-ray analysis or electron diffraction method etc. and dividing them by two.

Factors affecting Atomic Radius

Radius of an atom depends mainly upon the following factors :

(i) **Number of electronic shells :** More the number of electronic shells in the atom, larger is the size of atom.

(ii) **Nuclear charge :** Nuclear charge is given by the number of protons present in nucleus of the atom. Larger the nuclear charge, more is the nuclear pull on electronic shells, so smaller is the size of atom.

(iii) **Screening or Shielding effect :** It is the hindrance in nuclear pull created mainly by the electrons present in between nucleus and the outermost shell. Due to this hindrance the outer electrons feel lesser nuclear pull. Larger the number of such electrons, more is screening effect, so less is nuclear pull and larger is the size of atom.

Another factor interelectronic repulsion also affects the size of atom. However, it is discussed only in those cases where it is playing an appreciable role.

Periodicity in Atomic Radii

In a group the atomic radii increase from top to bottom with a rise in atomic number. It is because in a group the number of electronic shells increases from top to bottom. The nuclear charge also increases but its effect is almost (85 percent) counterbalanced by the increasing screening effect (as the number of electrons between nucleus and outermost shell is also increasing from top to bottom). For the sake of illustration the radii of Ist A group elements are being given here.

Li	Na	K	Rb	Cs	Fr
1.23 Å	1.57	2.03	2.16	2.35	—

In a period the atomic radii decrease with a rise in atomic number, *i.e.,* from left to right. It is because in a period the nuclear charge increases resulting in more and more nuclear pull and hence smaller atomic radii. In a period the number of electronic shells remains same and also the screening effect remains same. The decrease in radii of second period elements is being given below for the sake of illustration :

Li	Be	B	C	N	O	F	Ne
1.23	0.89	0.80	0.77	0.70	0.66	0.64	1.60 Å

It may be noted that decrease in atomic radii is not constant though the nuclear charge constantly increases by one as we move from left to right. It is because of interelectronic repulsion. The increase of electrons in the outermost shell results in a bit more and more interelectronic repulsion as we move from left to right in a period. This compensates a little bit of the effect of increased nuclear charge. The interelectronic repulsion seems to be increasing more and more as we move from left to right. It is evident by the fact that the decrease in atomic radii is much at the first but is quite low in between the elements of Vth and VIth groups and further low in between the elements of VIth and VIIth groups.

It is also to be noted that in each period the atomic radius of last element (noble gas) is quite large. He, Ne, Ar, Kr and Xe all have large value of atomic radius in their respective periods. This value is misleading as it is not the covalent radius, it is the true atomic radius. It should not be compared with the radii of the atoms of other elements in the period which have the covalent radii values. However, if somehow compared in the identical conditions, looking to the trend in periods the noble gas atomic radii are supposed to be slightly larger than the preceding element because of the enhanced interelectronic repulsion in the completed outer most shell in their atoms.

Q.2. What is ionic radii? How does ionic radii change with in a group and in a period of the periodic table? Why the size of cations are always smaller and size of anions are always greater than the parent atom?

Ans.

Ionic Radii

Ions are charged species and are formed when neutral atoms lose or gain electrons. The size of an ion in an ionic crystal is expressed in terms of ionic radius. The ionic radius of an ion may be defined as the distance from its nucleus to the point upto which the nucleus has influence on the electron cloud of the ion. The limits of electron cloud around nucleus cannot be determined with certainty. Therefore for measuring ionic radius, the internuclear distance in an ionic compound is determined by X-ray diffraction technique. This distance is taken as the sum of the radii of the two ions involved as shown in Fig. 1 If the ionic radius of one ion is known, that of the other ion can be calculated. The ions are of two types : (i) cations and (ii) anions.

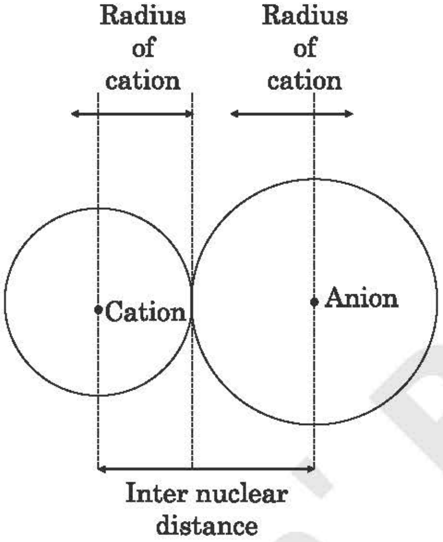


Fig. 1 : Ionic radii of a cation and an anion

Variation of Ionic Radii in a Group

Since the atomic size increases as we move down the group, therefore, ionic radius also increases in moving from top to bottom in a group. For example, ionic radii of alkali metals may be represented as :

Alkali metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radii	0.60 Å	0.95	1.33	1.48	1.69

Variation of Ionic Radii in a Period

Since the atomic size decreases in a period, therefore, ionic radius also decreases. In a period, the ionic radii of cations of elements of groups I-III and also anions of the elements of groups V-VII decrease with the increase in atomic number.

Groups	I	II	III	V	VI	VII
Cations	Na^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	F^-
Ionic radii	0.95 Å	0.65	0.50	1.71	1.40	1.36

Size of Cations

A cation is formed when an atom loses one or more outer electrons. A cation is always smaller than the corresponding atom because after the lose of electrons, the effective nuclear pull increases as the same number of protons have now to attract lesser electrons. Mostly the cation is much smaller than the corresponding atom because all the outermost shell electrons are generally lost in the formation of a cation, resulting in the decrease of one complete shell. The third factor, *i.e.*, screening effect also decreases here because after the formation of cation the inner shell becomes outermost resulting in the lesser number of intermediate electrons.

As an illustration, the atomic and ionic radii of sodium are given below :

Na_{11} 2, 8, 1 Na^{+}_{10} 2, 8
1.57 Å 0.98 Å

Also, in the case of iron :

Fe_{26} 2, 8, 14, 2 Fe^{2+}_{24} 2, 8, 14 Fe^{3+}_{23} 2, 8, 13
1.17 Å 0.76 Å 0.64 Å

The higher charge cation is smaller (*e.g.,* in Fe^{2+}, Fe^{3+}) because more the loss of electrons from the atom, more is the effective nuclear pull.

Size of Anions

An anion is formed when one or more electrons are added to the outermost shell of an atom. The anion is always larger than the corresponding atom because on addition of electrons the effective nuclear pull decreases as the same number of protons now have to attract more electrons. In the formation of anion the number of electronic shells generally remains unchanged as the electrons are added in the already existing outer shell. The shielding effect is also unchanged because inner shells remain same. Thus, it is mainly the less effective nuclear pull which is responsible for larger size of anion. The only other factor playing a role here is the interelectronic repulsion. Due to increased number of electrons in outer shell, the interelectronic repulsion increases, expanding the size of shell and thus making the anion larger. Atomic and ionic radii of chlorine are given below :

Cl_{17} (0.99 Å) 2, 8, 7 Cl^{-} (1.81 Å) 2, 8, 8

The ionic radii (cationic as well as anionic) increase from top to bottom in a group and decrease from left to right in a period just like the atomic radii.

Q.3. What do you understand by electronegativity? How do you determine electronegativity? What are the factors that affect electronegativity? How does electronegativity change with in a group and in a period of the periodic table?

Ans.

Electronegativity

When two atoms are bonded by a covalent bond, both of them share a pair of electrons. The tendency of the bonded atom in a molecule to attract this shared pair of electrons is termed its electronegativity. It differs from electron affinity since it is concerned with atoms in molecules and not with isolated atoms. Same atom when present in different molecules may be in entirely different environments. It is un likely, therefore, that electronegativity remains a constant quantity. It is, however, assumed to remain constant. Various attempts have been made to evolve a quantitative scale of electronegativity of these the following are noteworthy :

1. **Pauling scale :** Pauling devised an electronegativity scale based on experimentally derived values of bond energies. According to him, bond energy of a compound A-B for pure covalency is a geometric mean of the bond energies of *A—A* and *B—B, i.e.,*

For pure covalency $=[D_{A—A} \times D_{B—B}]^{1/2}$

But actual experimental value $D_{A—B}$ is found to be greater than this expected value. According to Pauling, Δ′, the difference between the actual bond energy and the bond energy for pure covalency is called the **ionic resonance energy**

or
$$\Delta' = \text{(Actual bond energy)}$$
$$- \text{(Bond energy for pure covalency)}$$
$$= D_{A—B}\ \text{(experimental)} - \sqrt{(D_{A—A} \times D_{B—B})}$$

For example, for the actual bond energies of H_2, F_2 and HF respectively are 436 kJ mol^{-1}, 563 kJ mol^{-1} and 159 kJ mol^{-1}

$$\therefore \qquad \Delta' \text{ for HF} = 536 - \sqrt{436 \times 159}$$
$$= 536 - 263 = 273\ \text{kJ mol}^{-1}$$

Similarly for HI, substituting the values for BE's H_2, I_2 and HI equal to 436, 151 and 298 kJ mol^{-1} respectively.

$$\Delta' \text{ for HI} = 298 - \sqrt{436 - 151} = (298 - 257)$$
$$= 41\ \text{kJ mol}^{-1}$$

The difference, Δ′ is due to electronegativity differences between the atoms. Pauling noted that D' is not an additive term. While $\sqrt{\Delta'}$ is additive, he concluded that $X_B — X_A = k\sqrt{D'}$ where X_B and X_A are the electronegativities of B and A and k is proportionally constant. When D' is zero, bonding electrons are shared equally.

In general, smaller atoms attract electron more than larger ones and are, therefore, more electronegative. Atoms with nearly filled shells of electrons (*e.g.*, halogens) will tend to have higher electronegativity than those with sparsely occupied shells. Electronegativity increases from left to right across a period and decreases as we descend a group.

Two atoms with similar electronegativities form covalent bond while an ionic bond results when the difference in electronegativity is large. Thus ionic character of a bond is dependent on the difference in electronegativity. When the electronegativity difference between the atoms is about 107, the bond is 50% ionic.

2. **Mulliken scale : R.S. Mulliken** proposed that electronegativity of an element is the arithmetic mean of first ionization energy which measures its tendency to hold its own outer electron, and its electron affinity which measures its tendency to attract electron of the element bonded with it.

Thus, electronegativity may be obtained from the relation :

$$\frac{\text{1st ionization energy} + \text{Electron affinity}}{2}$$

when the ionization energy and electron affinity are measured in kJ mol^{-1}.

The Mulliken (M) and Pauling (P) values are related approximately as :

$$X_B^M - X_A^M = 2.78\,(X_B^P - X_A)$$

3. **Allred and Rochow scale :** Allred and Rochow (1958) defined electronegativity as the electrostatic force exerted by the nucleus on the valence electrons. According to them,

$$\text{Electronegativity} = 0.359\frac{Z^*}{r^2} + 0.744$$

where Z^* is the effective nuclear charge experienced by the electron, e is the charge on the electron itself (4.8×10^{-10} *esu*) and r is the mean radius of the orbital which can be taken equal to the covalent radius of the atom (in Å).

Factors Which affect Electronegativity

The magnitude of electronegativity of an atom depends upon the following factors :

(i) **Size of the atom :** Electronegativity decreases with the increase in the size of the atom.

(ii) **State of hybridisation :** The state of hybridisation also affects the electronegativity of an atom. Greater is the *s* character in hybridisation state of an atom, greater will be its electronegativity. For example, the electronegativity of C in different hybridisation states are as follows :

Hybridisation state	*s*-character	Electronegativity
sp^3	25%	2.48
sp^2	33.3%	2.75
sp	50%	3.29

(iii) **Effective nuclear charge :** Higher the effective nuclear charge of an atom, greater is its tendency to pull the shared pair and consequently greater is its electronegativity.

(iv) **Oxidation state :** Higher the oxidation state of an atom, greater is its electronegativity. For example, the electronegativity of Fe^{3+} (o.s. = +3) is greater than that of Fe^{2+} (o.s. = +2).

Variation of Electronegativity in the Periodic Table

Electronegativity is a periodic property and varies regularly across a period or on going down a group. The increasing or decreasing trends are more pronounced in case of representative elements.

Variation across a Period

In general, the electronegativity increases on moving from left to right in a period. The elements of group 1 (alkali metals) possess the least values of electronegativities. These elements practically have no tendency to pull the shared electron pairs and are said to be the electropositive elements. Instead of attracting electrons, they have a tendency to lose electrons (electropositive character) and prefer to form ionic compouds. On the other hand, the elements of group 17 (halogens) possess the highest values of electronegativities in their respective periods. Thus, they are most electronegative elements and have a strong tendency to attract electrons.

Variation across a Group

In general, the electronegativity decreases on going down a group. This is due to a decrease in the effective nuclear charge with increase in atomic number in a group. Among all the elements, fluorine is the most electronegative element.

Q.4. What is ionization enthalpy or ionization energy? What are the factors that affect ionization energy? How does ionization energy change with in a group and in a period in the periodic table?

Ans.

Ionization Enthalpy or Energy

An electron in an atom is attracted by the positively charged nucleus. When an electron is to be removed from the atom, work is done against this nuclear attraction. In other words, energy is required for removing an electron from the atom. To under stand finer details of chemical behaviour of an element we must have a quantitative indication of the energy with which its atom binds its electrons. This we obtain from measurements of the ionization energy–the minimum energy required to remove an electron from a gaseous atom in its ground state to form a gaseous ion :

Gaseous atom + Ionization energy → Gaseous ion
+ Gaseous electron removed infinite distance away

It is expressed in kJ mol^{-1} of atoms. Since in the gaseous phase the atom and the ion are isolated from all external influences, the ionization energy is exactly the energy with which the atom binds its electron. It, therefore, gives a quantitative measure of the stability of the isolated atom.

In an atom, the energy required to remove the first electron from the gaseous atom to form a unipositive gaseous ion is termed its first ionization energy.

A beryllium atom has got four electrons outside the nucleus. Its first ionization energy is found to be 899.6 kJ Mol^{-1}

$$\text{Be}\,(g) + 899.6\ \text{kJ mol}^{-1} \longrightarrow \text{Be} + e^{-}(g)$$

It is found that another electron can be removed from Be^{+} by expending an energy of 1757 kJ mol^{-1} of Be^{+}.

$$\text{Be}^{+}(g) + 1757\ \text{kJ mol}^{-1} \longrightarrow \text{Be}^{2+}(g) + e^{-}(g)$$

This is known as its second ionization energy. The second ionization energy is the energy needed to remove one electron from one unipositive gaseous ion to form one bipositive gaseous ion. This is higher than the first ionization energy as the electron has to be removed a gainst the pull by a bipositive ion formed while in the earlier case (first ionization energy) the electron had to be pulled away against the attraction force due to the resulting unipositive ion.

Similarly, energy required to remove the third electron from the gaseous atom (*i.e.*, energy required to remove one electron from the gaseous bipositive ion obtained above) is termed its third ionization energy. Fourth, fifth or sixth ionization energy can be defined in a similar manner.

The ionization energy can be measured in a discharge tube containing the gas or vapour under low pressure. Initially the current flow through the tube is practically zero. As the voltage between the cathode and anode is increased, a well-defined voltage is reached at which the gas is ionized and there is a sudden large increase in the current flow through the tube. In other words, at this voltage an electron has acquired sufficient energy for its impact on an atom to produce ionization.

This well-defined value of the voltage is known as the **ionization potential** commonly expressed in volts and is numerically equal to the ionization energy in electron-volts (eV). One electron volt is equivalent to ($1.6\times10^{-19}\text{J}\times6.023\times10^{23}\text{ mol}^{-1}=96.48\text{kJ mol}^{-1}$). For example, when hydrogen gas under low pressure is taken in the discharge tube, a sudden very large increase in current flow occurs when the voltage is 13.58 volts. The ionization potential of hydrogen is 13.58 volts and the ionization energy of hydrogen atom is

$$13.58\text{ eV }(\equiv 13.58\times96.48=1310\text{ kJ mol}^{-1}).$$

Factors on which Ionization Energy Depends

Ionization energy depends on the following factors :

1. **Shielding effect :** As shown in Fig. 1, a valence electron in a multielectron atom is pulled by the nucleus and repelled by the inner shells of electrons. The valence electron does not, therefore, experience that pull of the total positive charge of the nucleus. Instead the effective pull is due to total charge minus the number of correct elections. Thus the increase in the number of inner electrons will tend to decrease the effective pull of the nucleus and hence ionization energy will decrease.

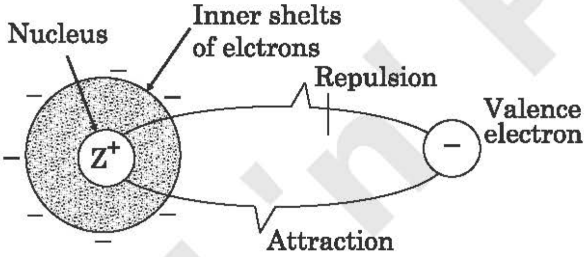


Fig. 1 : Effect of inner electron on a valence electron (shielding effect)

The foregoing discussion can be summarized to :

$$Z^* = Z - S$$

where Z^* is the effective nuclear charge, Z is the actual nuclear charge and S is the shielding or screening constant.

2 **Nuclear charge :** As the nuclear charge increases the electrons of the outer shells experience greater and greater pull by the positively charged nucleus with the result that it is more and more difficult to remove an electron from the atom or the ionization energy increases.

Since nuclear charge increases from left to right in a period, the ionization energy increases from left to right in a period.

3. **Principal quantum number, (n) :** How far an electron is located from the nucleus is determined by its principal quantum number. Further away the electron from the nucleus, more loosely would it be bound to it and more easy it would be to remove it. In other words, higher the value of *n*, less will be the energy required to remove the electron, *i.e.*, less will be its ionization energy.

As we move along a group from top to bottom value of *n* for the outer electron increases and hence the ionization energy decreases.

It is found that as we move to the right in the periodic table, Z^* (so also the ionization energy) gradually increases until it achieves a maximum at the noble gas.

4. **Azimuthal quantum number, *l*:** When electrons are added one by one to build up an atom, the electron being added does not remain completely outside the negative charge cloud constituted by previously added electrons. Rather the electron will penetrate the inner charge cloud to a greater or less extent. The result of this penetration effect is that the added electron will be attracted more strongly by the nucleus.

   For a given value of *n* the probability of finding the electron near the nucleus decreases as the value of l increases, *i.e*, the probability is in the order :

   $$s > p > d > f$$

   Therefore, the, *s* electron is better able to penetrate than a *p* electron which in turn penetrates better than a *d* election, and so on. Consequently the force of attraction on different electrons with the same value of *n* is in the order :

   $$s > p > d > f$$

   Hence the ionization energy of *s* electron is greater than that of a electron which in turn is greater than that of *d* electron, and so on.

5. **Completely filled or Half-filled subshells :** According to **Hund's rule** atoms with completely filled or half-filled subshells are stable. To pull out an electron from such atoms will require more energy since the more stable system (associated with less energy) is to pass to a less stable system (associated with more energy). The ionization energy of such atoms is, therefore, relatively high.

6. **The net charge on the atom or Ion :** The work done in removing an electron from an atom or ion is proportional to the charge on the residual ion. In removing the first electron, work (say w_1) is done against attraction by the unipositive ion. In removing the second electron, work (say, w_2) is done against attraction by the bipositive ion. The work done goes on increasing as third, fourth, fifth ....., *n*th electron is removed. In other words, successive ionization energies of various electrons are in the order :

   1st < 2nd < 3rd < 4th < 5th, and so on.

   As a result of the combined effect of these factors, the ionization energy tends to increase when we move from left to right and it tends to decrease on descending a group.

Variation in Ionisation Energy (IE)

In a group the ionisation energy (IE) decreases from top to bottom with the rise in atomic number. It is because in a group the number of electronic shells goes on increasing from top to bottom, increasing more and more the distance of outer electrons from nucleus. It results in lesser nuclear pull due to which low energy is required to be supplied to take out the electron. However, the nuclear charge also increases from top to bottom, but its effect is almost counterbalanced by screening effect which also increases from top to bottom (as inner shells are increasing). Thus, net result is that the IE values decrease from top to bottom. First IE values of the elements of group IA are being given below :

Li	Na	K	Rb	Cs
500 kJ mol^{-1}	496	420	403	376

In other words it may be said that as atomic radii increase from top to bottom in a group, the I.E. values decrease because outer electrons feel less and less nuclear pull with rise in atomic size.

In a period the IE values increase from left to right with a rise in atomic number. It is because in a period the nuclear charge goes on increasing from left to right due to which the outer electrons feel more and more nuclear pull resulting in higher IE values. The number of electronic shells remains unchanged in a period and the inner electrons also remain same giving almost no difference in screening effect. The IE values of second period elements are given below :

Li	Be	B	C	N	O	F	Ne
500	900	801	1085	1400	1314	1680	2080 kJ mol^{-1}

It may be said in other words that as the atomic radii decrease from left to right in a period, the IE values increase because outer electrons feel more and more nuclear pull with decreasing atomic size.

Q.5. What do you understand by electron gain enthalpy or electron affinity? What are the factors that affect electron affinity? How does electron affinity change with in a group and in a period?

Ans.

Electron gain Enthalpy or Electron Affinity

Energy is to be supplied to remove an electron from an atom and is measured in terms of ionisation energy. On the other hand, if an electron is added into an atom, energy is released. The energy released is measured in terms of electron affinity. Thus, whereas I.E. tells the case with which the electron is lost so that cation is formed, the electron affinity tells the ease with which the electron is accepted so that anion is formed. Thus, electron affinity is the measure of electron attracting property of an atom.

Electron affinity may be defined as the amount of energy released when an electron is added into the outermost shell of a gaseous atom (or ion) in its ground state.

$$A_{(g)} + e \longrightarrow A^{-}_{(g)} + \text{energy (electron affinity)}$$

Just like ionisation energy, the energy released on the addition of first electron is known as **first electron affinity**; energy released on the addition of second electron is known as **second electron affinity**, and so on. Unit of electron affinity is same as that of IE *i.e.*, kJ mol^{-1}.

Experimental measurement of electron affinity is quite difficult. It is measured indirectly.

Negative value of electron affinity : In the atoms of some elements, outermost shell is already so much stable that it never prefers the entry of new electron. Such atoms, rather, repel the new entering electron. If electron is still added in such atoms then instead of the release of energy, the energy is to be supplied, *i.e.*, such elements have negative values of electron affinity. For example, the atoms of noble gases are already most stable and hence they do not have any affinity for electrons. They have negative values of electron affinity. Similar is the case with Be and Mg etc. Since the negative values of electron affinity of such elements are quite small, they may roughly be regarded as zero each.

Second electron affinity : After the entry of one electron the neutral atom becomes a negatively charged ion. Now it does not prefer the entry of second electron. Due to its negative charge it repels the second new electron, if added. So, in this process instead of a release in energy the energy is to be supplied. Thus second electron affinity values are always negative.

For example, the second electron affinity values for O (for O^{2-}) and S (for S^{2-}) are –710 and –500 kJ mol^{-1} respectively.

Factor which affect Electron gain Enthalpy

Electron gain enthalpy is governed by several factors. Some of the important ones are as follows :

1. **Atomic size :** When the size of atom is large, the added electron is far from the nucleus and will experience less force of attraction by it. Consequently, the electron gain enthalpy will be less negative. Thus greater the size of an atom, less negative is the value of electron gain enthalpy.
2. **Nuclear charge :** In general, electron gain enthalpy values are more negative with increase in the nuclear charge. This is due to the fact that a higher nuclear charge helps in the addition of electron to the atom.
3. **Electronic configuration :** When an atom possesses a stable electronic configuration, *i.e.,* it possesses completely filled or half filled shells, it has very little or practically no tendency to accept the added electron. Consequently, the electron gain enthalpy values are large positive. Be, Mg, noble gases, etc., are elements of this type. Their atoms possess completely filled shells and do not add electrons. Therefore, the values of electron gain enthalpy for all these elements are large positive. Nitrogen possesses a half filled shell and requires absorption of energy for an electron to be added. Therefore, it has a positive value of electron gain enthalpy.

Variation of Electron Gain Enthalpy in the Periodic Table

Since, the electron gain enthalpy for most of elements is not known, the variation of electron gain enthalpy in the periodic table is not well defined. However, some general trends have been observed. These are as follows :

1. **Variation across a period :** In general, electron gain enthalpy values become more and more negative on moving from left to right in a period. This is because on moving from left to right in a period, the atomic size decreases while nuclear charge increases. Both these factors result into greater attraction for the added electron. Consequently, electron gain enthalpy values become more and more negative in a period. However, the general trend is not strictly followed in the periodic table.
2. **Variation in a group :** In general, electron gain enthalpy values become less negative on going down a group. On going down a group, the nuclear charge as well as the atomic size increase regularly. But the effect of increase in atomic size dominates over the increase in nuclear charge. Hence, the added electron experiences less attraction by the nucleus. Consequently, the electron gain enthalpy values become less negative as one moves down a group.

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UNIT-IV

Recapitulation of Basics of Organic Chemistry

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. What is inductive effect?

Ans. The **inductive effectve** or ***I*-effect** is a permanent effect and involves the displacement of σ-electrons along a saturated carbon chain due to the presence of an electron withdrawing group (–*I*-effect) or an electron repelling group (+*I*-effect) at one end of the chain resulting in the development of partial positive or negative charges in the decreasing order of magnitude.

$$\overset{\delta\delta\delta-}{C} \longrightarrow \overset{\delta\delta+}{C} \longrightarrow \overset{\delta+}{C} \xrightarrow{-I\text{-effect}} \overset{\delta-}{X}$$

(electron withdrawing group)

$$\overset{\delta\delta\delta+}{C} \longleftarrow \overset{\delta\delta+}{C} \longleftarrow \overset{\delta+}{C} \xleftarrow{+I\text{-effect}} \overset{\delta-}{X}$$

(electron repelling group)

Q.2. Write the order of –*I* effect of some common groups.

Ans. The order of –*I*-effect of some common groups is as follows :

$$—NO_2 > —CN > —COOH > —F > —Cl > —Br > —I > —OH > —C_6H_5—$$

Q.3. Write order of +*I* effect shown by alkyl groups.

Ans. The alkyl groups show +*I*-effect which decreases in the order 3° > 2° > 1°. Thus,

$$(CH_3)_3C > (CH_3)_2CH— > CH_3CH_2— > CH_3—$$

Q.4. When the inductive effect becomes negligible?

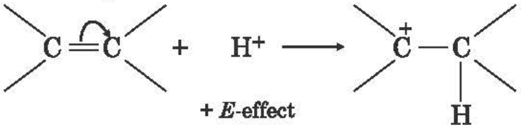
Ans. The inductive effect becomes almost negligible beyond C_3 of the chain.

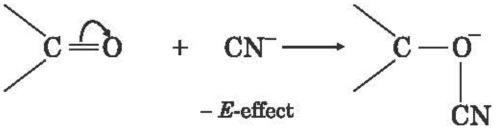
Q.5. What is hyperconjugation?

Ans. **Hyperconjugation effect** comes into existence when a C—H bond is present at the α-position to an unsaturated system and involves the interaction of α-electrons of C—H bond with π-electrons of the double bond of the unsaturated system resulting in the release of electrons from α-carbon and the polarisation of the double bond. Hyperconjugation is also termed as no bond resonance.

Q.6. What is electromeric effect?

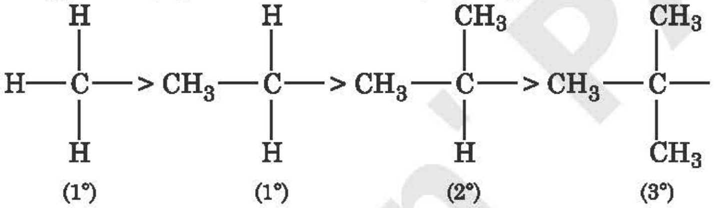
Ans. The **electromeric effect** or **E-effect** is a temporary effect and involves the complete transfer of the shared pair of π-electrons of a multiple bond to one of the shared atoms in the presence of an attacking reagent. When the electrons of π-bond are transferred to that atom of the double bond to which the reagent gets attached , it is called +*E*-effect. In case than electrons are transferred to that atom of double bond to which the reagent is not attached, the effect is called ***E*-effect**. For example,





Q.7. Write the order of hyperconjugation effect shown by alkyl groups.

Ans. The order of hyperconjugation effect for alkyl groups follows the following order :



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}- \; > \; CH_3-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}- \; > \; CH_3-\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}- \; > \; CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-$$

(1°) (1°) (2°) (3°)

Q.8. What is mesomeric effect?

Ans. Mesomeric effect or ***M*-effect** is the permanent effect involving the transfer of electrons relayed through π-electrons of multiple bonds in a chain of carbon atoms in a molecule. The effect comes into existence when an electron-withdrawing or electron-pumping group is in conjugation with a π-bond, or an atom or group having atleast one lone pair of electrons in conjugation with a π-bond. It is also referred to as **resonance effect** (*R*-effect).

When the transfer of electrons is away from the atom or group in conjugation with a π-bond, the effect is called +*M*-effect. In case the transfer of electrons is towards the atom or group in conjugation with a π-bond, the effect is called –*M*-effect.

Q.9. Write some groups showing +*M*-effect and –*M*-effect.

Ans. Some of the groups showing +*M*-effect are :

$$-\ddot{\underset{\cdot\cdot}{O}}-H, -\ddot{\underset{\cdot\cdot}{O}}-R, -\ddot{N}H_2 -\ddot{\underset{\cdot\cdot}{S}}-R, -\ddot{\underset{\cdot\cdot}{Cl}}:-\ddot{\underset{\cdot\cdot}{Br}}: \text{ etc.}$$

On the other hand, some of the groups showing –*M*-effect are :

$$>C=O, -NO_2, -C\equiv N, \text{etc.}$$

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you understand by bond length?

Ans.

Bond Length

The equlibrium distance between the nuclei of two atoms joined by the covalent bond is known as bond length or **bond distance**. It is determined in solid molecules by X-ray diffraction and in gaseous molecules by neutron diffraction studies and expressed in Angstrom unit ($1 \text{ Å} = 10^{-8}$ cm.)

The bond length of each kind of bond varies very little from compound to compound. Bond (length of single, double and triple bonds follow the order :

Single bond > Double bond > Triple bond

Normal bond length of some of the important covalent bonds is given in the Table :

Bond	Length (Å)	Bond	Length (Å)
C—C	1.54	H—H	0.74
C═C	1.34	C—O	1.43
C≡C	1.20	C═O	1.22
O—H	0.97	C—N	1.47
N—H	1.00	C═N	1.29
C—H	1.08	C≡N	1.16

Q.2. Write the factors that affects bond length.

Ans.

Factors affecting Bond Length

Bond length mainly depends on the following factors :

1. **Electronegativity :** If an atom is more electronegative than the other in a diatomic molecule, then the bond length will be comparatively shorter. For example, the bond length of C—F bond is found to be 1.36 Å, whereas it should be 0.77 +0.64 = 1.41 Å. The greater the difference in electronegativity between two atoms, the shorter will be the bond length. If the electronegativities of two atoms A and B are X_A and X_B, then bond length (r_{A-B}) is given by,

   $$r_{A-B} = r_A + r_B - 0.09\,(X_A - X_B)$$

   where r_A and r_B are the covalent radius of the two atoms.
2. **Bond order :** It is seen that as bond order or multiplicity of bond increases, the bond length decreases. For example, in CH_3—CH_3, the bond length of C—C bond (bond order = 1) is 1.54 Å, whereas in CH_2═CH_2, the bond length of C═C bond (bond order = 2) is 1.34 Å and in HC≡CH, the bond length of C≡C bond (bond order = 3) is 1.20 A.

   Similarly, in C—N, C═N, C≡N, the bond length is 1.47 Å, 1.29 Å and 1.16 Å, respectively,
3. **Hybridisation :** Bond length depends on the hybridised state of the bonded atoms in a molecule. It is due to the *s*-character in different types of hybridised orbitals. In sp^3-orbital, there is 25% *s*-character, while in *sp*-orbital there is 50% *s*-character. So, greater the *s*-character, smaller will be the orbital and smaller will be the bond length.
4. **Resonance and delocalisation :** Bond length is also affected by resonance. For example, the bond length of each C—C bond in benzene is 1.39 Å which is neither equal to C—C single bond (1.54 Å) nor to C═C double bond (1.34 Å). It is however, in between them, as benzene occurs as the following two resonance hybrids.

Q.3. Write a short note on bond angles.

Ans.

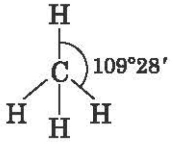
Bond Angle

The angle between two nearest atoms to central atom of a molecule is known as bond angle. It is represented in degree (°). It can be determined by infrared spectroscopy, microwave spectroscopy and electron diffraction methods. The diatomic molecules are linear and therefore, in these there is no meaning of bond angle but for triatomic and polyatomic molecules, the bond angle is very important for determining the structure of molecules.

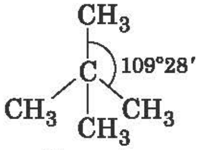
Factors Affecting Bond Angle

(i) **Hybridization of central atom :** The bond angle can be known by the hybridized state of central atom. The central carbon atom in C_2H_2, C_2H_4 and CH_4 is in *sp*, sp^2 and sp^3 hybridized state, respectively and therefore, bond angle ∠HCH in these compounds is 180°, 120° and 109°28'.

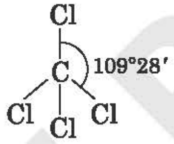
(ii) **Atoms or Groups attached to central atom :** The bond angle in *sp* hybridization is 109°28', in sp^2 it is 120° and in *sp* it is 180°. These bond angles are only when the atoms or groups attached to central atom are same.



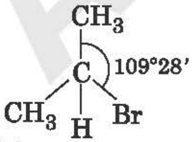
Methane



Neo pentane



Carbon tetra chloride



2-bromo propane

The bond angle deviates if different atoms or groups are attached to central atom. For example, in 2 bromo propane ∠CCBr is 114.1°. This is due to difference in the electronegativity of atoms attached to central carbon atom.

(iii) **Number of bonded pair of electrons :** The electronegativity of an orbital containing lone pair of electron is least. In CH_4, NH_3 and H_2O, there is an increase in the *p*-character of orbital attached to hydrogen, whereas there is an increase in the *s*-character of orbital containing lone pair of electron. In all these molecules, the central atom is sp^3 hybridized but the bond angle is 109.5°, 107° and 104.5°, respectively. The lone pair of electrons in CH_4, NH_3 and H_2O are 0, 1 and 2 respectively.

(iv) **Electronegativity of bonded atoms :** The bond angle decreases on decreasing the electronegativity of central atom.

Compound	NH_3	PH_3	AsH_3	SbH_3
Bond angle	107°	93.3°	91.8°	91°

Applications : The bond angle is used for determining the structure and symmetry of molecules. It also gives information about the hybridization of central atom and ionic character of bond.

Q.4. What do you understand by bond energy?

Ans.

Bond Energy

This is defined as the average amount of energy required to break a bond in one mole of the substance. Each bond has a characteristic value of this energy and is a measure of strength of that bond. The greater the bond energy, the stronger is the bond. It is determined by measurement of heat of reaction and by spectroscopic method. It is expressd in k.cal per mole or kJ per mole. The bond energies of some bonds are :

C—C = 83 k.cal/mole
C═C = 146 k.cal/mole
C≡C = 199 k.cal/mole
O—H = 111 k.cal/mole
C—N = 73 k.cal/mole
C—O = 86 k.cal/mole

$C—H = 99$ k.cal/mole　　$C{=}O = 179$ k.cal/mole
$N—H = 93$ k.cal/mole　　$C—Cl = 81$ k.cal/mole

Bond energy is the scale of direct measurement of bond strength. To break one mole hydrogen (H_2) gas into H-atoms, the required bond energy is 436 kJ, *i.e.,*

$$H—H \rightarrow H + H - 436\ \text{kJ}$$

So, the bond energy of H—H bond is 436 kJ/mole. Bond energy required to break a bond and to form the same bond is always the same. Bond breaking is an endothermic process, while bond forming is an exothermic process.

The energy required to break one mole of methane (CH_4) into atoms is 1653.5 kJ, *i.e.,*

$$CH_4 \rightarrow C + 4H - 1653.5\ \text{kJ}$$

So, the energy required to break C—H bonds in methane $= \frac{1653.5}{4} = 413.4$ kJ.

Q.5. Write the factors affecting bond energy.

Ans.

Factors Affecting Bond Energy

The following factors affect the bond energy :

1. **Electronegativity :** The greater the difference in electronegativities of the two atoms in a compound, the greater will be the bond energy. For example, the bond energy of HF is maximum (135.0 k.cal/mole) and that of HI is minimum (70.4 k.cal/mole).
2. **Atomic size :** Small atoms form smaller bonds and so the bonds formed between such atoms will have more bond strength.

   The atomic size of halogens is in the order of F< Cl< Br< I. Therefore, the order of bond energies of halogen acids will be H—F> H—Cl > H—Br > H—I.
3. **Type or Extent of overlapping :** We know that σ-bond is more strong than π-bond. Therefore, compounds having σ-bonds form stronger bonds than those having π-bonds. So, the bond energy of compounds having σ-bonds is greater than that of compounds having π-bonds.
4. **Hybridisation :** The bond energy for different types of hybridisation is in the order, $s < p < sp < sp^2 < sp^3$. This is because the *p*-character in the hybridised orbital increases in the above order.
5. **Bond order :** The higher the bond order of a multiple bond, greater will be the bond energy. For example, the bond energies of C—C, $C{=}C$, $C{\equiv}C$ bonds are 347.2, 610.0, 815.1 kJ/mole, respectively.
6. **Repulsion between lone pair of electrons of the binding atoms :** If the binding atoms have a lone pair of electrons, then the bond formed between them is less strong, because the lone pair of electrons do not get localised. The electron clouds of both atoms repulse each other and so the bond becomes weak and bond energy is decreased. The more the number of lone pair of electrons, the greater will be the repulsion and weaker will be the bond.

Q.6. Write a short note on Inclusion compounds.

Ans.

Inclusion Compounds

An inclusion compound is a complex in which one chemical compound (the 'host') form a cavity in which molecules of a second guest compound are located. The definition of inclusion compound is very broad, extending to channels formed between molecules in a crystal lattice in which guest molecules can fit. If the spaces in the host lattice are enclosed on all sides so that the guest species is 'trapped' as in a cage, the compound is known as a **clathrate**. In molecular encapsulation, a guest molecule is actually trapped inside another molecule.

Cyclodextrin Inclusion Compounds

Inclusion compounds have been reported between cyclodextrins and ferrocene. When a solution of both compounds in a 2 : 1 ratio in water is boiled for 2 days and then allowed to rest for 10 hours at room temperature, orange-yellow crystals are obtained. X-ray diffraction analysis of these crystals reveal a 4 : 5 inclusion complex with 4 molecules of ferrocene in the cavity of 4 cyclodextrin molecules with the fifth ferrocene molecule sandwiched between two stacks, of ferrocene-cyclodextrin dimers.

There is no chemical affinity between the host and guest molecules in the inclusion compounds. Formation of such compounds depends upon the size and shape of the guest molecules and the size of the cavities or channels created in the host molecules.

Urea Inclusion Compounds

Urea forms an inclusion compound with straight chain alkanes. Urea crystallises in hexagonal lattice, in the presence of guest molecules and traps them in the cavity. This is represented as under :

The channels in crystallised urea are of the dimensions 5A which can trap only the straight chain hydrocarbons. Branched chain hydrocarbons which are of bigger dimensions do not form inclusion compounds with urea. However thiourea which crystallises with bigger cavities can from inclusion compounds with branched chain hydrocharbon, the dimension of thiourea channel is appropriate in size and shape to trap the molecules of branched alkanes, cycloalkanes and chloroform etc.

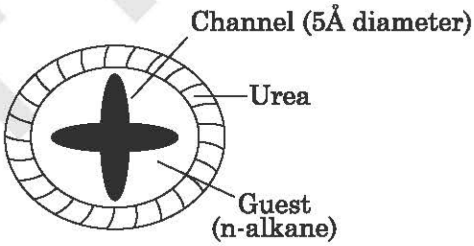


Fig. : Crystallised urea

Q.7. What are the uses of inclusion compounds?

Ans. **Important Uses of Inclusion Compounds**

The most common inclusion compound used in analytical chemistry is the use of starch-iodine compound. If starch has some impurities such as fatty acids, then it will not trap iodine to give a blue colour. The general use of inclusion compounds fall into two main categories :

1. **Resolution of Mixtures :**
   - (i) Removal of free fatty acids from oils or waxes by treatment with moist urea.
   - (ii) *cis-trans* isomers can be separated by urea complexation.
   - (iii) Removal of straight chain hydrocarbons present in petroleum through urea complexation from hydrocarbon mixture.
   - (iv) Separation of benzene from cyclohexane (both having very close boiling points). Both can be separated by treating the mixture with wet thiourea and filtering out the cyclohexane complex. The complex when shaken with water gives pure cyclohexane as water dissolves thiourea.
   - (v) Separation of saturated and unsaturated fatty acids by urea adduct formation.

2. **Storage of Substances :** Certain substances can be protected for long time in the form of inclusion complexes. For example, auto-oxidation of oleic acid does not occur when the acid is in the form of urea complex.

The clathrates of inert gases provide a convenient method of despersing the gases without restoring to high pressure cylinders.

Q.8. What are clathrates? Discuss in brief.

Ans.

Clathrates

The inclusion compounds of noble gases are termed as clathrates.

According to **Powell**, clathrate compounds consist of atoms or molecules of one substance called the 'guest' held in the crystalline cages formed by the molecules of a second substance called the 'host'.

The only type of interaction in these "cage compounds" is the relatively weak Van der Waals' forces and there is no chemical bonding. It is not necessary that all the cavities in the host structure are filled. As a result, the clathrates are normally non-stoichiometric compounds.

Essential Conditions for Clathrate Formation

(a) The presence of cavities of appropriate size in the crystal lattice of the 'host'.

(b) Size of the 'guest' particle should be such as to fit in the cavities of the 'host' without bringing any atoms closer together than corresponding to the Van der Waals' radii of the atoms.

Stability of Clathrate Compounds

Clathrate compounds once formed are quite stable due to the following reasons :

(i) The 'guest' molecules tightly fit in the cavities of the 'host' molecules.

(ii) The 'guest' molecules within the cages are at a minimum potential energy.

The 'guest' can escape from the 'host' only when the forces holding the molecular cages together are overcome. This can be achieved by the following two methods :

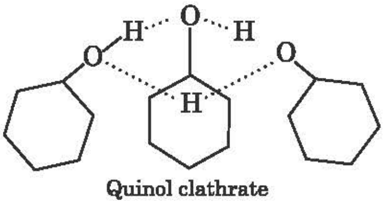
(i) By heating the crystals.

(ii) By dissolving them in a suitable solvent such as alcohol.

Q.9. Describe in brief the preparation and uses of clathrates.

Ans.

Preparation of Clathrates



Quinol clathrate

Clathrate compounds of argon, krypton and xenon have been isolated by locking up these gases in the cages of water, phenol or quinol. However, clathrate compounds of helium and neon have not yet been prepared because helium atoms are thought to be too small and difficult to deform or polarize as required by Van der Waals bonding to be imprisoned in the cages. The neon is borderline element and its clathrate could possibly be formed at pressures in excess of 160 atmospheres. It is predicted that in clathrate of neon, if formed, the neon atoms (being so small) will diffuse through the crystal from one cavity to another.

The other molecules to form clathrates with quinol are SO_2, O_2, H_2S and CH_3OH. During crystallisation, three molecules of quinol form a cup-shaped structure due to hydrogen bonding and two such cups give rise to a cage like structure for the guest molecule. The crystals are quite stable and exist for a pretty long time.

Uses of Clathrates

(i) Xenon-133 clathrate provides a compact source for gamma radiation.

(ii) Clathrates play an important role in some physiological actions, *e.g.*, it is thought that the anaesthetic action of xenon and many other anaesthetics is due to aqueous clathrate in physiologically strategic spots. When the anaesthetic is no longer administered, the clathrate equilibrium is destroyed, the clathrate decomposes and the consciousness returns.

(iii) Krypton-85 clathrate provides a safe and useful source of beta radiation which are useful for measuring thickness of gauges.

(iv) In the separation of noble gases. For example, neon can be separated from argon, krypton and xenon because neon is the only gas that does not form clathrates with quinol.

Q.10. Write a short note on charge transfer complex.

Ans.

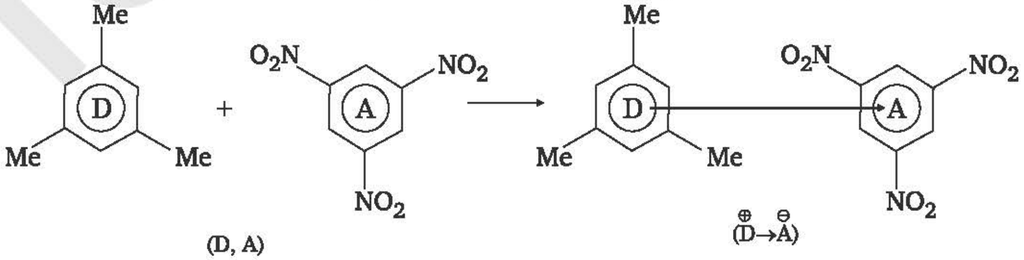
Charge Transfer Complexes

Molecular adducts formed by mixing an electron-rich molecule (called **donor molecule,** D) and an electron-defficient molecule (called **acceptor molecule,** A) in 1:1 ratio are termed as charge transfer complexes. A donor molecule is a molecule capable of donating either non-bonding or π-electrons. These complexes are considered to be hybrids of the following resonance forms :

$$D + A \rightleftharpoons \underset{(1)}{D \ldots\ldots\ldots A} \longleftrightarrow \underset{(2)}{\overset{\oplus\oplus}{DA}}$$

Form (1), being the major contributor, does not involve formal covalent bond and the binding forces between these molecules may be **weak coulombic forces.** A bonding of such type which results from attractive forces between donor and acceptor molecule is called **charge transfer interaction.**

Formation of the so called picrate by the action of picric acid and an aromatic hydrocarbon probably represents the most common example of such addition compounds. The nitro groups rather than a hydroxyl group are essential for the success of the reaction, as not only picric acid but other aromatic compounds such as 1, 3, 5-trinitrobenzene, form similar addition compounds. In these complexes the aromatic rings are held in parallel planes.



Charge transfer complex between picric acid and 1, 3, 5-trimethyl benzene.

The formation of charge-transfer complex is facilitated by the presence of electron-donating substituents in donor molecule and electron withdrawing substituents in acceptor molecule.

The distance between the donor and accepter molecules in charge transfer complexes is 3–3.5 Å. The extent of charge-separation in a charge-transfer complex is often reflected in ground state properties such as dipole moment. Charge transfer complexes display significant dipole moment.

Q.11. What is electromeric effect? Discuss in brief.

Ans.

Electromeric Effect

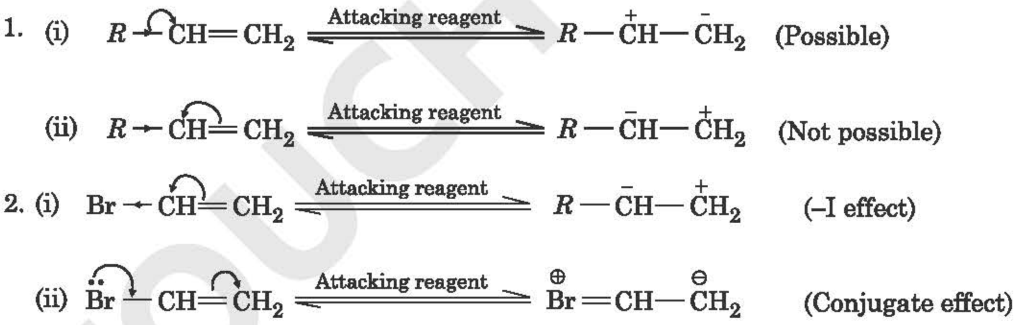
This is a temporary effect brought into play at the requirement of attacking reagent. In it a complete transfer of π-electron pair of double or triple bond to one of the atoms joined by the bond takes place. When multiple bond is present between two different atoms, electromeric shift towards more electronegative atom takes place.

$$>C=O \xrightleftharpoons{\text{Attacking reagent}} >\overset{+}{C}-\overset{-}{O}$$

When multiple bond is present between two similar atoms (For example, in alkenes and alkynes, multiple bond is present between two carbon atoms), then there are two possibilities :

Possibility (i) *Symmetric alkenes or Alkynes* : Here electromeric shift can take place in any direction.

Possibility (ii) *Asymmetric alkenes or Alkynes* : Here direction of shift of electrons is governed by the inductive effect or electromeric effect (conjugate effect) of the group present at doubly or triply bonded atom. Since conjugate effect is stronger, hence when both inductive as well as conjugate effects are operating in unsaturated molecule, conjugate effect usually overcome inductive effect. For example,



1. (i) $R \rightarrow CH=CH_2 \xrightleftharpoons{\text{Attacking reagent}} R-\overset{+}{C}H-\overset{-}{C}H_2$ (Possible)

(ii) $R \rightarrow CH=CH_2 \xrightleftharpoons{\text{Attacking reagent}} R-\overset{-}{C}H-\overset{+}{C}H_2$ (Not possible)

2. (i) $Br \leftarrow CH=CH_2 \xrightleftharpoons{\text{Attacking reagent}} R-\overset{-}{C}H-\overset{+}{C}H_2$ (–I effect)

(ii) $\ddot{B}r-CH=CH_2 \xrightleftharpoons{\text{Attacking reagent}} \overset{\oplus}{B}r=CH-\overset{\ominus}{C}H_2$ (Conjugate effect)

Since conjugate effect is stronger than (–*I*) effect hence electromeric shift (2)(ii) takes place.

There are two types of electromeric effects :

(a) **(+E) effect :** When complete transfer of π-electron pair takes place away from the atom or group at the requirement of attacking reagent.

$$\ddot{X}-CH=CH_2 \xrightleftharpoons{\text{Attacking reagent}} \overset{\oplus}{X}=C-\overset{\ominus}{C}-C$$

(b) **(–E) effect :** When complete transfer of π-electron pair takes place towards the atom or group at the requirement of attacking reagent.

$$Y=C-C=C- \xrightleftharpoons{\text{Attacking reagent}} \overset{\ominus}{Y}-C=C-\overset{\oplus}{C}-$$

Q.12. What is the difference between inductive and electromeric effect?

Ans. Differences between Inductive and Electromeric Effect

S.No.	Inductive effect	Electromeric effect
1.	It is shown by the compounds containing single bonds.	It is shown by the compounds containing double or triple bonds.
2.	It is a permanent effect and takes place due to the presence of an electron withdrawing or electron repelling group attached to one end of a saturated chain of carbon atoms.	It is a temporary effect and takes place when an attacking reagent attacks on the molecule containing a multiple bond.
3.	This effect involves a slight displacement of σ-electrons from one atom towards the other.	This effect involves the complete transfer of π-electrons of the multiple bond to one of the bonded atoms.
4.	The charges developed on the atoms of the chain are small fractional charges which decrease rapidly as one moves away from the electron withdrawing or electron repelling group.	The charge acquired by the atom that gains electrons is −1 while that acquired by the atom which loses electrons is +1.

Q.13. What is the difference between inductive and mesomeric effect?

Ans. Differences between Inductive and Mesomeric Effect

S.No.	Inductive effect	Mesomeric effect
1.	It occurs in the compounds containing single bonds.	It occurs in the compounds containing multiple bonds particularly in conjugated systems.
2.	It involves slight displacement of σ-electrons.	It involves the transfer of π-electrons.
3.	The charges developed on the atoms of the chain are partial and decrease rapidly on moving away from the electron withdrawing or electron-repelling group attached to the chain.	Due to complete transfer of π-electrons, the charges developed are full positive and negative. The terminal carbon bears almost the same charge as the first carbon atom of the chain.
4.	It is transmitted over a short distance and becomes almost negligible after third carbon of the chain.	In a conjugated system, it is transmitted over the entire molecule and suffers very little decrease in intensity.

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What are localised and delocalised chemical bonds? Give the difference between these two.

Ans. Localised and Delocalised Chemical Bonds

A chemical bond is a connection between two atoms. This connection occurs due to the overlapping of molecular orbitals. There are two major forms of bonds as localised and delocalised chemical bonds. Localised chemical bonds are the normal molecular orbital overlappings such as **sigma bonds** and **pi bonds**. However, delocalised chemical bonds are different. These bonds form when several localised bonds mix with each other. More details are below.

Localised Chemical Bonds : Localised chemical bonds are normal sigma and pi bonds or lone electron pairs that exist on a single atom. These bonds are concentrated on a limited region of a molecule. These regions have a concentrated electron distribution. In other words, the electron density of this region is very high.

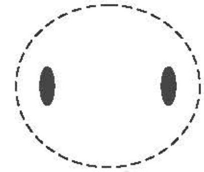


Fig. 1 : A sigma bond : A Localised chemical bond

A localised bond forms when two molecular orbitals of two separate atoms overlap with each other. Sigma bonds may form due to the overlap of two ***s*-orbitals**, two ***p*-orbitals** or *s-p* overlap.

Delocalised Chemical Bonds : Delocalised chemical bonds are the chemical bonds that do not associate with only a single atom but with several atoms or other chemical bonds. We call the electrons in these bonds as 'delocalised electrons'. Delocalization occurs in the conjugated pi system. A conjugated pi system has double bonds and single bonds in an alternating pattern.

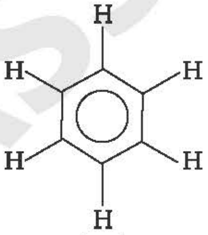
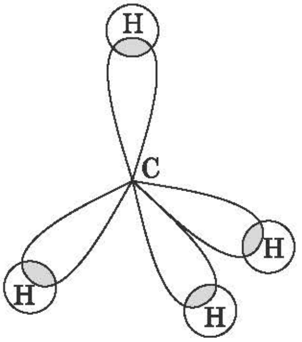


Fig. 2 : Delocalization of electrons

For example, the benzene ring has three single bonds and three double bonds in an alternating pattern. Each carbon atom in this ring has a *p*-orbital that does not undergo frontal overlapping. Therefore these *p*-orbitals can have side overlapping. This kind of overlapping is the delocalization. We can indicate this as two circles on the top of the benzene ring and the bottom of the ring. These electrons are free to move throughout the molecule because they do not have a permanent binding to a single atom or a covalent bond.



Consider methene molecule, there are four carbon-hydrogen sigma bonds.

These are all localized bonds since the positions of the overlapping orbitals are fixed. Now consider the case of 1, 3-butadiene. This is a conjugated diene.

All four carbon atoms in 1, 3-butadiene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with *s*-orbitals of the hydrogen atoms to form C—C and C—H σ bonds. Since the bonds result from the overlap of trigonal sp^2-orbitals, all carbon and hydrogen atoms lie in one plane.

Also each carbon atom in 1, 3-butadiene possesses an unhybridized *p* orbital. The *p* orbitals are perpendicular to the plane of σ bonds. The *p* orbital on C-2 can overlap with the *p* orbitals on C-1 and C-3. The *p* orbital on C-3 can overlap with the *p* orbitals on C-2 and C-4. That is, all four *p* orbitals overlap to form a large te molecular orbital (Fig. 3). Each pair of a electrons is thus attracted, not by two, but all four carbons.

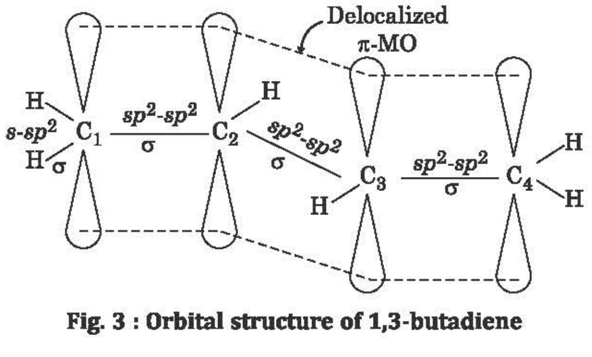
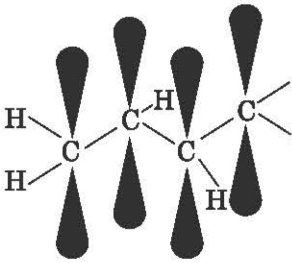
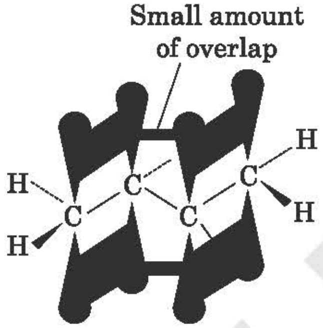


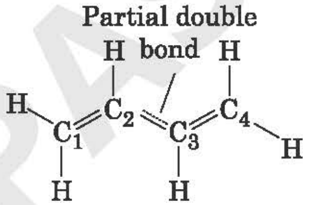
Fig. 3 : Orbital structure of 1,3-butadiene

The overlap of *p* orbitals of C-2 and C-3 in both directions, which allows the π electrons to be spread over a larger area, is referred to as delocalization. This delocalization of π electrons is responsible for greater stability of 1, 3-butadiene.

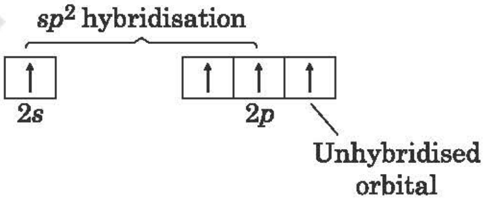
The C—C single bonds in 1, 3-butadiene are shorter (1.48 Å) than normal carbon-carbon single bonds. The C—C double bonds are longer (1.37 Å) than normal isolated carbon-carbon double bonds.







The delocalized molecular orbital contains four electrons. The central carbon-carbon single bond is shorter than the 1.54 Å bonds typical of alkanes because of its partial double bond character. The electrons forming two π bonds in the molecule of 1, 3-butadiene are thus delocalized chemical bonds.



Another example of delocalized bonds is provided by the structure of benzene. It has a hexagonal structure in which the six carbon atoms occupy the corners of a regular hexagon. All the carbon atoms are linked to each other by sigma bonds. Also each carbon is linked to one hydrogen by sigma bond. It may be noted that carbon atoms in benzene are sp^2 hybridised. Thus, all carbons lie in the same plane. There is one orbital in each carbon, which does not participate in hybridisation.

There are six such unhybridised orbitals these can overlap laterally in pairs to form three to bonds as shown in Fig. 4 (a) and (b). But the same situation exists as in 1, 3-butadiene. All the six orbitals overlap together forming a circular electron cloud above and below the benzene ring (Fig. 4).

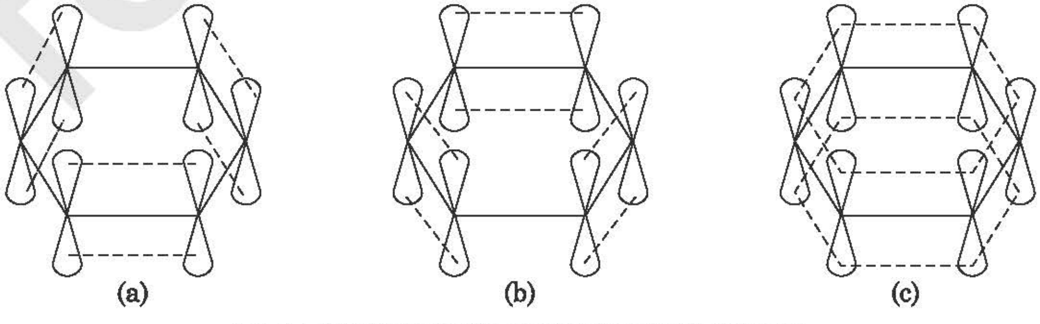

(a) (b) (c)

Fig. 4 : Overlapping of orbitals in benzene molecule

Difference Between Localised and Delocalised Chemical Bonds

Localised chemical bonds are normal sigma and pi bonds or lone electron pairs that exists on a single atom. These bonds form due to frontal overlapping between *s* orbitals, *p* orbitals or *s* and *p* orbitals. Moreover, these electrons are limited to a particular region between two separate atoms. Delocalised chemical bonds are the chemical bonds that do not associate with only a single atom but with several atoms or other chemical bonds. These bonds have electrons spread throughout the molecule that are free to move. These bonds form due to side overlapping of *p* orbitals. This is the main difference between localised and delocalised chemical bonds.

Localised vs Delocalised Chemical Bonds

Basis	Localised chemical bonds	Delocalised chemical bonds
Definition	Normal sigma and pi bonds or lone electron pairs which exists on a single atom.	Chemical bonds that do not associate with only a single atom but with several atoms or other chemical bonds.
Electrons in the Chemical Bond	Have localised electrons which are limited to a concentrated region between two separate atoms.	Have delocalized electrons which are free to move throughout the molecular structure.
Formation of the Bond	Form due to frontal overlapping of molecular orbitals.	Form due to side overlapping of molecular orbitals.

Q.2. What is hyperconjugation? Describe its applications.

Ans. Hyperconjugation (Baker-Nathan Effect)

Delocalization of electrons through overlap between the *p*-orbital occupied by the odd electron and adjacent σ orbitals of the alkyl group.

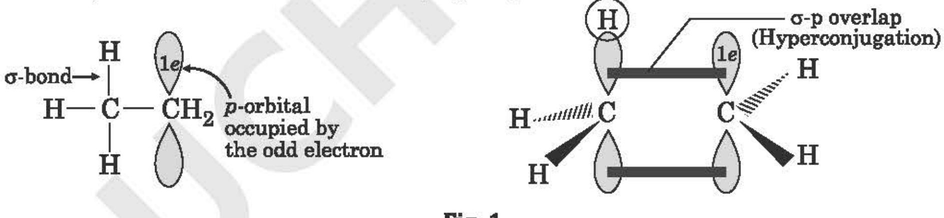


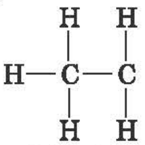
Fig. 1

Through this overlap individual electrons can to an extent help bind together three nuclei, two carbons and one hydrogen. This kind of delocalization involving σ bond orbitals is called **hyperconjugation.**

In resonance language, it is no-bond resonance.

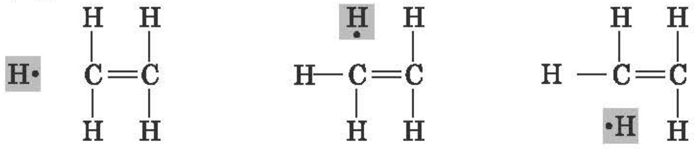
For example,

Ethyl radical



$$\begin{array}{ccccc} & & H & & H\\ & & | & & |\\ H & - & C & - & C\\ & & | & & |\\ & & H & & H \end{array}$$

has three hyperconjugation structures with 6 k cal/mol as resonance energy.



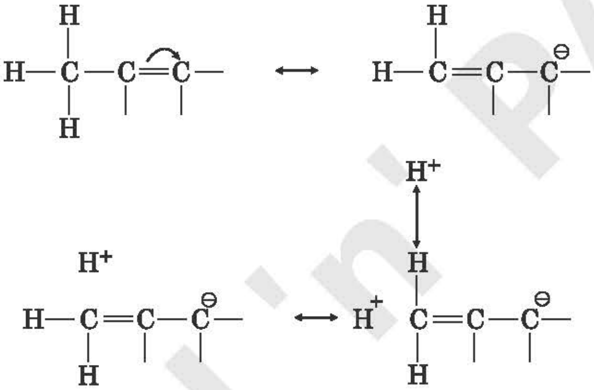
$$H\cdot \quad \begin{array}{ccc} H & & H\\ | & & |\\ C & = & C\\ | & & |\\ H & & H \end{array} \qquad \begin{array}{ccccc} & & \dot{H} & & H\\ & & & & |\\ H & - & C & = & C\\ & & | & & |\\ & & H & & H \end{array} \qquad \begin{array}{ccccc} & & H & & H\\ & & | & & |\\ H & - & C & = & C\\ & & & & |\\ & & \cdot H & & H \end{array}$$

with 6 k cal/mol as resonance energy

Types of Hyperconjugation

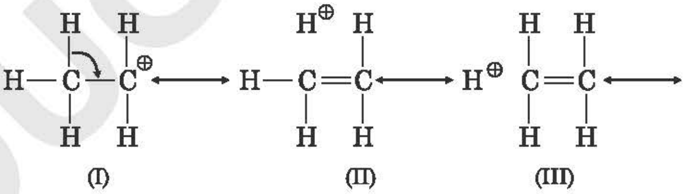
(a) **Sacrafacial hyperconjugation :** The essential condition is the attachment of alkyl group to double bond or triple bond.

Carbon atom of alkyl group attached to double bond must contain atleast one hydrogen atom in hyperconjugation.



It involves a short of sacrifice of bond and hence the name sacrafacial.

(b) **Isovalent hyperconjugation :** This kind of hyperconjugation involves no sacrifice of bonds. Ethyl radicals have the same number of real bonds as the classical structure.



Applications of Hyperconjugation

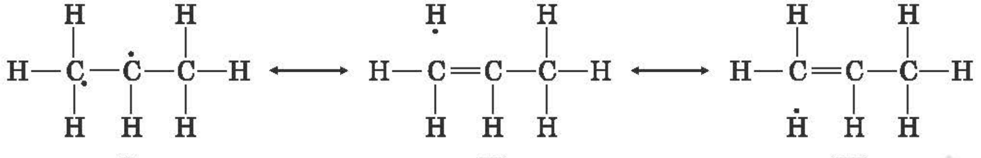
The concept of hyperconjugation is quite useful in explaining relative stabilities of a number of species such as alkyl free radicals, carbocations and alkenes. These are briefly discussed as follows:

1. **Relative stabilities of alkyl free radicals :** The order of the relative stabilities of different alkyl free radicals is :

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

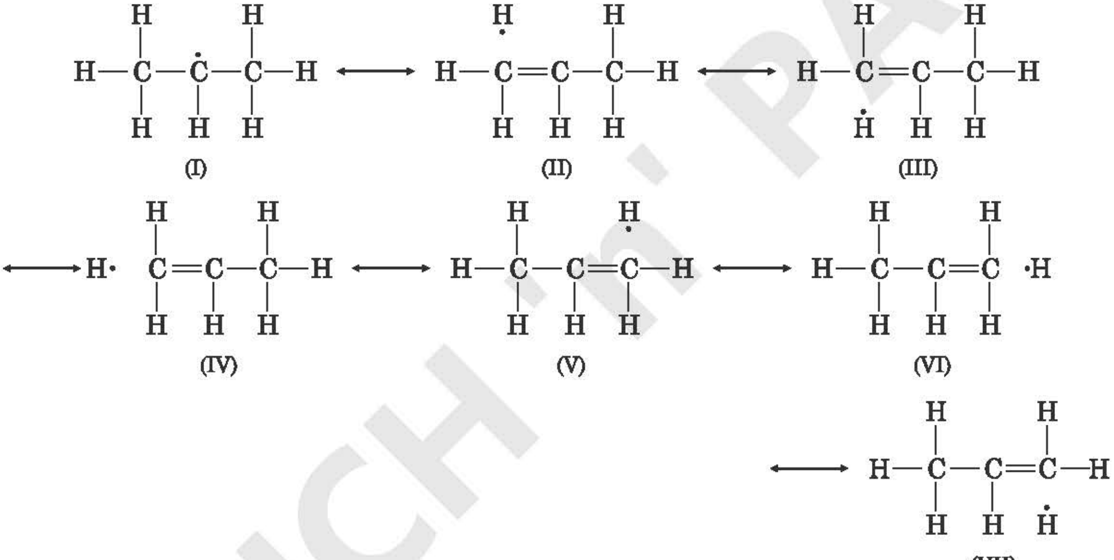
Tert-butyl	Isopropyl	Ethyl	Methyl
(3°)	(2°)	(1°)	(1°)

Ethyl free radical is regarded as a hybrid of four contributing structures.



But there is no possibily of any hyperconjugation in methyl free radical. Therefore, ethyl free radical is more stable than the methyl free radical.

In isopropyl free radical, there are two methyl groups attached to the carbon atom which has single electron. As a result, six contributing structures in addition to normal structure are possible as shown below :



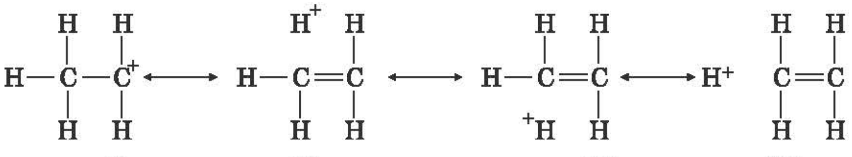
Similarly, nine contributing structures are possible for the tertiary butyl free radical in addition to its normal structure. Therefore, it is still more stable and thus, the order of the relative stabilities of the different alkyl free radicals can be explained.

2. **Relative stabilities of alkyl carbocations :** The order of relative stabilities of the alkyl carbocations is

$$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$$

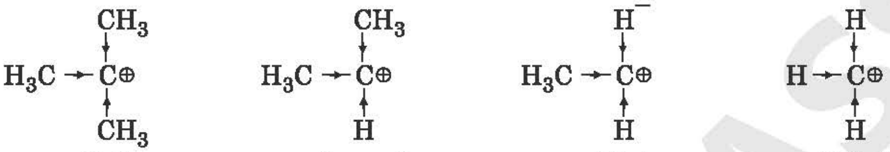
Tert-butyl Isopropyl Ethyl Methyl

and the order is the same as in case of free radicals. This can also be explained with the help of hyperconjugation. The ethyl carbocation (primary) has three contributing structures in addition to its normal structure based upon hyperconjugation.



It is more stable than methyl carbocation where no resonance is possible. Similarly, the contributing structures in isopropyl carbocation and tertiary butyl carbocation are six and nine respectively in addition to the normal structure. Hence these are more stabilised and relative order of their stabilities is justified.

The order of the relative stabilities of the different alkyl carbocations can also be explained with the help of inductive effect (+*I* effect).

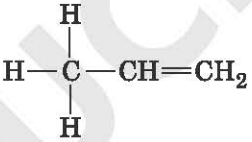

Tertiary butyl Isopropyl Ethyl Methyl

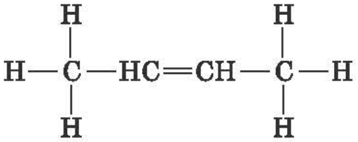
Because of the +*I* effect, the alkyl group will tend to increase the electron density on positively charged carbon atom neutralising its +ve charge to some extent. As the reactivity of carbocation is due to the positive charge on it, the reactivity will tend to decrease and the stability will correspondingly increase. Thus, greater the number of the alkyl groups present, greater will be the stability of carbocation and lesser will be the reactivity. Thus, the relative stabilities of different alkyl carbocations can be explained.

3. **Relative stabilities of alkenes :** The order of the relative stabilities of different alkenes is :

$$R_2C=CR_2 > R_2C=CHR > RCH=CHR > RCH=CH_2 > CH_2CH_2$$

This can be explained on the basis of hyperconjugation. The presence of alkyl group (say methyl group) on the double bonded carbon atom is likely to increase the number of contributing structures due to hyperconjugation.


Propene
(Three contributing structures)


2-butene
(Six contributing structures)

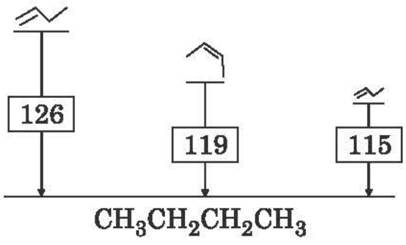
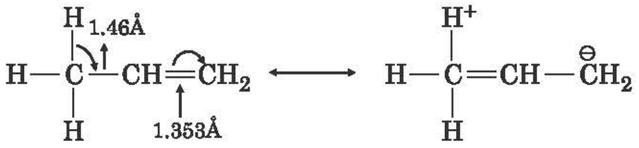


Fig. 2 : Stability of isomeric alkenes

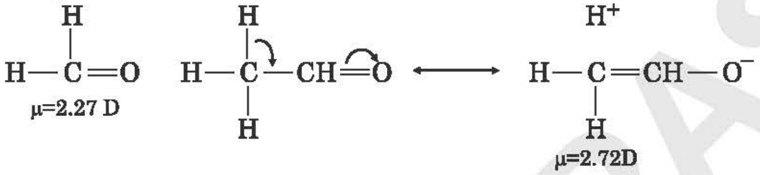
Thus, greater the number of the contributing structures, greater will be the stability of the alkene.

4. **Bond length :** Hyperconjugation, like conjugation and resonance, also affects bond length.

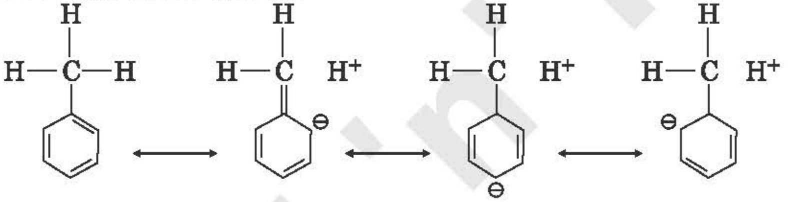


Bond length in propene is 1.46 Å in contrast to normal 1.54 Å (in propane). It is due to the partial double bond character acquired and hence a little shorter.

5. **Dipole moment :** Since hyperconjugation causes the separation of charges, it also affects the dipole moment in the molecule.



6. Ortho-para directiong property of methyl group in toluene is partly due to +*I* effect and partly due to hyperconjugation.



Q.3. What is inductive effect? Describe the applications of inductive effect.

Ans.

Inductive Effect

It is defined as the permanent displacement of electrons forming a covalent bond towards the more electronegative element or group.

Assuming electronegativity of $X > C > Y$ than the electron pair forming the $C—X$ bond is somewhat more attracted towards the atom X with the result X attains a partial negative charge (–δ) while the C attains a partial positive charge C (+δ) :

$$\therefore \quad C:X \quad \Rightarrow \quad \overset{\delta+}{C} \longrightarrow \overset{\delta-}{X}$$

Similarly, the electron pair forming the $C—Y$ bond can be represented as

$$C:Y \quad \Rightarrow \quad \overset{\delta-}{C} \longleftarrow \overset{\delta+}{X}$$

Inductive effect is represented by the symbol → the arrow pointing towards the more electronegative element or group of atoms.

It is always transmitted along a chain of carbon atoms but the extent of partial charge keep on decreasing away from polar bond and at third or fourth carbon atom it is almost zero for all practical purposes. This process of electron shift along a chain of atoms due to the presence of some polar bond in the molecule is termed as **inductive effect**.

It causes certain degree of polarity in the bond which in turn renders the bond much more liable to be attacked by other charged atoms or group.

Some atoms or groups exert an electron attracting inductive effect, others give rise to an electron repelling effect. For comparing the relative inductive effects of various groups, hydrogen is taken as standard.

Electron attracting (–*I* effect) is exerted by those atoms or groups which have greater electron attracting power than hydrogen.

Some of the groups in order of decreasing (–*I*) effect are :

$$^{+}NMe_3 > {}^{+}NH_3 > NO_2 > CN > COOH > F > Cl > Br > I > OAr > COOR > OR > OH > C_6H_5 > H$$

Electron repelling (+*I effect*) is exerted by those atoms or groups which have lesser electron attracting power than hydrogen. Some of the groups in order of decreasing (+*I*) effect are :

$$C_6H_5O^- > COO^- > CR_3 > CHR_2 > CH_2R > CH_3 > H$$

Applications of Inductive Effects

1. **Dipole moment :** Greater the inductive effect, more will be the dipole moment in the molecule since inductive effect leads to a dipolar character in the molecule.

   For example : Dipole moments

   $$CH_3—F > CH_3—Cl > CH_3—Br > CH_3—I$$

   Since the –*I* effect of F > Cl > Br > I.

2. **Bond length :** Greater the –*I* effect, smaller will be the bond length in the molecule since inductive effect leads to ionic character in the bond.

   For example, Bond length increases in the order

   $$CH_3F < CH_3Cl < CH_3Br < CH_3I$$

   Since the – *I* effect decreases in the order F > Cl > Br > I.

3. **Reactivity of alkyl halides :** Due to the presence of C—*X* polar bond in alkyl halides, alkyl halides are more reactive than the corresponding alkanes.

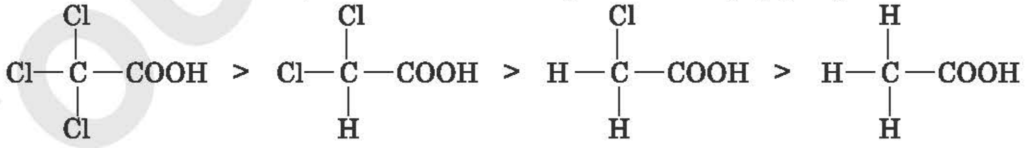
   Reactivity increases with increase of (+*I*) effect. We know (+*I*) effect of

   $$R_3C > R_2CH > RCH_2$$

   Hence reactivity of $R_3C—X > R_2CH—X > RCH_2—X$.

   Reactivity is directly related to C—*X* bond polarity.

4. **Strength of carboxylic acids :** Acidity of carboxylic acid is due to the ease with which it ionises to give proton and this ease increases with the strength of (–*I*) group attached at the a carbon of carboxylic acid or increasing number of (–*I*) groups.

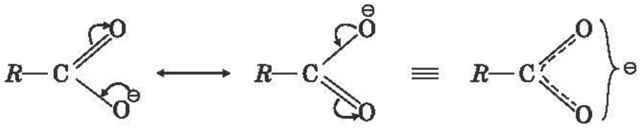


$$Cl—\overset{Cl}{\underset{Cl}{C}}—COOH > Cl—\overset{Cl}{\underset{H}{C}}—COOH > H—\overset{Cl}{\underset{H}{C}}—COOH > H—\overset{H}{\underset{H}{C}}—COOH$$

It is to be noted that carboxylic acids are acids because they release H^+ ions in solution. This proton release depends up –*I* effect of oxygen.

$$R—\overset{O}{\overset{\|}{C}}—O\leftarrow H \Rightarrow R—\overset{O}{\overset{\|}{C}}—O^- + H^+$$

are resonance stabilization of carboxylate anion.

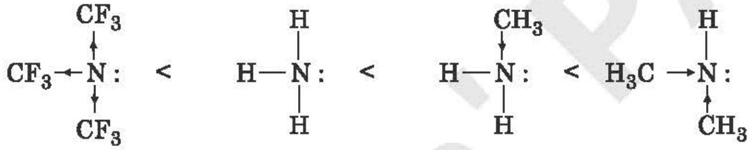


The (–*I*) effect of oxygen can be increased or decreased depending on the nature of *R*-group. If the *R*-group is also having (–*I*) effect, the net result is increase in acidity and *vice-versa*.

5. **Basic strength of amines :** Amines are basic because they are electron pair donor or they can accept proton. The readiness with which this happens determines the relative strength of amines. Relative basic strength of amines depends on inductive effect, steric effect and stabilization of cation by hydration. Let us discuss here only the inductive effect. Groups which have (+*I*) effect, when attached to nitrogen atom, make it simpler for the lone pair of electrons on nitrogen to be easily available hence they increase the basic strength.

   But the groups with (–*I*) effect make it difficult for the easy availability of lone pair of electrons on nitrogen hence they decrease the basic strength.

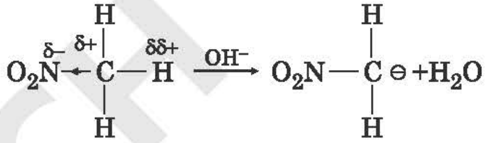
   Hence, increasing order of basic strength is as follows:



$$\mathrm{CF_3\leftarrow\underset{\underset{CF_3}{\downarrow}}{\overset{\overset{CF_3}{\uparrow}}{N}}:} \;<\; \mathrm{H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}:} \;<\; \mathrm{H-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{\downarrow}}{N}}:} \;<\; \mathrm{H_3C\rightarrow\underset{\underset{CH_3}{\uparrow}}{\overset{\overset{H}{|}}{N}}:}$$

Note : Inductive effect is always present in a molecule. it may be increased, temporarily and prior to some reactions or change by the approach of a charged ion (attacking reagent). Such a temporary effect is known as **inductometric effect.** This effect is time dependent and it always aids the reaction, never inhibits it.

For example,



$$\mathrm{\overset{\delta-}{O_2N}\leftarrow\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{\overset{\delta+}{C}}}-\overset{\delta\delta+}{H}} \xrightarrow{OH^-} \mathrm{O_2N-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\ominus + H_2O}$$

Q.4. What do you understand by mesomeric effect or resonance? Describe the applications of mesomeric effect.

Ans.

Mesomeric Effect or Resonance

Mesomeric effect is also a permanent effect. In this electrons are transferred :

(i) from a multiple bond to an atom or

(ii) from a multiple bond to a single covalent bond or

(iii) from an atom with lone pair (s) of electrons to the adjacent single covalent bond.

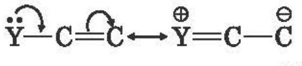
Mesomeric effect takes place in unsaturated and especially conjugated system *via* their π -orbitals (π-bonds). In this effect, complete charge separation takes place and full charges are created.

Types of Mesomeric Effect

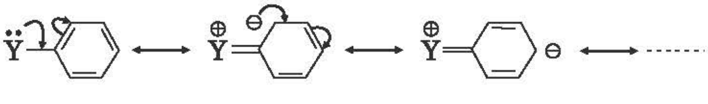
It is of two types :

1. **+M :** When the transference of electron pairs is away from the atom or group.

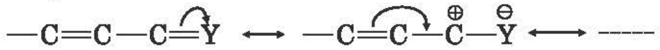
   For example,

(i) 

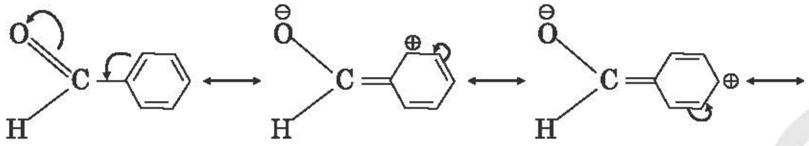
$$\mathrm{\ddot{Y}-C=C \longleftrightarrow \overset{\oplus}{Y}=C-\overset{\ominus}{C}}$$

(ii) 

2. **– M :** When the transference of electron pair is towards the atom or group. For example,

(i) 

$$-C=C-C\overset{\curvearrowright}{=}Y \longleftrightarrow -C=C-\overset{\oplus}{C}-\overset{\ominus}{Y} \longleftrightarrow \text{-----}$$

(ii) 

This phenomenon in which two or more structures, involving identical position of atoms can be written for a particular molecule, is called **resonance**. The various structures are called as **resonating** or **contributing** structures. It is to be noted that resonating structures have no real existence. They are useful because they allow us to describe molecules, radicals or ions for which a single lewis structure is not sufficient. The actual structure lies somewhere in between the various possible resonating structures and is called **resonance hybrid**. The difference in energy between the resonance hybrid and the most stable resonating structure is called as **resonance energy**.

Applications of Mesomeric Effects

1. **Dipole moment :** Dipole moment of $CH_3-CH_2-Cl > CH_2=CH-Cl$

   Due to resonance in vinyl chloride

   $$CH_2=CH-\ddot{C}l \longleftarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{C}l$$

2. **Bond length :** Benzene (C_6H_6) has three double bonds and three single bonds within the ring. So if it is written as 

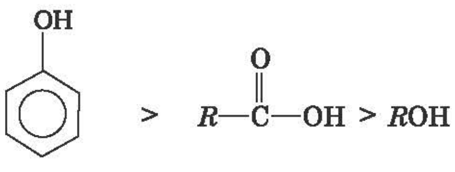
   It appears that there should be two different types of bond lengths corresponding to single (1.54 Å) and double bond (1.33 Å).

   But the fact is that all the bond lengths in the benzene ring are equal. This can be explained by writing following resonating structures of benzene :

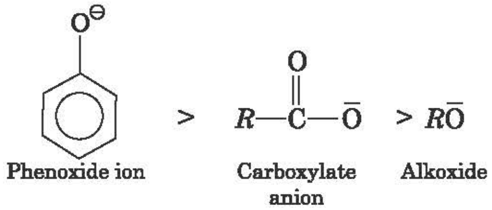
   

   With the net result, resonance hybrid has the structure where the position of single and double bonds are delocalised and hence each bond has partial single and partial double bond character and hence equal bond length.

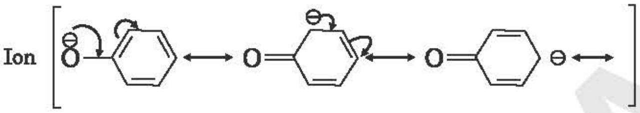
3. **Strength of acids :** Acidic strength of :

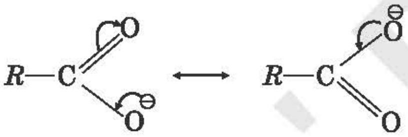
   because the stability of corresponding conjugate bases is in the order



This is due to the more resonance stabilisation of phenoxide ion.



Compared to carboxylate anion.

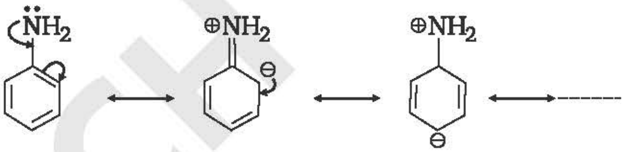


Alkoxide ion is not stabilized at all by resonance.

4. **Strength of bases :** Basic strength of : $RNH_2 > NH_3 > C_6H_5NH_2$.

   It is due to $(+I)$ effect of R in $R \rightarrow\!\!- \ddot{N}H_2$. Thus lone pair is more easily available.

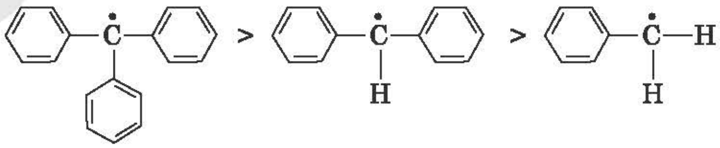
   But in C_6H_5—NH_2, Phenyl group has (–M effect).



   Hence the lone pair present at the nitrogen in aniline is delocalised in the ring by resonance, hence, it is not free for donation leading to decrease of basic strength of aniline.

5. **Stability of intermediates :** Greater the number of resonating structures for a given intermediate, more will be its stability.

   For example, stability of carbon free radicals is in the order :



❑

UNIT-V

Mechanism of Organic Reactions

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. What are reaction intermediates?

Ans. The fission of a covalent bond leads to the formation of certain.

Q.2. What is carbocation or carbonium ion?

Ans. Carbocations or carbonium ions are the species in which the central carbon atom carries a positive charge. They formed by the heterolytic fission of a C—X bond, where X is more electronegative than carbon.

Q.3. What are carbanions?

Ans. Carbanions are the species in which the central carbon atom carries a negative charge. They are formed by the heterolytic fission of a C—Y bond, where Y is less electronegative than carbon.

Q.4. Write the stability order of carbanions.

Ans. The stability of carbanions follows the order $1° > 2° > 3°$.

Q.5. What are free radicals?

Ans. A free radical is an atom or group of atoms having an unpaired electron. Free radical are produced on account of the homolytic fission of a covalent bond. These are short lived and highly reactive species.

Q.6. What are alkyl free radicals?

Ans. Alkyl free radical are planar species. The central carbon atom present in them is in a state of sp^2 hybridisation. The unpaired electron is present in the unhybridised $2p$ orbital of the central carbon atom.

Q.7. What are carbenes?

Ans. Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atom or groups and carries a lone pair of electrons.

Q.8. What are electrophiles?

Ans. The electrophilic reagents or electrophiles are those species which possess an affinity for electrons. They possess a deficiency of electrons and attack on electron rich centres in chemical reactions.

Q.9. What are nucleophiles?

Ans. The nucleophilic reagents or *nucleophiles* are those speciess which possess an affinity for the positive charge. They are electron rich species and possess at least one lone pair of electrons.

Q.10. Give some examples of electrophiles.

Ans. Examples of electrophiles are as follows :

1. **Positively charged electrophiles :** $H^+, H_3O^+, \overset{+}{N}O, \overset{+}{N}O_2, \overset{+}{Cl}, \overset{+}{Br}, I^+, C_6H_5N_2^+$ etc., and all carbocations.
2. **Neutal electrphiles :** BF_3, $AlCl_3$, free radical, carbenes, nitrenes, etc. Electrophiles act as *Lewis acids.*

Q.11. Give some examples of nucleophiles.

Ans. Examples of nucleophiles are as follows :

1. **Nagatively charged nucleophiles :** OH^-, OR^-, CN^-, H^-, Cl^-, Br^-, I^- etc., and all carbanions.
2. **Neutral nucleophiles :** $H-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-H$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-H$, $R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-R$, $R-\overset{\bullet\bullet}{N}H_2$, $\overset{\bullet\bullet}{N}H_3$, etc. Nucleophiles act as Lewis bases.

Q.12. Pick up from the following, the electrophiles and nucleophiles :

$$AlCl_3, PH_3, HNO_3, R_3N$$

Ans. **Electrophiles :** $AlCl_3$, HNO_3.

Nucleophiles : PH_3, R_3N.

Q.13. Pick up from the following, the electrophiles and nucleophiles :

$$CN^-, BF_3, NH_3, ROH, SnCl_4, H_3O^+, AlCl_3, SO_3$$

Ans. **Electrophiles :** BF_3, $SnCl_4$, SO_3, H_3O^+, $AlCl_3$.

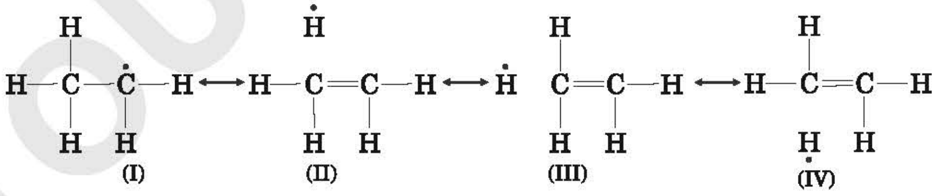
Nucleophiles : NH_3, ROH, CN^-.

Q.14. Arrange the following free-radicals in increasing order of stability and explain your answer.

$$\dot{C}_2H_5, (C_2H_5)_2\dot{C}(C_2H_5)_2(C_2H_5)_2\dot{C}H, \dot{C}H_3$$

Ans. The order of stability can be given considering the hyperconjugation phenomenon.

(i) Ethyl radical is a hybrid of four resonating structures.



Q.15. Which of the two, single and triplet carbene is more stable and why?

Ans. Triplet carbenes are more stable than singlet carbenes because two unhybridised *p*-orbitals contain one electron each while unshared pair of electrons in present in the third sp^2 hybrid orbital and the unhydridised *p*-orbital is empty.

Q.16. Arrange the following carbocations in the order of increasing stability :

$$C_6H_5CH_2^+, (C_6H_5)_2CH^+, (CH_3)_3C^+, (CH_3)_3CH^+$$

Ans. $(C_6H_5CH_2^+ < (C_6H_5)_2\ CH^+ < (CH_3)_2\ \overset{+}{C}H < (CH_3)\overset{+}{C}$

Q.17. Mention the methods by which you can infer that a particular reaction involves a free radical intermediate or not.

Ans. (i) Formation of free radicals is favoured by the presence of UV light, heat and organic peroxides.

(ii) Free radicals are paramagnetic due to the presence of unpaired electrons.

(iii) Reactions involving free radicals widely occur in the phase.

Q.18. Order of stability of carbocation is as under. Explain.

$$\underset{\text{(I)}}{(C_6H_5)_3\overset{+}{C}} > \underset{\text{(II)}}{(C_6H_5)_2\overset{+}{C}H} > \underset{\text{(III)}}{C_6H_5\overset{+}{C}H_2}$$

Ans. Carbocation (I) gives the maximum number of resonating structures, as this is linked to three benzene rings, hence this will have maximum stability. The order of stability in decreasing order is :

I > II > III

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What is homolytic fission of an organic compound?

Ans.

Homolytic Fission

When a covalent bond breaks up in such a way that each atom forming the covalent bond takes away one electron of the shared pair, the cleavage of bond is called homolytic fission or symmetrical fission.

$$A\bullet \,\vdots\, \bullet B \xrightarrow{\text{Homolytic fission}} \underset{\text{Free radicals}}{A^\bullet + B^\bullet}$$

The homolytic fission of a covalent bond leads to the formation of atoms or group of atoms having unpaired electrons. The atoms or groups of atoms containing an unpaired electron formed by the homolytic fission a covalent bond are termed as free radicals. The homolytic fission of a covalent bond is favoured by ultraviolet radiation, high temperature and the presence of organic peroxides.

Q.2. What is heterolytic fission of an organic compound?

Ans.

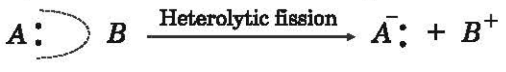
Heterolytic Fission

When a covalent bond breaks up in such a way that both the electrons belonging to the shared pair are taken away only by one of the atoms forming the covalent bond, the cleavage of bond is called heterolytic fission or unsymmetrical fission. The atom taking away both the shared electrons is obviously more electronegative.

For example, if atom *B* is more electronegative as compared to *A*, the heterolytic fission of bond *A*—*B* takes place as follows.

$$A \; :B \xrightarrow{\text{Heterolytic fission}} A^+ + :B^-$$

If *A* is more electronegative, the bond fission will take place as follows.



$$A: \; B \xrightarrow{\text{Heterolytic fission}} \overset{-}{A}: + B^+$$

The heterolytic fission of a covalent bond leads to the formation of charged species, *i.e.*, cations and anions. It usually occurs in the polar molecules and is favoured by polar solvents.

Q.3. Write a short note an electrophillic reagents or electrophiles.

Ans.

Electrophilic Reagents or Electrophiles

The electropilic (electro : electron, philic : loving *i.e.*, electron loving) reagents or electrophiles are those species which possess an affinity for electrons. These reagents possess a deficiency of electrons and therefore in chemical reactions they attack on those centres which are rich in electrons.

Electrophilic reagents possess an electron dificient atom or centre. This is why they have lust for electrons and attack at electron rich centres. Electrophilic reagents are of following two types :

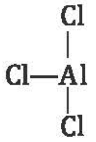
1. **Positively charged electrophiles :** Positively charged ions and carbocations possess a deficiency of electrons and therefore act as electrophiles. Some important ones are given below.

   H^+, H_3^+O, $\overset{+}{N}O$, $\overset{+}{N}O_2$, Cl^+, Br^+, I^+, $C_6H_5\overset{+}{N}_2$ (diazonium ion), RCH_2^+ (1° carbocations), $R_2\underset{+}{C}H$ (2° carbocations), $R_3\underset{+}{C}$ (3° carbocations) etc.

2. **Neutral electrophiles :** Some neutral species which possess a deficiency of electron act as neutral electrophiles. For example,

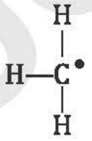
   (a) Species like BF_3, $AlCl_3$ etc., in which the central atom has only six electrons :

(Boron has 6 electrons in the valence shell)

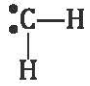


(Al has 6 electrons in the valence shell)

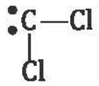
   (b) Free redicals, carbenes and nitrenes



Methyl free radical (carbon has 7 electons)



Methylene carbene (6 electrons)



Dichloro carbene (6 electrons)

Nitrene (6 electrons)

It is to be noted that each free radical is short of one electron while carbenes and nitrenes are short of pair of electrons.

Thus, both positively charged and neutral electrophiles are short of a pair of electrons (except free radicals which are short of 1 electron only). This is why they have a strong tendency to attack at electron rich centres and behave as **Lewis acids**. They always attack the substrate molecule at the site of highest electron density.

Q.4. Write a short note on nucleophilic reagent or nucleophiles.

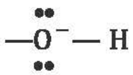
Ans. Nucleophilic Reagents or Nucleophiles

The nucleophilic (*nucleo* : nucleus, *philic* : loving *i.e.*, nucleus loving) reagents or nucleophiles are those species which possess an affinity for the positive charge. The nucleophiles are electron rich species and possess at least one lone pair of electrons. Therefore, in chemical reactions, they attack at those centres which are deficient in electrons. Nuclephilic reagents are of following two types :

1. **Negatively charged nucleophiles :** The species having an available electron pair and a negative charge act as negatively charged nucleophiles. For example,

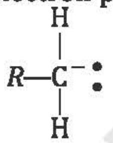
   OH^-, OR^-, CN^-, H^-, Cl^-, Br^-, I^-, RCH_2^-, R_2CH^-, R_3C^-, $RCOO^-$ etc.

   These speices possess an available electron pair along with a negative charge, *e.g.*,



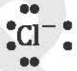
$-\ddot{\underset{..}{O}}^- - H$

(Hydroxyl ion)



$R-\overset{H}{\underset{H}{C}}^-:$

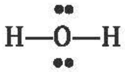
(Carbanion)



$:\ddot{\underset{..}{Cl}}^-:$

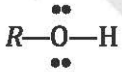
(Chloride ion)

2. **Neutral nucleophiles :** In some neutral molecules such as H_2O, $R—OH$ (alcohlos), $R—O—R$ (ethers), NH_3 $R—NH_2$ (amines). etc, the hetero atom possesses one or more lone pair of electrons.



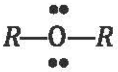
$H-\ddot{\underset{..}{O}}-H$

(Water)



$R-\ddot{\underset{..}{O}}-H$

(Alcohol)

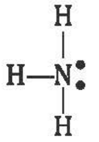


$R-\ddot{\underset{..}{O}}-R$

(Ether)

$R-\ddot{N}H_2$

(Amine)



$H-\overset{H}{\underset{H}{N}}:$

(Ammonia)

Such molecules are able to donate a lone pair at electrons to an electron deficient centre and therefore act as nucleophiles. Thus, both negatively charged and neutral nuclephiles possess lone pair of electron and can doname it to an electron deficient species. Therefore, in chemical reactions, they behave as **Lewis bases** and attack the substrate molecule at the site of lowest electron density.

Q.5. What is the difference between electrophiles and nucleophiles?

Ans. The main differences between nucleophiles and electrophiles are given below :

S.No.	Electrophiles	Nucleophiles
1.	Electron deficient,	Electron rich,
2.	Usually positively charged,	Usually negatively charged,
3.	Possesses an empty orbital to receive the electron pair from the nucleophile,	Possesses unshared pair of electrons which are not firmly held to the nucleus,
4.	Attack on electron rich centres,	Attack on electron deficient centres,
5.	**Examples :** NO_2^+, Br^+, BF_3, $FeCl_2$, SO_3, $SOCl_2$ etc.	**Examples :** OH^-, OCH_3^-, NH_3, H_2O etc.

SECTION-C LONG ANSWER TYPE QUESTIONS

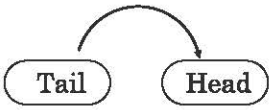
Q.1. What do you understand by curved arrow notations. Describe the detail.

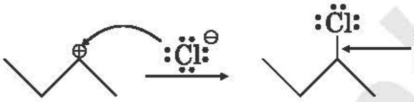
Ans.

Curved Arrow Notation

Curved arrows are very important in organic chemistry and using them correctly is essential in mastering the subject. In fact, it is like the operating system of organic chemistry, so the sooner you master the principle behind it, the easier it will be for you to understand many concepts in organic chemistry.

Every curved arrow has a head and a tail for showing the flow of electrons from high electron density to a low electron density center. The arrow must start from the middle of a lone pair or a covalent bond. For example,





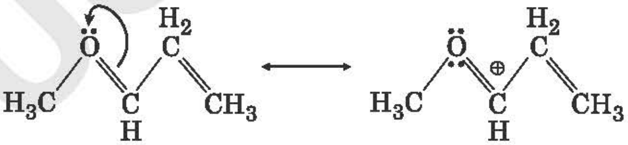
New bond formed by the Cl electrons

In this reaction, the electrons move from the Cl to the carbon and as a result, a new bond is formed. In the next example, the curved arrow shows the movement of the electron pair shared between the carbon and Br (that is from the C—Br bond) to the Br :

Breaking the bond, giving the e^- pair to Br

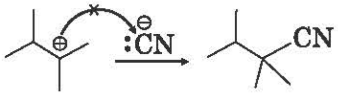
Therefore, this represents the breaking of the σ-bond.

If we started the arrow from a π bond, then that would indicate breakage of the π bond. For example :

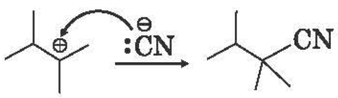


The key observation here is that curved arrows showed the flow of electrons. And that is the first and most important thing you need to remember about curved arrows :

Curved arrows show movement of electrons. Therefore, any curved arrow mechanism starts from a lone pair of electrons or a covalent bond. Do not start them from a positive charge or a plain atom with no lone pairs :

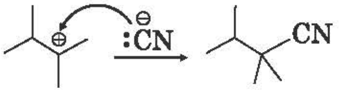


Wrong-arrow cannot start from a (+) charge



(✓) Right arrow from a lone pair

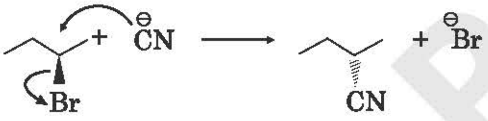
Starting from a negative charge is also acceptable.



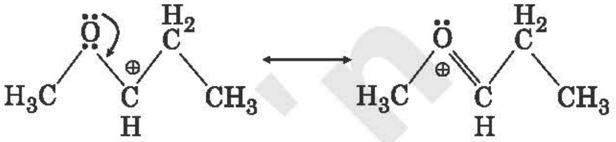
(✓) You can start arrow from (-) charge, it presumes moving the lone pair

Curved arrows in Resonance Structures

There are two main areas where curved arrows are used. The first one is their use is resonance structures and the second is their use in demonstrating the mechanisms of organic reaction. The big difference between these two is that in resonance structures the connectivity of atoms stays the same. This means that resonance structures represent the same entity only with different electron distribution.



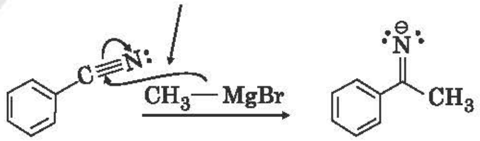
Chemical reaction : Connectivities of atoms change



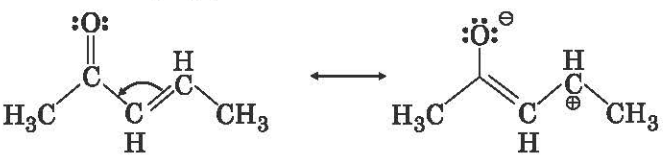
Resonance structures : Connectivities not changed

In fact, even the electrons do not move in resonance structures and we are simply showing them as such to keep track and explained certain properties and reactivity of compounds.

The main implication of the fact that resonance structures represent the same molecule/ion is that you cannot break any σ bonds as this would change the connectivity of atoms, hence different molecules would form. So, when initially we said that curved arrows must start either from lone pair of electrons or covenant bond, this statement is narrowed down for resonance structures : Curved arrows in resonance structures must start either from lone pair or π bonds.



Single (σ) bonds can break in reactions

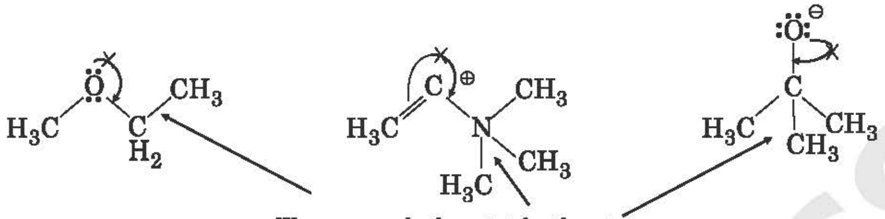


Only π bond can break in resonance

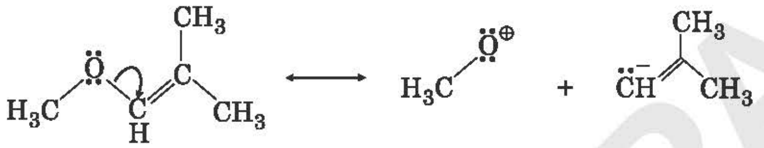
In general, the following two rules must be followed when drawing resonance structures :

(i) Do not exceed the octet on 2nd-row elements.

(ii) Do not break single bonds.



Wrong exceeds the octet for the atom



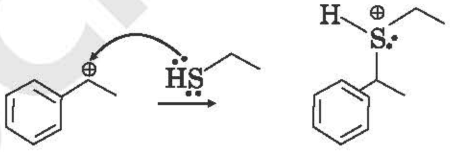
Wrong : breaking a single bond is not allowed in resonance structures

Curved Arrows in Organic Reaction Mechanisms

Curved arrows are a formal notation to help us understand the electron flow in organic reactions. This makes it easier to keep track of the bonds forming and breaking during the reaction as well as visualizing and explain more advanced features such as the region and stereochemistry of certain reactions.

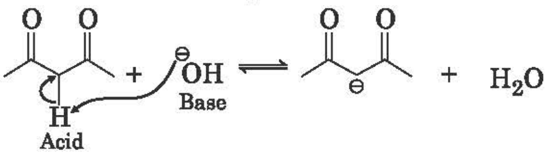
The electrons always flow from a high electron density region to a low electron density region. The molecules with a high electron density are nucleophiles *i.e.*, love nucleus. A molecule with a low electron density is classified as an electrophile *i.e.*, loves electrons.

The following is a nucleophilic addition reaction which is a very important class of organic reactions :



The arrow starting from the lone pair on the sulfur and pointing to the positively charged carbon makes a new covalent bond between them by a nucleophilic attack.

Another common important class of reactions that we can consider for learning the curved arrows is the acid-base reactions. For example,



Here, the hydroxide ion is the base and it attacks the proton connected to the carbon. So, this curved arrow shows a bond-forming between the oxygen and the hydrogen. The second arrow indicates breaking the bond between the hydrogen and the nitrogen as otherwise, the hydrogen would have left with two bonds which is not possible.

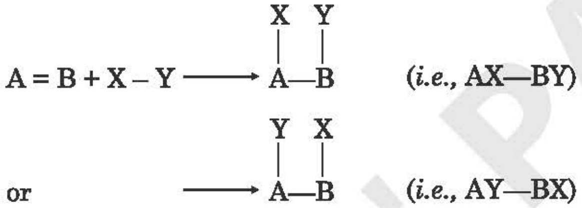
Q.2. What are addition reactions in organic compounds? Describe nucleophilic, electrophilic and free radical addition reactions their mechanism.

Ans.

Addition Reactions

Such reactions take place in unsaturated compounds (containing double or triple bonds). The attacking reagent, called as **addendum**, usually breaks into two similar or dissimilar fragments. One of these fragments adds on one of the carbons of the multiple bond while the other fragment adds on the other carbon of the multiple bond. Thus, the two reacting molecules (one of the attacking reagent and other of the reactant) add together to give, usually, a single molecule.

In general, an addition reaction may be represented as :



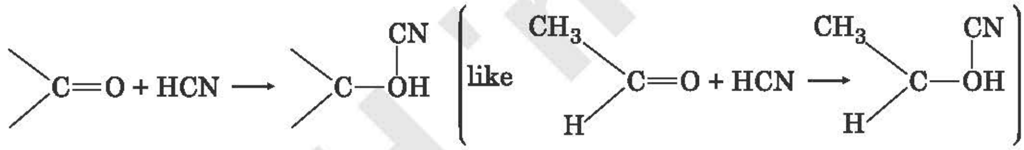
$$A = B + X - Y \longrightarrow \underset{}{\overset{X}{\underset{|}{}}}\!\!A\text{—}B\overset{Y}{} \quad (i.e., \text{AX—BY})$$

$$\text{or} \longrightarrow A\text{—}B \quad (i.e., \text{AY—BX})$$

Some more common examples of such reactions are :

(i) $CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br\text{—}CH_2Br$

(ii)



(iii) $CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2$ etc.

In triple bond compounds the addition may take place twice, *i.e.*,

$$CH \equiv CH + H_2 \longrightarrow CH_2 = CH_2 \xrightarrow{H_2} CH_3\text{—}CH_3$$

From the mechanistic point of view the addition reactions are divided into three types :

1. Electrophilic additions
2. Nucleophilic additions
3. Free radical additions.

1. Electrophilic Addition Reaction

It is an addition reaction in which the reactant (containing the multiple bond) is attacked by an electrophile. The attacking electrophile is, in fact, the electrophilic part of the addendum. A common example of such a reaction is the addition of bromine at ethene giving 1,2-dibromoethane :

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br\text{—}CH_2Br$$

The reaction is carried out in a solvent like chloroform or carbon tetrachloride.

Mechanism

The reaction takes place in following steps :

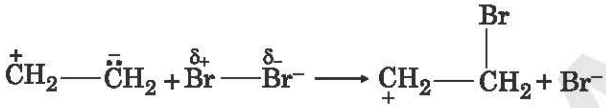
Though bromine is a non-polar molecule, in presence of high electron giving field of a double bond of alkene, it develops a polarity to facilitate the addition reaction :

$$Br_2 \longrightarrow \overset{\delta+}{Br}—\overset{\delta-}{Br}$$

The electromeric effect of Br_2 shifts the π electrons of double bond of ethene to any one of the doubly bonded carbon atoms (since both carbon atoms are identical) :

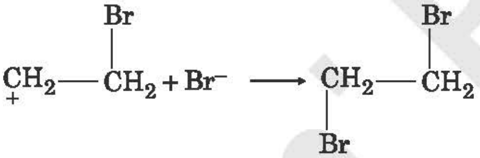
$$CH_2\overset{\frown}{=}CH_2 \longrightarrow \overset{+}{C}H_2—\overset{\cdot\cdot\,-}{C}H_2$$

The electrophilic part of bromine molecule (Br^+) now attacks the electron rich ethene to give a carbonium ion :



$$\overset{+}{C}H_2—\overset{\cdot\cdot\,-}{C}H_2 + \overset{\delta+}{Br}—\overset{\delta-}{Br^-} \longrightarrow \underset{+}{C}H_2—\overset{Br}{\overset{|}{C}H_2} + Br^-$$

Finally the nucleophilic part of bromine molecule adds to positive charged carbon of ethene to give the product :



$$\underset{+}{C}H_2—\overset{Br}{\overset{|}{C}H_2} + Br^- \longrightarrow \underset{Br}{\underset{|}{CH_2}}—\overset{Br}{\overset{|}{CH_2}}$$

It is a **trans** addition since the two adding fragments of the addendum (Br_2) approach the double bond from the opposite directions.

Additions of halogen acids (HX), H_2SO_4, H_2O etc. to alkenes and alkynes are all similar electrophilic addition reactions.

It is also to be made clear that when addition of an unsymmetrical addendum (like HBr, H_2SO_4 etc.) takes place to a symmetrical alkene like $CH_2=CH_2$ or $CH_3—CH=CH—CH_3$ etc., only one type of addition product ($CH_3—CH_2Br$ from ethene because $CH_2Br—CH_3$ is same, and $CH_3—CH_2—CHBr—CH_3$ from 2-butene because $CH_3—CHBr—CH_2—CH_3$ is same) is obtained. However, if addition takes place to an unsymmetrical alkene like $CH_3—CH=CH_2$ (propene), two electrophilic addition products are possible :

$$CH_3—CH=CH_2 + HBr \longrightarrow \underset{\text{2-bromopropane}}{CH_3—CHBr—CH_3} \longrightarrow \underset{\text{1-bromopropane}}{CH_3—CH_2—CH_2Br}$$

It is found that 2-bromopropane is the main product in such cases. **Markownikoff's** rule is a guiding rule to decide the main product in such reactions.

Markownikoff's Rule

Russian chemist Markownikoff gave a guiding rule to predict the main product expected to be obtained by the addition of an unsymmetrical addendum to an unsymmetrical alkene (or alkyne). According to this rule when addition takes place to an unsymmetrical alkene or alkyne, the negative part of addendum adds to that unsaturated carbon of alkene (or alkyne) which contains least number of hydrogen atoms. Thus, on the addition of HBr to $CH_3—CH=CH_2$, negative part of the addendum (*i.e.*, Br^-) adds to carbon atom number 2 of propene as carbon atom number 2 is the unsaturated carbon containing the least number of hydrogen atoms. It results in the formation of mainly the 2-bromopropane :

$$CH_3—CH=CH_2 + HBr \longrightarrow CH_3—CHBr—CH_3 \qquad \text{... 80\%}$$

$$\longrightarrow CH_3—CH_2—CH_2Br \qquad \text{... 20\%}$$

Peroxide Effect

The scientist Kharasch observed that when the addition to an unsymmetrical alkene takes place in the presence of a peroxide, the addition takes place contrary to Markownikoff's rule, *i.e.*, negative part of the addendum adds to that unsaturated carbon which has more hydrogen atoms. For example, when HBr adds to propene in the presence of benzoyl peroxide then 1-bromopropane is obtained mainly :

$$CH_3—CH=CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3—CH_2—CH_2Br$$

Mechanism

It is a free radical mechanism. It is important to remember here that the peroxide effect is applicable to the addition of HBr only. It is not applicable to the addition of HCl or HI, *i.e.*, if propene is allowed to add with HCl or HI, the product is well according to Markownikoff's rule even in the presence of a peroxide :

$$CH_3—CH=CH_2 + HCl \xrightarrow{(C_6H_5CO)_2O_2} CH_3—CHCl—CH_3$$

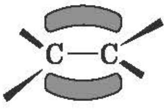
$$CH_3—CH=CH_2 + HI \xrightarrow{(C_6H_5CO_2)O_2} CH_3—CHI—CH_3$$

2. Nucleophilic Addition Reaction

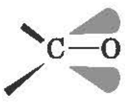
It is an addition reaction in which the reactant (containing a multiple bond) is attacked by a nucleophile, *i.e.*, initially the nucleophilic part of the addendum adds to the unsaturated carbon of the reactant. A conmon example of such a reaction is the addition of hydrogen cyanide to a carbonyl compound (aldehyde or ketone) resulting in the formation of a cyanohydrin :

Mechanism

The double bond in carbonyl group (>C=O) is quite different in nature to the double bond in alkene (>C=C<). Whereas the double bond in alkene has equal sharing between two bonded atoms, the double bond in carbonyl group has unequal sharing between the two bonded atoms because of the difference in electronegativities of carbon and oxygen. Thus, the π electron cloud is symmetrical in >C=C< but unsymmetrical in >C=O. In >C=O, the electron cloud is nearer to oxygen because of its higher electronegativity



(>C=C<)



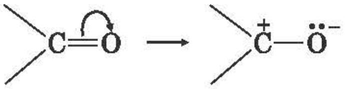
(>C=O)

As a result the carbon of >C=O group becomes electron deficient and susceptible to nucleophilic attack. Mechanism involves following steps :

The addendum produces the nucleophilie :

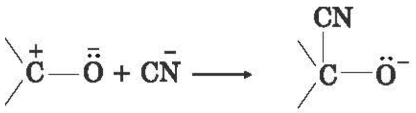
$$HCN \rightleftharpoons H^+ + \underset{\text{(Nucleophile)}}{CN^-} \qquad ...(1)$$

The electromeric effect of a addendum shifts the π-electrons of double bond of $>C=O$ group totally towards the more electronegative oxygen atom, resulting in the development of a positive charge at carbon atom :



...(2)

Development of positive and negative charges in $>C=O$ group whereas makes the oxygen to be quite stable (since it is highly electronegative and prefers to attain the negative charge), it makes the carbon to feel sufficiently electron deficient and, thus, susceptible to nucleophilic attack. This is the reason why initially the nucleophile CN^- attacks the carbon instead of the attack of electrophile H^+ at oxygen.



...(3)

Now the other part (H^+) of the addendum adds to the negative charged oxygen giving the final product, *i.e.*, a cyanohydrin :

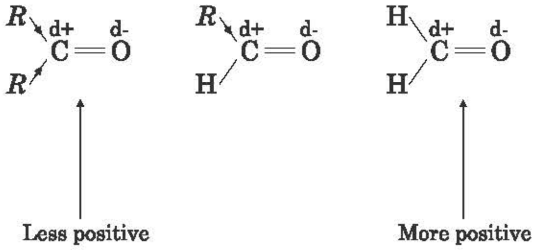
...(4)

Additions of sodium bisulphite ($NaHSO_3$), ammonia (NH_3), Grignard reagent (RMgX) etc. to a carbonyl compound are also the similar nucleophilic addition reactions.

Relative Reactivity of Formaldehyde, Acetaldehyde and Acetone towards Nucleophilic Additions

Out of formaldehyde, acetaldehyde, and acetone, the formaldehyde is most susceptible to nucleophilic attack and, hence, is most reactive. Acetone is least reactive. It can be explained as follows :

It has been seen above that nucleophilic attack takes place because the carbon of $>C=O$ group becomes electron deficient. In ketones (alkanones), the positive inductive effect of two alkyl groups pushes the electrons towards this carbon, reducing its electron deficiency and thus, making it less susceptible to nucleophilic attack.



In acetaldehyde (ethanal), due to the presence of one alkyl group the electron donating effect is less and so the electron deficiency of carbon of $>C=O$ group is not reduced so much. It makes acetaldehyde to be comparatively more reactive. In formaldehyde (methanal), no $+I$ effect of any alkyl group exists and the carbon of $>C=O$ group remains much electron deficient. It makes it most highly susceptible to nucleophilic attack.

Along with the electronic factor explained above, the steric effect also plays a role here. The ketones have two alkyl groups on carbon of $>C=O$ group and these groups hinder the attack on it. Aldehydes have only one and formaldehyde has none.

Also, larger (bulky) the alkyl group attached to a carbonyl group, more is the steric hindrance, so less is the reactivity of such a ketone. For the same reason, dipropyl ketone" is less reactive than acetone.

3. Free Radical Addition Reaction

It is an addition reaction in which the multiple bond containing compound (the reactant) is attacked by a free radical given by the addendum, *i.e.,* the addition takes place *via* free radical formation. Such reactions take place only in the presence of a source which may produce a free radical from the addendum. This free radical is responsible to initiate the reaction. The source may be in the form of a compound or in the form of sunlight or air etc. A common example of free radical reaction is the addition of hydrogen bromide to propene in the presence of benzoyl peroxide. 1-bromopropane is obtained (peroxide effect) mainly instead of 2-bromo propane, *i.e.,* the addition takes place contrary to Markownikoff's rule :

$$CH_3-CH=CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-CH_2-CH_2Br$$

Mechanism

The organic peroxide (benzoyl peroxide) splits into free radicals in the presence of sunlight :

$$\left.\begin{array}{l} (C_6H_5CO)_2O_2 \longrightarrow 2C_6H_5COO \\ C_6H_5COO \longrightarrow C_6H_5 + CO_2 \end{array}\right\} \quad \text{...(1)}$$

The free radical so produced reacts with the addendum HBr and produces the main attacking free radical (Br) :

$$C_6H_5 + HBr \longrightarrow C_6H_6 + Br \quad \text{...(2)}$$

The Br free radical quickly attacks the π electrons of propene and adds to one of the unsaturated carbons of the double bond. There are two possible addition products :

$$\left.\begin{array}{l} CH_3-CH=CH_2 + Br \longrightarrow \underset{\text{(I)}}{CH_3-CH-CH_2Br} \\ \qquad\qquad\qquad\qquad\quad \longrightarrow \underset{\text{(II)}}{CH_3-CHBr-CH_2} \end{array}\right\} \quad \text{...(3)}$$

Out of the two, the free radical (I) is more stable since it is a secondary free radical than the free radical (II) which is a primary free radical. So (I) is predominantly formed.

Finally the hydrogen from HBr adds to the unpaired electron centre and the product $CH_3CH_2CH_2Br$ is formed :

$$CH_3-CH-CH_2Br + HBr \longrightarrow CH_3-CH_2-CH_2Br + Br \quad \text{...(4)}$$

Br radical formed in step (4) is used in step (3) again and, thus, steps (3) and (4) continue till the end of the reaction.

Steps (1) and (2) are used only to initiate the reaction, therefore termed as initiation steps. Steps (3) and (4) go on propagating the reaction further and, therefore, termed as propagation steps. If two free radicals come in contact, the chain may be terminated in demand of free radical. Such a step is termed as **chain termination** step, *e.g.,*

$$\left.\begin{array}{ll} & Br + Br \longrightarrow Br_2 \\ \text{or} & C_6H_5 + C_6H_5 \longrightarrow C_6H_5-C_6H_5 \end{array}\right\} \quad \text{...(5)}$$

Peroxide effect is applicable to the addition of only the HBr to propene. Addition of HCl or HI to propene goes according to Markownikoff's rule even in the presence of organic peroxides. It is because only in HBr the free radical formation is favoured. Free radical formation is not favoured in HCl or HI. The bond energy of HCl (431 kJ) is much higher than the bond energy of HBr (366 kJ) and disfavours the dissociation into free radicals. In HI, though the bond dissociation energy is low, the addition of iodine atom to a double bond is an endothermic reaction and so less favourable.

Polymerisation is also an addition reaction and takes place via similar free radical mechanism if carried in the presence of a source of free radicals, *e.g.*, the polymerisation of ethene in the presence of an organic peroxide resulting in the formation of polythene :

$$n\mathrm{CH_2{=}CH_2} \xrightarrow{R\text{—O—O—}R} (\mathrm{—CH_2—CH_2—})_n$$

However, the polymerisation reaction may take place *via* ionic mechanism also (electrophilic or nucleophilic addition). It depends upon the catalyst used.

Q.3. What are substitution reactions in organic compounds? Describe, nucleophilic, electrophilic and free radical substitution reactions and their mechanism.

Ans.

Substitution Reactions

In such reactions an atom or a group of atoms in a reactant is replaced by another atom or group of atoms given by the other reactant. This type of reactions may also be called as **replacement reactions** and, in general, they can be represented as follows :

$$\mathrm{A—B + X—Y \longrightarrow A—X + B—Y}$$

or

$$\mathrm{\longrightarrow A—Y + B—X}$$

Some common examples of such reactions are :

(i) $$\mathrm{CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl}$$

(ii) $$\mathrm{C_2H_5Br + \underset{(aq)}{KOH} \longrightarrow C_2H_5OH + KBr}$$

(iii) $$\mathrm{C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O} \text{ etc.}$$

From the view point of their mechanism, substitution reactions may be divided into three kinds :

$$\left.\begin{array}{l}\text{1. Nucleophilic substitutions}\\ \text{2. Electrophilic substitutions}\end{array}\right\}\text{(Ionic mechanism)}$$

3. Free radical substitutions (Free radical mechanism)

1. Nucleophilic Substitution Reactions

The substitution reactions which are brought about by the attack of a nucleophile are termed as nucleophilic substitution reactions and are represented as S_N (substitution, nucleophilic) reaction.

In a nucleophilic substitution reaction, a weaker nucleophile is usually replaced by a stronger nucleophile. For example,

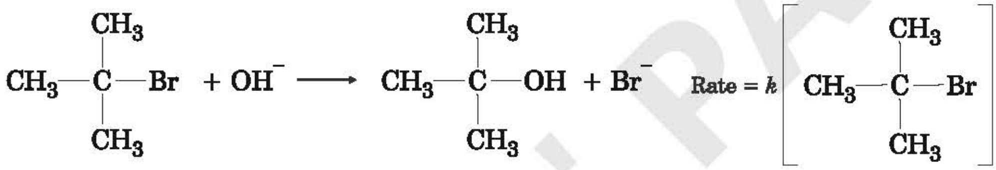
$$\underset{\substack{\text{Alkyl halide}\\ \text{(Substrate)}}}{\mathrm{R—}X} + \underset{\substack{\text{Hydroxide ion}\\ \text{(Stronger}\\ \text{nucleophile)}}}{\mathrm{OH^-}} \longrightarrow \underset{\substack{\text{Alcohol}\\ \text{(Substitution}\\ \text{product)}}}{R\mathrm{—OH}} + \underset{\substack{\text{Halide ion}\\ \text{(Weaker}\\ \text{nucleophile)}}}{X^-}$$

Nucleophilic substitution (S_N) reactions are of following two types :

(i) **S_N1 reactions :** The S_N1 (substitution, nucleophilic, unimolecular) reactions are those nucleophilic substitution reactions in which the rate of reaction depends only upon the concentration of the substrate and not upon the concentration of the attacking nucleophile, *i.e.*,

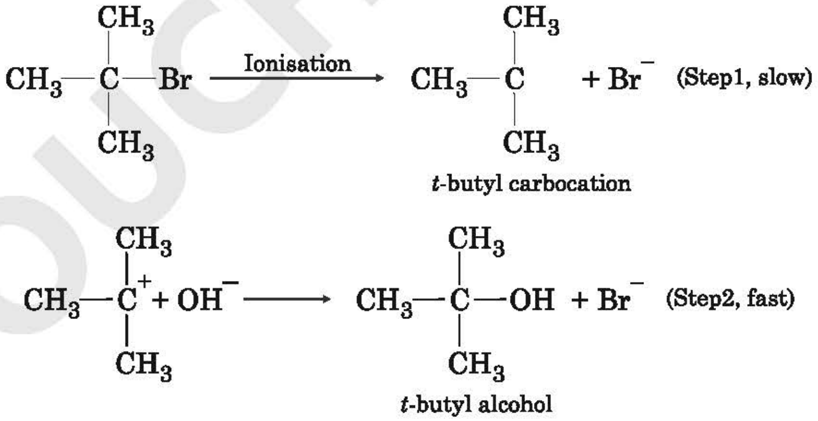
$$\text{Rate} \propto [\text{Substrate}]$$

Such reactions are first order reactions and the rate law involves only the concentration of the substrate. All tertiary alkyl halides undergo substitution by S_N1 mechanism. For example,



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + OH^- \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Br^- \quad \text{Rate} = k\left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br\right]$$

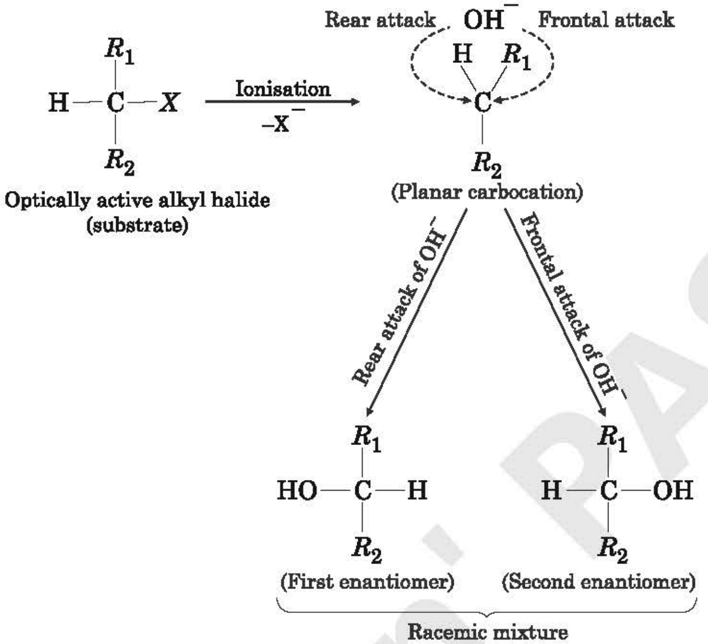
The rate law suggests that the reaction occurs in two steps. The first step involves the slow ionisation of the alkyl halide to produce a carbocation. This step is slow and is obviously the rate determining step. In the second step, the carbocation being a reactive species, rapidly reacts with the nucleophile to give the substitution product. This step is very fast and does not contribute to the rate of reaction. Thus, the mechanism of the above reaction can be written as follows.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow{\text{Ionisation}} CH_3-\overset{CH_3}{\underset{CH_3}{C}} + Br^- \quad \text{(Step1, slow)}$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + OH^- \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Br^- \quad \text{(Step2, fast)}$$

Stereochemistry of S_N1 reactions : The intermediate species involved in S_N1 reactions are carbocations which are planar species. Since, a carbocation is planar, the attacking nucleophile can attack on it with equal ease from the either face (*i.e.,* either from front or from rear). Therefore, if the alkyl halide is optically active, theoretically a 1:1 mixture of the two enantiomers should be obtained. Hence, the product should be a racemic mixture. For example,

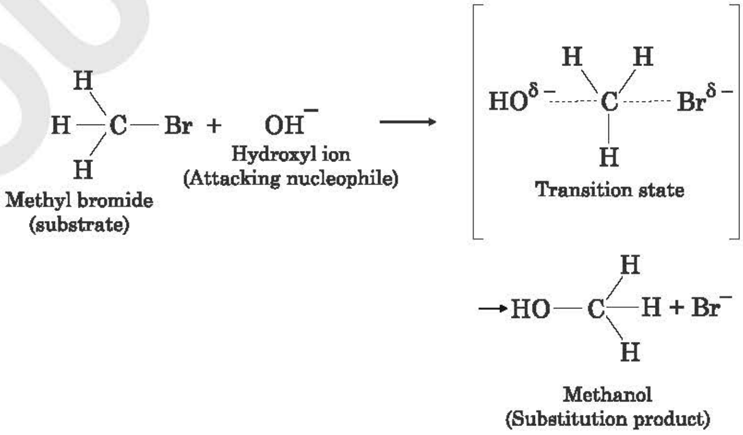


However, in actual practice, the product may not be completely racemised as the inverted product may exceed its enantiomer.

(ii) **S_N2 reactions :** The S_N2 (substitution, nucleophilic, bimolecular) reactions are those nucleophilic substitution reactions in which the rate of reaction depends upon the concentration of the substrate as well as on the concentration of the attacking nucleophile. Thus, a S_N2 reaction is a second order reaction and has the rate law :

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

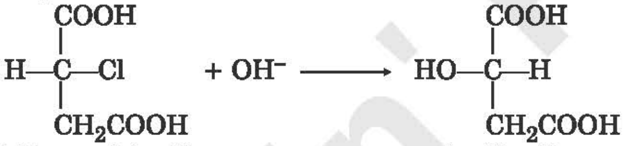
Obviously, the rate determining step involves the participation of both the substrate and the nucleophile. S_N2 reactions occur through a transition state as shown below.



The attacking nucleophile (OH^- in the above case) attacks on the substrate (CH_3Br in the above case) at the face most remote from the existing nucleophile (Br^- in the above case).

Thus, the attack of the nucleophile occurs from the rear of the substrate molecule. In the transition state, both the attacking nucleophile (OH^-) and the already existing nucleophile (Br^-) are partially bonded to the carbon atom of the substrate molecule (shown by dotted lines). As the attacking nucleophile (OH^-) is a stronager one, the electron density drifts towards it and a permanent C—OH bond is formed. At the same time, the C---Br bond is broken and Br^- leaves the transition state from the front side. The energy needed for the cleavage of C---Br bond is partly provided by the energy liberated in the formation of C—OH bond.

Stereochemistry of S_N2 reactions : As mentioned above, in an S_N2 reaction, the attacking nucleophile attacks the substrate molecule from the rear side and the already present nucleophile leaves the molecule from the front side. Therefore, a S_N2 reaction is always followed by an inversion in configuration. The inversion of configuration is commonly known as **Walden inversion.** If the substrate is optically active, the substitution product obtained as a result of S_N2 reaction is also optically active and has the opposite effect on the plane polarised light. For example,



$$\begin{array}{c} COOH \\ | \\ H—C—Cl \\ | \\ CH_2COOH \end{array} + OH^- \longrightarrow \begin{array}{c} COOH \\ | \\ HO—C—H \\ | \\ CH_2COOH \end{array}$$

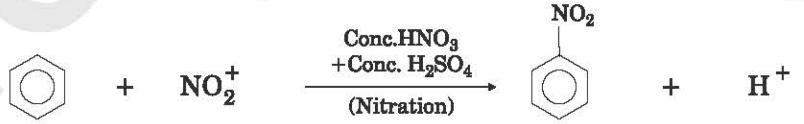
d-chlorosuccinic acid (+) *l*-malic acid (–)

All primary aliphatic halides undergo substitution by S_N2 mechanism. The secondary alkyl halides undergo substitution either by S_N1 or by S_N2 mechanism depending upon the experimental conditions.

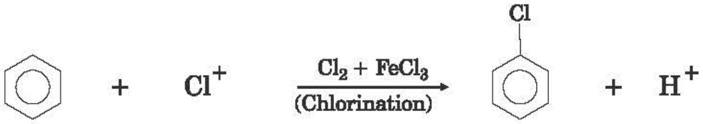
2. Electrophilic Substitution Reactions

The substitution reactions which are brought about by the attack of electrophiles are referred to as electrophilic substitution reactions and are represented as S, (substitution, electrophilic) reactions.

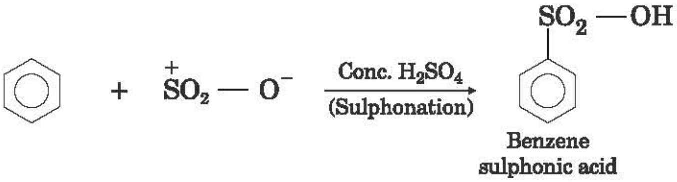
In an electrophilic substitution reaction, a stronger electrophile attacks on the substrate molecule. As a result, a weaker electrophile leaves the molecule. Such reactions are typical of arenes and their derivatives. Some examples of electrophilic substitution reactions commonly shown by arenes and their derivatives are halogenation, nitration, sulphonation and **Friedel-Crafts reactions**. Alkanes also undergo electrophilic substitution reactions but to a much lesser extent. Some electrophilic substitution reactions of benzene are given as follows :

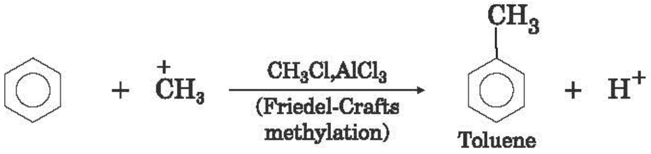


Benzene (Substrate) Nitronium ion (Attacking electrophile) Nitrobenzene (Substitution product) Hydrogen ion (Relased electrophile)



Chloronium ion Chlorobenzene





3. Free Radical Substitution Reactions

The substitution reactions which are brought about by the attack of free radicals are called free radical substitution reactions.

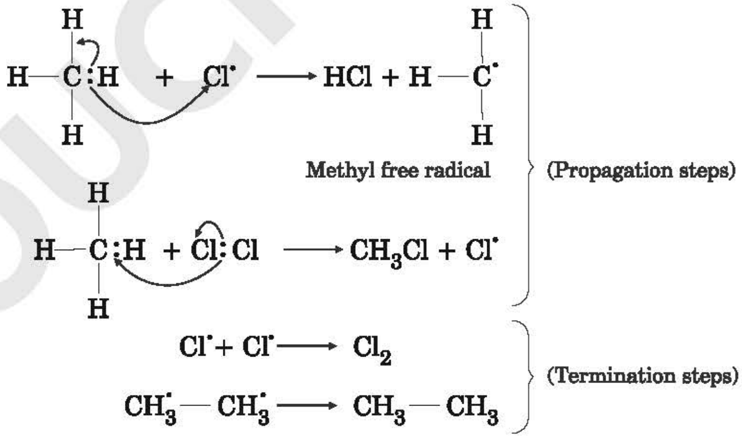
The chlorination of alkanes in the presence of sunlight or heat is a well known example of this type of reactions.

$$CH_4 + Cl_2 \xrightarrow[\text{or } 520\text{-}670\text{ K}]{h\nu} CH_3Cl + HCl$$

A free radical substitution reaction occurs in three steps : (i) initiation, (ii) propagation, and (iii) termination.

For example, the chlorination of methane takes place as given below :

$$Cl : Cl \xrightarrow[\substack{\text{or heat}\\ \text{(Homolytic}\\ \text{fission)}}]{h\nu} \underbrace{Cl^{\bullet} + Cl^{\bullet}}_{\substack{\text{Chlorine}\\ \text{free}\\ \text{radicals}}} \text{ (Initiation step)}$$



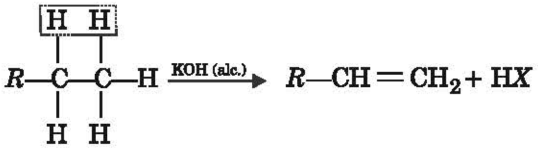
Q.4. What are elimination reactions in organic compounds? Discuss their mechanism.

Ans.

Elimination Reactions

The reactions involving the loss of two or four atoms or groups from the same or the adjacent carbon atoms in a substrate molecule leading to the formation of a multiple bond are called elimination reactions.

The dehydrohalogenation of alkyl halides in the presence of alcoholic potassium hydroxide is a typical example of this type of reactions. This involves the loss of hydrogen and halogen atoms and leads to the formation of a double bond as shown below.



$$R-\underset{H}{\overset{\boxed{H}}{C}}-\underset{H}{\overset{\boxed{H}}{C}}-H \xrightarrow{\text{KOH (alc.)}} R-CH=CH_2+HX$$

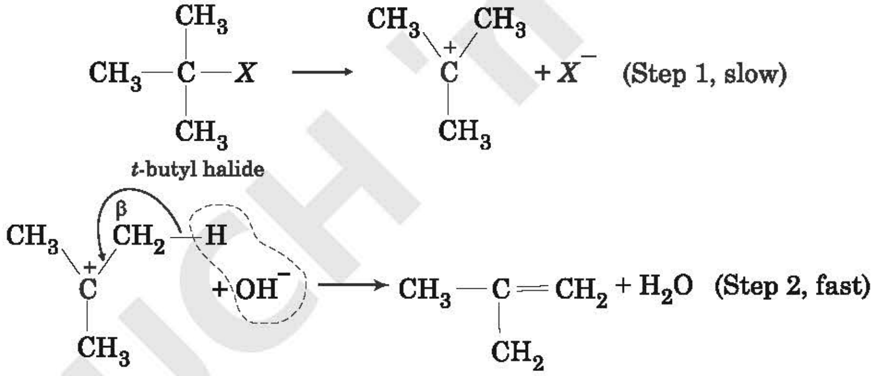
Elimination reactions are of following two types.

1. E_1 Reactions (Unimolecular Elimination Reactions)

The E_1 (elimination, unimolecular) reactions are those reactions in which the rate of reaction depends only upon the concentration of the substrate, *i.e.*,

$$\text{Rate} \propto [\text{Substrate}]$$

Like S_N1 reactions, the E_1 reactions occur in two steps. The first step involves the ionisation of the alkyl halide (substrate) to form a carbonium ion. This step is show and is the rate determining step. The second step is fast and involves the abstraction of a proton by the base (attacking species) from the adjacent β-carbon atom leading to the formation of an alkene. For example,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-X \longrightarrow (CH_3)_2\overset{+}{C}-CH_3 + X^- \quad \text{(Step 1, slow)}$$

t-butyl halide

$$CH_3-\overset{+}{C}(CH_3)-\overset{\beta}{CH_2}-H + OH^- \longrightarrow CH_3-\underset{CH_2}{C}=CH_2 + H_2O \quad \text{(Step 2, fast)}$$

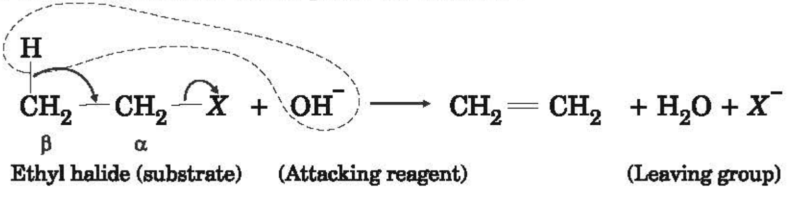
(2-methylpropene)

2. E_2 Reactions (Bimolecular Elimination Reactions)

The E_2 (elimination, bimolecular) reactions are those elimination reactions in which the rate of reaction depends upon the concentration of both the substrate and the attacking species, *i.e.*,

$$\text{Rate} \propto [\text{substrate}]\,[\text{Attacking species}]$$

E_2 reactions occur in one step only. The attacking species (*e.g.*, OH^-) abstracts a proton from the β-carbon atom resulting in the simultaneous release of the leaving group (*e.g.*, X^- ion) from the α-carbon atom of the substrate. For example, the dehydrohalogenation of an halide in the presence of alcoholic KOH takes place as follows :



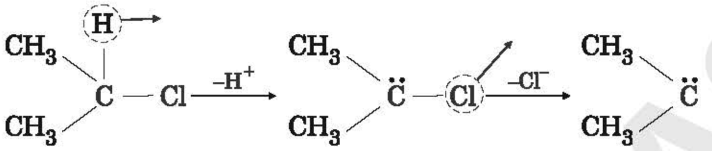
$$\underset{\beta}{\overset{H}{CH_2}}-\underset{\alpha}{CH_2}-X + OH^- \longrightarrow CH_2=CH_2 + H_2O + X^-$$

Ethyl halide (substrate) (Attacking reagent) (Leaving group)

Classification of Elimination Reactions

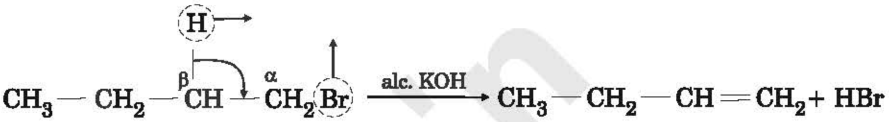
Elimination reactions are also classified as α (alpha), β (beta) or γ (gamma) elimination reactions :

(i) **α-elimination reactions :** In this type of reactions, the two atoms or groups are removed from the position of the substrate molecule. This produces electron deficient reactive intermediate species which further react to give stable products. For example,



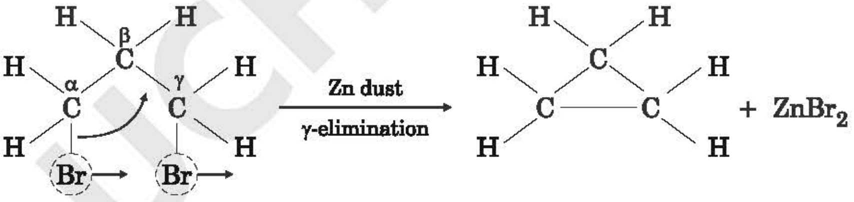
Dimethylcarbene
(A reative
intermediate)

(ii) **β-elimination reactions :** This type of reactions involve the elimination of the atoms or groups from the adjacent positions (α, β) of the substrate. For example,



$$CH_3-CH_2-\overset{\beta}{CH}(H)-\overset{\alpha}{CH_2}Br \xrightarrow{\text{alc. KOH}} CH_3-CH_2-CH=CH_2+HBr$$

(iii) **γ-elimination reactions :** In this type of reactions, the loss of two atoms or groups occurs from a γ-positions. Consequently, a three membered ring is formed. For example,



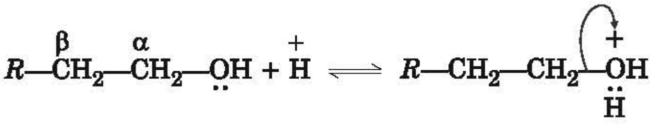
1,3 -dibromocyclopropane Cyclopropane

Dehydration of Alcohols : Alcohols in presence of dehydrating agent such as conc. H_2SO_4, H_3PO_4, anhydrous $ZnCl_2$ etc., undergo dehydration to form olefins.

$$R\text{—}CH_2.CH_2OH \xrightarrow[170°C]{\text{Conc. } H_2SO_2} R.\,CH{=}CH_2 + H_2O$$

The mechanism of the reaction involves following step :

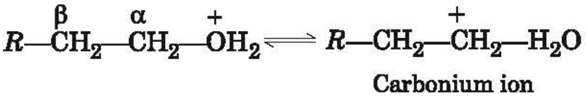
In the first step, the H^+ from the acid (H_2SO_4) is attached to the oxygen of —OH group through one of the lone pairs of electrons present on oxygen forming an oxonium ion.



$$R-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-\ddot{O}H + \overset{+}{H} \rightleftharpoons R-CH_2-CH_2-\overset{+}{\ddot{O}}H(H)$$

Alcohol Oxonium ion

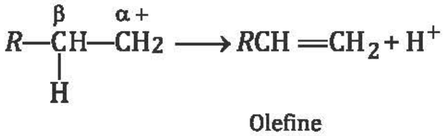
In the **next step**, the oxonium ion dissociates into water and carbonium ion.



$$R-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-\overset{+}{O}H_2 \rightleftharpoons R-CH_2-\overset{+}{C}H_2-H_2O$$

Carbonium ion

In the last step, one of the C^{β}—H bond electrons are attracted by the carbon having 6 electrons only to form an olefin, liberating H^+.



$$R-\underset{\displaystyle H}{\overset{\beta}{C}}H-\overset{\alpha +}{C}H2 \longrightarrow RCH=CH_2+H^+$$

Olefine

Q.5. What are carbocations? Discuss their formation, orbital structure, stability and reactions.

Ans.

Carbocations (Carbonium Ions)

The chemical species which possess a positively charged carbon centre are called carbocations. The central carbon bearing positive charge in a carbocation contains six electrons in its valence shell. Earlier, these ions were termed as **carbonium ions.**

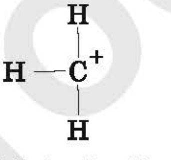
A carbocation is formed by the heterolytic fission of the C—X bond (where *X* is more electronegative than carbon) present in an organic molecule as shown below.

$$R-\underset{\displaystyle R}{\overset{\displaystyle R}{C}}-X \xrightarrow{\text{Heterolytic fission}} R-\underset{\displaystyle R}{\overset{\displaystyle R}{C^+}}+X^-$$

During the heterolytic fission, the shared pair of electrons of the C—*X* bond is taken away by the more electronegative species *X* resulting in the development of a positive charge on carbon and a carbocation is formed.

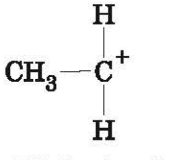
Classification

Carbocation are classified on the basis of the nature of carbon atom bearing positive charge. Thus, we have **primary** (1°), **secondary** (2°), and **tertiary** (3°) carbocations as shown below.



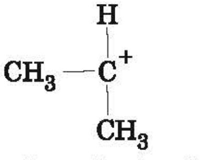
$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C^+}}$$

Methyl carbocation
(1°)



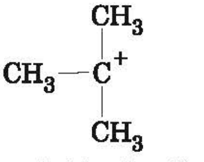
$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle H}{C^+}}$$

Ethyl carbocation
(1°)



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

Isopropl carbocation
(2°)

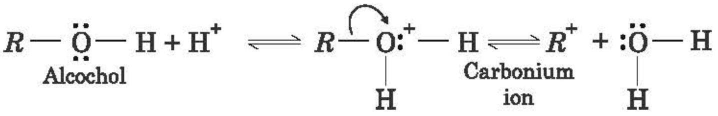


$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C^+}}$$

t-butyl carbocation
(3°)

Formation of Carbonium Ion

(i) **By the addition of acids to alcohols, esters, ethers, acid anhydrides etc :** Alcohols, acid etc. produce carbonium ions when dissolved in acid solution.



$$R-\ddot{\underset{\cdot\cdot}{O}}-H+H^+ \rightleftharpoons R-\underset{\displaystyle H}{O}{:}^+-H \rightleftharpoons R^+ + :\underset{\displaystyle H}{\ddot{O}}-H$$

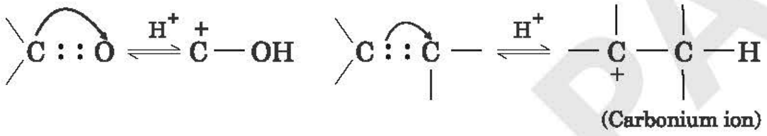
Alcochol

Carbonium ion

(ii) **By the attack of carbonium ion upon a saturated hydrocarbon :** Carbonium ions are also formed by the action of a carbonium ion upon a saturated hydrocarbon under suitable conditions.

$$R_1\text{—H} + \overset{\oplus}{R} \rightleftharpoons \underset{\text{Carbonium ion}}{\overset{\oplus}{R_1}} + R\text{—H}$$

(iii) **By the addition of acids to unsaturated compounds :** In the presence of acids (protons), the shared electron pair forming a multiple bond is displaced from its normal position and the bond assumes a more polarized form. When an unsaturated compound is dissolved in a proton donating solvent, equilibrium in the different system is established resulting in the formation of carbonium ion.



(iv) **By the addition of acids to organic halides :** Organic halides on treatment with acids produce carbonium ions.

$$R-\ddot{X} + H^+ \rightleftharpoons R-\overset{+}{\underset{..}{\ddot{X}}}-H \rightleftharpoons R^+ + :\underset{..}{\ddot{X}}-H$$

Carbonium ion

Orbital Structure

The central carbon atoms present in a carbocation is in a state of sp^2 hybridisation. The three sp^2 hybrid orbital of this carbon lie in one plant at an angle of 120°. These orbital overlap with the orbitals of H atom or alkyl groups to form σ-bonds. The unhybridised $2p$ orbital remains vacant in a carbocation (Fig). The positive charge is present on the central carbon which is sp^2 hybridised. Due to sp^2 hybridisation, carbocations are planar species.

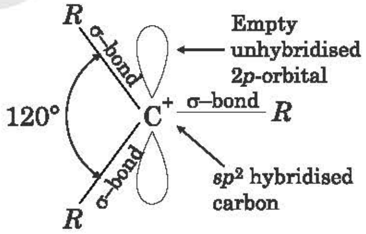
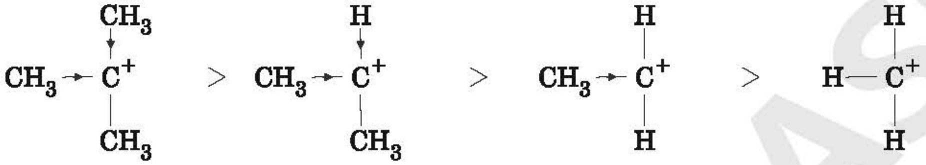


Fig. Orbital structure of a carbocation

Stability

Carbocations are formed as reaction intermediates and are very reactive. This is because the central carbon bearing a positive charge contains only six electrons in its valence shell and has a great tendency to complete the octet. Hence, a carbocation combines readily with any substance that can donate a pair of electrons to it.

The stability of different types of carbocations is in the order 3° > 2° > 1°. The relative stability of carbocations can be explained on the basis of **inductive effect**. When an electron repelling group (such as an alkyl group) is attached to the central carbon bearing positive charge, the magnitude of positive charge on the central carbon decreases due to pumping of electrons by the electron repelling group (dispersal of positive charge by + *I*-effect) and makes the carbocation more stable. Since, a 3° carbocation contains three alkyl group attached to the central carbon +*I*-effect is the strongest in it and consequently it is most stable. On the other hand, since a 1° carbocation contains either one or no alkyl group attached to the central carbon, atom, the disperal of positive charge due to +*I*-effect is minimum and hence 1° carbocation is the least stable. Thus,



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

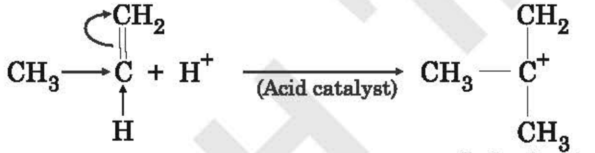
t-butyl carbocation (3°) (Most stable)
Isopropoly carbocation (2°)
Ethyl carbocation (1°)
Methyl carbocation (1°) (Least stable)

Since, the order of reactivity is the reverse of stability reactivity of carbocations follows the order 1° > 2° > 3°.

Reactions of Carbonium Ion

1. **Union with alkene :** This results in the formation of large carbonium ions.

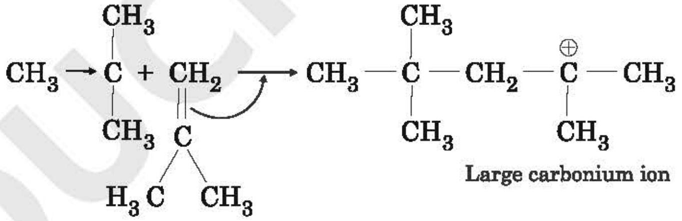
(i)



$$CH_3 \longrightarrow \overset{\overset{CH_2}{\|}}{\underset{\underset{H}{\uparrow}}{C}} + H^+ \xrightarrow[\text{(Acid catalyst)}]{} CH_3 - \overset{\overset{CH_2}{|}}{\underset{\underset{CH_3}{|}}{C^+}}$$

Carbonium ion

(ii)



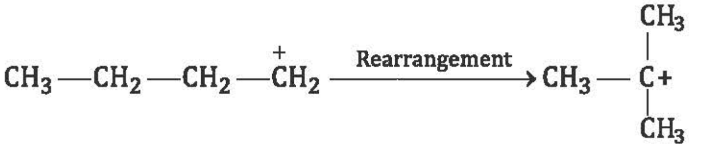
$$CH_3 \rightarrow \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} + \underset{\underset{H_3C \quad CH_3}{\underset{C}{\|}}}{CH_2} \longrightarrow CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2 - \overset{\oplus}{\underset{\underset{CH_3}{|}}{C}} - CH_3$$

Large carbonium ion

2. **Rearrangement :** The carbonium ion may undergo rearrangement to form a more stable carbonium ion.

$$CH_3 - CH_2 - CH_2 - \overset{-}{C}H_2 \xrightarrow{\text{Rearrangement}} CH_3 - CH_2 - \overset{-}{C}H - CH_3$$

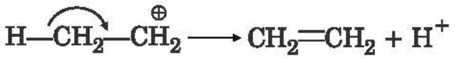
Primary carbonium ion [less stable]
Secondary carbonium ion [more stable]



$$CH_3 - CH_2 - CH_2 - \overset{+}{C}H_2 \xrightarrow{\text{Rearrangement}} CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C+}}$$

Tertiary carbonium ion [most stable]

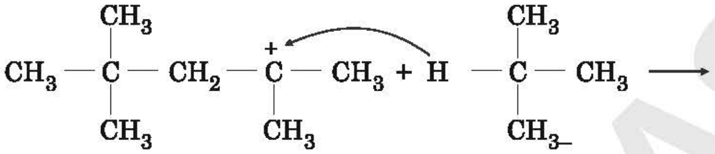
3. **Elimination of a hydrogen ion :** Carbonium ion may eliminate a proton resulting in the formation of an olefin.



$$H-CH_2-\overset{\oplus}{C}H_2 \longrightarrow CH_2{=}CH_2 + H^+$$

Ethylene

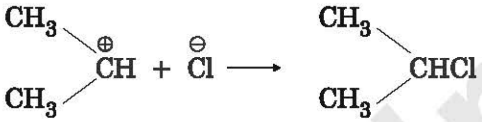
4. **Abstraction of a hydrogen ion :** This results in the formation of a paraffin.



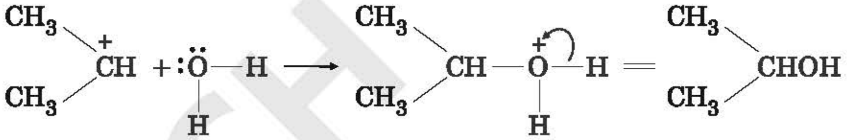
Carbonium ion as produced in reaction (3)

2-methylpropane

5. **Union with a negative ion or electron rich molecule :** This result in the formation of a stable molecule.



Isopropyl alcohol



Protonated alcohol

Isopropyl alcohol

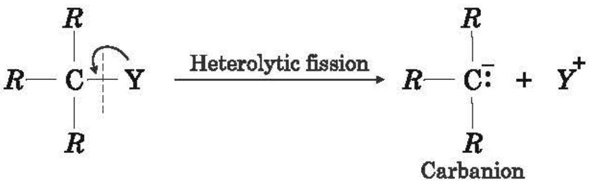
Q.6. What are carbanions? Discuss their formation, orbital structure, stability and reactions.

Ans.

Carbanions

The chemical species which possess a negatively charged carbon centre are called **carbanions**. The central carbon bearing the negative charge contains a pair of available electrons. It has a complete octet.

A carbanion is formed by the heterolytic fission of the C—*Y* bond (where *Y* is less electronegative than carbon) present in an orgainc molecule as shown below.

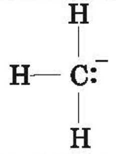


Carbanion

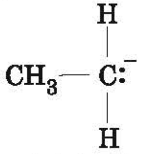
During the heterolytic fission, the shared pair C—*Y* bond remains with the central carbon. This develops a negative charge on it and a carbanion is obtained.

Classification

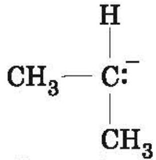
Like carbocations, carbanions are also classified on the basis of the nature of carbon bearing the negative charge. Thus, we have **primary** (1°), **secondary** (2°) and **tertiary** (3°) carbanions as shown below :



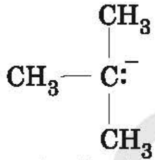
Methyl carbanion (1°)



Ethyl carbanion (1°)



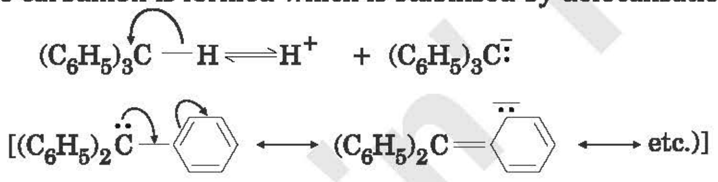
Isopropyl carbanion (2°)



t-butyl carbanium (3°)

Formation of Carbanions

Carbanions are formed only from those compounds which contain a functional group capable of weakening a nearby C—H bonds. For example, Saturated hydrocabons are completely inert to strong bases but in the presence of electron withdrawing groups the C—H bond is weakened and the carbanion is formed which is stabilised by delocalisation.

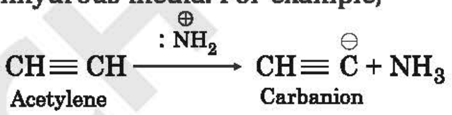


$$(C_6H_5)_3C-H \rightleftharpoons H^+ + (C_6H_5)_3C\bar{:}$$

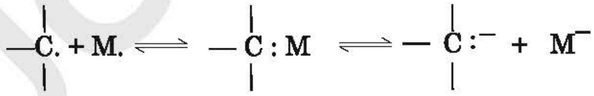
$$[(C_6H_5)_2\ddot{C}-C_6H_5 \longleftrightarrow (C_6H_5)_2C=C_6H_5 \longleftrightarrow \text{etc.})]$$

Carbanion

Compounds, which lose a proton less readily may be converted into carbanions by treatment with very strong bases in anhydrous media. For example,



$$CH\equiv CH \xrightarrow{:\overset{\oplus}{N}H_2} CH\equiv \overset{\ominus}{C} + NH_3$$

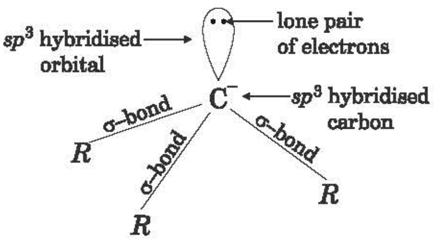


$$-\overset{|}{\underset{|}{C}}. + M. \rightleftharpoons -\overset{|}{\underset{|}{C}}:M \rightleftharpoons -\overset{|}{\underset{|}{C}}:^- + M^-$$

Free radical Organometallic compound Carbanion

Orbital Structure

The central carbon atom present in a carbanion (the carbon which bears negative charge) is in a state of sp^3 hybridisation. Among the four sp^3 hybrid orbitals, the three hybrid orbitals overlap with the orbitals of alkyl group or H-atoms and form σ-bonds. The fourth sp^3 hybrid orbital contains the lone pair of electrons. Thus, a carbanion usually assumes a pyramidal structure as shown in Fig.



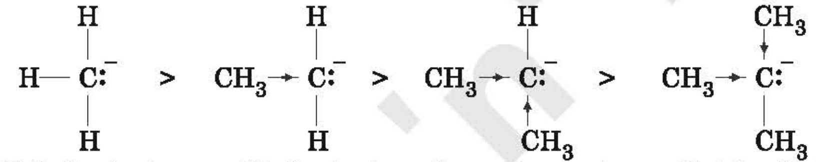
Orbital structure of a carbanion

Stability

Although the central carbon atom in a carbanion possesses an octet the carbanions are very reactive intermediates. This is due to the presence of a negative charge on the central carbon atom. Since the central carbon atom possesses an easily available pair of electrons, carbanions are readily attacked by electron deficient species (electrophiles).

The stability of carbanions is in the order 1° > 2° > 3°.

The relative stability of carbanions can be explained in terms of **inductive effect**. Greater the number of alkyl groups attached to the central carbon atom, greater is the increase in the magnitude of negative charge on central carbon due to +*I* effect and lesser is the stability of the carbanion. In a 3° carbanion, three alkyl group are attached to the central carbon atom bearing the negative charge. The alkyl groups are electron repelling groups and have a tendency to increase the magnitude of negative charge on the central carbon. This decreases the stability of the ion. On the other hand, a 1° carbanion contains either one or no alkyl groups attached to the central carbon atom. Hence, the magnitude of negative charge either increases slightly or remains almost the same. This is why 1° carbanions are most stable. Thus,



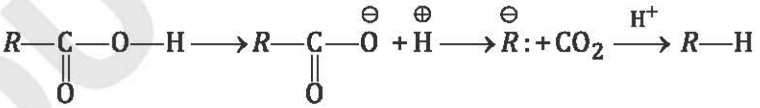
$$H-\overset{H}{\underset{H}{C}}:^{-} > CH_3\rightarrow\overset{H}{\underset{H}{C}}:^{-} > CH_3\rightarrow\overset{H}{\underset{CH_3}{C}}:^{-} > CH_3\rightarrow\overset{CH_3}{\underset{CH_3}{C}}:^{-}$$

Methyl carbanion (1°) (Most stable) Ethyl carbanion (1°) Isopropyl carbanion (2°) *t*-butyl carbanium (3°) (Least stable)

The reactivity of carbanions follows the order 3° > 2° > 1°.

Reactions of Carbanions

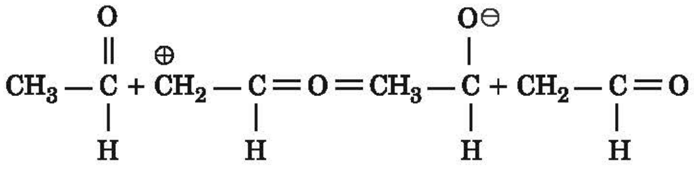
1. **Decarboxylation :** Decarboxylation of carboxylic acids involve formation of carbanion.



$$R-\underset{O}{\underset{\|}{C}}-O-H \longrightarrow R-\underset{O}{\underset{\|}{C}}-\overset{\ominus}{O} + \overset{\oplus}{H} \longrightarrow \overset{\ominus}{R}: + CO_2 \xrightarrow{H^+} R-H$$

Acid Carbanion Alkane

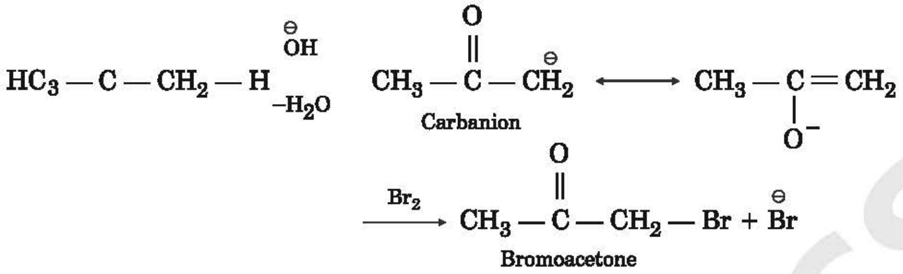
2. **Addition reactions :** Carbanions take part in a wide variety of addition reactions, such as addition to carbanyl group, Perkin and Benzoin reactions and aldol condensation etc.



$$CH_3-\overset{O}{\overset{\|}{\underset{H}{\underset{|}{C}}}} + \overset{\oplus}{CH_2}-\underset{H}{\underset{|}{C}}=O=CH_3-\overset{O\ominus}{\overset{|}{\underset{H}{\underset{|}{C}}}} + CH_2-\underset{H}{\underset{|}{C}}=O$$

Carbanion Aldol anion

3. **Halogenation of ketones :** halogenation of ketone (*e.g.*, bromination of acetone) takes place *via* carbanion formation.



$$HC_3-C-CH_2-H \xrightarrow[-H_2O]{\overset{\ominus}{O}H} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{C}H_2 \longleftrightarrow CH_3-\underset{\underset{\displaystyle O^-}{|}}{C}=CH_2$$

Carbanion

$$\xrightarrow{Br_2} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-Br+\overset{\ominus}{Br}$$

Bromoacetone

Q.7. What are free radicals? Discuss their formation, orbital structure, stability and reactions.

Ans.

Free Radicals

A free radical may be defined as an atom or group of atoms having an unpaired electron. These are produced on account of the homolytic fission of a covalent bond in the presence of heat or light.

$$A\bullet \,\vdots\, \bullet B \xrightarrow[\text{Homolytic fission}]{\text{Heat or light}} \underset{\text{Free radicals}}{A^{\bullet} + B^{\bullet}}$$

For example, homolytic fission of Cl—Cl bond in Cl_2 molecule in the presence of ultraviolet light gives chlorine free radicals.

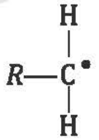
$$Cl-Cl \xrightarrow{\text{UV Light}} \underset{\text{Chlorine free radicals}}{Cl^{\bullet} + Cl^{\bullet}}$$

Free radicals are short lived and highly reactive. This is because they have a strong tendency to pair up their unpaired electrons.

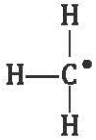
Classification

Depending upon the nature of carbon carrying the unpaired electron, the free radicals may be classified in the following three categories :

1. **Primary free radicals (1° free radicals) :** These possess unpaired electron on a primary (1°) carbon atom. For example,

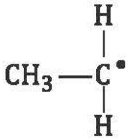


$$R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^{\bullet}$$



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^{\bullet}$$

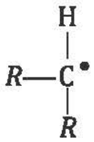
Methyl free radical



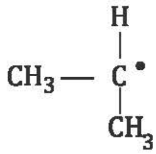
$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^{\bullet}$$

Ethyl free radical

2. **Secondary free radicals (2° free radicals) :** These possess unpaired electron on a secondary (2°) carbon atom. For example,



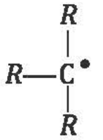
$$R-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^{\bullet}$$



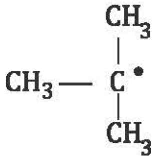
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{}^{\bullet}$$

2-propyl free radical
(Isopropyl free radical)

3. **Tertiary free radicals (3° free radicals) :** These possess unpaired electron on a tertiary (3°) carbon atom. For example,



$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{C^{\bullet}}}$$



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^{\bullet}}}$$

2-methyl-2-propyl free radical
(*t*-butyl free radical)

Formation of Free Radicals

(I) Long lived free radical : These may be prepared by the following method :

Chemical method of Gomberg : Long lived radicals, *e.g*,. triphenylmethyl radical my be prepared by treating triphenylmethyl chloride in benzene with finely powdered silver or zinc dust at room temperature for several days.

$$2\,(C_6H_5)_3\,C-Cl + 2Ag \xrightarrow[\text{Room temp.}]{\text{Benzene, }CO_2} \underset{\text{Triphenylmethyl radical}}{2\,(C_6H_5)_3\,C}$$

$$\overset{\text{Dimerisation}}{\rightleftharpoons} \underset{\text{Hexaphenylethane (Colourless)}}{(C_6H_5)_3\,C-C\,(C_6H_5)_3} + 2AgCl$$

The precentage dissociation of dimer to triphenylmethyl radical is increased if liquid SO_2 is taken as a solvent in place of benzene. The degree of dissociation also increases with increase in dilution and temperature.

(II) Short lived Free radicals : These may be prepared as follows :

Decomposition of peroxides : The peroxides having weak covalent bond (~ 30 kcal/mole) undergo thermal decomposition to form free radicals.

$$\underset{\text{Dibenzoyl peroxide}}{C_6H_5CO-O-O-CO\,C_6H_5} \xrightarrow[CCl_4]{60\text{–}100\,°C} 2C_6H_5COO \rightarrow \underset{\text{Phenyl radical}}{2C_6H_5} + 2CO_2$$

The formation of phenyl radical is inferred by the formation of Chlorobenzene, hexachloroethane and biphenyl etc in the reaction mixture.

$$\underset{\text{Diphenyl}}{C_6H_5-C_6H_5} \xleftarrow{\text{Dimerisation}} \underset{\text{Phenyl radical}}{C_6H_5} + \underset{\text{(solvent)}}{CCl_4} \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + CCl_3$$

$$\xrightarrow{\text{Dimerisation}} \underset{\text{Hexachloroethane}}{CCl_3-CCl_3}$$

Orbital Structure

Alkyl free radical are planar species. The central carbon atom present in an alkyl free radical is in a state of sp^2 hybridisation. The three sp^2 hybrid orbitals of the central carbon atom lie in a plane at an angle of 120° and overlap with the orbitals of H atoms or alkyl groups to form σ bonds. The unhybridised 2*p* orbital of the central carbon atom contains the unpaired electron as shown in Fig.

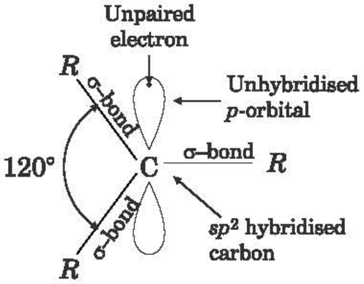
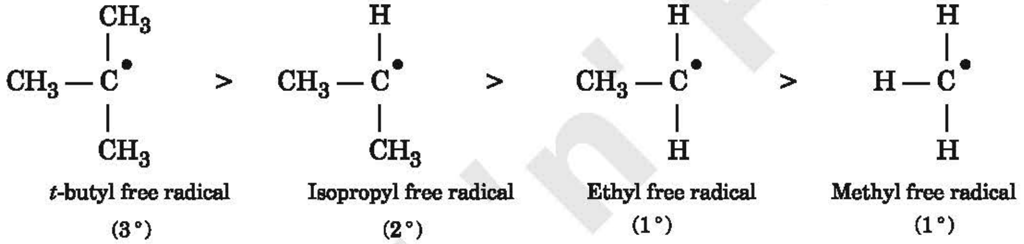


Fig. : Orbital structure of an alkyl free radical (*R* = an alkyl group or H-atom).

Stability

Free radical are very short lived species and therefore they are quite reactive. Their order of stability follows the order 3° > 2° > 1°. Thus, the relative stability of CH_3, CH_3CH_2, $(CH_3)_2CH$ and $(CH_3)_3C$ free radical is in the order :



$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

t-butyl free radical (3°) Isopropyl free radical (2°) Ethyl free radical (1°) Methyl free radical (1°)

The relative stability of free radicals can be explained on the basis of **hyperconjugation effect**. Greater the hyperconjugation effect, greater is the electron release towards the terminal carbon and lesser is the stability of the free radical. Since hyperconjugation effect is minimum for a *t*-butyl group, *t*-butyl free radical is most stable.

Reactions of Free Radicals

1. **Addition reactions :** These are as follows :
   - (i) **With halogen :** Free radicals react and add a halogen molecule.

$$2(C_6H_5)_3\,C + I_2 \longrightarrow 2\,(C_6H_5)_3C—I$$

   - (ii) **With olefins :** Free radicals undergo polymerisation.

$$\underset{}{CH_3} + CH_2{=}CH_2 \longrightarrow \underset{(A)}{CH_3—CH_2—CH_2} \xrightarrow{CH_2=\,CH_2}$$

$$CH_3—CH_2—\underset{(A')}{CH_2}—CH_2—CH_2$$

$$A + A' \longrightarrow \underset{\text{Polythene}}{A—A'}$$

   - (iii) **With hydrogen :** Free radical are reduced to hydrocarbon molecules.

$$\underset{\text{Triphenylmethyl radical}}{2(C_6H_5)_3\,C} + H_2 \xrightarrow{Zn/CH_3COOH} \underset{\text{Triphenyl methane}}{2\,(C_6H_5)_3\,C—H}$$

   - (iv) **With metals :** Free radical form organometallic compounds.

$$(C_6H_5)_3\,C + Na \longrightarrow \underset{\text{Triphenyl methyl sodium}}{(C_6H_5)_3\,C—Na}$$

(v) **With oxygen :** Free radical form peroxides.

$$2(C_6H_5)_3\,C + O_2 \longrightarrow \underset{\text{Peroxide (Colourless)}}{(C_6H_5)_3\,C—O—O—C\,(C_6H_5)_3}$$

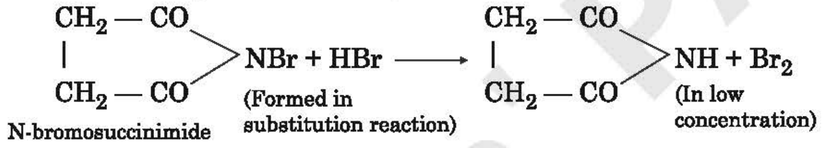
(vi) **With nitric oxide :** Free radicals from nitroso compounds.

$$(C_6H_5)_3C + NO \longrightarrow \underset{\text{Nitrosotriphenyl methane}}{(C_6H_5)_3\,C—NO}$$

2. **Disproportionation :** In this reaction free radical is reduced at the expense of other radical which gets oxidised.

$$C_2H_5 + C_2H_5 \xrightarrow{\text{High temp.}} \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Ethylene}}{C_2H_4}$$

3. **Bromination with N-bromo succinimide :** It is used for allylic bromination of propene at room temperature in CCl_4 solvent.



$$Br—Br \longrightarrow Br + Br\ (\textit{Chain initiation})$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + Br \longrightarrow CH_2—CH{=}CH_2 + HBr$$

$$CH_2—CH{=}CH_2 + Br—Br \longrightarrow \underset{\text{Allyl bromide}}{CH_2Br—CH{=}CH_2} + Br$$

It should be noted that addition is not favoured in low concentration of bromine.

Q.8. What are carbenes? Discuss their formation, orbital structure, reactions and applications.

Ans.

Carbenes

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries a lone pair of electrons.

Formation : These are usually produced either by **photolysis** (photochemical decom-position) or by **pyrolysis** (thermal decomposition) of diazoalkanes and ketenes. For example,

$$CH_2N_2 \xrightarrow{h\nu \text{ or } \Delta} \underset{\text{Methylene carbene}}{:CH_2} + N_2$$

$$CH_2{=}C{=}O \xrightarrow{h\nu \text{ or } \Delta} \underset{\text{Methylene carbene}}{:CH_2} + CO$$

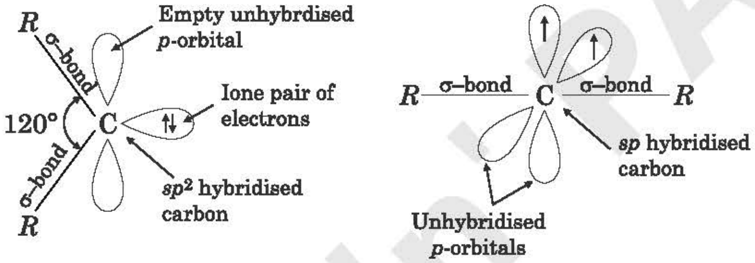
$$\underset{\text{Chloroform}}{CHCl_3} \xrightarrow{C_2H_5ONa} \underset{\text{Dichloro carbene}}{:CCl_2} + HCl$$

Carbenes are short lived and highly reactive species. This is because the central carbon atom in a carbene possesses an incomplete octet (only six electrons in the valence shell) and has a strong tendency to achieve an octet.

Orbital Structure

Carbenes are of two type– **singlet** and **triplet carbenes**. In a singlet carbene, the central carbon atom is in a state of sp^2 hybridasation. Among the three sp^3 hybrid orbitals, two overlap with the orbital of monovalent atoms or groups to form two σ-bonds while the third sp^2 hybrid orbital contains the lone pair of electrons. The unhybridised *p*-orbital is empty [Fig. 1 (a)]. Thus, a singlet carbene has a **bent structure**. In a **triplet carbene**, the central carbon atom is in a state of *sp* hybridisation. The two *sp* hybrid orbitals overlap with the orbitals of monovalent atoms or groups to form two σ-bonds. The two unhybridised *p*-orbitals contain one electron each (electrons belonging to the lone pair). Thus, a triplet carbene has a linear structure as shown in Fig. 1 (b).

It is to be noted that a triplet carbene is more stable than a singlet carbene.



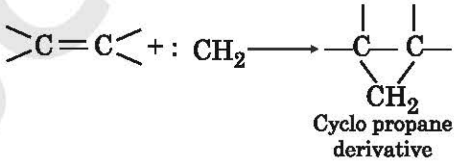
(a) Singlet carbene **(b) Triplet carbene**

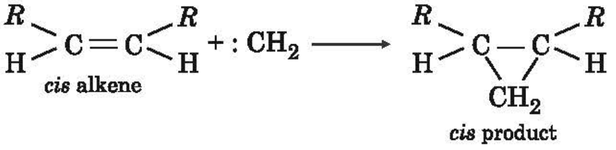
Fig. 1

Reactions

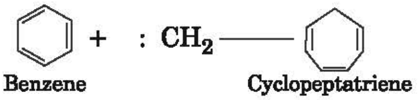
Carbenes are highly reactive unstable compounds. They are always prepared in the presence of the compound with which they react. Some of the important reactions are :

(i) **Addition to C═C bonds :** Carbenes add on alkenes to form cyclo propane derivatives.



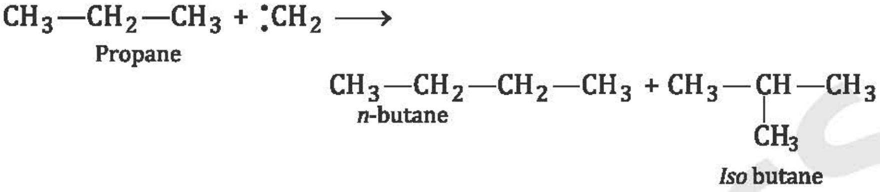


Carbenes also add to aromatic systems when ring expansion takes place.



(ii) **Addition reactions to alkanes :** Ethane adds methylene ($:CH_2$) to form propane and propane reacts with methylene to give *n*-butane and isobutane.

$$\underset{\text{Ethane}}{CH_3{-}CH_3} + :CH_2 \longrightarrow \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$



$$\underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3} + :CH_2 \longrightarrow \underset{n\text{-butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} + \underset{\textit{Iso}\text{ butane}}{CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3}$$

Applications

Carbenes are the reactive intermediates in a number of reactions such as Reimer **Tiemann reaction**, carbylamine reaction, Wittig reaction. In these reactions, $:CCl_2$ is formed as reaction intermediate.

Q.9. What are arynes? Discuss in detail.

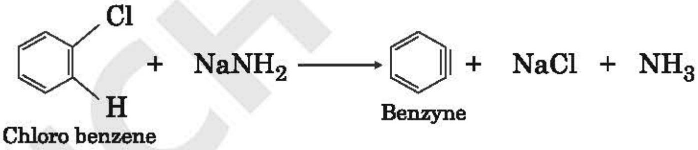
Ans.

Arynes or Benzyne (C_6H_4)

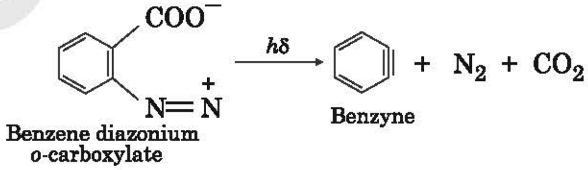
Benzyne is neutral, highly reactive intermediate in which aromatic character is not much disturbed. It is formed as an intermediate compound during nucleophilic substitution of aromatic compounds. It contains carbon-carbon triple bond which is quite different from that of acetylene.

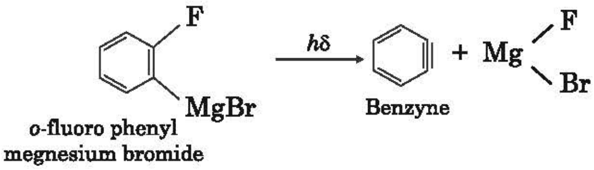
Formation of Benzyne

(i) By the action of strong bases such as sodamide or metal alkoxide (potassium *t*-butoxide) on aryl halides.



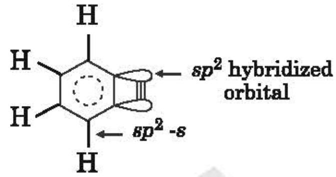
(ii) By the decomposition of benzene diazonium *o*-carboxylate or *o*-fluoro phenyl magnesium bromide.





Structure

The carbon-carbon triple bond present is benzyne is different from the tripe bond of acetylene. In acetylene each carbon atom is *sp*-hybridized. These two *sp*-hybridized orbitals form σ-bonds with *sp*-hybridized orbital of carbon and *s*-orbital of hydrogen. The remaining two unhybridized *p*-orbitals form two π-bonds. Such a structure is not possible in benzyne due to hexagonal geometry of benzene ring. Thus, a new bond of benzyne is formed by sideways overlapping of sp^2 hybridized orbitals of two adjacent carbon atoms as shown below :



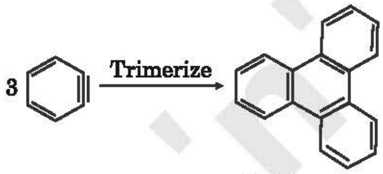
Structure of benzyne

Reactions

It is very reactive compound. This is because in this compound π-bond is formed by sideways overlapping of sp^2 orbitals which is very unstable. Some of its reactions are :

(i) In the absence of any reagent, two or three molecules of benzyne react together to form diphenylene and triphenylene, respectively.

Benzyne   Diphenylene

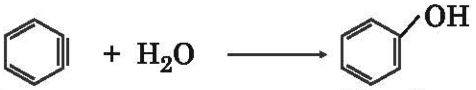


Triphenylene

(ii) It reacts with nucleophilic reagents to form addition compounds.

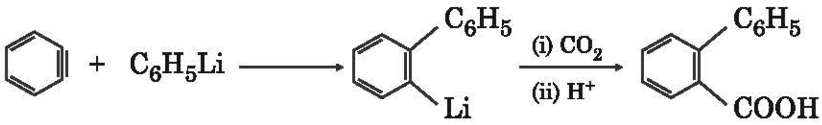
Benzyne   Liquid   Aniline

Benzyne   Methyl aniline



Benzyne   Phenol

(iii) It reacts with phenyl lithium to form phenyl lithium compound which is used in the sysnthesis.



Phenyl lithium compound   Biphenyl 2-carboxylic acid

Q.10. Discuss in detail about Nitrenes.

Ans.

Nitrenes or Imidogens

Nitrenes are the organic species having the general formal $R-\ddot{N}\colon$

They are similar to carbenes and contain a nitrogen atom with one bond and two non-bonded electron pairs, *i.e.*, $-\ddot{N}\colon$. They are electron deficient and have only six electrons in the outermost shell. They are highly reactive and act as strong electrophiles as they need a pair of electrons to complete the octet. The parent compound nitrene, $H-\ddot{N}\colon$ is also known as imidogen, azene or imene. Nitrenes can exist in the singlet and triplet states. The triplet state is the ground state and most nitrenes exist in this state.

Formation of Nitrenes

Alkyl and acyl nitrenes may be prepared by the decompostion of alkyl azides, alkyl isocyantes or acyl azides in the presence of light or heat.

$$\underset{\text{Alkyl azide}}{R-N_3} \xrightarrow{\text{light}} \underset{\text{Alkyl nitrene}}{R-\ddot{N}\colon} + N_2$$

$$\underset{\text{Methyl azide}}{CH_3-N_3} \xrightarrow{\text{light}} \underset{\text{Methyl nitrene}}{CH_3-\ddot{N}\colon} + N_2$$

$$\underset{\text{Phenyl azide}}{C_6H_5-N_3} \xrightarrow{\text{light}} \underset{\text{Phenyl nitrene}}{C_6H_5-\ddot{N}\colon} + N_2$$

$$\underset{\text{Alky isocyanate}}{R-N=C=O} \xrightarrow{\text{light}} \underset{\text{Alkyl nitrene}}{R-\ddot{N}\colon} + CO$$

$$\underset{\text{Methyl iso cyante}}{CH_3-N=C=O} \xrightarrow{\text{light}} \underset{\text{Methyl nitrene}}{CH_3-\ddot{N}\colon} + CO$$

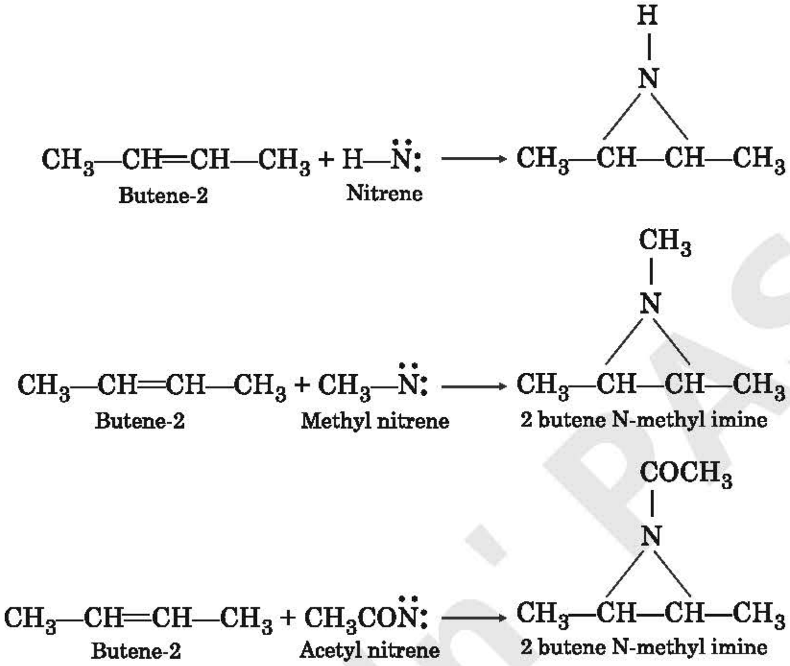
$$\underset{\text{Acyl azide}}{RCON_3} \xrightarrow{\text{light}} \underset{\text{Acyl nitrene}}{R-CO\ddot{N}\colon} + N_2$$

$$\underset{\text{Acetyl azide}}{CH_3CON_3} \xrightarrow{\text{light}} \underset{\text{Acetyl nitrene}}{CH_3CO\ddot{N}\colon} + N_2$$

Reactions

Nitrenes are highly reactive unstable compounds. Some of the important reactions are :

(i) **Addition to C=C bonds :** Nitrenes add on alkenes to form cyclic products.



(ii) **Addition reactions to alkanes :** Iso butane reacts with acetyl nitrene to form acetyl *t*-butyl amine.

$$\underset{\text{Iso butane}}{(CH_3)_3CH} + \underset{\text{Acetyl nitrene}}{CH_3CO\ddot{N}:} \longrightarrow \underset{\text{Acetyl } t\text{-butyl amine}}{(CH_3)_3CNHCOCH_3}$$

(iii) **Dimerization :** Two molecules of nitrene combine to form azo compounds.

$$\underset{\text{Phenyl nitrene}}{2C_6H_5—\ddot{N}:} \xrightarrow{\text{light}} \underset{\text{Azo benzene}}{C_6H_5—N{=}N—C_6H_5}$$

Applications

Nitrenes have important synthetic applications and they are reactive intermediates in a number of reactions such as **Hofmann, Curtius** and lossen rearrangement.

❑

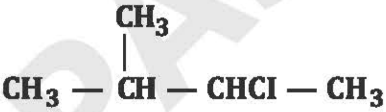
UNIT-VI

Stereochemistry

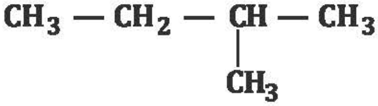
SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. Which of the following compounds exhibit enantiomerism?

(i) $CH_2OH\,CHOH\,CHO$

(ii) 

$CH_3 - \underset{}{\overset{CH_3}{\overset{|}{CH}}} - CHCl - CH_3$

(iii) 

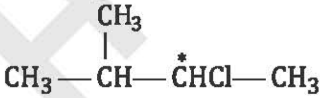
$CH_3 - CH_2 - \underset{CH_3}{\underset{|}{CH}} - CH_3$

(iv) $CH_3CHOHCH_3$

(v) CH_2NH_2COOH

Ans. Compounds (i) and (ii) have chiral carbons marked with asterisks and hence these two compounds show enantiomerism.

$CH_2OH\overset{*}{C}HOHCHO$



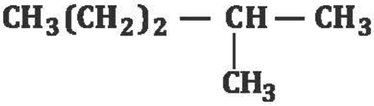
$CH_3 - \overset{CH_3}{\overset{|}{CH}} - \overset{*}{C}HCl - CH_3$

Compounds (iii), (iv) and (v) have no chiral carbon atom in the molecule.

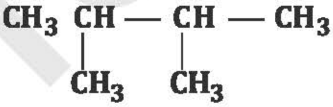
Hence, they do not show enantiomerism.

Q.2. Give below are the structural formulae of all alkanes with molecular formula C_6H_{14}. Which of these exhibit enantiomerism?

(i) $CH_3(CH_2)_4CH_3$

(ii) 

$CH_3(CH_2)_2 - \underset{CH_3}{\underset{|}{CH}} - CH_3$

(iii) 

$CH_3\,\underset{CH_3}{\underset{|}{CH}} - \underset{CH_3}{\underset{|}{CH}} - CH_3$

(iv) $(CH_3)_3\,C - CH_2CH_3$

Ans. There is no carbon in any of the compounds above which is chiral *i.e.*, attached to four different groups.

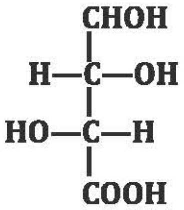
Chirality is the necessary condition for a molecule to exhibit enantiomerism. Hence none of the compounds above shows enantiomerism.

Q.3. Point out the optically active compounds out of the following :

(i) $CH_2OH - CHOH - CHO$

(ii) $CH_3 - CHOH - CH_2OH$

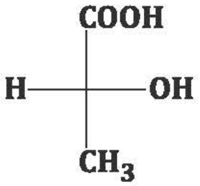
(iii)



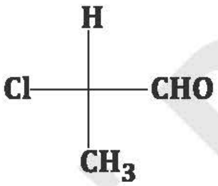
Ans. Compounds (i) and (ii) have one chiral carbon (the middle one) and hence both these compounds are optically active compounds. (iii) has two chiral carbons (the middle ones) and therefore this compounds is also optically active.

Q.4. Assign *R* or *S* configuration to each of the following :

(i)

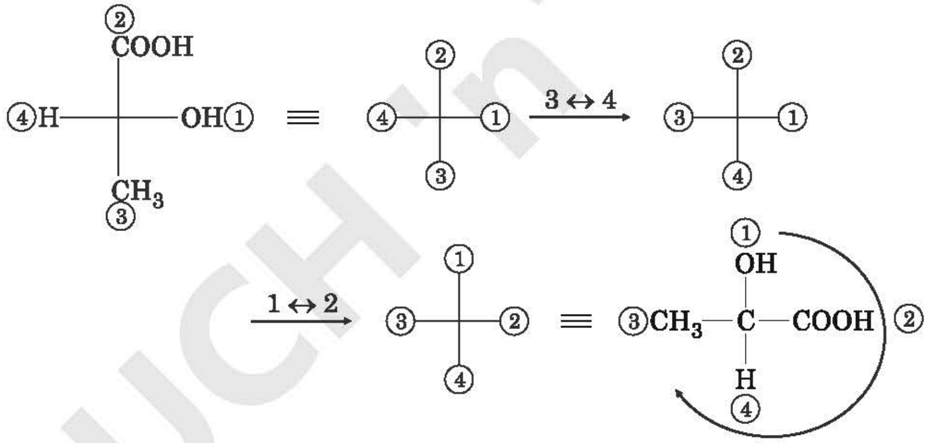


(ii)



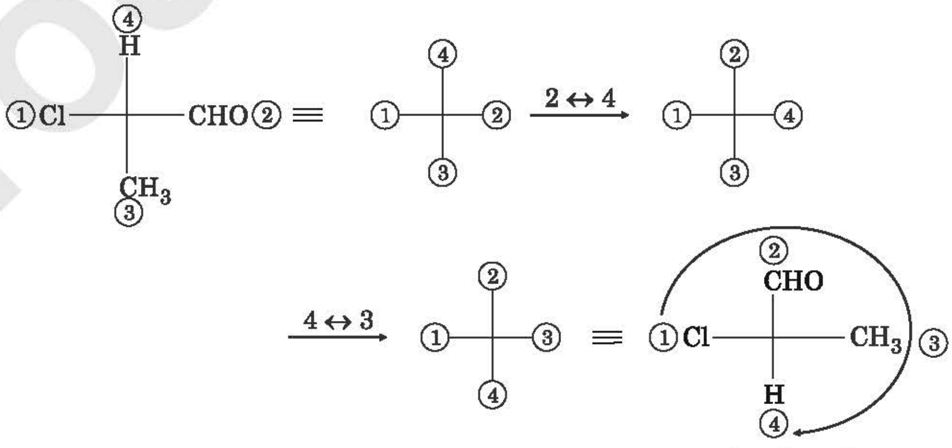
Ans.

(i)



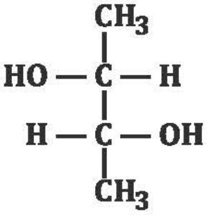
R-configuration

(ii)

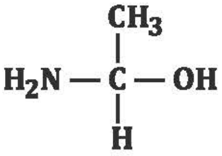


R-configuration

Q.5. Assign (*R*) or (*S*) configuration to the following compounds :

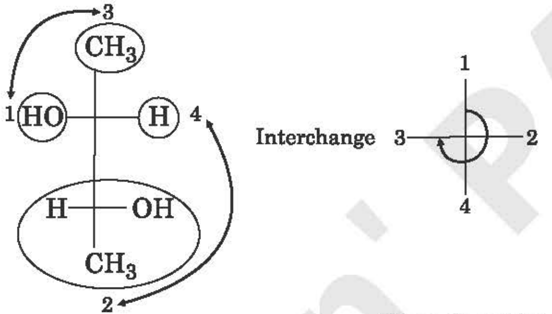


(*A*)

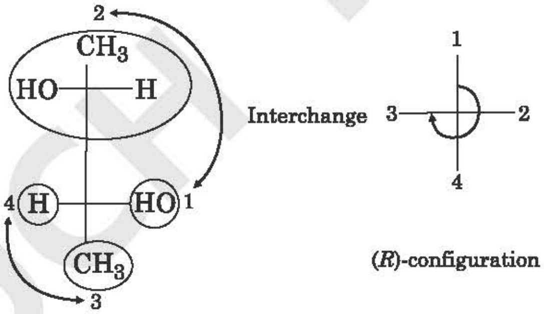


(*B*)

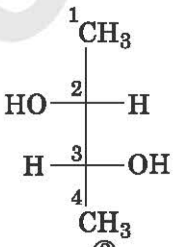
Ans.



(*A*)

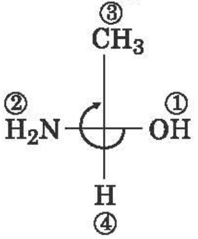


∴ (*A*) ≡



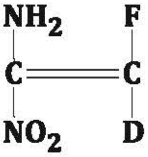
≡ (2*R*, 3*R*)-configuration

(*B*)

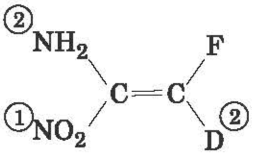


≡ (*R*)-configuration

Q.6. Assign *E* – *Z* nomenclature to the following compounds :



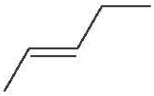
Ans.



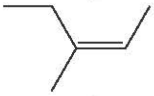
(E)-configuration.

Q.7. Write *E* and *Z* configuration of the compounds :

(i)

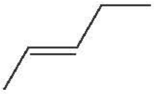


and **(ii)**

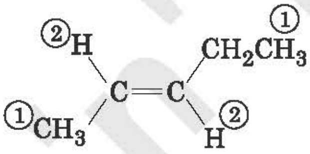


Ans.

(i)

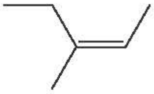


≡

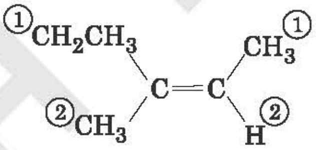


(*E*)-

(ii)



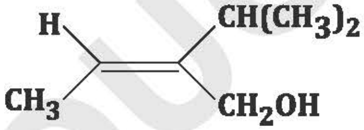
≡



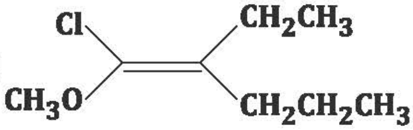
(*Z*)-

Q.8. Assign *E* or *Z* configuration to each of the following :

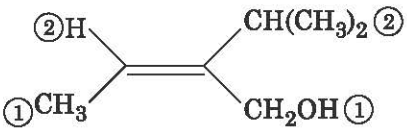
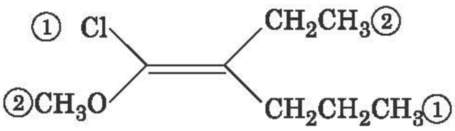
(i)



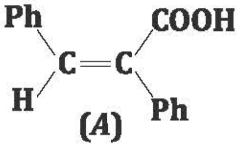
(ii)



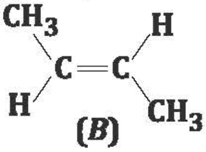
Ans.

S.No.	**Molecule**	**Configuration**
(i)		(*Z*)
(ii)		(*E*)

Q.9. Assign *E* or *Z* configuration to the following compounds :

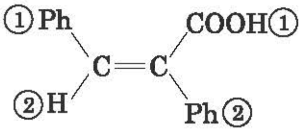


(*A*)

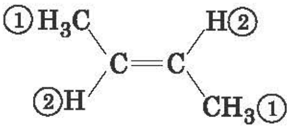


(*B*)

Ans.



(*Z*)-configuration



(*E*)-configuration

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you mean by centre of symmetry or centre of inversion?

Ans.

Centre of Symmetry or Centre of Inversion (CI)

Centre of symmetry is a point such that, if a line is draw from any atom or group of the molecule to this point and extended an equal distance beyond this point, another identical atom or group will be found just at the end of the line. For example, A cube and ethane molecule both have centre of symmetry as shown in Fig. below :

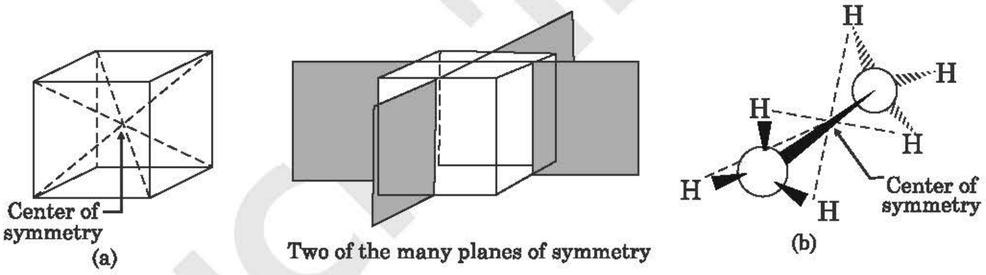


Fig. Center of symmetry : (a) A cube has center of symmetry and several planes of symmetry. A cube is achiral. (b) The staggered form of the ethane molecule also has a center of symmetry and so is achiral.

Q.2. What is plane of symmetry or mirror plane?

Ans.

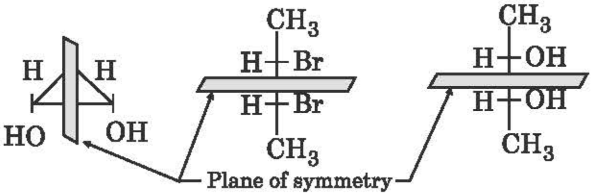
Plane of Symmetry or Mirror Plane

A plane of symmetry is one which divides the molecule into two equal halves so that each half is the mirror image of the other half.

In general, all planar molecules possesses atleast one plane of symmetry, identical with molecular plane.

For example, all alkenes have plane of symmetry which is the plane of double bond.

When a molecule has plane of symmetry it will not be optically active, even though it might contain chiral carbon. For example, meso compounds

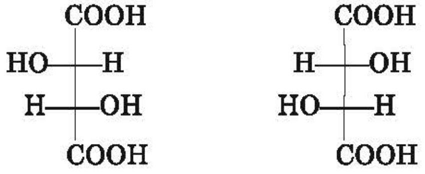


Q.3. What are enantiomers? Discuss in brief.

Ans.

Enantiomers

Chiral molecules which are non- superimposable mirror images of each other are enantiomers.



Enantiomers

They have opposite crystal structures and configurations. They rotate plane of plane polarized light in opposite directions but to the same extent. The physical properties of enantiomers *e.g.*, boiling point, melting point and solubility in optically inactive solvents) are identical. In symmetrical environments, their chemical properties are also identical. This means that two optically active forms of enantiomers behave similarly towards achiral reagent, achiral solvent and achiral catalyst. The enantiomers react at different rates and form products in different amounts in asymmetric environment. They have different solubilities in same chiral solvent. They react at different rates, if any one of the reagent solvent or catalyst is chiral.

A substance composed of equimolecular amounts of a pair of enantiomers is a **racemic modification.**

Laboratory synthesis of an enatiomer in symmetric environment leads to racemic form. But if one tries to synthesize an enantiomer by the use of an optically active reagent, optically active products are obtained. This may contain : (a) One enantiomer is excess over the other or (b) a pure enantiomer.

From a racemic modification, optically active substances may also be obtained by using optically active reagent, catalyst and solvent. In nature on finds pure optical isomers instead of racemic forms, this is because optically active enzymes are involved in such synthetic processes.

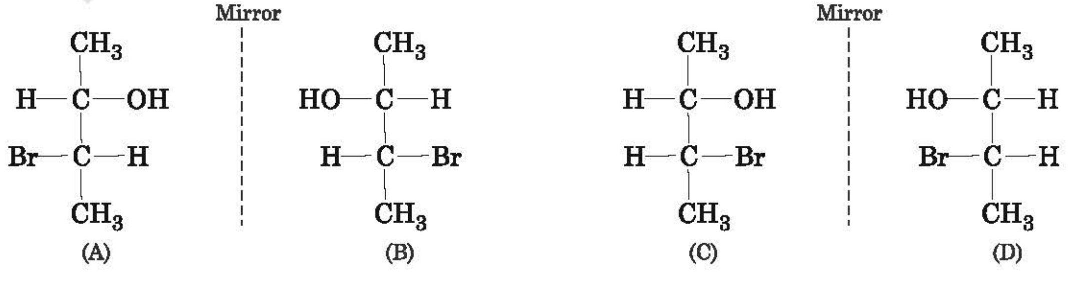
Enantiomerism is the phenomenon of existence of enentiomers in a single structural formula but in opposite configuration.

Q.4. What are diastereomers? Explain with example.

Ans.

Diastereomers

In general, each asymmetric carbon atom in a molecule doubles the number of theoretically possible isomers. Hence, molecule with n asymmetric carbon atoms should have 2^n stereoisomers. Following figure shows the four isomers of 3-bromo-2-butanol, which has two asymmetric carbon atoms :



Notice that (A) is the mirror image of (B); (C) is the mirror image of (D). Thus the four isomers are two pairs of **enantiomers**. Now compare (A) with (C). They are neither superimposable nor are they mirror images. They are called **diastereomers**. (A) and (D) are also diastereomers, as are (B) and (C), and (B) and (D). Stereoisomers that are not mirror images of each other as called **diasteremers**.

Diastereomers have different properties. Two diastereomers will have different melting point, boiling points and solubilities. They will have different chemical reactivities toward most reagents.

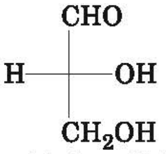
Q.5. Write short note on threo and erythro diasteromers.

Ans.

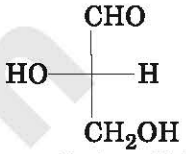
Threo and Erythro Notations

Diastereomers are optical isomers of compound which are not mirror images of each other and hence are not enantiomers. For example, *d*-tartaric acid is a diastereomer of mesotartaric acid. But the two are not enantiomers.

As for as the absolute configuration of a compound is concerned we derive it from the configuration of glyceraldehyde which has been taken as arbitrary standard.



D (+) glyceraldehyde



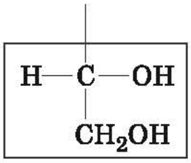
L (–) glyceraldehyde

D and *L* stand for the configuration while (+) and (–) signs denote the actual direction of rotation of plane polarised light. If H and OH are on the LHS and RHS of central carbon, it donates *D* configuration. It OH and H are on the LHS and RSH of central carbon it denotes *L* configuration.

Any compound that can be obtained from or converted into *D* (+) glyceraldehyde has *D* configuration. Similarly any compound that can be obtained from or converted into *L* (–) glyceraldehyde has *L* configuration.

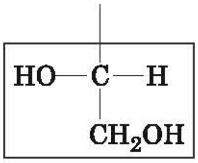
Thus, when we have to decide the configuration of compounds (particularly sugars) containing more than three carbons, we shall check the configuration of lower two carbons as show below :

X



D-series

Y

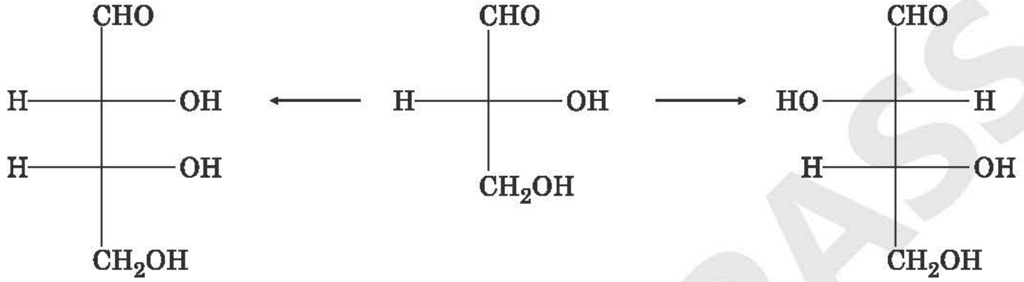


L-series

If the arrangement corresponds to X, the compound has *D* configuration. If the arrangement corresponds to Y, the compound belongs to *L* configuration.

Let us take the example of $CHO\,\overset{*}{C}H\,OH\,\overset{*}{C}HOH\,CH_2\,OH$. This contains two asymmetric carbon atoms marked with asterisks. There are four optical isomers possible, all of which are known.

If the H on the third carbon atom (from the bottom) is on the left hand side, the compound is **erythro**, while if the H on the third carbon atom is on the right hand side, the compound is **threo**. The structures of *D*-erythrose and *D*-threose which may be assumed to be obtained from *D*-glyceraldehyde are given below



D(–) Erythrose (I) *D*(+) Glyceraldehyde *D*(–) Threose (II)

Q.6. Give the difference between enantiomers and diastereomers.

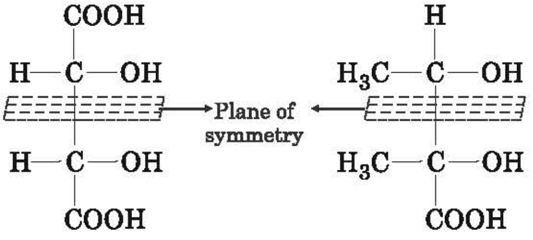
Ans. Differences between Enantiomers and Diastereomers

S.No.	Enantiomers	Diastereomers
1.	Optical isomers that are mirror images of each other are known as enantiomers.	Optical isomers that are not mirror images of each other are known as diastereomers.
2.	They have identical physical properties (mp, bp etc). They differ only in their action towards plane polarised light	They have different physical properties like mp, bp, density, refractive index.
3.	Optical isomers have identical chemical properties except their action towards optically active compounds.	Show similar but not identical chemical properties.
4.	They are optically active.	Diastereomers other than geometrical isomers may or may not be optically active.
5.	They equimolar mixture of two enantiomers (racemic mixture) can be separated by resolution.	On account of difference in their physical properties they can be separated from one another through techniques like fractional distillation, chromatography etc.

Q.7. What are meso compounds and racemic mixture?

Ans. Meso Compound

"A compound, having two or more asymmetric carbon atom, which superimposes on its mirror image and hence is optically inactive is known as meso compound. A meso compound is optically inactive due to internal compensation as the molecule has a plane of symmetry. Therefore, molecule as a whole is not disymmetric because one half of the molecule is exactly the mirror image of other. Meso form can't be resolved into optically active form because optical inactivity is present within the molecule.



Meso-tartaricacid

Meso-2,3-dihydroxy butane

One half is the mirror image of the other

Meso-form differs form the active forms in physical and chemical properties.

Property	Meso form	Active forms/Isomers
M.P.	140°C	170°C
Density	less	more
Solubility	less	more

Racemic Mixture

"An equimolar mixture of *d* and *l*-forms is known as racemic mixture." Optical rotations caused by *D* and *L*-forms are exactly equal but opposite in direction. Therefore, rotation of one form is compensated by the opposite rotation of other form and mixture as a whole is optically inactive. Thus, racemic mixture is optically inactive due to external compensation. hence a racemic mixture can be separated into *D* and *L*-forms.

Q.8. Discuss in brief the resolution of racemic mixtures.

Ans.

Resolution of Racemic Mixtures

Synthesis of an optically active compound produces a mixture of both (+)- and (–)-isomers in equal amount. Such a mixture is called a racemic mixture or a **racemate**. The separation of a racemic mixture into its two optically active components (+ and – isomers) is known as resolution. Following methods are used :

1. Chemical Resolution

Optically active isomers of the same compound resemble one another so closely in all properties except optical that it is not possible to separate them by ordinary laboratory methods. If, however, the racemic mixture is made to combine with another optically active compound, differences are set up which can be exploited for separation. Suppose for example, that racemic lactic acid is allowed to combine with the optically active base, (–)-strychnine. The salts formed will be :

(–)-strychnine (+)-lactate and
(–)-strychnine (–)-lactate

These salts are not true enantiomers. They differ considerable in properties and in particular, in solubility in various solvents. By fractional crystallisation from a suitable solvent, they can be separated. Then treatment with dilute mineral acid removes the optically active base and leaves the two separate samples of (+)-lactic acid and (–)-lactic acid.

In a similar way, a racemic mixture of optically active forms of a base can be separated by the use of an optically active acid.

2. Biochemical Resolution

When certain bacteria or moulds are added to a solution of a racemic mixture they bring about the decomposition of one of the optically active forms more rapidly than the other. For example,. *Penicillium glaucum* decomposes (+)- tartaric acid more readily than the (−)-isomer so that the latter can be obtained from the residue after treatment with the would.

Q.9. Write a short note on racemisation.

Ans.

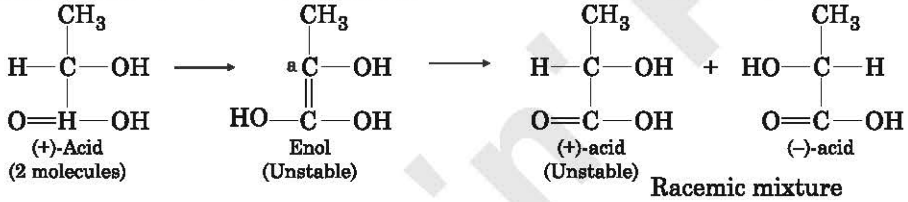
Racemisation

Conversion of an optically active compound into a racemic mixture is called racemisation. Racemic mixture is a mixture containing equal amounts of (+)- and (−)-isomers. Thus,

$$2\ (+)\text{-A} \rightarrow (+)\text{-A} + (-)\text{-A}$$

$$\text{or } 2\ (-)\text{-A} \rightarrow (+)\text{-A} + (-)\text{-A}$$

Racemisation can be accomplished by means of heat, light or by conversion of the isomer into an optically inactive intermediate which reverts to the racemic mixture. The conversion of either of the optically active lactic acids into a racemic mixture by heating its aqueous solution may proceed through an *enol* intermediate.

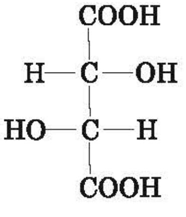
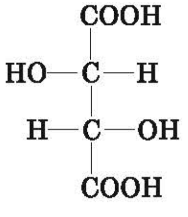
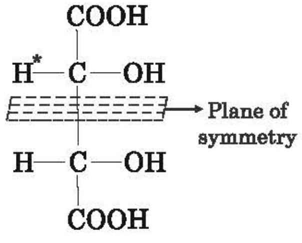


When the proton migrates back to the carbon atom, the process can involve the opening of either of the two linkages of the double bond and can produce either the original configuration or the opposite of it.

Q.10. Give the difference between racemic mixture and meso compounds.

Ans.

Differences between Racemic Mixture and Meso Compound

S.No.	Racemic mixture	Meso Compound
1.	A racemic mixture contains equimolar amounts of enantiomers.	A meso compound is one which is optically inactive although have more than one chiral carbons.
2.	Recemic mixture is optically inactive due to external compensation.	Meso compound is optically inactive due to internal compensation.
3.	It can be resolved into optically active forms.	It can't be resolved into optically active forms.
4.	Enantiomers which are the part of racemic mixture are disymmetric in nature. *e.g.*, Equimolar mixture of *D*-and *L*-tartaric acid.  *d*-form  *l*-form	The molecule as a whole is not disymmetric, as its has "plane of symmetry". *e.g.*, Tartaric acid.  **Meso-form**

Q.11. Discuss Walden inversion in short.

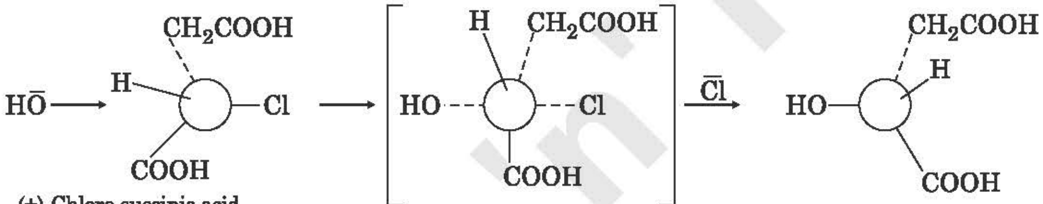
Ans.

Walden Inversion

When a group attached to an asymmetric carbon atom is replaced, the configuration of the new compound may be opposite to the original. That is, the product is the enantiomer (mirror image) of the expected substance. This phenomenon is known as **Walden inversion.** Factors which determine whether or not an inversion will occur are the nature of the reagent the nature of the solvent, the temperature and the nature of the substance being acted upon.

The mechanism of Walden inversion involves three steps :

1. Approach of the attacking group from the side of the molecule opposite to the position of the group which is later replaced.
2. Formation of an intermediate transition state in which three groups and the asymmetric carbon atom lie in one plane, and
3. Separation of the group being replaced. This change is analogous to an umbrella being blown inside out. The conversion of (+) chlorosuccinic acid into (–) malic acid is an example of Walden inversion.



(+)-Chloro succinic acid

(–)-Malic acid

Q.12. Write a short note on configuration.

Ans.

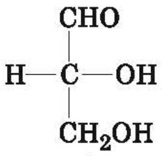
Configuration

"The arrangement of atoms or groups around the asymmetric centre is known as configuration." Configuration is used to characterise a particular stereoisomer. There are two important conventions, that are used to assign the configuration of organic compounds :

1. Relative configuration (*D* and *L*), 2. Absolute configuration (*R* and *S*).

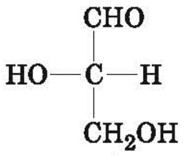
1. Relative Configuration

In this system the configuration of a compound is assigned with reference to an arbitrary standard glyceraldehyde. The two forms of glyceraldehyde were arbitrarily assigned the *D* and *L* configuration as follows :



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

D-configuration
(+)-glyceraldehyle



$$\begin{array}{c} CHO \\ | \\ HO-C-H \\ | \\ CH_2OH \end{array}$$

L-configuration
(–)-glyceraldehyle

At asymmetric carbon atom	At asymmetric carbon atom
If (a) — OH on right hand side	If (a) — OH on left hand side
(b) — H on left hand side	(b) — H on right hand side
Configuration – *D* – form	Configuration – *L* – form

If the configuration at the asymmetric carbon atom of a compound can be related to *D*(+) glyceraldehyde the compound belongs to *D*-series and if it can be related to *L*(–) glyceraldehyde, the compound belongs to the *L*–series.

2. Absolute configuration

D and *L* system of assigning the configuration has the following limitations :

(i) Configuration of the same molecule may be related to both *D* and *L* series simulta -neously.

(ii) Difficult to apply it to molecules having complicated structures.

(iii) Difficult to apply it to the compounds having more than one asymmetric carbon atom.

These ambiguities are removed by *R* and *S* system of nomenclature.

Q.13. Write the difference between conformation and configuration.

Ans. Differences between Configuration and Conformation

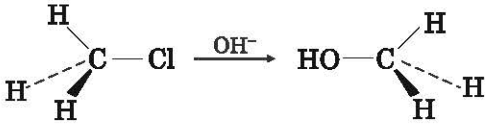
S.No.	Conformation	Configuration
1.	Configuration of a molecule is the spatial arrangement of atoms and groups about a rigid part of the molecule, *i.e.*, about a double bond or ring and about a dissymmetric part of the molecule.	Conformations of a molecule are the different spatial arrangements of its atoms and groups that arise due to the rotation of a part of the molecule about a single bond.
2.	Configurations are isolable.	Conformers are non-isolable.
3.	A molecule can have only one configuration, *i.e.*, a different configuration is a different molecule.	A molecule could have an infinite number of conformations.
4.	Conformations have low energy barrier, which varies from 4.2 to 46 kJ per mole.	Difference of energy between two configuration is more than 84 kJ/mole.
5.	Interconversions of configuration involve bond breaking and bond reforming processes.	Interconversion of conformations involve rotation of a part of a molecule about a single bond.
6.	Configuration are not easily interconvertible.	Conformations are easily interconvertible, they get converted even at room temperature.

Q.14. Discuss in brief the retention and inversion of configuration.

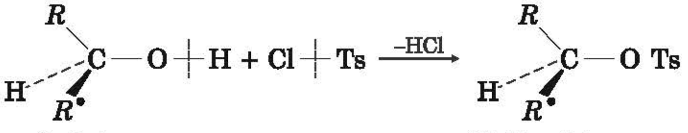
Ans. Retention and Inversion of Configuration

A reactant with a chiral molecule in a reaction gives a product which may have the same configuration as the reactant or an opposite configuration. If the configuration of the reactant and product is the same, the reaction is said to proceed with retention of configuration. And if the reactant and the product have opposite configurations, the reaction is said to occur with inversion of configuration consider the following examples.

S_N2 reaction of alky halide with OH^- ions. This reaction takes place with **inversion** of configuration as shown below :



Reaction of a secondary alcohol with tosyl chloride (*p*-toluenesulphonyl chloride) in the presence of pyridine. This reaction takes place with retention of configuration and the product is alkyl tosylate.



Alcohol Alkyl tosylate

SECTION-C LONG ANSWER TYPE QUESTIONS

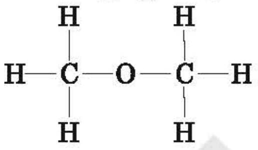
Q.1. What do you understand by isomerism? What are the type of isomerism? Discuss structural isomerism in detail.

Ans.

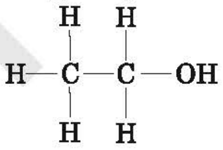
Isomerism

"Compounds having same molecular formula but differ in physical and chemical properties are known as isomers and the phenomenon is known as isomerism". *e.g.*,

(i) The molecular formula C_2H_6O represents the following compounds :



and

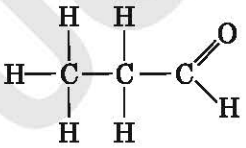


Dimethyl ether (C_2H_6O)

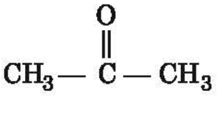
Ethyl alcohol (C_2H_6O)

Their physical and chemical properties are entirely different. Therefore diethyl ether and ethyl alcohol are isomers.

(ii) C_3H_6O



and



Propanal

Acetone

Types of Isomerism

Isomerism are mainly of two types :

1. Structural isomerism, 2. Stereo isomerism.

Structural Isomerism

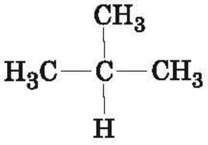
"Compounds having same molecular formula but have different structural formula are known as structural isomerism and the phenomenon is known as structural isomerism." Structural isomerism are of following types :

(i) **Chain isomerism :** Chain isomerism is due to different arrangement of carbon chains, *i.e.*, branched *or* straight. *e.g.*,

(a) **C_4H_{10}** : Butane has the following chain isomers :

$CH_3—CH_2—CH_2—CH_3$

n-butane
(Straight chain)

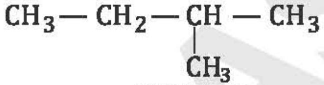


Iso-butane
(Branched chain)

(b) **C_5H_{12}** : Pentane has three chain isomers :

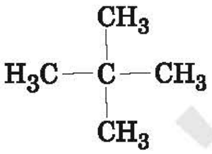
$H_3C — CH_2 — CH_2 — CH_2 — CH_3$

n-pentane



$CH_3—CH_2—\underset{CH_3}{\underset{|}{CH}}—CH_3$

Isopentane



Neopentane

(ii) **Position isomerism :** This type of isomerism is only due to different positions of the same functional group, substituent, double or triple bond. *e.g.*,

(a) **C_4H_8** has the following two position isomers (due to different position of double bonds) :

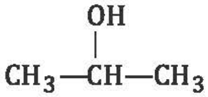
$CH_3—CH_2—CH{=}CH_2$
1-butene

$CH_3—CH{=}CH—CH_3$
2-butene

(b) **C_3H_7OH**

$CH_3—CH_2—CH_2—OH$

1-propanol
(*n*-propyl alcohol)



$CH_3—\overset{OH}{\overset{|}{CH}}—CH_3$

2-propanol
(Iso-propyl alcohol)

Due to different positions of the same functional group—OH.

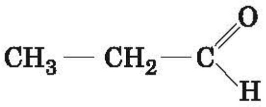
(iii) **Functional isomerism :** This type of isomerism is due to the different functional groups. *e.g.*,

(a) **C_2H_6O**

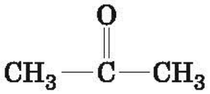
$CH_3—CH_2—OH$
Ethanol
(Functional group—OH)

$CH_2—O—CH_3$
Dimethyl ether
(Functional group—O—)

(b) **C_3H_6O**



Propanal
(Functional group —CHO)



Propanone
(Functional group > C=O)

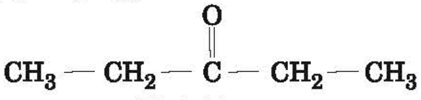
(iv) **Metamerism :** Unequal distribution of carbon atoms on both sides of same functional group leads to metamerism. *e.g.*,

(a) $\mathbf{C_4H_{10}O}$

$CH_3-CH_2-O-CH_2-CH_3$
Diethyl ether
(Functional group—O—)
Groups attached to functional group are
CH_3-CH_2- and CH_3-CH_2-

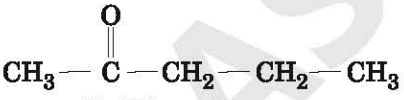
$CH_3-O-C_3H_7$
Methyl propyl ether
(Same functional group—O—)
Groups attached to functional group are
CH_3- and $CH_3CH_2CH_2-$

(b) $\mathbf{C_5H_{10}O}$



$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Diethyl ketone

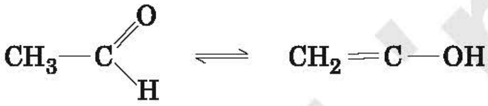


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

Methyl propyl ketone

(v) **Tautomerism :** Tautomerism refers to the reversible inter-conversion of isomers. When the two inter-convertible isomers contain > C═O group and enolic (double bond + OH) it is known as **keto-enol tautomerism**. There exists a dynamic equilibrium between the tautomers. *e.g.*,

(a) $H-C\equiv N \rightleftharpoons H-N\overset{=}{\rightarrow}C$

(b)


Acetaldehyde Vinyl alcohol

(c)


$CH_3-\overset{\overset{H}{\|}}{C}-CH_2-COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{\|}}{C}=CH-COOC_2H_5$

Acetoacetic ester (Ketonic form) keto-enol tautomerism Enolic form

Q.2. What is optical isomerism? Describe in detail.

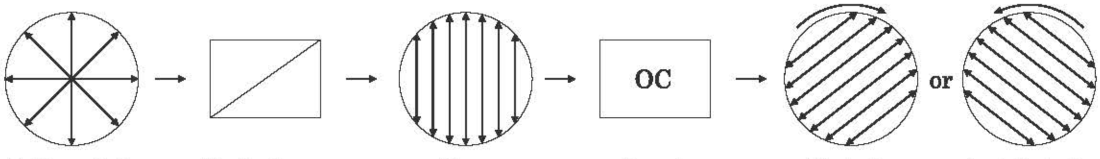
Ans.

Optical Isomerism

When an ordinary light is passed through a nicol prism, the vibrations of light are adjusted in a single plane and a light whose vibrations occur in one plane is termed as plane polarized light. Some substances have the ability to rotate the plane polarised light either to the right (clockwise) or to the left (anti-clockwise) direction.

Substances, which are capable of rotating the plane of polarised are said to be optically active. The property of rotating the plane polarised light is called **optical activity**.

Polarimeter is used to determine and measure the optical activity of a substance in terms of angle of rotation of the planes in degrees.



The angle of rotation depends upon the following factors :

(i) Nature of substance

(ii) Wavelength of light

(iii) Concentration of solution

(iv) Nature of solvent

(v) Length of path through which polarised light passes.

Thus optical activity is expressed in terms of specific rotation (α_{sp}).

$$\alpha_{sp} = \frac{\alpha_{obs}}{l \times c}$$

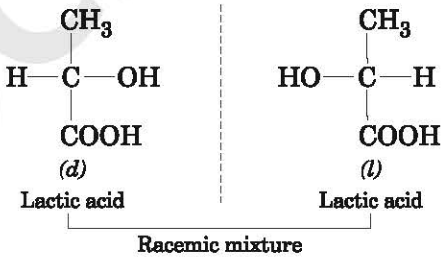
where $\alpha_{obs} \rightarrow$ Observed rotation
$l \rightarrow$ Length of solution in decimeter
$c \rightarrow$ Number of grams per ml in the solution

Optical Isomers

Compounds having similar chemical and physical properties but differ only in behaviour towards polarized light are called optical isomers and this phenomena is called as **optical isomerism.**

On the a basis of optical activity the organic compounds are divided into three types :

1. **Dextro-rotatory :** The optical isomer which rotates the plane of polarised light to the right direction (clockwise) is known as dextro-rotatory and designed (+) or *d*.
2. **Laevo-rotatory :** The optical isomer which rotates the plane polarised light to the left (anti-clockwise) is known as laevo-rotatory isomers and is designated (–) or *l*.
3. **Racemic mixture :** If the optical power of *d* and *l* isomers are equal in magnitude and opposite in sign then an equimolar mixture of the two forms, will be optically inactive, the mixture is termed as racemic mixtures or *dl* form of (+, –).

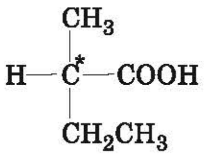


$\mathrm{H-\overset{CH_3}{\underset{COOH}{C}}-OH}$ (*d*) Lactic acid; $\mathrm{HO-\overset{CH_3}{\underset{COOH}{C}}-H}$ (*l*) Lactic acid

Racemic mixture

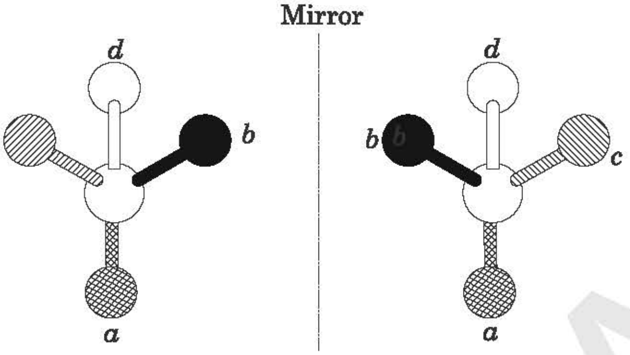
Important Terms in Optical Isomerism

1. **Chiral molecule :** A chiral molecule is defined as that centre of carbon atom which is attached with four dissimilar groups or atoms. Such a carbon atom is called an **asymmetric carbon atom**. For example,



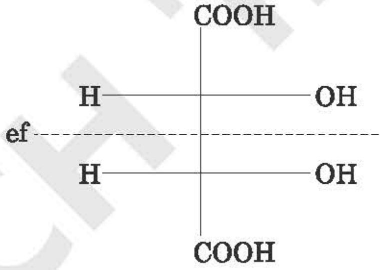
$\mathrm{H-\overset{CH_3}{\underset{CH_2CH_3}{\overset{*}{C}}}-COOH}$

A chiral molecule is a stereoisomer whose mirror image is not super-imposable.

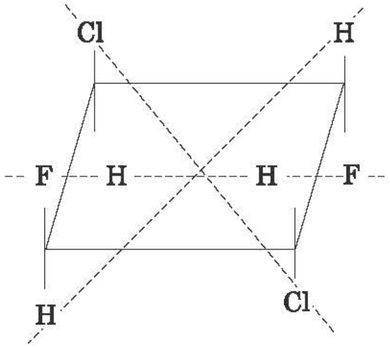


Note : For a optical activity the chiral molecule does not contain a **plane of symmetry** and **centre of symmetry**.

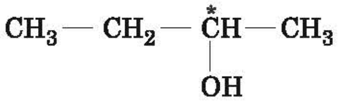
2. **Plane of symmetry :** When the molecules is divided into two equal halves, then it will become optically inactive because the upper half rotates in positive (+ve) direction or negative (–ve) direction and the lower halves rotates in (–ve) direction or (+ve) direction. These two rotations cancel each other and the compound become optically inactive. For example, *meso* tartaric acid.



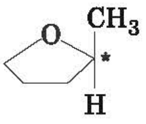
3. **Centre of symmetry :** A molecule is said to have a centre of symmetery if it all straight lines that can be drawn through the centre of the molecule atoms at the same distance from the centre.



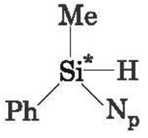
4. **Chiral centre :** A chiral centre is an atom bonded tetrahedrally to four different atoms or groups of atoms. A chiral centre is usually a C atom, but may be N, S, P, Si, etc. Chiral centre are indicated with an asterik (*). For example,



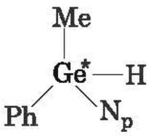
(a)



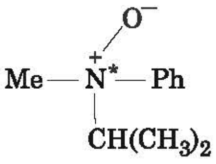
(b)



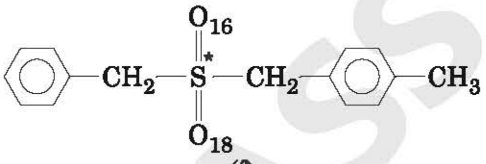
(c)



(d)



(e)



(f)

Q.3. What is *R-S* system of nomenclature?

Ans.

R-S System of Nomenclature

The optical activity of the organic compounds can be assigned by *R-S* system. *R* (from *rectus*, Latin for right) and *S* (from *sinister*, Latin for left).

A priority sequence (proposed by Cahn, Ingold and Prelog) is assigned to the four groups attached to the chiral center.

"The arrangement of the groups is viewed in decreasing order of priorities and looking so if the eye travels in clockwise direction, the configuration is *R* and if the eye travels in anticlockwise direction, then the configuration is *S*."

Golden Rule

If the lowest priority group lies towards left or fight and after assiging the priorities the eye travels in clockwise direction, then system is *S*, and if anticlockwises direction, then system is *R*. Similarly, the lowest priority group lies towards top or bottom and after assiging the priorities, the clockwise system is *R* and anticlockwise system is *S*.

Cahn, Ingold and Prelog (CIP) Priority Sequence Rule

(i) Higher priority is assigned to the atoms of higher atomic number. For example in H, Cl, Br, I the order of precedence is as follows :

$$I > Br > Cl > H$$

(ii) If isotope of the same elements are attached, the isotope with higher mass number is given higher order of precedence. For example, ${}^{1}_{1}H$, ${}^{2}_{1}H$, the order of precedence is ${}^{2}_{1}H > {}^{1}_{1}H$.

(iii) If there are several groups, the order of precedence is also decide on the basis of atomic number of first atom of the group. For example, COOH, — Cl, —SO_3H, —OH, —NH, —CH_3, the order of precedence is as follows :

$$-Cl > -SO_3H > -OH > -NH\,CH_3 > -COOH$$

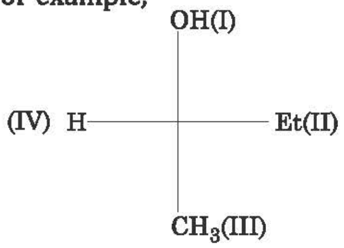
(iv) When the order of precedence of the groups cannot be settled on the first atom, the second atom of the substituent atom is considered. For example,
— COOH, — CN, — CH_2CH_3 — CH_3

$$-COOH > -CN > -CH_2CH_3 > -CH_3$$

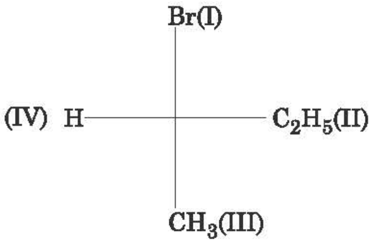
(v) A double or triple bonded atoms are considered equivalent to two or three such atoms.

For example, $>C=O$ can be considered as $>C<^{O}_{O}$ similarly, — $C \equiv N$ can be considered as

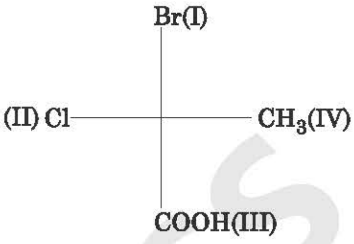
For example,



(S)



(S)



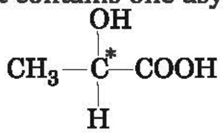
(R)

Q.4. (i) Describe the optical isomerism of lactic acid.
(ii) Describe the optical isomerism of tartaric acid.

Ans.

(i) Optical Isomerism of Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is an example of a compound which shows acid optical isomerism. It contains one asymmetric carbon atom.



$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C^*}}-COOH$$

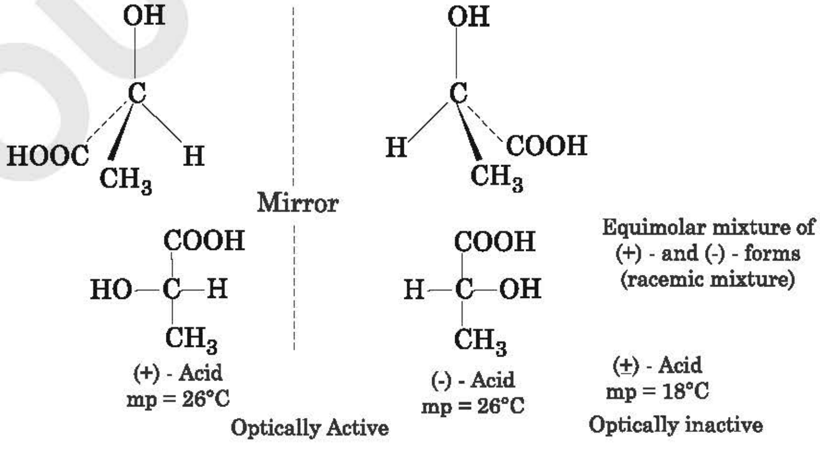
The assymmetric carbon is shown by an asterisk.

Lactic acid

Two three dimensional structures are possible for lactic acid fig.

These structures are not identical because they cannot be superimposed on each other. One is the mirror image of the other. Such nonsuperimposable mirror image forms are optical isomers and are called **enantiomers**. Thus, three forms of lactic acid are known. Two are optically active and the third is optically inactive.

1. **(+) Lactic acid :** It rotates the plane of polarised light to the right (clockwise direction) and is called **dextrorotatory**.
2. **(–) Lactic acid :** It rotates the plane of polarised light to the left (anticlockwise direction) and is called **laevorotatory**. (–) Lactic acid is the mirror image of (+) lactic acid and *vice-versa*.

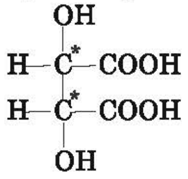


Isomers of Lactic acid. In the upper line two three-dimensional structures are shown. In the lower line a commonly used. Fischer projection is given. The vertical lines represent bonds going away from the observer/reader and horizontal lines represent bonds coming toward the observer.

3. **(±) Lactic acid :** It does not rotate the plane of polarised light. That is it is optically inactive. It is an equimolar mixture of (+). and (–). forms (racemic mixture).

(ii) Optical Isomerism of Tartaric Acid

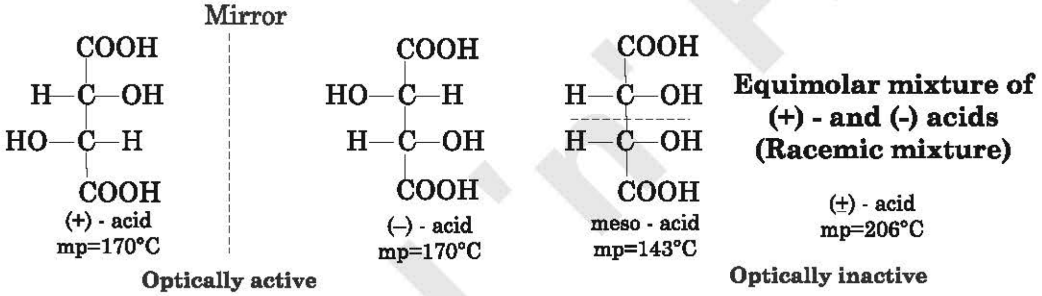
Tartaric acid (2, 3-dihydroxybutanedioic acid) contains two asymmetric carbon atoms :



The two asymmetric carbon are shown by asterisks.

Tartaric acid

Four forms of tartaric acid are known in Fig. Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image. That is, they are **enantiomers**.



Isomers of tartaric acid

1. **(+)-Tartaric acid :** It rotates the plane of polarised light to the right (clockwise direction) and is called **dextrorotatory**.
2. **(–)-Tartaric acid :** It rotates the plane of polarise light to the left (anticlockwise direction) and is called laevorotatory. (–)-tartaric acid is the mirror image of (+)-tartaric and and *vice-versa*.
3. **Meso-tartaric acid :** It possesses a plane of symmetry and is consequently optically inactive. The optically inactive form is said to be **internally compensated** (optical rotation of one asymmetric carbon is cancelled by that of the other).
4. **(±) Tartaric acid :** It does not rotate the plane of polarised light. That is, it is optically inactive. It is an equimolar mixture of (+)-and (–)-forms (racemic mixture).

Q.5. What do you understand by geometrical isomerism? Describe *E-Z* system of nomenclature of organic compounds.

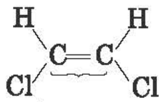
Ans. Geometrical Isomerism and Geometrical Isomers

Such isomers which possess, same structural and molecular formula but differ in arrangement of atom or group in space around a double bond are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

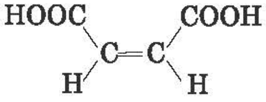
Geometrical isomers are of two types :

1. ***Cis* isomers :** This isomer which have similar group on the same side or plane of the double bond is known as *'cis'* isomer.

For example,



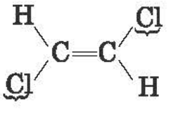
Same side
(*cis*)



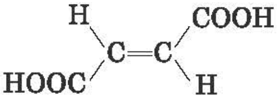
Maleic acid
(*cis* form)

2. ***Trans* isomers :** The isomer which have similar group on the opposite side or plane around the double bond is known as '*trans*' isomer. For example,

(i)

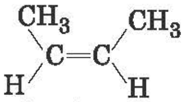


Opposite side (*trans*)

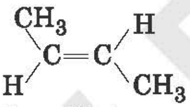


Fumaric acid (*trans*)

(ii)

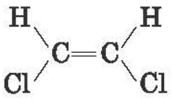


Cis-2-butene

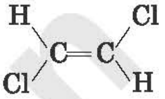


Trans-2-butene

(iii)

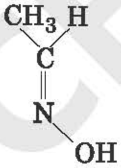


Cis-1, 2-dichloroethene

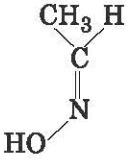


Trans-2-dichloroethene

Geometrical isomerism is also shown by other compounds containing C=N or N=N bonds such as oximes and certain cyclic compounds.



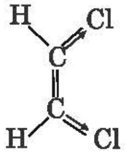
Syn
(Equivalent to *cis*)



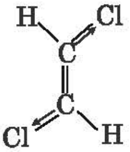
Anti
(Equivalent to *trans*)

Syn and anti isomerism is not possible in Ketoxime.

Cis and *trans* isomers are generally distinguished by dipole moment. *Cis*-form has a definite value of dipole moment while *trans* form has zero dipole moment.



$\mu = 1.84$ D



$\mu = 0$

Properties of Geometrical Isomers

Geometrical isomers show following properties :

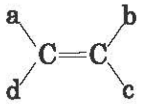
1. *Trans* isomer is general has a low melting point (mp) and high boiling points (pp).

2. The *cis* isomer has high dipole moment and *trans* has nearly zero dipole moment.
3. *Trans* isomer are more stable than *cis* isomer.

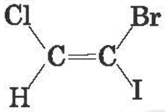
E and *Z* Nomenclature

The geometrical isomers can be designed by the new type of nomenclature, *i.e.*, *E* and *Z*. This nomenclature is used in place of *cis* and *trans* because there are some limitations in *cis* and *trans* nomenclature.

The '*cis* and *trans* designating cannot be used if four groups or atoms attached to the carbon atoms of double bond' are different.



or



In such above cases, *E* and *Z* system of nomenclature is used and this system is based on a priority sequence rule invented by **Cahn, Ingold** and **Prelog**. In this system the two atoms or groups attached to each of the double bond carbon are put in order of precedence.

Cahn, Ingold and Prelog (CIP) Sequence Rule

(i) The symbol *E* is assigned to an isomer is which groups of atoms of higher priority are on the opposite sides.

(ii) Higher priority is assigned to the atoms of higher atomic number. For example in H, Cl, Br and I the order of precedence is as follows :

$$I > Br > Cl > H$$

(iii) The symbol *Z* is assigned to an isomer in which the groups of atoms of higher priority are on the same side.

(iv) If isotope of the elements are attached, the isotope with higher mass number is given higher order of precedence. For example, ${}^{1}_{1}H$, ${}^{2}_{1}H$, the order of precedence is ${}^{2}_{1}H > {}^{1}_{1}H$.

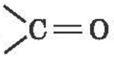
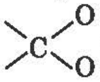
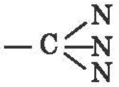
(v) If there are several groups, the order of precedence is decide on the basis of atomic number of first atom of the group. For example, COOH, — Cl, — SO_3H, — OH, —NH,—CH_3, the order of precedence is as follows :

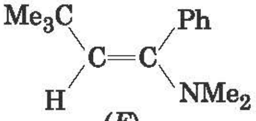
$$—Cl > —SO_3H > —OH > —NHCH_3 > —COOH$$

(vi) When the order of precedence of the groups cannot be settled on the first atom, the second atom of the substituent atom are considered. For example, —COOH,—CN, —CH_2CH_3—CH_3.

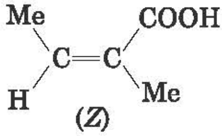
$$—COOH > —CN > —CH_2CH_3 > —CH_3$$

(vii) A double or triple bonded atoms are considered equivalent to two or three such atoms.

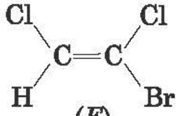
For example,  can be considered as,  similarly, — C≡N can be considered as 

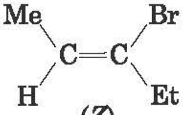
(a) 

(*E*)

(b) 

(*Z*)

(c) 
(E)

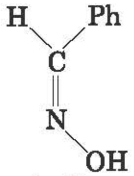
(d) 
(Z)

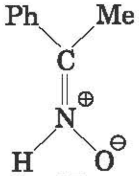
Q.6. Describe the geometrical isomerism of oximes. How will you determine the configuration of oximes? Also give the geometrical isomerism of alicyclic compounds.

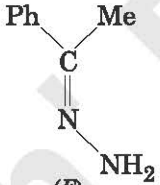
Ans.

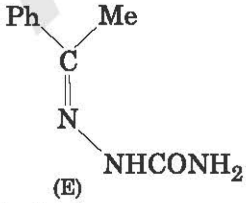
Geometrical Isomerism of Oximes

Nitrogen compounds containing $>C=N-$ as well as $-N=N-$ bond exhibit geometrical isomerism. The important classes of compounds exhibiting geometrical isomerism due to $>C=N-$ bond are : (i) oximes, (ii) nitrones, (iii) hydrazones and (iv) semicarbazones.


Anti(Z)
Benzaldoxime

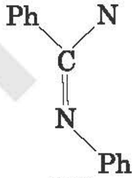

(E)
Nitrone

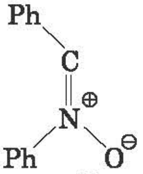

(E)
Hydrazone


(E)
Semicarbazone

Examples of compounds exhibiting geometrical isomerism due to $-N=N-$ bonds are :


syn(Z)
Diazoate


anti(E)
Azobenzene

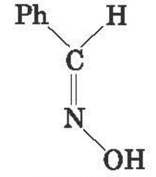

syn (E)
Azoxybenzene

Oximes are the most common compounds and we will discuss their geometrical isomerism in detail.

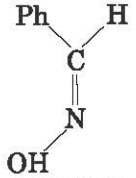
Both the carbon and nitrogen atoms in oximes are sp^2 hybridised. The $>C=N$ bond in oximes consists of one σ and one π-bond. There is no free rotation about $>C=N$, hence oximes of aldehydes and unsymmetrical ketones exhibit geometrical isomerism.

Nomenclature

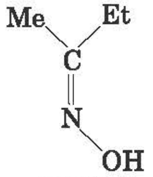
The prefixes *syn* and *anti* are used instead of *cis* and *trans*. In th *syn* the hydroxyl group on nitrogen and hydrogen or the first-named of the two groups on the carbon are on the same side, while in the *anti*-isomer they are on the opposite sides. The *E – Z* system of nomenclature is also applied to oximes and it is more convenient. If the group with greater priority and the hydroxyl group are on the same side of the double bond, the configuration is *Z*, if on the opposite sides it is *E*. For example,



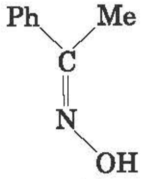
syn (*E*)
Benzaldoxime



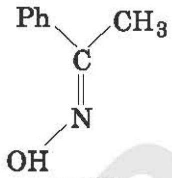
anti (*Z*)
Benzaldoxime



syn (*Z*)
Ethylmethylketoxime



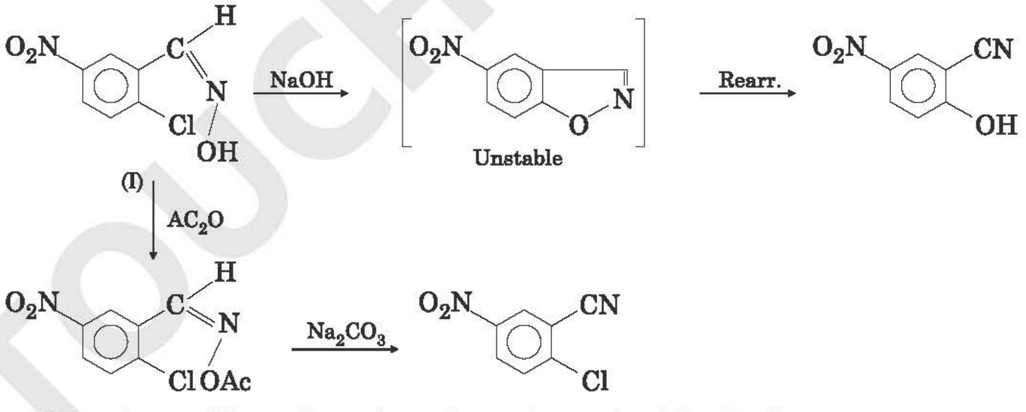
syn (*E*)
Methylphenylketoxime



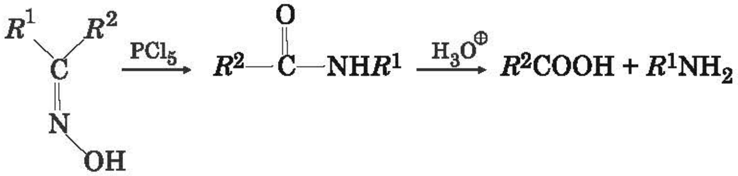
anti (*Z*)
Methylphenylketoxime

Determination of the Configuraton of Oximes

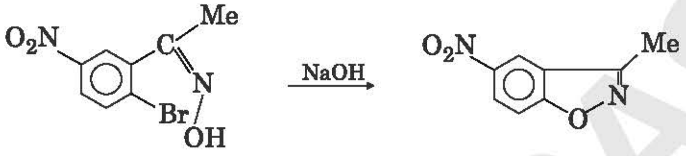
The configurations of geometrical isomers of **aldoximes** are determined by their relative ease of dehydration. For example, the *anti*-aldoxime I (*anti*-2chloro-5-nitrobenzaldoxime) readily undergoes cyclisaton, hence this form is *anti*-isomer. This isomer gives cyanide on treatment with acetic anhydride followed by aqueous sodium carbonate. Thus, *anti*-aldoxime does not give cyanide. Hence, using *anti*-elimination as the criterion for these reactions, the configurations of *syn*-and *anti*-forms can be determined.



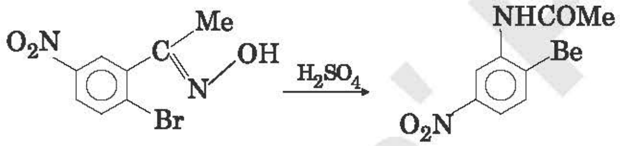
The configurations of **ketoximes** have been determined by **Beckmann rearrangement**. When treated with acidic reagents such as H_2SO_4, acid chlorides, acid anhydride, PCl_5, P_2O_5 etc. ketoximes undergo Beckmann rerrangement to give a substituted amide by migration of the group which is *anti* to the hydroxyl group. The structure of the amide obtained is determined by their hydrolysis to the corresponding carboxylic acid and amine which indicates the configuration of the parent oxime because the group *R*-incorporated in the amine must be *anti* to the hydroxyl group in the oxime.



That the group *anti* to the hydroxyl group actually migrates was shown by the following reaction :



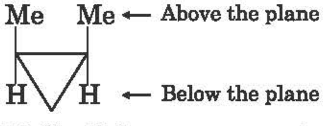
2-bromo-5-nitroacetophenone oxime



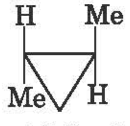
Out of the two isomeric ketoximes of 2-bromo-5-nitroacetophenone, one undergoes cyclisation with NaOH, hence it must be *syn*-methyl isomer. The other isomer is unaffected by NaOH, but on treatment with H_2SO_4 it undergoes **Beckmann rearrangement** to give *N*-substituted acetamide; thus group *anti* to the hydroxyl group migrates.

Geometrical Isomerism of Alicyclic Compounds

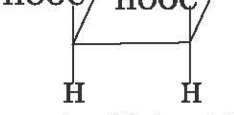
We have noted that geometrical isomerism is due to frozen rotation about a bond. Since there is no rotation about the ring-carbons, suitably substituted cycloalkanes, *e.g.*, cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc. also exhibit *cis-trans* isomerism. Thus, in disubstituted cycloalkanes where the two substituents are located on different carbons two geometrical isomers are possible in each case. The isomer in which the two substituents are located on the same face or side of the ring is called the *cis*-isomer, and in which the two substituents are on the opposite sides is called the *trans*-isomer. For example,



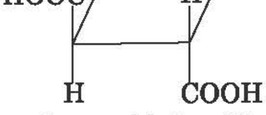
cis-1,2-dimethyl-cyclopropane



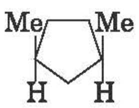
trans-1,2-dimethyl-cyclopropane



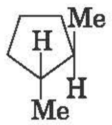
cis-cyclobutane-1,2-dicarboxylic acid



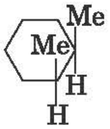
trans-cyclobutane-1,2-dicarboxylic acid



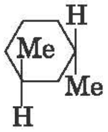
cis-1, 3-dimethyl-cyclopentane



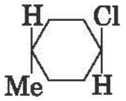
trans-1, 2-dimethyl-cyclopentane



cis-1, 2-dimethyl-cyclohexane



trans-1, 3-dimethyl-cyclohexane



trans-1-chloro-4-methyl-cyclohexane

Q.7. Describe projection formula of a tetrahedral carbon.

Or **Discuss flying-wedge projection, Newman projection, Fischer projection and Sawhorse projection formulae.**

Ans. Projection Formula of a Tetrahedral Carbon

It is not easy to represent a tetrahedron on a plane by drawing. The general practice is to form models with ball and stick; where balls are atoms and sticks are bonds (Fig. 1). Then projection formula for the model is drawn on the plane of the paper ; this shows only two dimensions, the other dimension is imagined. There are following method of doing so, there are :

1. Flying-wedge projection, 2. Newman projection, 3. Fischer projection, 4. Sawhorse projection

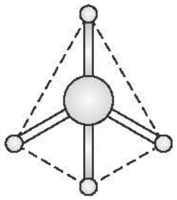
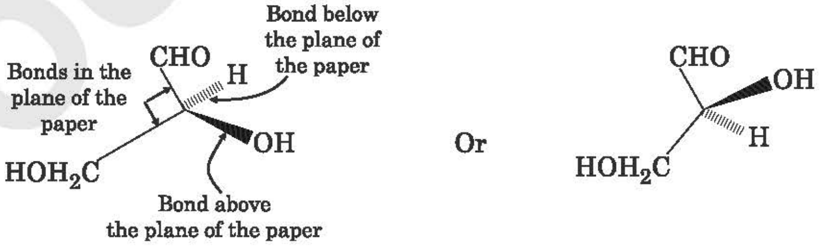


Fig. 1

1. Flying-wedge Projection or Three-dimensional Representation

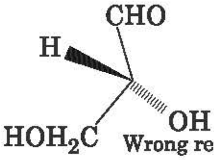
The flying-wedge projection is the most common three dimensional representation of a three dimensional molecule on a two dimensional surface. This representation is used only for chiral molecules having chiral centres. In this representation, the ordinary lines represents bonds in the plane of the paper, a solid wedge (◀) represents a bond above the plane of the paper and a dashed wedge (⫼) or broken line (---) represents a bond below the plane of the paper. For example, (S)-glyceral dehyde can be shown as flying-wedge as in given below :



Flying-wedge formula for (*s*)-glyceraldehyde

The bond which is above the plane of the paper is always towards the observer. Similarly the bond which is below the plane of the paper is always pointing away from the observer.

It is important to note that the ligands (or atoms or groups) above and below the plane should be represented adjacent to each other with no plane ligand between them. Thus give below fig. is not correct for glyceradehyde.

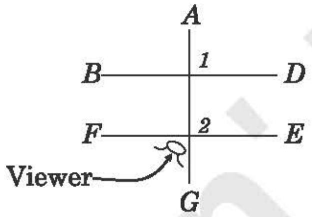


Wrong representation of glyceraldehyde

2. Newman Projection Formula

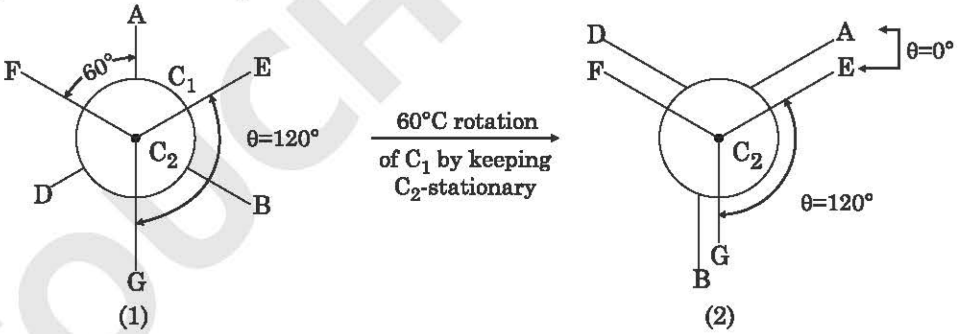
Newman projection is a very common way to represent a conformation of compounds containing minimum two carbon atoms joined togather.

In this projection, the molecule is viewed along the bond joining the key carbon atoms. Here the molecule (example molecule A) is viewed along the axis of a carbon-carbon band (C-1 and C-2).



The front carbon (*i.e.*, C-2) is represented by a **dot** and the back carbon (*i.e.*, C-1) by a circle. The reaming three bonds on each carbon are shown by small straight lines at angle of 120°.

In this projection, the line joining the two essential carbons (*i.e.*, front and back) represented by dot (*i.e.*, centre of circle) and circle is not visible.



(1) (2)

In Newmann projection (1) $A-(C-1)-(C-2)-G$ bonds are in the same plane.

Similarly $B-(C-1)-(C-2)-F$ are in same plane

$D-(C-1)-(C-2)-E$ are in same plane

In Newmann projection (1), the dihedral angle between ligands

A and *F* is 60°
F and *D* is 60°
D and *G* is 60°
G and *B* is 60°
B and *E* is 60°
E and *A* is 60°

When dihedral angle between one ligand on C–1 and other ligand on C–2 is 60° the conformation is known as staggered conformation.

If backcarbon (*i.e.*, $C-1$) is rotated to 60° (clockwise or anticlockwise) by keeping front carbon (*i.e.*, $C-2$) stationary, then we get conformation (2). In this conformation dihedral angle between two ligands (A and F say) is 0°. When dihedral angle is zero degree, the conformation is known as **eclipsed conformation**. Hence conformation (2) is eclipse conformation.

3. Fischer Projection

We simply draw a cross and attach to the ends the four groups (a, b, c and d) that are attached to the chiral centre. The **chiral center** is understood to be located where the lines cross. The horizontal lines represent bonds coming towards us out of the plane of the paper. The vertical lines represent bonds going away from us behind the plane of the paper.

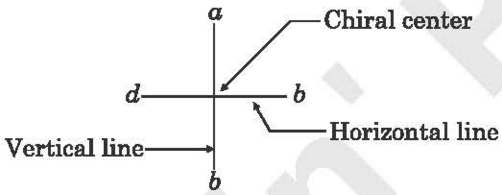


Fig. 2 : Fischer projection of chiral carbon.

To represent a molecule in a Fischer projection (after the great German chemist Emil Fischer), one should view each chiral carbon in a molecule in such a way that two of the bonds to this carbon are vertical and pointing away from the observer, and two are horizontal and pointing toward the observer. When this view is projected on a plane Fig. 3, we get Fischer projection.

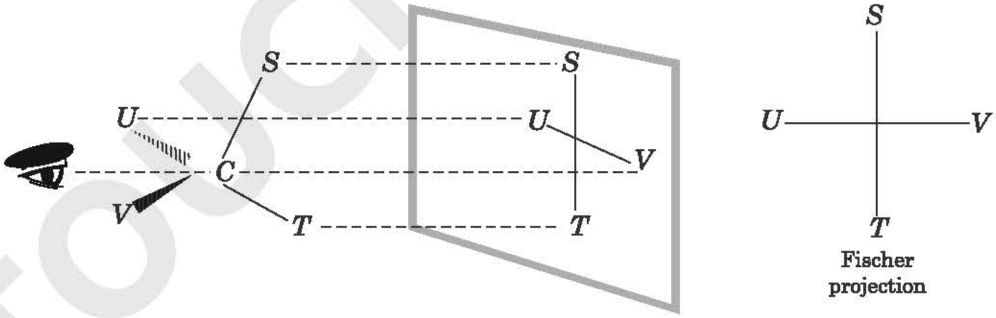
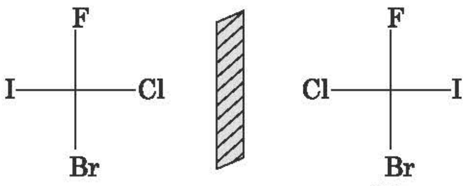


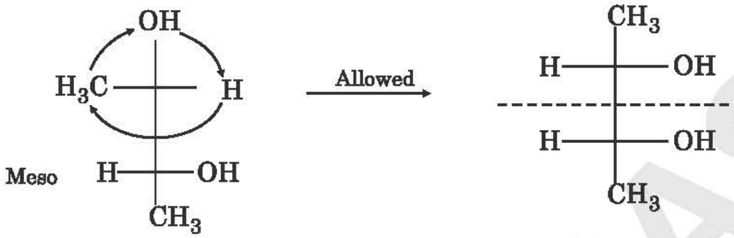
Fig. 3 : Fischer projections for a compound with one chiral carbon, the vertical groups, in the projection are assumed to be away from the observer. Note that the chiral carbons in the Fischer projection are not written explicitly ; they are assumed to be at the crossing points in the projection.

Importance of Fischer Projections

(i) It is easy to recognize enantiomers and mese compounds from the appropriate Fischer projections because planes of symmetry in the actual molecules reduce to lines of symmetry in their projections.

Enantiomers

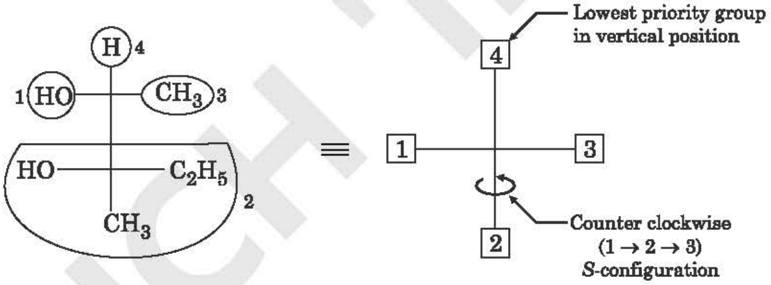




(ii) It is simple to determine the configuration of a chiral carbon by applying the *R*, *S*–system to a Fischer projection.

To do this, we first draw an equivalent Fischer projection (if required) in which the groups of lowest priority is in one of the two vertical positions. Then we apply the priority rules to the remaining three groups.

When the lowest-priority group is in a vertical position in Fischer projection, it is oriented "away" from the observer as required for application of the priority rules.



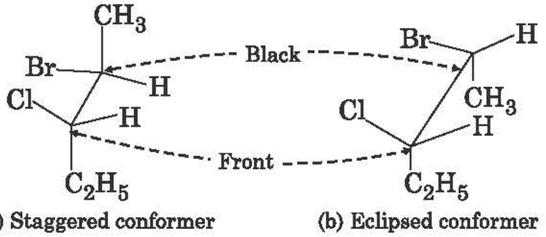
4. Sawhorse Projection

In it, the backbone carbons are represented by a diagonal line, and the terminal carbons are shown in groups.

A sawhorse projection can reveal staggered and eclipsed conformations in molecules.

(i) The atoms and groups attached to each backbone carbon fit in the voids around the group on the adjacent carbon in **staggered conformer**.

(ii) The atoms and groups on adjacent carbons are in line with each other in **eclipsed conformation**.



(a) Staggered conformer (b) Eclipsed conformer

A sawhorse projection allows better visualization of the three-dimensional geometry between adjacent carbon atoms.

Note that Fischer projection can be transformed to eclipsed sawhorse projection. The top carbon group of the Fischer projection of 2-bromo-3-chloropentane become the back carbon group of the sawhorse projection, so conformer (*B*) of Fischer projection is equivalent to conformer (*b*) of sawhorse projection.

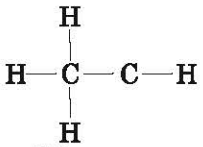
Q.8. Where do you understand by conformation? Describe the conformation of (i) Ethane (ii) Butane (*n*-butane) and (iii) Cyclohexane

Ans.

Conformation

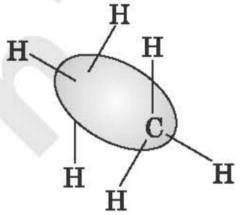
The different arrangement of atoms of groups in space which can be converted into one another by rotation about $C-C$ single bond in a molecule are known as conformation.

Conformational isomers are known as **conformers.** Conformers are therefore rotational isomers. For, *e.g.*, In $H_3C - CH_3$ (ethane) molecule when one of the carbon atoms of the ethane molecule is rotated about C—C single bond keeping the other carbon fixed many conformations of ethane are obtained. Out of these two extreme conformation are **staggered** and **eclipsed conformations,** shown given below Fig.

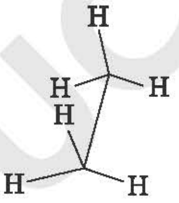


$H-\overset{H}{\underset{H}{C}}-C-H$

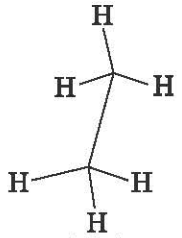
Ethane



Ethane molecule. Carbon-carbon single bond. s bond



Eclipsed conformation of ethane

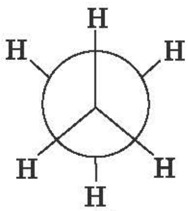


Staggered conformation of ethane

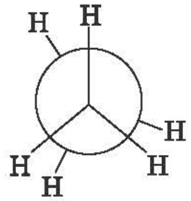
The intermediate conformations are known as **skew conformations.**

(i) Conformations of Ethane

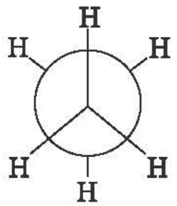
In ethane (C_2H_6) each carbon atom is sp^3-hybridised. The σ bond joining two carbon atoms has cylinderical symmetry about the line joining the carbon nuclei show given below fig. The rotation about C — C single bond is not free. The energy required to rotate the ethane molecule is 3k cal/mol. This energy is known as tortional energy. The energy available at room temperature is sufficient for the rotation of ethane molecule about the C — C single bond. This rotation change the geometry of the molecule and following six conformations are possible :



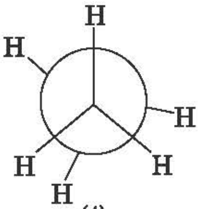
(1)



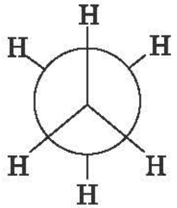
(2)



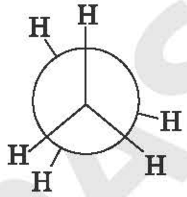
(3)



(4)

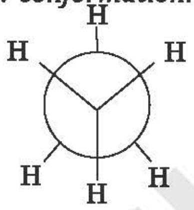


(5)

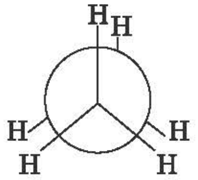


(6)

Out of these six conformations, three (1, 3 and 5) are **staggered form** in which H - atoms are as far apart as possible. The remaining three conformation (2, 4 and 6) are known as **eclipsed conformations** in which hydrogen atoms completely eclipse each other shown given below fig. In between the two extremes there are infinite number of intermediate conformations and are known as *Skew conformation.*



Staggered conformation
(Newman projection)



Eclipsed conformation
(Newman projection)

"The staggered conformations have the least potential energy due to the least tortional strain (repulsive interaction between bonds on adjacent atoms leads to restricted rotation which in turn causes torsional strain) and hence has the maximum stability." The greater repulsion between the electron clouds of C — H bonds in eclipsed conformation increases the potential energy and thus lowers the stability. The skew conformations have energy in between them.

Therefore, the potential energy of ethane molecule is minimum for staggered conformation increases with the rotation and reaches maximum at eclipsed conformation (Fig. 1), *i.e.*,

Order of potential energy : Eclipsed > Skew > Staggered

Stability of ethane molecule : Eclipsed < Skew < Staggered

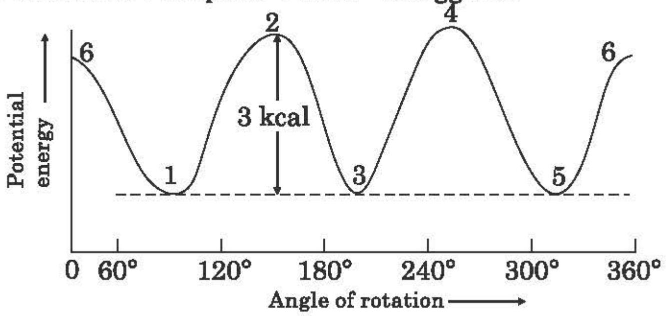
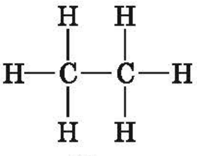


Fig. 1

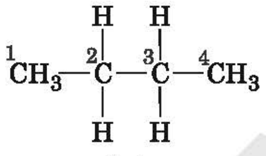
Most of the ethane molecules, exist in the most stable, staggered conformation (99%). The angle between C — H bonds is known as dihedral angle. Staggered conformation occurs at dihedral angle 60°. While eclipsed conformation occurs at dihedral angle 0° or 120°. The rotation in ethane molecule is therefore restricted.

(ii) Conformation of Butane



$H_3C{-}CH_3$

Ethane

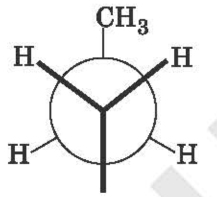


$\overset{1}{C}H_3{-}\overset{2}{C}H_2{-}\overset{3}{C}H_2{-}\overset{4}{C}H_3$

Butane

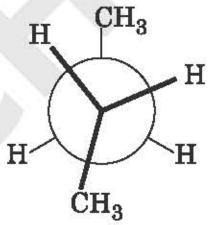
The middle C — C single bond in *n*-butane is similar to ethane but one hydrogen atoms at each carbon atom is replaced by methyl group (—CH_3). The rotation about C —2 and C — 3 single bonds gives many conformations of normal butane. (1) The staggered conformation in which the —CH_3 groups are as far apart as possible is known as *anti or trans* **conformation.** It is the most stable conformation. (2) The staggered rotamers in which two methyl groups are only 60° apart is known as **Gauche conformation.** (3) The other possible conformation is the eclipsed conformation, in which eclipsing occurs between hydrogen atoms and methyl groups.

The various conformation of *n*-butane is shown in the fig. C—C single bond in *n*-butane is rotated through 360°, six conformation are obtained , out of which three are staggered and three eclipsed.



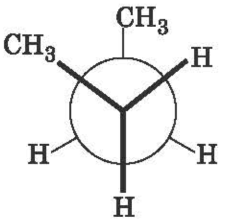
Anti-staggered 1

$\rightleftharpoons$



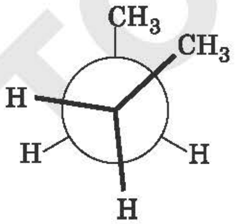
Eclipsed 2

$\rightleftharpoons$



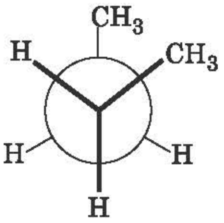
Gauche-staggered 3

$\rightleftharpoons$



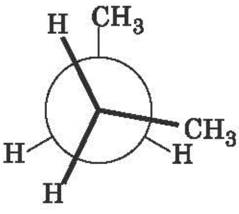
Eclipsed 4

$\rightleftharpoons$



Gauche-staggered 5

$\rightleftharpoons$



Eclipsed 6

The anti and gauche form are free torsional strain due to their staggered conformation. However the bulky — CH_3 group which are only 60° apart in gauche conformation may cause steric strain. The crowding of the bulky —CH_3 groups causes Van der Waals forces of repulsion between them which in-turn causes steric strain in molecule. But there is no steric strain in anti-form. Therefore gauche forms have higher energy and lesser stability than the anti form. In fully eclipsed form both the torsional and steric strains are maximum and is least stable.

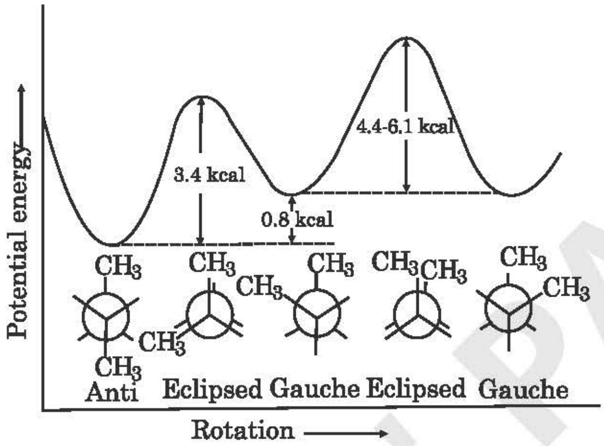


Fig. 2 : Potential Energy Changes During Rotation About the C(2)-C(3) bond in *n*-butane

(iii) Conformations of Cyclohexane

Cyclohexane is not a planar molecule. If it is so, the C—C—C bond angle should be 120°. On this basis, it should not be stable. In fact cyclohexane is a stable molecule. **Sachse** and **Mohr** has given two conformations of cyclohexane showing the relative spatial disposition of hydrogen atoms in them as shown in fig. 3. All the pairs of C—C bonds in the chair form of cyclohexane are perfectly staggered bonds and in boat form, there are eclipsed bonds. In the chair conformation, therefore, the angle strain as well as torsional strain are absent.

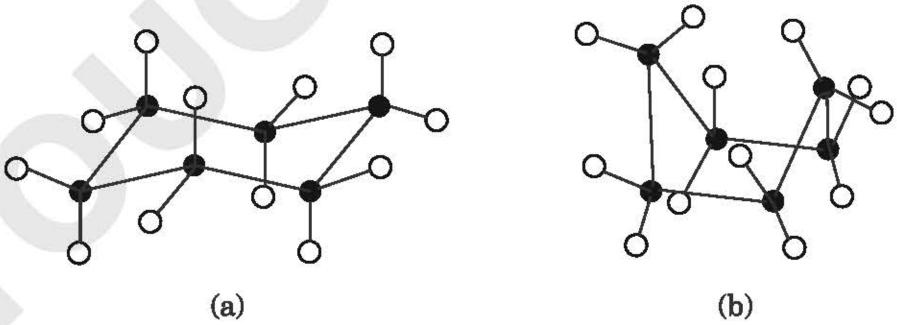
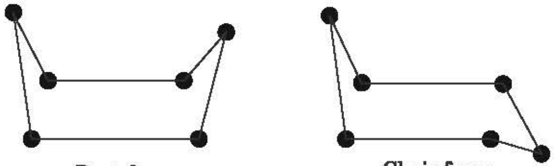

(a) (b)

Fig. 3 : Chair and boat conformations of cyclohexane

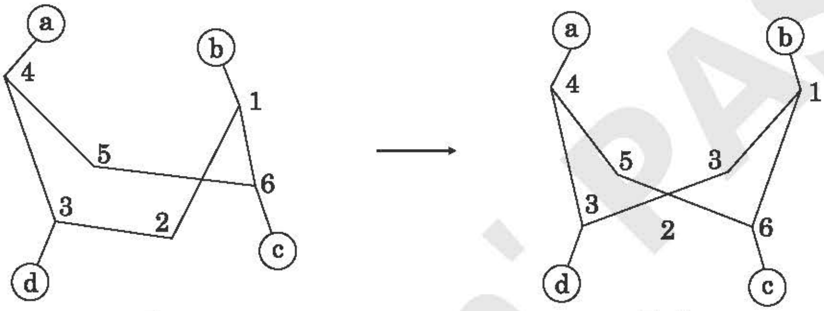
The boat conformation has appreciable torsional strain and steric strain due to the crowding of C_1 and C_4 hydrogens, although, although it has no angle strain. The boat form should thus be much less stable than the chair form. It has been seen that the chair conformation of cyclohexane has 7.0 kcal mole^{-1} less energy (thus more stable) than the boat conformation. On paper, the two routine conformation of cyclohexane are shown in fig. 4.



Boat form Chair form

Fig. 4

Besides the above conformations, cyclohexane has several other conformations as shown in fig.



Boat Twist

This theory is also confirmed by **Ruzicka**, who synthesised cycloketone containing 30 carbon atoms. The stability of muscone $C_{16}H_{30}O$, civetone $C_{17}H_{30}O$ has also been explained on the basis of their multiplanar stainless structures. ❑

UNIT-VII

Basic Computer System

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. What is number system in computer?

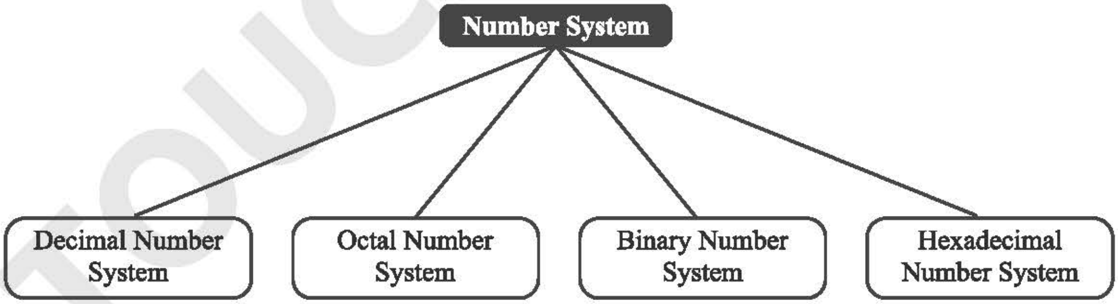
Ans. A method of writing or expressing numbers of a given set using digits or either symbols is called Number System. There are many number systems like Decimal, Octal, Binary and Hexadecimal which use their own set of symbols to represent numbers. As you know, computer is a machine which understands only binary number system which is made up of just two digits *i.e.* 0 and 1.

Q.2. What is the need of the number system?

Ans. When we type or enter some information, we use letters, numbers or words to represent it in the system, but a computer uses digits to represent and process this information. So, the information which we enter is first converted into digital form. We use the decimal number system in our day to day life while a computer represents all kinds of data and information like text, graphics, etc. in Binary number System.

Q.3. Write the types of number system.

Ans. Various number system which are used to represent all kinds of the data like text, numbers, graphics are :



Each number system contains a unique set of digits which are used to represent any value in that number system.

Number System	Base	Set of Unique Digits
Binary	2	0, 1
Octal	8	0-7
Decimal	10	0-9
Hexadecimal	16	0-9, A-F

Q.4. Convert the decimal number 26, *i.e.,* $(26)_{10}$ to binary.

Sol.

2	26
2	13 – 0
2	6 – 1
2	3 – 0
	1 – 1

The binary equivalent of $(26)_{10}$ is 11010

In other words, $(26)_{10} = (11010)_2$

Start listing the last quotient and all remainders from here.

Q.5. Convert the decimal number 64, *i.e.*, $(64)_{10}$ to binary.

Sol.

2	64
2	32 – 0
2	16 – 0
2	8 – 0
2	4 – 0
2	2 – 0
	1 – 0

$(64)_{10} = (1000000)_2$

Q.6. What is $(1111)_2$ in decimal number?

Sol.

$$(1111)_2 = 1\times 2^3 + 1\times 2^2 + 1\times 2^1 + 1\times 2^0$$
$$= 8 + 4 + 2 + 1 = 15$$
$$(1111)_2 = (15)_{10}$$

Q.7. Convert $(10111)_2$ to decimal number.

Sol.

$$(10111)_2 = 1\times 2^4 + 0\times 2^3 + 1\times 2^2 + 1\times 2^1 + 1\times 2^0$$
$$= 16 + 0 + 4 + 2 + 1 = 23$$
$$(10111)_2 = (23)_{10}$$

Q.8. Convert 101.101 to decimal number.

Position	2	1	0		–1	–2	–3
Face value	1	0	1	•	1	0	1
Weights	2^2	2^1	2^0		2^{-1}	2^{-2}	2^{-3}

Sol.

$$101.101 = 1\times 2^2 + 0\times 2^1 + 1\times 2^0 + 1\times 2^{-1} + 0\times 2^{-2} + 1\times 2^{-3}$$
$$= 1\times 4 + 0 + 1\times 1 + 1/2 + 0 + 1/8$$
$$= 4 + 1 + 0.5 + 0.125 = 5.625$$
$$(101.101)_2 = (5.625)_{10}$$

Q.9. Convert the following decimal numbers to binary :

(i) $(89)_{10}$ **(ii) $(146)_{10}$**

Sol. (i) $(89)_{10} = (?)_2$

2	89	Remainder	
2	44	1	(LSB) ↑
2	22	0	
2	11	0	
2	5	1	
2	2	1	
2	1	0	(MSB)
2	0	1	

$\therefore \quad (89)_{10} = (1011001)_2$

Q.10. Convert the following decimal number to binary : $(0.6875)_{10}$

Sol.

	Carry	
$0.6875 \times 2 = 1.3750$	1	(MSB) ↑
$0.3750 \times 2 = 0.7500$	0	
$0.7500 \times 2 = 1.5000$	1	
$0.5000 \times 2 = 1.0000$	1	(LSB)

$\therefore \quad (0.6875)_{10} = (0.1011)_2$

Verification, $(0.1011)_2 = 1 \times 2^{-1} + 0 \times 2^{-2} + 1 \times 2^{-3} + 1 \times 2^{-4}$

$$= \frac{1}{2} + 0 + \frac{1}{8} + \frac{1}{16}$$

$$= 0.5 + 0.125 + 0.0625 = (0.6875)_{10}$$

Q.11. Convert : (i) $(0.6875)_{10}$ and $(0.155)_{10}$ to octal.

Sol. (i) $(0.6875)_{10} = (?)_8$

	Carry	
$0.6875 \times 8 = 5.5000$	5	(MSB) ↓
$0.5000 \times 8 = 4.0000$	4	(LSB)

$\therefore \quad (0.6875)_{10} = (0.54)_8$

(ii) $(0.115)_{10} = (?)_8$

	Carry	
$0.115 \times 8 = 0.920$	0	(MSB) ↑
$0.920 \times 8 = 7.360$	7	
$0.360 \times 8 = 2.880$	2	
$0.880 \times 8 = 7.040$	7	
$0.040 \times 8 = 0.320$	0	
$0.320 \times 8 = 2.560$	2	
$0.560 \times 8 = 4.480$	4	(LSB)

upto 7 decimal places

$(0.115)_{10} = (0.0727024)$

Q.12. Convert $(76.43)_8$ to decimal.

Sol.

$$\begin{aligned}(76.43)_8 &= 6\times 8^0 + 7\times 8^1 + 4\times 8^{-1} + 3\times 8^{-2}\\ &= 6 + 56 + 4\times 0.125 + 3\times 0.015625\\ &= 62 + 0.500 + 0.046875\\ &= (62.546875)_{10}\end{aligned}$$

Q.13. Convert $(564.3)_{10}$ to octal.

Sol. $(564.3)_{10} = (?)_8$

8	564	Remainder	
8	70	4	(LSB)
8	8	6	↓
8	1	0	
	0	1	(MSB)

	Carry	
$0.3\times 8 = 2.4$	2	(MSB)
$0.4\times 8 = 3.2$	3	↓
$0.2\times 8 = 1.6$	1	
$0.6\times 8 = 4.8$	4	
$0.8\times 8 = 6.4$	6	
$0.4\times 8 = 3.2$	3	(LSB)

upto 6 decimal places.

$\therefore$ $(564.3)_{10} = (1064.231463)_8$

Q.14. Convert the following octal numbers into binary :

(i) $(47.12)_8$ (ii) $(537)_8$ (iii) $(160.5)_8$

Sol. (i) $(47.12)_8 =$

$$\begin{array}{ccccc} 4 & 7 & : & 1 & 2\\ \downarrow & \downarrow & & \downarrow & \downarrow\\ 100 & 111 & & 001 & 010\end{array}$$

$\therefore$ $(47.12)_8 = (100111.001010)_2$

(ii) $(537)_8 =$

$$\begin{array}{ccc} 5 & 3 & 7\\ \downarrow & \downarrow & \downarrow\\ 101 & 011 & 111\end{array}$$

$\therefore$ $(537)_8 = (101011111)_8$

(iii) $(160.5)_8 =$

$$\begin{array}{ccccc} 1 & 6 & 0 & : & 5\\ \downarrow & \downarrow & \downarrow & & \downarrow\\ 001 & 110 & 000 & & 101\end{array}$$

$\therefore$ $(160.5)_8 = (001110000.101)_2$

Q.15. Convert $(1010.0001\ 1111\ 01011000)_2$ into hexadecimal number.

Sol. $(1010.0001111101011000)_2 = (?)_6$

$$\begin{array}{ccccccc} = 1010 & : & 0001 & & 1111 & 0101 & 1000 \\ \downarrow & & \downarrow & & \downarrow & \downarrow & \downarrow \\ A & & 1 & & F & 5 & 8 \end{array}$$

$= (A.\ 1F58)_6$

Q.16. Convert the following hexadecimal numbers to decimal numbers :

(i) $(FFFF)_{16}$ **(ii) $(E5)_{16}$**

Sol. (i) $(F\ F\ F\ F)_{16} = (?)_{10}$

$$\begin{aligned} &= F\times16^0 + F\times16^1 + F\times16^2 + F\times16^3 \\ &= 15\times1 + 15\times16 + 15\times256 + 15\times4096 \qquad (\because F = 15) \\ &= 15 + 240 + 3840 + 61440 \\ &= (65535)_{10} \end{aligned}$$

(ii) $(E\ 5)_{16} = (?)_{10}$ $= 5\times16^0 + E\times16^1$

$$\begin{aligned} &= 5\times1 + 14\times16 \qquad (\because E = 14) \\ &= 5 + 224 \\ &= (229)_{10} \end{aligned}$$

Q.17. Compute $(1100)_2 - (11)_2$

Sol. $(1100)_2 - (11)_2 = (?)_2$

$$\begin{array}{rcccc} & 1 & 1 & 0 & 0 \\ - & 0 & 0 & 1 & 1 \\ \hline & 1 & 0 & 0 & 1 \end{array}$$

As in the decimal system, we start subtraction from the RHS. We need to borrow from the second column from RHS. But the upper number in the second column is already 0. Thus, it needs to borrow from the third column from RHS. It may be assumed that second column borrows from third column. The number in the third column becomes 0. In the second column, it becomes 2, out of which 1 is borrowed by the number in the first column. The difference in the first column will be $(2-1)$, *i.e.*, 1. Now 1 is left in the second column.The difference in the second column will be $(1-1)$, *i.e.*, 0. The upper number in the third column is now 0. Therefore the difference in third column will be $(0-0)$, *i.e.*, 0.

Q.18. Compute $(1010)_2 + (1111)_2$.

Sol. $(1010)_2 + (1111)_2 = (?)_2$

$$\begin{array}{lccccccl} & 1 & 1 & 1 & & & \longrightarrow \text{carry} \\ \text{Augend} & & 1 & 0 & 1 & 0 & \\ \text{Addend} & + & 1 & 1 & 1 & 1 & \\ \hline & 1 & 1 & 0 & 0 & 1 & \end{array}$$

We start the addition from the RHS as we do in Decimal system. As soon as the sum becomes two or more, we carry 1 to the next position on the left and continue addition.

Q.19. Compute $(1101)_2 \times (101)_2$

Sol.

$$\begin{array}{ccccccc} & & & 1 & 1 & 0 & 1 \\ & & & \times & 1 & 0 & 1 \\ \hline & & & 1 & 1 & 0 & 1 \\ & & 0 & 0 & 0 & 0 & \times \\ & 1 & 1 & 0 & 1 & \times & \times \\ \hline 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ \hline \end{array}$$

Binary Division : Binary division is performed by successive subtraction of the divisor from the dividend. The quotient bits are thus framed. The following rules are obeyed :

$$0 \div 1 = 0$$

$$1 \div 1 = 1$$

Q.20. Convert the following hexadecimal numbers into binary :

(i) $(6\ F\ 2\ E)_{16}$ (ii) $(D\ 4\ 3\ F\ 7)_{16}$ (iii) $(5\ F\ 4.24)_{16}$

Ans. (i) $(6\ F\ 2\ E)_{16} = (?)_2$

$$(6\ F2\ E)_{16} = \begin{array}{cccc} 6 & F & 2 & E \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 0110 & 1111 & 0010 & 1110 \end{array}$$

$\therefore\ (6\ F\ 2\ E)_{16} = (0110\ 1111\ 0010\ 1110)_2$

(ii) $(D\ 4\ E\ 3\ F\ 7)_{16} = (?)_2$

$$(D\ 4\ E\ 3\ F\ 7)_{16} = \begin{array}{cccccc} D & 4 & E & 3 & F & 7 \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 1101 & 0100 & 1110 & 0011 & 1111 & 0111 \end{array}$$

$\therefore\ (D\ 4\ E\ 3\ F\ 7)_{16} = (1101\ 0100\ 1110\ 0011\ 1111\ 0111)_2$

$$\text{(iii) } (5\ F\ 4.24)_{16} = \begin{array}{cccccc} 5 & F & 4 & . & 2 & 4 \\ \downarrow & \downarrow & \downarrow & . & \downarrow & \downarrow \\ 0101 & 1111 & 0100 & & 0010 & 0100 \end{array}$$

$\therefore\ (5\ F\ 4.24)_{16} = (0101\ 1111\ 0100.\ 0010\ 0100)_2$

Q.21. What is binary number system?

Ans. The binary number system is made up of only two digits, i.e., zero and one (0 and 1). Since this system uses two digits, it has the base 2. All digital computers use this number system and convert the input data from the decimal format into its binary equivalent.

SECTION-B SHORT ANSWER TYPE QUESTIONS

Q.1. What do you understand by computer hardware and software? Write the differences between hardware and software.

Ans.

Computer Hardware

Hardware refers to the physical components of a computer. Computer Hardware is any part of the computer that we can touch these parts. These are the primary electronic devices used to build up the computer. Examples of hardware in a computer are the Processor, Memory Devices, Monitor, Printer, Keyboard, Mouse, and the Central Processing Unit.

Computer Software : Software is a collection of instructions, procedures, documentation that performs different tasks on a computer system. we can say also Computer Software is a programming code executed on a computer processor. The code can be machine-level code or the code written for an operating system. Examples of software are Ms Word, Excel, Power Point, Google Chrome, Photoshop, MySQL etc.

Differences Between Hardware and Software

S.No.	Hardware	Software
1.	Hardware is a physical parts computer that cause processing of data.	Software is a set of instruction that tells a computer exactly what to do.
2.	It is manufactured.	It is developed and engineered.
3.	Hardware can not perform any task without software.	software can not be executed without hardware.
4.	As Hardware are physical electronic devices, we can see and touch hardware.	We can see and also use the software but can't actually touch them.
5.	It has four main categories: input device, output devices, storage, and internal components.	It is mainly divided into System software, Programming software and Application software.
6.	Hardware is not affected by computer viruses.	Software is affected by computer viruses.
7.	It can not be transferred from one place to another electrically through network.	But, it can be transferred.
8.	If hardware is damaged, it is replaced with new one.	If software is damaged, its backup copy can be reinstalled.
9.	Ex: Keyboard, Mouse, Monitor, Printer, CPU, Hard disk, RAM, ROM etc.	Ex: Ms Word, Excel, Power Point, Photoshop, MySQL etc.

Q.2. Write a short note on computer code.

Ans.

Computer Code

In computer programming, *computer code* refers to the set of instructions, or a system of rules, written in a particular programming language (*i.e.*, the source code).

It is also the term used for the source code after it has been processed by a compiler and made ready to run on the computer (*i.e.*, the object code).

In addition to building computer programs and mobile applications, code is used heavily for innovative concepts such as artificial intelligence and machine learning.

Coding in computer science : As stated previously, in computer science, *code* refers to the computer program algorithms, made up of symbols from a source alphabet, that represent the set of rules on what actions the program is expected to perform.

Essentially, it is our human language, translated by a coder, into lines of code that a computer can understand and respond to. It allows programmers to create software programs, operating systems and mobile applications.

Within computer language, specifically, there are a number of ways in which machine code can be used to provoke action or facilitate functionality.

Different coding languages : When writing code, there are a number of different coding languages in use today and each has different benefits and applications they are most commonly used for, such as :

1. **PHP :** PHP is a general scripting language used heavily in web development.
2. **Java :** Java is an object-oriented programming language built to have minimal dependencies for implementation and requires compilation. It is heavily used in back-end software
3. **JavaScript :** JavaScript is an all-text programming language that, unlike Java, can be run on a browser only.
4. **Python :** Python is another general-purpose programming language designed to emphasize readability.

Difference between Code and Markup Language

As it relates to websites and webpages, markup language also becomes part of machine language as it dictates to the system how a page should be formatted.

It is sometimes confused with or used interchangeably with *programming language* (or *code*). But there are some important distinctions to recognize.

The main difference between the two is that markup language is readable by both machines and humans, and, again, it is a set of instructions for how a webpage should be laid out.

Conversely, programming code is the instructions given to a machine to create a computer program. While these two operate in the same universe, they are used for different purposes.

Examples of markup languages include :

(i) HTML (Hypertext Markup Language)
(ii) XML (Extensible Markup Language)
(iii) SAML (Security Assertion Markup Language)
(iv) DCML (Data Center Markup Language)
(v) SGML (Standard Generalized Markup Language)

Q.3. What are the features of an operating system?

Ans.

Features of Operating System (OS)

1. Protected and supervisor mode.
2. Allows disk access and file systems Device drivers Networking Security.
3. Program Execution.
4. Memory management Virtual Memory Multitasking.
5. Handling I/O operations.
6. Manipulation of the file system.
7. Error Detection and handling.
8. Resource allocation.
9. Information and Resource Protection.

Q.4. Write in brief the advantages and disadvantages of using operating system.

Ans.

Advantages of using Operating System

1. Allows you to hide details of hardware by creating an abstraction.
2. Easy to use with a GUI.
3. Offers an environment in which a user may execute programs/applications.
4. The operating system must make sure that the computer system convenient to use.
5. Operating System acts as an intermediary among applications and the hardware components.

6. It provides the computer system resources with easy to use format.
7. Acts as an intermediator between all hardware's and software's of the system.

Disadvantages of using Operating System

1. If any issue occurs in OS, you may lose all the contents which have been stored in your system.
2. Operating system's software is quite expensive for small size organization which adds burden on them. Example Windows.
3. It is never entirely secure as a threat can occur at any time.

Q.5. Discuss in brief the kernel in operating system.

Ans.

Kernel in Operating System

The kernel is the central component of a computer operating systems. The only job performed by the kernel is to the manage the communication between the software and the hardware. A Kernel is at the nucleus of a computer. It makes the communication between the hardware and software possible. While the Kernel is the innermost part of an operating system, a shell is the outermost one.

Features of Kennel

1. Low-level scheduling of processes.
2. Inter-process communication.
3. Process synchronization.
4. Context switching.

Types of Kernels

There are many types of kernels that exists, but among them, the two most popular kernels are :

1. **Monolithic :** A monolithic kernel is a single code or block of the program. It provides all the required services offered by the operating system. It is a simplistic design which creates a distinct communication layer between the hardware and software.
2. **Microkernels :** Microkernel manages all system resources. In this type of kernel, services are implemented in different address space. The user services are stored in user address space, and kernel services are stored under kernel address space. So, it helps to reduce the size of both the kernel and operating system.

Q.6. Write the difference between 32-bit and 64-bit operating system.

Ans.

Difference between 32-Bit *vs* 64 Bit Operating System

Parameters	32-Bit	64-Bit
Architecture and Software	Allow 32 bit of data processing simultaneously	Allow 64 bit of data processing simultaneously
Compatibility	32-bit applications require 32-bit OS and CPUs.	64-bit applications require a 64-bit OS and CPU.
Systems Available	All versions of Windows 8, Windows 7, Windows Vista, and Windows XP, Linux, etc.	Windows XP Professional, Vista, 7, Mac OS X and Linux.
Memory Limits	32-bit systems are limited to 3.2 GB of RAM.	64-bit systems allow a maximum 17 Billion GB of RAM.

Q.7. Write a short note on computer programming.

Ans.

Computer Programming

It is the process of telling a computer to do certain things by giving it instructions. These instructions are called programs. A person who writes instructions is a computer programmer. The instructions come in different languages; they are called programming languages. There are many programming languages. Sometimes, programmers use special software, such as integrated development environments (IDEs), which have many special parts, including a text editor, to help them to type and edit programs.

Computers understand instructions directly if those instructions are written in machine code, special characters that can be processed by the computer but are difficult for humans to read. Writing these instructions directly in machine code takes a long time and is difficult, so instructions are written in a language easier for people to use, which the computer converts into "computer form" instructions (in other words, machine code) so the computer can follow them. The simplest of these is assembly language. Programs written in a language more like English are converted by a compiler. Some languages, called interpreted languages, use interpreters instead of assemblers or compilers.

Once a program has been compiled the instructions in it are written into a file that contains a series of numbers that the computer can understand. These files are generally called These machine-instructions will be loaded into the memory computer's so that the can run them when the executable is opened. In the event that data is not transferred correctly, it can result in.

Q.8. Write a short note on software products.

Ans.

Software Products

Below are the few examples of software products :

1. **Microsoft Office** suite comprises various applications which form the core of computer usage in today's world. The core applications and services in office are :
   (a) **MS Access :** It is Database Management Software (DBMS).
   (b) **MS Excel :** It is a data processing application.
   (c) **MS Power Point :** It is used to create audiovisual presentations.
   (d) **MS One Note :** It is a note-taking application.
   (e) **MS Outlook :** It is the e-mail client of the office suite.
   (f) **MS World :** It is useful in creating text documents.
2. **Chemsketch** is a Chemical Drawing Package that allows to draw chemical structures including organics, organometallics, polymers and Markus structures. It includes feature to calculate molecular properties, 2D and 3D structure cleaning and viewing, functionality for naming structures and prediction of a log P.
3. **Hyperchem :** The suit features multiple visualization options with the animated presentation of chemical calculations, molecular mechanics and dynamics.
4. **MATLAB :** It is used by engineering and scientists to analyse data, create models and develop algorithms.
5. **Scilab :** It is used for fluid dynamics simulations, numerical optimization and modeling, statistical analysis image enhancement, for signal processing, simulation of explicit and implicit dynamical systems.

Q.9. Write a short note on decimal number system.

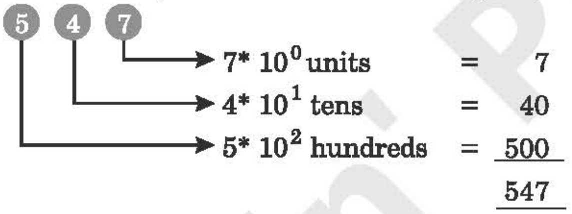
Ans.

Decimal Number System

In our daily life, we use decimal number system. Most of our arithmetic operations are performed with decimal numbers only. Decimal number system consists of ten digits, *i.e.*, 0 to 9 with the base 10. Each number can be used individually or they can be grouped to form a numeric value, *e.g.*, 82, −256, 52.87, etc. The value of each digit in a number depends upon the following :

1. The face value of the digit.
2. The base of the number system.
3. The position of the digit in the number.

Each position represents a specific power of the base (10). The right most digit of a number is called **Least Significant Digit**, whereas the left most digit is called **Most Significant Digit**. For example, the number 547 can be represented in the following way: **Example :**



$7* 10^0$ units = 7

$4* 10^1$ tens = 40

$5* 10^2$ hundreds = 500

547

Observation : The positional value of each digit increases ten folds as we move from right to left. In the above mentioned example, 5, 4, and 7 are the face values and their place values are hundreds, tens and units, respectively. The place value of a digit depends on its position in the number.

Now we will discuss various types of number systems that are used in a computer.

Q.10. Write a short note on hexadecimal number system.

Ans.

Hexadecimal Number System

This number system consists of 16 digits, numbers 0-9 and the letters A-F, where A-F represent decimal numbers from 10 to 15. That means, A is equivalent to 10, B is equivalent to 11, C refers to 12, and so on. The base of this number system is 16. This number system is also known as **Hex**. The procedure of converting hexadecimal to decimal is similar to the methods shown in the previous pages, with the only difference being the change of base.

To convert a hexadecimal number to decimal, multiply the numbers starting from the right-hand side with increasing power of 16, starting from 0 and then calculating the sum of all the products.

Example 1:

$(3B)_{16}$

$=(3\times16^1)+(11\times6^0)$

$=48+11=59$

Thus $(3B)_{16}=(59)_{10}$

Example 2:

$(4D2)_{16}$

$=(4\times16^2)+(13\times16^1)+(2\times16^0)$

$=1024+208+2=1234$

Thus $(4D2)_{16}=(1234)_{10}$

Q.11. What is octal number system?

Ans.

Octal Number System

The Octal number system (Oct) consists of 8 digits, from 0 to 7, with the base 8. The concept of Octal number system came from the Native Americans as they used to count numbers by using the space between their fingers rather than using their fingers. The procedure of 'Octal to Decimal' conversion is similar to 'Binary to Decimal' conversion. The only difference is the change of base.

To convert an octal number to a decimal number, start multiplying the digits of the number from the right-hand side with increasing power of 8 starting from 0 and finally calculating the sum of all the products.

Example 1:

$(345)_8 = (3 \times 8^2) + (4 \times 8^1) + (5 \times 8^0)$

$= 192 + 32 + 5 = 229$

Thus $(345)_8 = (229)_{10}$

Example 2:

$(317)(_8 = (3 \times 8^2) + (1 \times 8^1) + (7 \times 8^0)$

$= 192 + 8 + 7 = 207$

Thus $(317)_8 = (207)_{10}$

Q.12. Explain the conversion of decimal into binary number system.

Ans. Conversion of Decimal into Binary Number System

The equivalence between binary and decimal numbers can be understood with the given examples. To convert a decimal number into a binary number, follow the given steps :

Step 1 : Divide the given decimal number with the base 2.

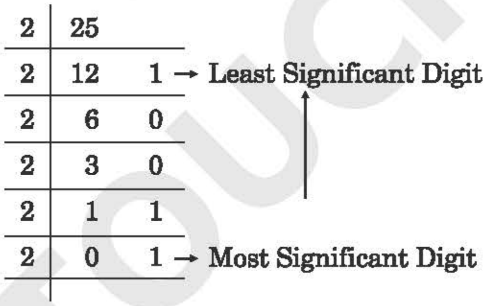
Step 2 : Write down the remainder and divide the quotient again by 2.

Setp 3 : Repeat the step 2 till the quotient is zero.

Step 4 : Write the remainders obtained in each step in the reverse order to form the binary equivalent of the given decimal number, *i.e,* placing the Least Significant Digit at the top and the Most Significant Digit at the bottom.

Consider the following examples :

Example 1:

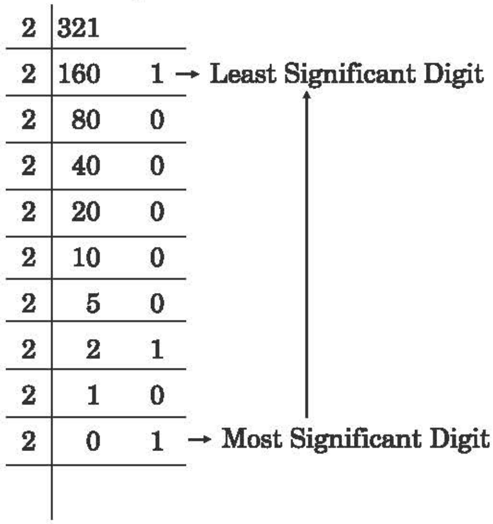


2	25		
2	12	1	→ Least Significant Digit
2	6	0	
2	3	0	
2	1	1	
2	0	1	→ Most Significant Digit

Thus $(25)_{10} = (11001)_2$

The base of number is given as subscript.

Example 2:



2	321		
2	160	1	→ Least Significant Digit
2	80	0	
2	40	0	
2	20	0	
2	10	0	
2	5	0	
2	2	1	
2	1	0	
2	0	1	→ Most Significant Digit

Thus $(321)_{10} = (101000001)_2$

Observe, that the remainders obtained in each step are written in the reverse order.

Q.13. Explain the conversion of binary to decimal number system.

Ans.

Conversion of Binary to Decimal Number

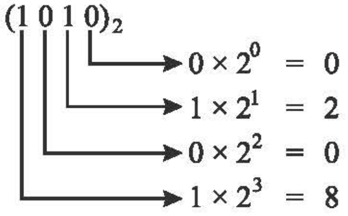
To convert a binary number into its equivalent decimal number, follow these steps :

(i) Multiply each binary number with its positional value, which is in terms of power of 2, starting from the extreme right digit.

(ii) Increase the power one by one, keeping the base fixed as 2.

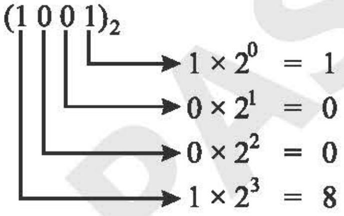
(iii) Calculate the sum of all the products to get the decimal number.

Example 1:



Thus $(1010)_2 = (10)_{10}$

Example 2:



Thus $(1001)_2 = (9)_{10}$

Example 3 : $(110001001)_2$

$$= (1\times2^8)+(1\times2^7)+(0\times2^6)+(0\times2^5)+(0\times2^4)+(1\times2^3)+(0\times2^2)+(0\times2^1)+(1\times2^0)$$

$$= 256+128+0+0+0+8+0+0+1$$

$$= 393$$

Thus $(110001001)_2 = (393)_{10}$

SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. What are input devices? Explain.

Ans.

Input Devices

Following are some of the important input devices which are used in a computer : Keyboard, Mouse, Joy Stick,Light pen, Track Ball, Scanner, Graphic Tablet, Microphone, Magnetic Ink Card Reader (MICR), Optical Character Reader (OCR), Bar Code Reader, Optical Mark Reader (OMR).

1. **Keyboard :** Keyboard is the most common and very popular input device which helps to input data to the computer. The layout of the keyboard is like that of traditional typewriter, although there are some additional keys provided for performing additional functions.

   Keyboards are of two sizes 84 keys or 101/102 keys, but now keyboards with 104 keys or 108 keys are also available for Windows and Internet.

   The keys on the keyboard are as follows :

   (i) **Typing Keys :** These keys include the letter keys (A-Z) and digit keys (09) which generally give the same layout as that of typewriters.

   (ii) **Numeric Keypad :** It is used to enter the numeric data or cursor movement. Generally, it consists of a set of 17 keys that are laid out in the same configuration used by most adding machines and calculators.

(iii) **Function Keys :** The twelve function keys are present on the keyboard which are arranged in a row at the top of the keyboard. Each function key has a unique meaning and is used for some specific purpose.

(iv) **Control keys :** These keys provide cursor and screen control. It includes four directional arrow keys. Control keys also include Home, End, Insert, Delete, Page Up, Page Down, Control(Ctrl), Alternate(Alt), Escape(Esc).

(v) **Special Purpose Keys :** Keyboard also contains some special purpose keys such as Enter, Shift, Caps Lock, Num Lock, Space bar, Tab, and Print Screen.

2. **Mouse :** Mouse is the most popular pointing device. It is a very famous cursor-control device having a small palm size box with a round ball at its base, which senses the movement of the mouse and sends corresponding signals to the CPU when the mouse buttons are pressed. Generally, it has two buttons called the left and the right button and a wheel is present between the buttons. A mouse can be used to control the position of the cursor on the screen, but it cannot be used to enter text into the computer.

   Advantages : Some advantages of mouse are as follows :

   (i) Easy to use
   (ii) Not very expensive
   (iii) Moves the cursor faster than the arrow keys of the keyboard.

3. **Joystick :** Joystick is also a pointing device, which is used to move the cursor position on a monitor screen. It is a stick having a spherical ball at its both lower and upper ends. The lower spherical ball moves in a socket. The joystick can be moved in all four directions. The function of the joystick is similar to that of a mouse. It is mainly used in Computer Aided Designing (CAD) and playing computer games.

4. **Light Pen :** Light pen is a pointing device similar to a pen. It is used to select a displayed menu item or draw pictures on the monitor screen. It consists of a photocell and an optical system placed in a small tube. When the tip of a light pen is moved over the monitor screen and the pen button is pressed, its photocell sensing element detects the screen location and sends the corresponding signal to the CPU.

5. **Track Ball :** Track ball is an input device that is mostly used in notebook or laptop computer, instead of a mouse. This is a ball which is half inserted and by moving fingers on the ball, the pointer can be moved. Since the whole device is not moved, a track ball requires less space than a mouse. A track ball comes in various shapes like a ball, a button, or a square.

6. **Scanner :** Scanner is an input device, which works more like a photocopy machine. It is used when some information is available on paper and it is to be transferred to the hard disk of the computer for further manipulation. Scanner captures images from the source which are then converted into a digital form that can be stored on the disk. These images can be edited before they are printed.

7. **Digitizer :** Digitizer is an input device which converts analog information into digital form. Digitizer can convert a signal from the television or camera into a series of numbers that could be stored in a computer. They can be used by the computer to create a picture of whatever the camera had been pointed at. Digitizer is also known as Tablet or Graphics Tablet as it converts graphics and pictorial data into binary inputs.

A graphic tablet as digitizer is used for fine works of drawing and image manipulation applications.

8. **Microphone :** Microphone is an input device to input sound that is then stored in a digital form. The microphone is used for various applications such as adding sound to a multimedia presentation or for mixing music.
9. **Magnetic Ink Card Reader (MICR) :** MICR input device is generally used in banks as there are large number of cheques to be processed every day. The bank's code number and cheque number are printed on the cheques with a special type of ink that contains particles of magnetic material that are machine readable. This reading process is called Magnetic Ink Character Recognition (MICR). The main advantages of MICR is that it is fast and less error prone.
10. **Optical Character Reader (OCR) :** OCR is an input device used to read a printed text. OCR scans the text optically, character by character, converts them into a machine-readable code, and stores the text on the system memory.
11. **Bar Code Readers :** Bar Code Reader is a device used for reading bar coded data (data in the form of light and dark lines). Bar coded data is generally used in labelling goods, numbering the books, etc. It may be a handheld scanner or may be embedded in a stationary scanner. Bar Code Reader scans a bar code image, converts it into an alphanumeric value, which is then fed to the computer that the bar code reader is connected to.
12. **Optical Mark Reader (OMR) :** OMR is a special type of optical scanner used to recognize the type of mark made by pen or pencil. It is used where one out of a few alternatives is to be selected and marked. It is specially used for checking the answer sheets of examinations having multiple choice questions.

Q.2. What do you understand by output devices? Explain.

Ans.

Output Devices

An output device is any hardware equipment to display, project, or physically reproduce the results of data processed by a computer. It converts electronic information into a format, which can be understood by humans. Output devices are peripheral hardware devices that are either wired or wireless.

The different types of output devices are as follows :

1. **Monitor :** The monitor is the most common output device. It displays information in a pictorial form or commonly referred to as pixels. More the pixels, the better is the picture clarity and sharpness. It includes a screen, circuitry, and the box, in which the circuit is enclosed. The user can view the processed data on the screen. There are two types of Monitor screens. They are as follows :
   (i) Cathode Ray Tube Monitor (CRT)
   (ii) Flat Panel Screen Monitors
2. **Printer :** A printer is a hardware device that produces a hard copy version of the processed data from the computer. It is a device that accepts texts and graphic output from the computer and transmits the image data to the printer, usually on paper. Printers are the most common output device to print text or photos. Some printers can print only in black and white, but today, almost all the printers can print monochrome and color prints. The modern-day printers used in homes have high DPI (dots per

inch), which generates high-quality images. The printers are classified into two main types :

   (i) Impact printers
   (ii) Non-Impact printers.

3. **Headphones :** The headphones or called earphones are hardware output devices that are either plugged in the computer or can be wireless. We can listen to audio or watch the video privately without disturbing others. Headphones come in various shapes and sizes. Some headphones utilize Styrofoam or soft fabric around the earpiece to provide a comfortable fit. The most common type of headphones is earbuds, which are small shaped in a specific manner that fits inside the ear.
4. **Computer Speakers :** Computer speakers are the most common output devices used with a computer. The speakers receive audio as input from the computer or a sound card then this input may be either in analog or digital form. Most computer speakers have internal amplifiers which can increase the volume or the amplitude of the sound based on users' requirements. External speakers are connected to a computer only if a user requires louder sounds, more bass, or surround sound.
5. **Projector :** A projector is an output device that can take images produced by a computer and project them onto a screen or surface. The older versions of the projectors used to create the image by shinning the light through a small transparent lens while the newer version projectors can project the image directly by using a laser. The projectors used nowadays are known as video projectors. The projectors can produce still images or moving images. Projectors are used in classrooms, offices, auditoriums, and also at places of worship, as it enables a group of people to watch videos, presentations, or pictures generated from a single computer.
6. **GPS (Global Positioning System) :** A global Positioning System or GPS is a network of satellites to know the exact location of an object on earth. The GPS is composed of a sender and a receiver computer. The GPS comprises 24 satellites, expanded in space about 12000 miles above the earth's surface. The GPS and satellite interact using microwave signals to give information regarding location, vehicle speed, etc. GPS is nowadays used in smartphones, vehicles, and many other tracking devices.
7. **Sound Card :** The sound card, also known as an audio adapter is the expansion card or integrated circuit to receive and produce sound. The sound cards operate with the help of a software application and a device driver. Microphones are the input device that receives the audio signals, and speakers or headphones are the output devices to send audio data. The sound card has a dual purpose of converting the input audio data into analog audio that can be played by the speakers, can convert the analog audio from microphones into digital data. The computer doesn't need a sound card. It is either a built-in motherboard or comes as an expansion slot.
8. **Video Card :** A video card is also an expansion card that is attached to the motherboard. It processes the images and video and enhances their display quality. Most computers have basic video and graphics capabilities, but a video card is required for getting faster and more detailed graphics.
9. **Braille Reader :** A Braille Reader is an electronic device that allows a blind person to read the text displayed on the monitor screen. The computer sends a text to the Braille

Reader, where it is translated into Braille format and displayed by raising rounded pins through a flat surface. Braille readers are available in various sizes like large units of keyboard size for computers and small units for laptops and tablets.

10. **Speech-Generating device :** The speech-generating device, also known as voice output communication aids, converts the text to speech. The SGD speaks out loud the command entered in the form of text by the user. This device is useful for individuals suffering from speech impairments.
11. **J plotter :** J plotter or simply plotter is a kind of hardware output device similar to a printer used to draw vector graphics. Plotter generates a digitally represented hard copy of the design.A graphics card sends the design to the plotter, and a pen is used to form the design. It is usually used in engineering and basically draws a certain image on a number of straight lines.

Q.3. Describe CPU and computer memory in detail.

Ans.

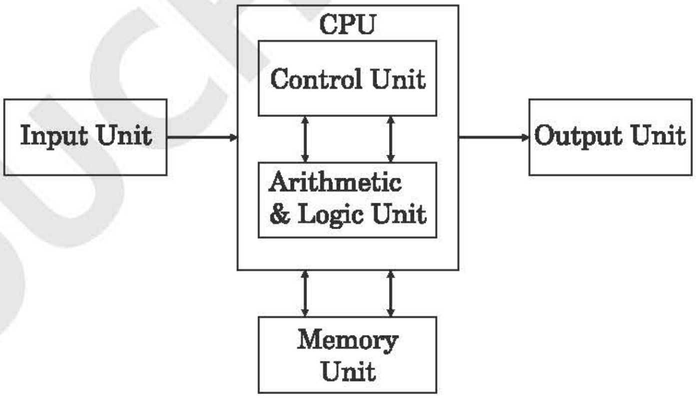
Computer - CPU (Central Processing Unit)

Central Processing Unit (CPU) consists of the following features :

1. CPU is considered as the brain of the computer.
2. CPU performs all types of data processing operations.
3. It stores data, intermediate results, and instructions (program).
4. It controls the operation of all parts of the computer.

CPU itself has following three components :

1. Memory or Storage Unit
2. Control Unit
3. ALU (Arithmetic Logic Unit)



Memory or Storage Unit

This unit can store instructions, data and intermediate results. This unit supplies information to other units of the computer when needed. It is also known as internal storage unit or the main memory or the primary storage or Random-Access Memory (RAM). Its size affects speed, power, and capability. Primary memory and secondary memory are two types of memories in the computer. Functions of the memory unit are :

1. It stores all the data and the instructions required for processing.
2. It stores intermediate results of processing.

3. It stores the final results of processing before these results are released to an output device.
4. All inputs and outputs are transmitted through the main memory.

Computer-Memory

A memory is just like a human brain. It is used to store data and instructions. Computer memory is the storage space in the computer, where data is to be processed and instructions required for processing are stored. The memory is divided into large number of small parts called cells. Each location or cell has a unique address, which varies from zero to memory size minus one. For example, if the computer has 64k words, then this memory unit has 64 * 1024 = 65536 memory locations. The address of these locations varies from 0 to 65535.

Memory is primarily of three types :

1. **Cache Memory :** Cache memory is a very high-speed semiconductor memory which can speed up the CPU. It acts as a buffer between the CPU and the main memory. It is used to hold those parts of data and program which are most frequently used by the CPU. The parts of data and programs are transferred from the disk to cache memory by the operating system, from where the CPU can access them.

   Advantages : The advantages of cache memory are as follows :
   - (i) Cache memory is faster than main memory.
   - (ii) It consumes less access time as compared to main memory.
   - (iii) It stores the program that can be executed within a short period of time.
   - (iv) It stores data for temporary use.

   Disadvantages : The disadvantages of cache memory are as follows :
   - (i) Cache memory has limited capacity.
   - (ii) It is very expensive.
2. **Primary Memory (Main Memory) :** Primary memory holds only those data and instructions on which the computer is currently working. It has a limited capacity and data is lost when power is switched off. It is generally made up of semiconductor device. These memories are not as fast as registers. The data and instruction required to be processed resides in the main memory. It is divided into two subcategories RAM and ROM.

   Characteristics of Main Memory : These are as follows :
   - (i) These are semiconductor memories.
   - (ii) It is known as the main memory.
   - (iii) Usually volatile memory.
   - (iv) Data is lost in case power is switched off.
   - (v) It is the working memory of the computer.
   - (vi) Faster than secondary memories.
   - (vii) A computer cannot run without the primary memory.
3. **Secondary Memory :** This type of memory is also known as external memory or non-volatile. It is slower than the main memory. These are used for storing data/information permanently. CPU directly does not access these memories, instead they are accessed via input-output routines. The contents of secondary memories are first transferred to the main memory, and then the CPU can access it. For example, disk, CD-ROM, DVD, etc.

Characteristics of Secondary Memory : These are as follows :

(i) These are magnetic and optical memories.
(ii) It is known as the backup memory.
(iii) It is a non-volatile memory.
(iv) Data is permanently stored even if power is switched off.
(v) It is used for storage of data in a computer.
(vi) Computer may run without the secondary memory.
(vii) Slower than primary memories.

Control Unit

This unit controls the operations of all parts of the computer but does not carry out any actual data processing operations. Functions of this unit are :

1. It is responsible for controlling the transfer of data and instructions among other units of a computer.
2. It manages and coordinates all the units of the computer.
3. It obtains the instructions from the memory, interprets them, and directs the operation of the computer.
4. It communicates with Input/Output devices for transfer of data or results from storage.
5. It does not process or store data.

ALU (Arithmetic Logic Unit)

This unit consists of two subsections namely :

1. **Arithmetic Section :** Function of arithmetic section is to perform arithmetic operations like addition, subtraction, multiplication, and division. All complex operations are done by making repetitive use of the above operations.
2. **Logic Section :** Function of logic section is to perform logic operations such as comparing, selecting, matching, and merging of data.

Q.4. What do you understand by computer operating system? Describe the functions of operating system and different types of computer operating systems.

Ans.

Operating System

An Operating System (OS) is a software that acts as an interface between computer hardware components and the user. Every computer system must have at least one operating system to run other programs. Applications like Browsers, MS Office, Notepad Games, etc., need some environment to run and perform its tasks.

The OS helps you to communicate with the computer without knowing how to speak the computer's language. It is not possible for the user to use any computer or mobile device without having an operating system.

Types of Operating System (OS)

Following are the popular types of OS (Operating System) :

1. **Batch Operating System :** Some computer processes are very lengthy and time-consuming. To speed the same process, a job with a similar type of needs are batched together and run as a group.

The user of a batch operating system never directly interacts with the computer. In this type of OS, every user prepares his or her job on an offline device like a punch card and submit it to the computer operator.

2. **Multi-Tasking/Time-sharing Operating systems :** Time-sharing operating system enables people located at a different terminal(shell) to use a single computer system at the same time. The processor time (CPU) which is shared among multiple users is termed as time sharing.
3. **Real time OS :** A real time operating system time interval to process and respond to inputs is very small. Examples : Military Software Systems, Space Software Systems are the Real time OS example.
4. **Distributed Operating System :** Distributed systems use many processors located in different machines to provide very fast computation to its users.
5. **Network Operating System :** Network Operating System runs on a server. It provides the capability to serve to manage data, user, groups, security, application, and other networking functions.
6. **Mobile OS :** Mobile operating systems are those OS which is especially that are designed to power smartphones, tablets, and wearables devices.

Some most famous mobile operating systems are Android and iOS, but others include BlackBerry, Web, and watch OS.

Functions of Operating System

Some typical operating system functions may include managing memory, files, processes, Input-Output system and devices, security, etc.

Below are the main functions of Operating System :

Memory Management
Processor Management
File Management
Device Management
I/O Management
Secondary Storage Management
Security
Command Interpretation
Networking
Communication Management
Job accounting

In an operating system software performs each of the function :

1. **Process management :** Process management helps OS to create and delete processes. It also provides mechanisms for synchronization and communication among processes.
2. **Memory management :** Memory management module performs the task of allocation and de-allocation of memory space to programs in need of this resources.
3. **File management :** It manages all the file-related activities such as organization storage, retrieval, naming, sharing, and protection of files.
4. **Device Management :** Device management keeps tracks of all devices. This module also responsible for this task is known as the Input-Output controller. It also performs the task of allocation and de-allocation of the devices.

5. **Input-Output System Management :** One of the main objects of any OS is to hide the peculiarities of that hardware devices from the user.
6. **Secondary-Storage Management :** Systems have several levels of storage which includes primary storage, secondary storage, and cache storage. Instructions and data must be stored in primary storage or cache so that a running program can reference it.
7. **Security :** Security module protects the data and information of a computer system against malware threat and authorized access.
8. **Command interpretation :** This module is interpreting commands given by the and acting system resources to process that commands.
9. **Networking :** A distributed system is a group of processors which do not share memory, hardware devices, or a clock. The processors communicate with one another through the network.
10. **Job accounting :** Keeping track of time and resource used by various job and users.
11. **Communication management :** Coordination and assignment of compilers, interpreters, and another software resource of the various users of the computer systems.

Most Popular Operating Systems

There are five main types of operating systems. These five OS types are likely what run your phone, computer, or other mobile devices like a tablet. Whether you're just a normal computer and phone user or someone hoping to get involved in an IT career, knowledge of applications and systems types will help you maintain security and user access, perform routine operations, and much more.

1. **Microsoft Windows :** The Windows OS has been around since the 1980s and has had several versions and updates (including Windows 95, Windows Vista, Windows 7/8/10, etc.) Microsoft Windows is one of the popular operating system types and is preloaded on most new PC hardware. With each new Windows update or release, Microsoft continues to work on improving their users' experience, hardware, and software, making Windows more accessible and easier to use.

   Microsoft Windows contains a control panel, a desktop and desktop assistant, disk cleanup, event viewer, and more. Many users prefer Microsoft Windows because they say it's compatible with many other kinds of software. Many kinds of computer programs run best on Microsoft Windows because they're developed by Microsoft.
2. **Apple macOS :** Head-to-head in the competition with Microsoft Windows is Apple's macOS. macOS and Windows are both examples of proprietary operating systems, meaning that the company conceptualized, designed, developed, and now sells their own OS. They're designed and sold by the companies and aren't meant to be tampered with or tweaked by users. Apple and Macintosh computers run on the proprietary macOS and OS X system, the first of which launched 20 years ago. There are also previous versions or updates which include:

   (i) Kodiak (OS X 10 Beta), (ii) Lion (OS X 10.7), (iii) Mountain Lion (OS X 10.8), (iv) Mavericks (OS X 10.9), (v) Yosemite (OS X 10.10), (vi) El Capitan (OS X 10.11), (vii) Sierra (macOS 10.12), (viii) High Sierra (macOS 10.13), (ix) Mojave (macOS 10.14), (x) Catalina (macOS 10.15), (xi) Big Sur (macOS 11).

The macOS and Apple/Mac products are also known and beloved by their users for ease of use and continually improving user experience. Fast processing speeds, a simple desktop interface, and a wide variety of helpful resources make users excited about macOS. Many users relish the instant connection with their computers and mobile phone hardware, and enjoy the lack of bugs and hackers that Apple systems are known for.

3. **Google's Android OS :** The OS that companies including Google use to run its Android mobile smartphones and tablets is based on Linux distribution and other open source software. Android OS is the primary OS for Google mobile devices like smartphones and tablets. Android has gained increasing popularity since its release as an alternative to Apple's iOS for smartphone users and is continuing to increase in popularity with new updates and exciting features.
4. **Apple iOS :** Apple's iOS is another mobile operating system used exclusively for iPhones, some of the most popular mobile devices on the market. iOS integrations have regular updates, new expansions to software, and continually are offering new features for users even if they have older devices.

   Many users appreciate the unique user interface with touch gestures, and the ease of use that iOS offers. This operating system also allows other Apple devices to connect, giving users easy connections to other devices or people.
5. **Linux Operating System :** Linux is different from Windows and Apple in that it's not a proprietary software, but rather a family of open source systems. In other words, anyone can modify and distribute it. Linux may be the least known on this list, but it's free and available in many different open source versions. Linux is popular because of its ease of customization and offers a variety of options to those who understand how to use it. If you know how to customize and work with operating systems, Linux is an ideal choice. And if this kind of coding and back-end work is interesting to you, it may be a good idea to purchase a Linux system and get started on manipulating it.

Q.5. Describe different types of programming languages.

Ans.

Computer Programming Languages

Computer programming languages allow us to give instructions to a computer in a language the computer understands. Just as many human-based languages exist, there are an array of computer programming languages that programmers can use to communicate with a computer. The portion of the language that a computer can understand is called a "binary." Translating programming language into binary is known as "compiling." Each language, from C Language to Python, has its own distinct features, though many times there are commonalities between programming languages.

These languages allow computers to quickly and efficiently process large and complex swaths of information. For example, if a person is given a list of randomized numbers ranging from one to ten thousand and is asked to place them in ascending order, chances are that it will take a sizable amount of time and include some errors.

Python

Python is an advanced programming language that is interpreted, object-oriented and built on flexible and robust semantics.

Uses of Python in Professions and Industries : Python developers, software engineers, back end developers, Python programmers. Used by employers in information technology, engineering, professional services and design

Major Organizations : Google, Pinterest, Instagram, YouTube, Drobox, NASA, ESRI

Specializations and Industries : Web and Internet development (frameworks, micro-frameworks and advanced content management systems); scientific and numeric computing; desktop graphical user interfaces (GUIs)

Importance : Python lets you work quickly to integrate systems as a scripting or glue language. It's also suited for Rapid Application Develop (RAD).

1. The game Civilization 4 has all its inner logic, including AI, implemented in Python.
2. NASA uses Python in its Integrated Planning System as a standard scripting language.

Features : These are as follows :

1. Simple to learn and easily read.
2. Associated web frameworks for developing web-based applications.
3. Free interpreter and standard library available in source or binary on major platforms.

Java

Java is a general-purpose, object-oriented, high-level programming language with several features that make it ideal for web-based development.

Uses of Java in Professions and Industries : These are as follows :

1. Software engineers, Java developers.
2. Used by employers in communications, education, finance, health sciences, hospitality, retail and utilities.

Major Organizations : V2COM, Eclipse Information Technologies, eBay, Eurotech

Specializations and Industries : Internet of Things (IoT), Enterprise Architecture, Cloud Computing

Importance : Java is used to develop enterprise-level applications for video games and mobile apps, as well as to create web-based applications with JSP (Java Server Pages). When used online, Java allows applets to be downloaded and used through a browser, which can then perform a function not normally available.

1. Programs that use or are written in Java include Adobe Creative Suite, Eclipse, Lotus Notes, Minecraft and OpenOffice.
2. Java is the core foundation for developing Android apps.

Features : These are as follows :

1. Application portability.
2. Robust and interpreted language.
3. Extensive network library.

Originally known as Oak, Java was developed in 1990 at Sun Microsystems to add capabilities to the C++ language. Java was developed according to the principle of WORA (Write Once Run Anywhere). The language was introduced to the public in 1995 and is now owned by Oracle.

HTML (Hypertext Markup Language)

HTML is the standard markup language used to create web pages; it ensures proper formatting of text and images (using tags) so that Internet browsers can display them in the ways they were intended to look.

Uses of HTML in Professions and Industries : These are as follows :

1. Web developers, technical editors, email designers, software engineers.
2. Used by employers in Information Technology, Engineering, Design, Professional Services, Management, Marketing, Customer Services and Sales.

Major Organizations : Apple, Cyber Coders, Apex Systems, CareerBuilder

Specializations and Industries Where HTML is Used Most : Web Development, Email Programming

Importance : HTML is used to create electronic documents (pages) displayed online. Visit any page and you will see an example of HTML in action.

- The diversity and complexity in the structure and appearance of today's sites is made possible with HTML.

Features : These are as follows :

1. Easy to use and learn the basics of HTML.
2. Free and accessible.
3. Multiple versions available.

HTML was created by physicist Tim Berners-Lee in 1990 to allow scientists to share documents online. Before then, all communication was sent using plain text. HTML made "rich" text possible (*i.e.*, text formatting and visual images).

JavaScript

JavaScript is a client-side programming language that runs inside a client browser and processes commands on a computer rather than a server. It is commonly placed into an HTML or ASP file. Despite its name, JavaScript is not related to Java.

Uses of Java Script in Professions and Industries : These are as follows :

1. JavaScript developers, Web developers, software engineers.
2. Used by employers in Information Technology, Engineering, Design, Marketing, Finance and Healthcare.

Major Organizations : WordPress, Soundcloud, Khan Academy, Linkedin, Groupon, Yahoo and many others

Specializations and Industries Where JavaScript is Used Most : Front End Website Development, Gaming Development

Importance : JavaScript is used primarily in Web development to manipulate various page elements and make them more dynamic, including scrolling abilities, printing the time and date, creating a calendar and other tasks not possible through plain HTML. It can also be used to create games and APIs.

1. The agency Cyber-Duck in Britain uses public APIs, created with JavaScript, to pull in data about crime and enables users to review a local area.
2. Tweetmap, created by Pete Smart and Rob Hawkes using JavaScript, represents a world map that is proportionally sized according to the number of tweets.

Features : These are as follows :

1. Basic features are easy to learn.
2. Multiple frameworks.
3. Users can reference Jquery, a comprehensive Javascript library.

JavaScript was designed by Netscape and originally known as LiveScript, before becoming JavaScript in 1995.

C Language

C Language is a structure-oriented, middle-level programming language mostly used to develop low-level applications.

Uses of C Language in Professions and Industries : These are as follows :

1. Software developers, computer engineers, business and systems analysts, IT and Web content administrators, embedded software engineers.
2. Used by employers in Information Technology, Engineering, Management, Healthcare and Professional Services.

Major Organizations : Microsoft, Apple, Oracle, Cisco, Raytheon

Specializations and Industries Where C Language is Used Most : Embedded Systems, Systems Programming, Artificial Intelligence, Industrial Automation, Computer Graphics, Space Research, Image Processing and Game Programming

Importance : C Language is used to develop systems applications that are integrated into operating systems such as Windows, UNIX and Linux, as well as embedded softwares. Applications include graphics packages, word processors, spreadsheets, operating system development, database systems, compilers and assemblers, network drivers and interpreters.

1. Facebook's TAO systems is programmed mostly using C language.
2. Most device drivers are still developed using C Language.

Features : These are as follows :

1. Simple to learn; there are only 32 keywords to master.
2. Easy to write systems programs such as compilers and interpreters.
3. Foundational language for beginners.

The C Language was developed in 1972 at Bell Labs specifically for implementing the UNIX system. It eventually gave rise to many advanced programming languages, including C++, Java C#, JavaScript and Pearl.

C++

C++ is a general purpose, object-oriented, middle-level programming language and is an extension of C language, which makes it possible to code C++ in a "C style". In some situations, coding can be done in either format, making C++ an example of a hybrid language.

Uses of C++ in Professions and Industries : These are as follows :

1. C++ software engineers, C++ software developers, embedded engineers, programmer analysts.
2. Used by employers in Information Technology, Engineering, Professional Services, Design, Quality Control and Management.

Major Company and Organization Users : Google, Mozilla, Firefox, Winamp, Adobe Software, Amazon, Lockheed Martin

Specializations : System/Application Software, Drivers, Client-Server Applications, Embedded Firmware

Importance : The C++ language is used to create computer programs and packaged software, such as games, office applications, graphics and video editors and operating systems.

1. The Blackberry OS is developed using C++.
2. The newest Microsoft Office suite was developed using C++.

Features : These are as follows :

1. Often the first programming language taught at college level.
2. Quick processing and compilation mechanism.
3. Robust standard library (STL).

Released in 1983 and often considered an object-oriented version of C language, C++ was created to compile lean, efficient code, while providing high-level abstractions to better manage large development projects.

Q.6. What is Internet? Describe the applications or uses of Internet.

Ans.

Internet

The Internet is an increasingly important part of everyday life for people around the world. But if we've never used the Internet before, all of this new information might feel a bit confusing at first.

Throughout this tutorial, we'll try to answer some basic questions we may have about the Internet and how it's used. When we're done, we'll have a good understanding of how the Internet works, how to connect to the Internet, and how to browse the Web.

The Internet is a global network of billions of computers and other electronic devices. With the Internet, it's possible to access almost any information, communicate with anyone else in the world, and do much more.

We can do all of this by connecting a computer to the Internet, which is also called going online. When someone says a computer is online, it's just another way of saying it's connected to the Internet.

The World Wide Web-usually called the Web for short-is a collection of different websites we can access through the Internet. A website is made up of related text, images, and other resources. Websites can resemble other forms of media-like newspaper articles or television programs-or they can be interactive in a way that's unique to computers.

The purpose of a website can be almost anything : a news platform, an advertisement, an online library, a forum for sharing images, or an educational site like us!

Once we are connected to the Internet, we can access and view websites using a type of application called a web browser. Just keep in mind that the web browser itself is not the Internet; it only displays websites that are stored on the Internet.

Applications of internet

This is the basic uses of the internet which are as follows :

1. Seek information on anything across the globe on a real-time basis.
2. Communicate, collaborate with others.
3. Telecommute to the office or work from home.
4. Do transactions with business entities.
5. Down load files from a remote.
6. Get educated and entertained.
7. Carry out social.
8. Do group activities.
9. Collect operational data from remote equipment (stationary as well as moving).
10. Process data while it is streamed to the central server.
11. Get real-time data on the surrounding devices, systems, weather to automate activities.

12. Design a decision-taking system as against the decision support system.
13. Connect people, stakeholders, machines and everything.

Uses of the Internet in our Daily Life

The following points will help us learn why the internet is important. How the internet changed the world. What are the advantages for us if we're connected to the internet? How the internet is influencing our life. So, Let's begin:

1. **Uses of the Internet in Students daily life :** Students have a free platform to learn throughout their lifetime. People in the age group 18 to 35 are among the most frequent users of the Internet today and these people are mostly students from all over the world. They are using the Internet to learn new skills and even acquire degrees in professional online courses.

   Similarly, educators like us are using the Internet for teaching and sharing our knowledge and experience with the world. There are many websites that help to explore what our hidden potential is and which profession would suit we the best.
2. **Uses of the Internet to increase the speed of daily tasks :** Our routine is initiated by the Internet. It is the first thing in the morning we do- see our notifications and emails. The Internet has made human life so much easier, now the biggest and toughest tasks are done in minutes. No matter it is a simple email, pizza order, shopping or money transfer it is so much easier by the use of the Internet in life.
3. **Uses of the Internet for business promotion and innovation :** We also use the Internet to promote our business. We can sell our products by using various e-Commerce solutions on the Internet. e-commerce is booming on the Internet and we can see new services and creative businesses starting up every single day, which in turn is creating jobs and thereby reducing unemployment.

   I think if our youth of India or from other countries learn and use the Internet seriously they can get hundreds of options for their careers on the Internet. I believe that the uses of the Internet in business have brought about an exciting stir in the business world and it will not hold back anymore.

   Use of Google Ad words, Facebook ads and content marketing are common in product and services marketing on the Internet. People are always looking for ways on the Internet to grow their businesses.
4. **Uses of the Internet for shopping in our daily life :** Shopping has become a hassle-free task now and almost anybody can order products online after comparison with other websites. The boom and the resultant competition in the online shopping business are evident. Shopping sites are more interesting because of the huge discounts different companies are offering customers.

   People are attracted to them and this is good news especially for the Indian shopper because of our frugal spending habits. The customer can pay cash for the delivery of a product delivered to his house in a few hours and can return the product if he is not satisfied with it.

   Shopping on the Internet is affordable, convenient, and saves time. The Use of flipkart.com, alibaba.com, amazon.com, paytm.com, snapdeal.com, etc. for online shopping is common. That's how the Internet is affecting our shopping habits in daily life. And all this process is called e-Commerce. e-Commerce has changed business and now it's an important part of our life.

Q.7. Describe the computer arithmetic *i.e.*, binary addition, subtraction, multiplication and division with examples.

Ans.

Computer Arithmetic

As a computer understands only the binary code, so the data entered into the computer by the user is converted into binary code for processing. This processing may involve various kinds of arithmetic operations, such as addition, subtraction, multiplication, division, etc., on the binary numbers.

1. Binary Addition : The technique used to add binary numbers inside the computer is very easy and simple. This is performed in the same way as you perform addition with decimal numbers. The following table illustrates the addition of two binary digits :

x	y	$z = x + y$
0	0	$0+0=0$
0	1	$0+1=1$
1	0	$1+0=1$
1	1	$1+1=10$

Example 1 : Compute $(1000)_2 + (1111)_2$

$$\begin{array}{r} 1\;0\;0\;0 \\ +\;1\;1\;1\;1 \\ \hline 1\;0\;1\;1\;1 \\ \hline \end{array}$$

Example 2 : Compute $(11111)_2 + (1011)_2$

$$\begin{array}{rl} 1\;1\;1\;1 & \text{carry over} \\ 1\;1\;1\;1\;1 & \\ +\;0\;1\;0\;1\;1 & \\ \hline 1\;0\;1\;0\;1\;0 & \\ \hline \end{array}$$

2. Binary Subtraction : The rules given in the table must be followed to perform binary subtraction :

x	y	$z = x + y$
0	0	$0+0=0$
1	0	$1-0=1$
1	1	$1-1=0$
0	1	$0-1=1$

Example 1.

Compute $(1111)_2 - (1010)_2$

$$\begin{array}{r} 1\;1\;1\;1 \\ -\;1\;0\;1\;0 \\ \hline 0\;1\;0\;1 \\ \hline \end{array}$$

Example 2.

Compute $(1100)_2 - (11)_2$

Again

Borrowed 1 Borrowed 1

10

Balance Balance Number is now

$$\begin{array}{ccccc} & & 0 & 1 & 10 \\ & 1 & 1 & 0 & 0\;\underline{-1} \\ - & 0 & 0 & 1 & 1\;\underline{\;\;1} \\ \hline & 1 & 0 & 0 & 1 \\ \hline \end{array}$$

Example 3.

Compute $(1100)_2 - (1010)_2$

Borrowed 1

$$\begin{array}{ccccc} & & & 1 & \\ & 1 & 1 & 0 & 0 \\ - & 1 & 0 & 1 & 0 \\ \hline & 0 & 0 & 1 & 1 \\ \hline \end{array}$$

3. Binary Multiplication : The rules for performing multiplication using binary numbers is same as that of the decimal numbers. The given table illustrates the multiplication of two binary digits :

x	y	$x * y = z$
0	0	$0*0=0$
0	1	$0*1=0$
1	0	$1*0=0$
1	1	$1*1=1$

Example 1.

Compute $(101)_2 \times (11)_2$

```
        1 0 1
      × 1 1
      -------
        1 0 1
    + 1 0 1 ×
  -----------
  Sum= 1 1 1 1
```

Example 2.

Compute $(1111)_2 \times (101)_2$

```
          1 1 1 1
        × 1 0 1
        ---------
          1 1 1 1
        0 0 0 0 ×
    + 1 1 1 1 × ×
    -------------
    1 0 0 1 0 1 1
```

Example 3.

Compute $(101)_2 \times (100)_2$

```
          1 0 1
        × 1 0 0
        -------
          0 0 0
        0 0 0 ×
    + 1 0 1 × ×
    -----------
      1 0 1 0 0
```

4. Binary Division : The method to perform division of two binary numbers is same as that of decimal numbers. See the example given below :

Example 1 : Compute $(110)_2 \div (10)_2$

```
              11     <---- Quotient
          --------
          10| 110    <---- Dividend
           |  10
           v  ---
   Divisor   010
              10
             ---
              00  <---- Remainder
             ---
```

Example 2 : Compute $(10000111)_2 \div (1001)_2$

```
             01111            <---- Quotient
         --------------
       1001| 10000111 <---- Dividend
         |   1001
         v   ------
   Divisor   001111
               1001
             ------
               01001
               1001
               -----
               01001
                 1001
               ------
                 0000 <---- Remainder
               ------
```

❑

UNIT-VIII

Mathematical Concepts for Chemistry

SECTION-A VERY SHORT ANSWER TYPE QUESTIONS

Q.1. If $\log 2 = 0.3010$ and $\log 3 = 0.4771$; find the value of :
(i) log 6 (ii) log 5 (iii) log $\sqrt{24}$

Sol. (i) $\log 6 = \log(2\times 3) = \log 2 + \log 3 = 0.3010 + 0.4771 = 0.7781$

(ii) $\log 5 = \log\frac{10}{2} = \log 10 - \log 2 = 1 - 0.3010 = 0.6990$ $(\because \log 10 = 1)$

(iii) $\log\sqrt{24} = \log(24)^{1/2} = \frac{1}{2}\log(2^3\times 3)$

$$= \frac{1}{2}[3\log 2 + \log 3] = \frac{1}{2}[3\times 0.3010 + 0.4771]$$

$$= 0.69005$$

Q.2. Find the slope of the line making inclination of 60° with the positive direction of x-axis.

Sol. Given that inclination of a line with the positive direction of x-axis is 60°.

$\therefore$ $\theta = 60°$.

Hence, slope of line, $m = \tan\theta = \tan 60° = \sqrt{3}$.

Q.3. Find the equation of a line parallel to y-axis and passing through $(-2, 5)$.

Sol. The equation of a line parallel to y-axis is of the form

$$x = a \qquad \text{...(i)}$$

Given that the line passes through the point $(-2, 5)$.

Putting $x = -2$ and $y = 5$ in eq (i), we get

$$-2 = a$$

Putting value of a in eq (i), we get

$$x = -2,$$

which is the required equation.

Q.4. Find the equation of line parallel to x-axis and passing through $(1, 4)$.

Sol. The equation of a line parallel to x-axis is of the form

$$y = a. \qquad \text{...(i)}$$

Given that the line passes through the point (1, 4)

Putting $x = 1$ and $y = 4$ in eq (i) we get

$$4 = a$$

Putting value of a in eq (i) we get

$$y = 4$$

which is the required equation.

Q.5. Find the derivative of $2x^4 + x$ *w.r.t.x*.

Sol. Suppose $f(x) = 2x^4 + x$

Then, $f'(x) = \frac{d}{dx}(2x^4 + x) = \frac{d}{dx}(2x^4) + \frac{d}{dx}(x) = 2\frac{d}{dx}(x^4) + \frac{d}{dx}(x) = 2(4x^3) + 1 = 8x^3 + 1.$

Q.6. Find the derivative of $\dfrac{x^4 + 3x^3 + 4x^2 + 2}{x^3}$.

Sol. Suppose $f(x) = \dfrac{x^4 + 3x^3 + 4x^2 + 2}{x^3} = x + 3 + 4x^{-1} + 2x^{-3}$

Then,

$$\begin{aligned} f'(x) &= \frac{d}{dx}(x + 3 + 4x^{-1} + 2x^{-3}) \\ &= \frac{d}{dx}(x) + \frac{d}{dx}(3) + \frac{d}{dx}(4x^{-1}) + \frac{d}{dx}(2x^{-3}) \\ &= 1 + 0 + (-4x^{-2}) + (-6x^{-4}) = 1 - \frac{4}{x^2} - \frac{6}{x^4}. \end{aligned}$$

Q.7. Differentiate $\log_7(\log x)$ *w.r.t.x*.

Sol. Suppose $y = \log_7(\log x)$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx} = \frac{d}{dx}[\log_7(\log x)] = \frac{d}{dx}\left[\frac{\log(\log x)}{\log 7}\right] = \frac{1}{\log 7}\frac{d}{dx}[\log(\log x)]$$

$$= \frac{1}{\log 7}\frac{\frac{d}{dx}(\log x)}{\log x} = \frac{1}{x \log x \log 7}$$

Q.8. Evaluate the following integrals :

(i) $\int(-3)dx$ (ii) $\int(\sin 5)dx$ (iii) $\int 2^5 dx$ (iv) $\int e^{e^e} dx$

Sol. (i) $\int(-3)\,dx = -3x + C$ (ii) $\int(\sin 5)\,dx = (\sin 5)\,x + C$

(iii) $\int 2^5\,dx = 2^5 x + C$ (iv) $\int e^{e^e}\,dx = e^{e^e} x + C.$

Q.9. Evaluate the following integrals :

(i) $\int \frac{1}{5 - 2x} dx$ (ii) $\int(3x - 1)^{-1} dx$ (iii) $\int \frac{1}{x} dx$

Sol. (i) $\int \frac{1}{5-2x}\,dx = \frac{\log|5-2x|}{\frac{d}{dx}(5-2x)} + C = -\frac{\log|5-2x|}{2} + C.$

(ii) $\int (3x-1)^{-1}\,dx = \frac{\log|3x-1|}{\frac{d}{dx}(3x-1)} + C = \frac{\log|3x-1|}{3} + C.$

(iii) $\int \frac{1}{x}\,dx = \frac{\log|x|}{\frac{d}{dx}(x)} + C = \log|x| + C.$

Q.10. Evaluate the following integrals :

(i) $\int e^{7-3x}\,dx$ (ii) $\int e^{2x+3}\,dx$ (iii) $\int e^{x}\,dx$

Sol. (i) $\int e^{7-3x}\,dx = \frac{e^{7-3x}}{\frac{d}{dx}(7-3x)} + C = -\frac{e^{7-3x}}{3} + C$

(ii) $\int e^{2x+3}\,dx = \frac{e^{2x+3}}{\frac{d}{dx}(2x+3)} + C = \frac{e^{2x+3}}{2} + C$ (iii) $\int e^{x}\,dx = \frac{e^{x}}{\frac{d}{dx}(x)} + C = e^{x} + C.$

Q.11. Find the value of following integrals :

(i) $\int \sin(4-5x)\,dx$ (ii) $\int \sin(2x-3)\,dx$

(iii) $\int \sin x\,dx$

Sol. (i) $\int \sin(4-5x)\,dx = -\frac{\cos(4-5x)}{\frac{d}{dx}(4-5x)} + C = \frac{\cos(4-5x)}{5} + C$

(ii) $\int \sin(2x-3)\,dx = -\frac{\cos(2x-3)}{\frac{d}{dx}(2x-3)} + C = -\frac{\cos(2x-3)}{2} + C$

(iii) $\int \sin x\,dx = -\frac{\cos x}{\frac{d}{dx}(x)} + C = -\cos x + C.$

Q.12. Evaluate the following integrals :

(i) $\int \operatorname{cosec}^2(4-x)\,dx$ (ii) $\int \operatorname{cosec}^2 x\,dx$

Sol. (i) $\int \operatorname{cosec}^2(4-x)\,dx = -\frac{\cot(4-x)}{\frac{d}{dx}(4-x)} + C = \cot(4-x) + C.$

(ii) $\int \operatorname{cosec}^2 x\,dx = -\frac{\cot x}{\frac{d}{dx}(x)} + C = -\cot x + C.$

Q.13. Find the value of following integrals :

(i) $\int_0^{\pi/4} \sin 2x\, dx$ **(ii) $\int_0^{\infty} e^{-x} dx$**

Sol. (i) $\int_0^{\pi/4} \sin 2x\, dx = \left[-\frac{\cos 2x}{2}\right]_0^{\pi/4} = 0 - \left(-\frac{1}{2}\right) = \frac{1}{2}.$

(ii) $\int_0^{\infty} e^{-x}\, dx = [-e^{-x}]_0^{\infty} = \left[-\frac{1}{e^x}\right]_0^{\infty} = 0 - (-1) = 1$

Q.14. Evaluate the following integrals :

(i) $\int_1^2 (4x^3 - 5x^2 + 6x + 9)dx$ **(ii) $\int_2^3 x^2\, dx$**

Sol. (i) $\int_1^2 (4x^3 - 5x^2 + 6x + 9)\, dx = \left[x^4 - \frac{5x^3}{3} + 3x^2 + 9x\right]_1^2$

$$\left[16 - \frac{40}{3} + 12 + 18\right] - \left[1 - \frac{5}{3} + 3 + 9\right] = \frac{64}{3}$$

(ii) $\int_2^3 x^2\, dx = \left[\frac{x^3}{3}\right]_2^3 = 9 - \frac{8}{3} = \frac{19}{3}.$

Q.15. Evaluate : $\int_0^{\pi/4} \frac{1}{1 + \sin x} dx$

Sol. $\int_0^{\pi/4} \frac{1}{1 + \sin x} dx = \int_0^{\pi/4} \frac{1 - \sin x}{(1 + \sin x)(1 - \sin x)} dx = \int_0^{\pi/4} \frac{1 - \sin x}{\cos^2 x} dx$

$$= \int_0^{\pi/4} [\sec^2 x - \sec x \tan x]\, dx$$

$$= [\tan x - \sec x]_0^{\pi/4} = (1 - \sqrt{2}) - (0 - 1) = 2 - \sqrt{2}.$$

Q.16. Evaluate :

(i) $5! - 6!$ **(ii) $\frac{7!}{4!}$** **(iii) $6!$** **(iv) $\frac{12!}{10!3!}$**

(v) $7! + 3!$

Sol. (i) $5! - 6! = (5 \times 4 \times 3 \times 2 \times 1) - (6 \times 5 \times 4 \times 3 \times 2 \times 1) = 120 - 720 = -600$

(ii) $\frac{7!}{4!} = \frac{7 \times 6 \times 5 \times 4!}{4!} = 210$

(iii) $6! = 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$

(iv) $\frac{12!}{10!3!} = \frac{12 \times 11 \times 10!}{10! \times 3 \times 2 \times 1} = 22$

(v) $7! + 3! = (7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1) + (3 \times 2 \times 1) = 5040 + 6 = 5046$

Q.17. Evaluate : (i) $3!\times 2! = 6!$ (ii) $3! + 2! = 5!$

Sol. (i) We have, $3!\times 2! = (3\times 2\times 1)\times(2\times 1) = 6\times 2 = 12$

Also, $6! = 6\times 5\times 4\times 3\times 2\times 1 = 720$. Hence, $3!\times 2! \neq 6!$

(ii) We have $3! + 2! = (3\times 2\times 1) + (2\times 1) = 6 + 2 = 8$

Also, $5! = 5\times 4\times 3\times 2\times 1 = 120$. Hence, $3! + 2! \neq 5!$

Q.18. Evaluate : $\dfrac{n!}{r!(n-r)!}$, when $n = 5, r = 2$.

Sol. Given that $n = 5, r = 2$

Then, $\dfrac{n!}{r!(n-r)!} = \dfrac{5!}{2!3!} = \dfrac{5\times 4\times 3!}{2\times 3!} = 10.$

Q.19. Prove the following :

(i) ${}^nP_n = {}^nP_{n-1}$ (ii) ${}^nP_n = 2\,{}^nP_{n-2}$ (iii) ${}^nP_r = n\,{}^{n-1}P_{r-1}$

Sol. (i) ${}^nP_{n-1} = \dfrac{n!}{[n-(n-1)]!} = \dfrac{n!}{1!} = n! = {}^nP_n$

(ii) $2\,{}^nP_{n-2} = 2\times\dfrac{n!}{[n-(n-2)]!} = 2\times\dfrac{n!}{2!} = n! = {}^nP_n$

(iii) $n\,{}^{n-1}P_{r-1} = n\times\dfrac{(n-1)!}{[(n-1)-(r-1)]!} = \dfrac{n(n-1)!}{(n`-r)!} = \dfrac{n!}{(n-r)!} = {}^nP_r$

Q.20. In how many ways can the letters of the word STRANGE be arranged to form the words not beginning with *T*?

Sol. Here, the order is important and the repetition of letters is not allowed.

So, each arrangement is a permutation.

For leftmost position, we arrange 6 distinct letters (S, R, A, N, G, E), taken one at a time and for other positions, we arrange remaining 6 distinct letters, taken all at a time.

Hence, required number of words = ${}^6P_1\times{}^6P_6 = \dfrac{6!}{5!}\times\dfrac{6!}{0!} = 4320.$

Q.21. In how many ways can 4 red, 3 yellow and 2 green discs be arranged in a row if the discs of the same colour are indistinguishable?

Sol. Here, the order is important and the repetition of discs cannot be done.

So, each arrangement is a permutation.

We arrange 9 discs (4 red, 3 yellow, 2 green), taken all at a time.

We have, $n = 9, p_1 = 4, p_2 = 3, p_3 = 2$

Hence, required number of ways = $\dfrac{n!}{p_1!\,p_2!\,p_3!} = \dfrac{9!}{4!\,3!\,2!} = 1260$

Q.22. In how many ways can 5 persons be seated along a round table?

Sol. Here, each arrangement is a stationary circular permutation.

We have, $n = 5$ and $r = 5$

Hence, required number of arrangements = $\dfrac{{}^nP_r}{r} = \dfrac{{}^5P_5}{5} = \dfrac{5!}{5\times 0!} = 24.$

Q.23. Evaluate :

(i) $^{40}C_{40}$ (ii) $^{6}C_{2}$ (iii) $C(13,3)$

Sol. (i) $^{40}C_{40}=\frac{40!}{40!(40-40)!}=\frac{40!}{40!0!}=1$ (ii) $^{6}C_{2}=\frac{6!}{2!(6-2)!}=\frac{6!}{2!4!}=\frac{6\times5\times4!}{2\times1\times4!}=15$

(iii) $C(13,3)=\frac{13!}{3!(13-3)!}=\frac{13!}{3!10!}=\frac{13\times12\times11\times10!}{3\times2\times1\times10!}=286$

Q.24. Find r, if $^{15}C_{3r}={}^{15}C_{r+3}$.

Sol. We know that if $^{n}C_{a}={}^{n}C_{b}$, then either $a=b$ or $n=a+b$

Given that $^{15}C_{3r}={}^{15}C_{r+3}$

Then, either $3r=r+3$ or $15=3r+(r+3)$ *i.e.*, either $r=\frac{3}{2}$ or $r=3$

But, $r=\frac{3}{2}$ is not possible, as r is always an integer. Hence, $r=3$.

Q.25. If $^{n}C_{8}={}^{n}C_{2}$, then find $^{n}C_{2}$.

Sol. We know that if $^{n}C_{a}={}^{n}C_{b}$ then either $a=b$ or $n=a+b$

Given that $^{n}C_{8}={}^{n}C_{2}$

Then, $n=8+2=10$ $[\because 8\neq2]$

Hence, $^{n}C_{2}={}^{10}C_{2}=\frac{10!}{2!(10-2)!}=\frac{10!}{2!8!}=\frac{10\times9\times8!}{2\times1\times8!}=45.$

SECTION-B (SHORT ANSWER TYPE) QUESTIONS

Q.1. Find the log of the following :

(i) log of 1000 on base 0.01 (ii) log of $216\sqrt{6}$ on base 6

Sol. (i) Suppose $\log_{0.01}(1000)=x$

or $(0.01)^{x}=1000=10^{3}$

or $\left(\frac{1}{100}\right)^{x}=10^{3}$ or $10^{-2x}=10^{3}$

or $-2x=3$ or $x=\frac{-3}{2}$

(ii) Suppose $\log_{6}216\sqrt{6}=x$

or $(6)^{x}=216\sqrt{6}=6^{3}.6^{1/2}=6^{7/2}$ or $x=\frac{7}{2}$

Q.2. Solve the following equations :

(i) $3^{1+x}=7^{x/2}$ (ii) $21^{x}=2^{2x+1}.5^{x}$

(log 2 = 0.3010, log 3 = 0.4771 and log 7 = 0.8451)

Sol. (i) $3^{1+x} = 7^{x/2}$

taking log, $\log 3^{1+x} = \log 7^{x/2}$

or $(1+x)\log 3 = \frac{x}{2}\log 7$ or $(1+x)(0.4771) = \frac{x}{2}(0.8451)$

or $0.9542 + 0.9542x = 0.8451x$ or $x = -8.7$

(ii) $21^x = 2^{2x+1}.5^x$

taking log, $\log 21^x = \log(2^{2x+1} \times 5^x) = \log 2^{2x+1} + \log 5^x$

or $x\log 21 = (2x+1)\log 2 + x\log 5$

or $x\log(3\times 7) = (2x+1)\log 2 + x\log 10/2$

or $x\log 3 + x\log 7 = 2x\log 2 + \log 2 + x\log 10 - x\log 2$

or $x\log 3 + x\log 7 = x\log 2 + \log 2 + x$ $(\because \log 10 = 1)$

or $x(0.4771) + x(0.8451) = x(0.3010) + 0.3010 + x$

or $x = \frac{0.3010}{0.0212} = 14.198$

Q.3. Prove that : $\log\frac{75}{16} - 2\log\frac{5}{9} + \log\frac{32}{243} = \log 2$

Sol. $\log\frac{75}{16} - 2\log\frac{5}{9} + \log\frac{32}{243}$

$= [\log 75 - \log 16] - 2[\log 5 - \log 9] + [\log 32 - \log 243]$

$= [\log(3\times 5\times 5) - \log 2^4] - 2[\log 5 - \log 3^2] + [\log 2^5 - \log 3^5]$

$= \log(3\times 5^2) - \log 2^4 - 2\log 5 + 2\log 3^2 + \log 2^5 - \log 3^5$

$= \log 3 + 2\log 5 - 4\log 2 - 2\log 5 + 4\log 3 + 5\log 2 - 5\log 3 = \log 2.$

Q.4. Prove that : $\log\frac{26}{51} + \log\frac{119}{91} = \log 2 - \log 3$

Sol. $\log\frac{26}{51} + \log\frac{119}{91} = \log 26 - \log 51 + (\log 119 - \log 91)$

$= \log(13\times 2) - \log(17\times 3) + \log(17\times 7) - \log(13\times 7)$

$= \log 13 + \log 2 - [\log 17 + \log 3] + [\log 17 + \log 7] - [\log 13 + \log 7]$

$= \log 13 + \log 2 - \log 17 - \log 3 + \log 17 + \log 7 - \log 13 - \log 7 = \log 2 - \log 3$

Q.5. If a, b, c, d are four positive numbers, prove that

$\log_b a \times \log_c b \times \log_d c = \log_d a.$

Sol. L.H.S. $= \log_b a \times \log_c b \times \log_d c$

$= \frac{\log_m a}{\log_m b} \times \frac{\log_m b}{\log_m c} \times \frac{\log_m c}{\log_m d}$ (by base changing formula)

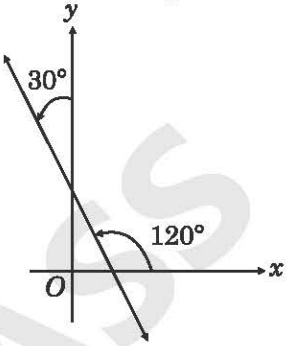
$= \frac{\log_m a}{\log_m d} = \log_d a =$ R.H.S.

Hence, $\log_b a \times \log_c b \times \log_d c = \log_d a$.

Q.6. Find the slope of the line, which makes an angle of 30° with the positive direction of y-axis measured anticlockwise.

Sol. Given that a line makes an angle of 30° with the positive direction of y-axis measured anticlockwise.

So, the line makes an angle of 120° with the positive direction of x-axis measured anticlockwise.



$\therefore$ $\theta = 120°$

Hence, slope of line, $m = \tan\theta = \tan 120°$

$$= \tan(180° - 60°)$$

$$= -\tan 60° = -\sqrt{3}.$$

Q.7. Find the slope of the lines :

(i) Passing through the points $(3, -2)$ and $(-1, 4)$

(ii) Passing through the points $(3, -2)$ and $(7, -2)$

(iii) Passing through the points $(3, -2)$ and $(3, 4)$.

Sol. (i) Given points are $(3, -2)$ and $(-1, 4)$

Then, slope of the line passing through the given points is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{4 - (-2)}{-1 - 3} = -\frac{3}{2}$$

(ii) Given points are $(3, -2)$ and $(7, -2)$

Then, slope of the line passing through the given points is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-2 - (-2)}{7 - 3} = \frac{0}{4} = 0$$

(iii) Given points are $(3, -2)$ and $(3, 4)$

Then, slope of the line passing through the given points is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{4 - (-2)}{3 - 3} = \frac{6}{0}, \text{ which is not defined.}$$

Q.8. Show that the line through the points (5, 6) and (2, 3) is parallel to the line through the points $(9, -2)$ and $(6, -5)$.

Sol. Suppose m_1 be the slope of the line passing through the points (5, 6) and (2, 3).

Then, $m_1 = \frac{3 - 6}{2 - 5} = 1$

Now suppose m_2 be the slope of the line passing through the points $(9, -2)$ and $(6, -5)$

Then, $m_2 = \frac{-5 - (-2)}{6 - 9} = 1$

Since, $m_1 = m_2$

Hence, the given lines are parallel to each other.

Q.9. Find the derivative of the following functions w.r.t. x:

(i) $2x - \frac{3}{4}$ **(ii) $x^{-4}(3 - 4x^{-5})$** **(iii) $4\sqrt{x} - 2$**

Ans. (i) Suppose $f(x)=2x-\frac{3}{4}$.

Then, $$f'(x)=\frac{d}{dx}\left(2x-\frac{3}{4}\right)=\frac{d}{dx}(2x)-\frac{d}{dx}\left(\frac{3}{4}\right)=2\frac{d}{dx}(x)-\frac{d}{dx}\left(\frac{3}{4}\right)=2(1)-0=2$$

(ii) Suppose $f(x)=x^{-4}(3-4x^{-5})=3x^{-4}-4x^{-9}$

Then, $$f'(x)=\frac{d}{dx}(3x^{-4}-4x^{-9})=\frac{d}{dx}(3x^{-4})-\frac{d}{dx}(4x^{-9})$$
$$=3\frac{d}{dx}(x^{-4})-4\frac{d}{dx}(x^{-9})=3(-4x^{-5})-4(-9x^{-10})=-12x^{-5}+36x^{-10}$$

(iii) Suppose $f(x)=4\sqrt{x}-2$.

Then, $$f'(x)=\frac{d}{dx}(4\sqrt{x}-2)=\frac{d}{dx}(4\sqrt{x})-\frac{d}{dx}(2)$$
$$=4\frac{d}{dx}\left(x^{1/2}\right)-\frac{d}{dx}(2)=4\left(\frac{1}{2}x^{-1/2}\right)-0=2x^{-1/2}.$$

Q.10. Find the derivative of the following functions w.r.t. x :

(i) $2\sin x$ (ii) $\tan^n x$ (iii) $\cos^3 x$

Sol. (i) Suppose $f(x)=2\sin x$.

Then, $$f'(x)=\frac{d}{dx}(2\sin x)=2\frac{d}{dx}(\sin x)=2\cos x.$$

(ii) Suppose $f(x)=\tan^n x$.

Then, $$f'(x)=\frac{d}{dx}(\tan^n x)=n\tan^{n-1}x\frac{d}{dx}(\tan x)=n\tan^{n-1}x\sec^2 x.$$

(iii) Suppose $f(x)=\cos^3 x$.

Then, $$f'(x)=\frac{d}{dx}(\cos^3 x)=3\cos^2 x\frac{d}{dx}(\cos x)=-3\cos^2 x\sin x.$$

Q.11. Find the derivative of $(\sec x-1)(\sec x+1)$ w.r.t. x.

Sol. Suppose $f(x)=(\sec x-1)(\sec x+1)$

Then, $$f'(x)=\frac{d}{dx}[(\sec x-1)(\sec x+1)]$$
$$=(\sec x-1)\frac{d}{dx}(\sec x+1)+(\sec x+1)\frac{d}{dx}(\sec x-1)$$
$$=(\sec x-1)\left[\frac{d}{dx}(\sec x)+\frac{d}{dx}(1)\right]+(\sec x+1)\left[\frac{d}{dx}(\sec x)-\frac{d}{dx}(1)\right]$$
$$=(\sec x-1)[\sec x\tan x+0]+(\sec x+1)[\sec x\tan x-0]$$
$$=(\sec x\tan x)[(\sec x-1)+(\sec x+1)]$$
$$=(\sec x\tan x)[2\sec x]=2\sec^2 x\tan x.$$

Q.12. Find the derivative of the following functions w.r.t. *x*:

(i) $\dfrac{\sec x - 1}{\sec x + 1}$ **(ii)** $\dfrac{\sin x + \cos x}{\sin x - \cos x}$

Sol. (i) Suppose $f(x) = \dfrac{\sec x - 1}{\sec x + 1}$

Then $$f'(x) = \frac{d}{dx}\left(\frac{\sec x - 1}{\sec x + 1}\right) = \frac{(\sec x + 1)\frac{d}{dx}(\sec x - 1) - (\sec x - 1)\frac{d}{dx}(\sec x + 1)}{(\sec x + 1)^2}$$

$$= \frac{(\sec x + 1)\left[\frac{d}{dx}(\sec x) - \frac{d}{dx}(1)\right] - (\sec x - 1)\left[\frac{d}{dx}(\sec x) + \frac{d}{dx}(1)\right]}{(\sec x + 1)^2}$$

$$= \frac{(\sec x + 1)(\sec x \tan x - 0) - (\sec x - 1)(\sec x \tan x + 0)}{(\sec x + 1)^2}$$

$$= \frac{(\sec x + 1)(\sec x \tan x) - (\sec x - 1)(\sec x \tan x)}{(\sec x + 1)^2}$$

$$= \frac{(\sec x \tan x)(\sec x + 1 - \sec x + 1)}{(\sec x + 1)^2} = \frac{2\sec x \tan x}{(\sec x + 1)^2}.$$

(ii) Suppose $f(x) = \dfrac{\sin x + \cos x}{\sin x - \cos x}$

Then, $$f'(x) = \frac{d}{dx}\left(\frac{\sin x + \cos x}{\sin x - \cos x}\right)$$

$$= \frac{(\sin x - \cos x)\frac{d}{dx}(\sin x + \cos x) - (\sin x + \cos x)\frac{d}{dx}(\sin x - \cos x)}{(\sin x - \cos x)^2}$$

$$= \frac{(\sin x - \cos x)\left[\frac{d}{dx}(\sin x) + \frac{d}{dx}(\cos x)\right] - (\sin x + \cos x)\left[\frac{d}{dx}(\sin x) - \frac{d}{dx}(\cos x)\right]}{(\sin x - \cos x)^2}$$

$$= \frac{(\sin x - \cos x)(\cos x - \sin x) - (\sin x + \cos x)(\cos x + \sin x)}{(\sin x - \cos x)^2}$$

$$= \frac{-(\sin x - \cos x)^2 - (\sin x + \cos x)^2}{(\sin x - \cos x)^2}.$$

Q.13. Differentiate the following w.r.t. *x*:

(i) $\cos\sqrt{x}$ **(ii)** $\sin(ax + b)$ **(iii)** $\sin(\log\cos x)$ **(iv)** $\cot(5x^\circ)$

(v) $\sec(\tan\sqrt{x})$ **(vi)** $\tan(e^{\cos x})$

Sol. (i) Suppose $y=\cos\sqrt{x}$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx}=\frac{d}{dx}[\cos\sqrt{x}]=-\sin\sqrt{x}\,\frac{d}{dx}(\sqrt{x})=-\sin\sqrt{x}\left[\frac{\frac{d}{dx}(x)}{2\sqrt{x}}\right]=-\frac{\sin\sqrt{x}}{2\sqrt{x}}.$$

(ii) Suppose $y=\sin(ax+b)$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx}=\frac{d}{dx}[\sin(ax+b)]=\cos(ax+b)\,\frac{d}{dx}(ax+b)=\cos(ax+b)\left[\frac{d}{dx}(ax)+\frac{d}{dx}(b)\right]$$

$$=\cos(ax+b)\left[a\,\frac{d}{dx}(x)+0\right]=a\cos(ax+b).$$

(iii) Suppose $y=\sin(\log\cos x)$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx}=\frac{d}{dx}[\sin(\log\cos x)]=\cos(\log\cos x)\,\frac{d}{dx}[\log\cos x]$$

$$=\cos(\log\cos x)\,\frac{\frac{d}{dx}(\cos x)}{\cos x}=\cos(\log\cos x)\,\frac{\left[-\sin x\,\frac{d}{dx}(x)\right]}{\cos x}$$

$$=-\tan x\cos(\log\cos x).$$

(iv) Suppose $y=\cot(5x^\circ)$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx}=\frac{d}{dx}[\cot(5x^\circ)]=-\operatorname{cosec}^2(5x^\circ)\,\frac{d}{dx}(5x^\circ)=-\operatorname{cosec}^2(5x^\circ)\,\frac{d}{dx}\left(\frac{5\pi}{180}x\right)$$

$$=-\operatorname{cosec}^2(5x^\circ)\left(\frac{5\pi}{180}\right)\frac{d}{dx}(x)=-5^\circ\operatorname{cosec}^2(5x^\circ).$$

(v) Suppose $y=\sec(\tan\sqrt{x})$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx}=\frac{d}{dx}[\sec(\tan\sqrt{x})]=\sec(\tan\sqrt{x})\tan(\tan\sqrt{x})\,\frac{d}{dx}(\tan\sqrt{x})$$

$$=\sec(\tan\sqrt{x})\tan(\tan\sqrt{x})\left[\sec^2\sqrt{x}\,\frac{d}{dx}(\sqrt{x})\right]$$

$$=\sec(\tan\sqrt{x})\tan(\tan\sqrt{x})\left[\sec^2\sqrt{x}\,\frac{\frac{d}{dx}(x)}{2\sqrt{x}}\right]$$

$$=\sec(\tan\sqrt{x})\tan(\tan\sqrt{x})\sec^2\sqrt{x}\,\frac{1}{2\sqrt{x}}.$$

(vi) Suppose $y = \tan(e^{\cos x})$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx} = \frac{d}{dx}[\tan(e^{\cos x})] = \sec^2(e^{\cos x})\frac{d}{dx}(e^{\cos x})$$

$$= \sec^2(e^{\cos x})\left[e^{\cos x}\frac{d}{dx}(\cos x)\right]$$

$$= \sec^2(e^{\cos x})e^{\cos x}(-\sin x) = -\sin x\, e^{\cos x}\sec^2(e^{\cos x})$$

Q.14. Differentiate $\log\sqrt{\frac{1+\cos x}{1-\cos x}}$ w.r.t. x.

Sol. Suppose $y = \log\sqrt{\frac{1+\cos x}{1-\cos x}} = \log\left(\frac{1+\cos x}{1-\cos x}\right)^{1/2} = \frac{1}{2}\log\left(\frac{1+\cos x}{1-\cos x}\right)$

$$= \frac{1}{2}[\log(1+\cos x) - \log(1-\cos x)]$$

Differentiating both sides w.r.t. x, we get

$$\frac{dy}{dx} = \frac{1}{2}\frac{d}{dx}[\log(1+\cos x) - \log(1-\cos x)]$$

$$= \frac{1}{2}\left[\frac{d}{dx}\{\log(1+\cos x)\} - \frac{d}{dx}\{\log(1-\cos x)\}\right] = \frac{1}{2}\left[\frac{\frac{d}{dx}(1+\cos x)}{1+\cos x} - \frac{\frac{d}{dx}(1-\cos x)}{1-\cos x}\right]$$

$$= \frac{1}{2}\left[-\frac{\sin x}{1+\cos x} - \frac{\sin x}{1-\cos x}\right] = -\frac{\sin x}{2}\left[\frac{1}{1+\cos x} + \frac{1}{1-\cos x}\right]$$

Q.15. What is the maximum area of a rectangle of perimeter 176 cm?

Sol. Suppose x and y are the length and breadth of the rectangle, respectively. Then,

$$2(x+y) = 176 \quad \text{or} \quad x + y = 88$$

Area, $A = xy = x(88-x)$

$\therefore$ $\frac{dA}{dx} = 88 - 2x$ and $\frac{d^2A}{dx^2} = -2 < 0$

$$\frac{dA}{dx} = 0 \Rightarrow x = 44$$

$\therefore$ $x = 44$ is a point of maxima.

$\therefore$ Maxima area $= 44(88-44) = 44 \times 44 = 1936\ \text{cm}^2$

Q.16. Evaluate the following integrals :

(i) $\int(4x+1)^{-7/3}\,dx$ (ii) $\int(7-3x)^5\,dx$ (iii) $\int x^8\,dx$

Sol. (i) $\int (4x+1)^{-7/3}\,dx = \dfrac{(4x+1)^{-4/3}}{\left(-\frac{4}{3}\right)\frac{d}{dx}(4x+1)} + C = -\dfrac{3\,(4x+1)^{-4/3}}{16} + C.$

(ii) $\int (7-3x)^5\,dx = \dfrac{(7-3x)^6}{(6)\frac{d}{dx}(7-3x)} + C = -\dfrac{(7-3x)^6}{18} + C.$

(iii) $\int x^8\,dx = \dfrac{x^9}{(9)\frac{d}{dx}(x)} + C = \dfrac{x^9}{9} + C.$

Q.17. Evaluate the following integrals :

(i) $\int 4^{7-6x}\,dx$ **(ii)** $\int 2^x\,dx$ **(iii)** $\int 3^{2x-5}\,dx$

Sol. (i) $\int 4^{7-6x}\,dx = \dfrac{4^{7-6x}}{\log 4\,\frac{d}{dx}(7-6x)} + C = -\dfrac{4^{7-6x}}{6\log 4} + C.$

(ii) $\int 2^x\,dx = \dfrac{2^x}{\log 2\,\frac{d}{dx}(x)} + C = \dfrac{2^x}{\log 2} + C.$

(iii) $\int 3^{2x-5}\,dx = \dfrac{3^{2x-5}}{\log 3\,\frac{d}{dx}(2x-5)} + C = \dfrac{3^{2x-5}}{2\log 3} + C.$

Q.18. Evaluate : $\int (x^3 + x^{-3} + x - 5)\,dx$

Sol. $\int (x^3 + x^{-3} + x - 5)\,dx = \int x^3\,dx + \int x^{-3}\,dx + \int x\,dx - 5\int 1\,dx$

$$= \frac{x^4}{4} + \frac{x^{-2}}{(-2)} + \frac{x^2}{2} - 5x + C$$

$$= \frac{x^4}{4} - \frac{1}{2x^2} + \frac{x^2}{2} - 5x + C.$$

Q.19. Evaluate :

(i) $\int \dfrac{1}{x\log x}\,dx$ **(ii)** $\int \dfrac{\log x}{x}\,dx$

Sol. (i) Suppose $I = \int \dfrac{1}{x\log x}\,dx$

Put $\log x = y$ or $\dfrac{1}{x} = \dfrac{dy}{dx}$ or $\dfrac{1}{x}\,dx = dy$

$\therefore$ $I = \int \dfrac{1}{y}\,dy = \log|y| + C = \log|\log x| + C$

(ii) Suppose $I = \int \frac{\log x}{x}\,dx$

Put $\quad \log x = y \quad$ or $\quad \frac{1}{x} = \frac{dy}{dx} \quad$ or $\quad \frac{1}{x}\,dx = dy$

$$\therefore \quad I = \int y\,dy = \frac{y^2}{2} + C = \frac{1}{2}(\log x)^2 + C.$$

Q.20. Evaluate the following integrals :

(i) $\int_0^{\pi/4} \sin^3 2x \cos 2x\,dx$ (ii) $\int_4^9 \frac{\sqrt{x}}{(30 - x^{3/2})^2}\,dx$

Sol. (i) Suppose $I = \int_0^{\pi/4} \sin^3 2x \cos 2x\,dx$

Put $\quad \sin 2x = y$

or $\quad 2\cos 2x\,dx = dy \qquad$ If $x = 0$, then $y = 0$

or $\quad \cos 2x\,dx = \frac{1}{2}dy \qquad$ If $x = \frac{\pi}{4}$, then $y = 1$

$$\therefore \quad I = \frac{1}{2}\int_0^1 y^3\,dy = \frac{1}{2}\left[\frac{y^4}{4}\right]_0^1 = \frac{1}{2}\left[\frac{1}{4} - 0\right] = \frac{1}{8}.$$

(ii) Suppose $\quad I = \int_4^9 \frac{\sqrt{x}}{(30 - x^{3/2})^2}\,dx$

Put $\quad 30 - x^{3/2} = y$

or $\quad -\frac{3}{2}x^{1/2}\,dx = dy \qquad$ If $x = 4$, then $y = 22$

or $\quad \sqrt{x}\,dx = -\frac{2}{3}dy \qquad$ If $x = 9$, then $y = 3$

$$\therefore \quad I = -\frac{2}{3}\int_{22}^{3} \frac{1}{y^2}\,dy = -\frac{2}{3}\left[-\frac{1}{y}\right]_{22}^{3} = -\frac{2}{3}\left[-\frac{1}{3} - \left(-\frac{1}{22}\right)\right] = \frac{19}{99}.$$

Q.21. How many numbers greater than 1000000 can be formed by using the digits 1, 2, 0, 2, 4, 2, 4?

Sol. 7-digit numbers by using the digits 1, 2, 0, 2, 4, 2, 4.

Here, the order is important and the repetition of digits is not allowed.

So, each arrangement is a permutation.

We arrange 7 digits (one 1, three 2's, one 0, two 4's), taken all at a time.

We have, $n = 7$ and $p_1 = 1, p_2 = 3, p_3 = 1, p_4 = 2.$

So, number of such arrangements $= \frac{n!}{p_1!\,p_2!\,p_3!\,p_4!} = \frac{7!}{1!3!1!2!} = 420$

But, such arrangements also include those numbers which have the digit 0 at the million's place. Such numbers are not 7-digit numbers.

We count the numbers having 0 at the million's place.

We fix 0 at million's place and count the arrangements possible with the remaining 6 digits. We arrange 6 digits (one 1, three 2's, two 4's), taken all at a time.

We have, $n=6$ and $p_1=1, p_2=3, p_3=2.$

So, number of such arrangements $=\dfrac{n!}{p_1!p_2!p_3!}=\dfrac{6!}{1!3!2!}=60$

Hence, required number of numbers $=420-60=360.$

Q.22. Prove that : $\dfrac{{}^nC_r}{{}^{n-1}C_{r-1}}=\dfrac{n}{r}$.

Sol. L.H.S. $=\dfrac{{}^nC_r}{{}^{n-1}C_{r-1}}=\dfrac{\left[\dfrac{n!}{r!(n-r)!}\right]}{\left[\dfrac{(n-1)!}{(r-1)![(n-1)-(r-1)]!}\right]}=\dfrac{\left[\dfrac{n!}{r!(n-r)!}\right]}{\left[\dfrac{(n-1)!}{(r-1)!(n-r)!}\right]}$

$$=\frac{n!}{r!(n-r)!}\times\frac{(r-1)!(n-r)!}{(n-1)!}=\frac{n(n-1)!}{r(r-1)!(n-r)!}\times\frac{(r-1)!(n-r)!}{(n-1)!}=\frac{n}{r}=\text{R.H.S.}$$

Q.23. How many numbers are there between 99 and 1000 having 7 in the units place?

Sol. *Aim :* To find the numbers between 99 and 1000 (*i.e.*, 3-digit numbers) having 7 in the units place.

Here, the order is important and the repetition of digits is allowed.

So, we can apply multiplication principle.

Number of choices for one's place $=1.$

Number of choices for ten's place $=10$

Number of choices for hundred's place $=9.$

Hence, by multiplication principle, the number of required numbers $=1\times10\times9=90.$

Q.24. In how many ways can 4 different rings be worn in 3 fingers?

Sol. Here, the order is important and the repetition of fingers is allowed (*i.e.*, each ring can be put in any of the 3 fingers).

So, we can apply multiplication principle.

Number of possible choices for first ring $=3$

Number of possible choices for second ring $=3$

Number of possible choices for third ring $=3$

Number of possible choices for fourth ring $=3.$

Hence, by multiplication, principle, required number of outcomes $=3\times3\times3\times3=81.$

Q.25. A coin is tossed three times. Find the probability of getting :

(i) either one head or two heads

(ii) neither two heads nor three heads.

Sol. Sample space on tossing a coin three times is

$$S=\{HHH, HHT, HTH, THH, HTT, THT, TTH, TTT\}$$

$\therefore$ Total number of cases $=8$

(i) P(either one head or two heads) $= P$(one head) $+ P$(two heads) $- P$(one and two heads)

$$= \frac{3}{8} + \frac{3}{8} - 0 = \frac{3}{4}.$$

(ii) P(neither two heads nor three heads)

$= 1 - P$(either two heads or three heads)

$= 1 - [P$(two heads)$+ P$(three heads) $- P$(two and three heads)$]$

$$= 1 - \left[\frac{3}{8} + \frac{1}{8} - 0\right] = \frac{1}{2}.$$

Q.26. What is the probability of 53 Sundays in a leap year?

Sol. Total number of days in a leap year $= 366$

Since, each week contains one Sunday.

$\therefore$ 52 weeks (*i.e.*, 364 days) contain 52 Sundays.

$\therefore$ Number of remaining days $= 366 - 364 = 2.$

The remaining days may occur as (Sunday, Monday), (Monday, Tuesday), (Tuesday, Wednesday), (Wednesday, Thursday), (Thursday, Friday), (Friday, Saturday) or (Saturday, Sunday).

$\therefore$ Total number of cases $= 7$

A leap year will contain 53 Sundays, if the remaining days occurs as (Sunday, Monday) or (Saturday, Sunday).

$\therefore$ Number of favourable cases $= 2$

Hence, required probability $= \frac{2}{7}.$

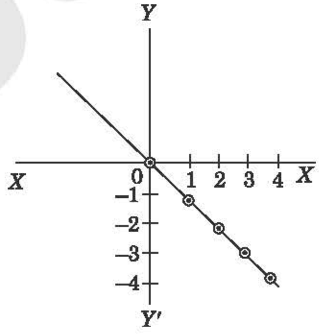
SECTION-C LONG ANSWER TYPE QUESTIONS

Q.1. Draw the graphs and find the slopes :

(i) $x + y = 0$ **(ii) $2x - y = 3$**

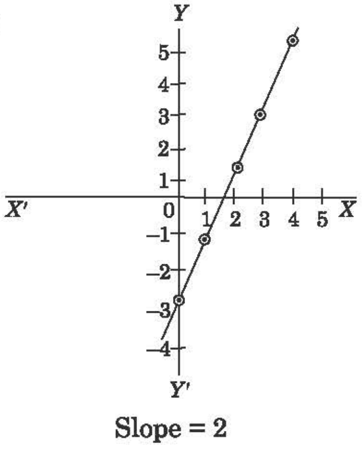
Ans.

(i)



Slope = – 1

(ii)



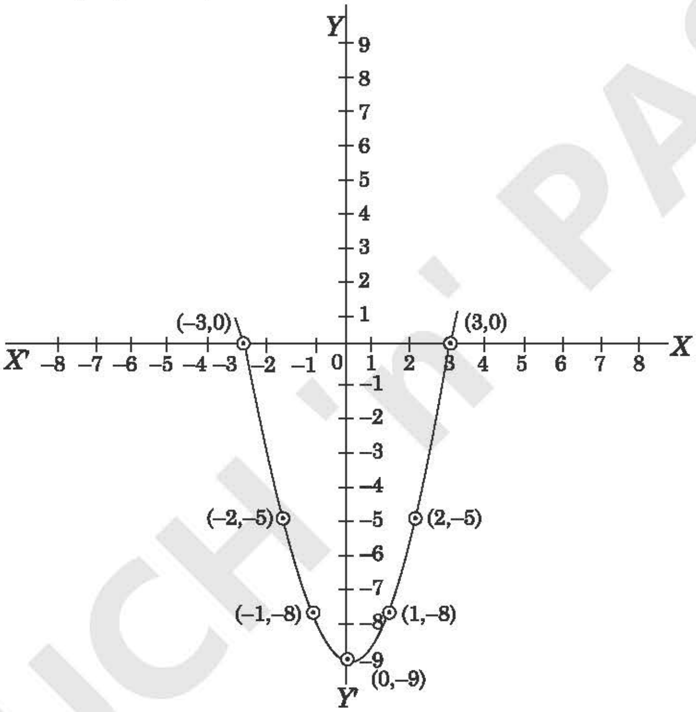
Slope = 2

Q.2 Sketch the curve $y = x^2 - 9$.

Sol. First of all we get table of values for $y = x^2 - 9$ by taking x as independent and y as dependent variable. We get the table of values as under :

x	-3	-2	-1	0	1	2	3
y	0	-5	-8	9	-8	-5	0

Plot these points in the graph and join it with free hand as shown below :



Q.3. Find the maximum and minimum values of $x^3 - 3x^2 - 9x$.

Sol. $f(x) = x^3 - 3x^2 - 9x$ or $y = x^3 - 3x^2 - 9x$

Differentiating with respect to x $\quad \dfrac{dy}{dx} = 3x^2 - 6x - 9$

Differentiating again with respect to x $\quad \dfrac{d^2y}{dx^2} = 6x - 6$

For maximum or minimum value of x $\quad \dfrac{dy}{dx} = 0$

$$\Rightarrow \quad 3x^2 - 6x - 9 = 0 \qquad \left[\because \frac{dy}{dx} = 3x^2 - 6x - 9\right]$$

or $\quad x^2 - 2x - 3 = 0$

or $\quad (x+1)(x-3) = 0$

$\therefore \qquad x = -1, 3$

At $x = -1$, $\dfrac{d^2 y}{dx^2} = 6(-1) - 6 = -6 - 6 = -12$ (negative) $\quad \therefore$ Maxima at $x = -1$

At $x = 3$, $\dfrac{d^2 y}{dx^2} = 6(3) - 6 = 18 - 6 = 12$ (positive) $\quad \therefore$ Minima at $x = 3$.

Q.4. In how many ways can 3 boys and 3 girls be seated along a round table if :
(i) no restriction is imposed?
(ii) two particular boys must sit together?
(iii) two particular boys never sit together?

Sol. Here, each arrangement is a stationary circular permutation.

(i) *We arrange 3 boys and 3 girls with no restriction imposed.*

We arrange 6 children, taken all at a time.

We have, $n = 6$ and $r = 6$.

Hence, required number of arrangements $= \dfrac{{}^nP_r}{r} = \dfrac{{}^6P_6}{6} = \dfrac{6!}{6 \times 0!} = 120$.

(ii) *We arrange 3 boys and 3 girls such that two particular boys must sit together.*

We consider the 2 particular boys as a single object X.

We arrange the object X and 4 other children, taken all at a time.

We have, $n = 5, r = 5$.

So, number of such arrangement $= \dfrac{{}^nP_r}{r} = \dfrac{{}^5P_5}{5} = \dfrac{5!}{5 \times 0!} = 24$.

We count the number of arrangements possible in the object X.

We arrange 2 particular boys, taken all at a time.

We have, $n = 2, r = 2$.

So, number of arrangement in object $X = {}^nP_r = {}^2P_2 = \dfrac{2!}{0!} = 2$.

Hence, required number of arrangements $= 24 \times 2 = 48$.

Q.5. (a) A coin is tossed two times. Find the probability of getting :
(i) two heads (ii) at least one tail
(b) Two coins are tossed once. Find the probability of getting :
(i) no head (ii) exactly one tail

Ans. (a) Sample space on tossing a coin two times is $S = \{HH, HT, TH, TT\}$.

$\therefore$ Total number of cases $= 4$.

(i) Favourable cases of getting two heads $= \{HH\}$

$\therefore$ Number of favourable cases $= 1$

Hence, required probability $= \dfrac{1}{4}$.

(ii) Favourable cases of getting at least one tail $= \{HT, TH, TT\}$

$\therefore$ Number of favourable cases $=3$. Hence, required probability $=\frac{3}{4}$.

(b) Sample space on tossing two coins once is $S = \{HH, HT, TH, TT\}$

$\therefore$ Total number of cases $=4$

(i) Favourable cases of getting no head $= \{TT\}$

$\therefore$ Number of favourable cases $=1$. Hence, required probability $=\frac{1}{4}$.

(ii) Favourable cases of getting exactly one tail $= \{HT, TH\}$

$\therefore$ Number of favourable cases $=2$. Hence, required probability $=\frac{2}{4}=\frac{1}{2}$.

Q.6. A number is selected from the numbers 1, 2, ..., 50. Find the probability of getting :

(i) an even number **(ii) a prime number**

(iii) a prime number < 10 **(iv) a prime number and even number**

(v) a multiple of 4 **(vi) a perfect square.**

Sol. Sample space is $S = \{1, 2, \ldots, 50\}$

$\therefore$ Total numbers $=50$

(i) Favourable cases of getting an even number $= \{2, 4, 6, \ldots, 48, 50\}$

$\therefore$ Number of favourable cases $=25$. Hence, required probability $=\frac{25}{50}=\frac{1}{2}$.

(ii) Favourable cases of getting a prime number $=\left\{\begin{matrix} 2,3,5,7,11,13,17,19, \\ 23,29,31,37,41,43,47 \end{matrix}\right\}$

$\therefore$ Number of favourable cases $=15$. Hence, required probability $=\frac{15}{50}=\frac{3}{10}$.

(iii) Favourable cases of getting a prime number $<10 = \{2, 3, 5, 7\}$

$\therefore$ Number of favourable cases $=4$. Hence, required probability $=\frac{4}{50}=\frac{2}{25}$.

(iv) Favourable cases of getting a prime number and even number $= \{2\}$

$\therefore$ Number of favourable cases $=1$. Hence, required probability $=\frac{1}{50}$.

(v) Favourable cases of getting a multiple of $4 = \{4, 8, 12, \ldots, 44, 48\}$

$\therefore$ Number of favourable cases $=12$. Hence, required probability $=\frac{12}{50}=\frac{6}{25}$.

(vi) Favourable cases of getting a perfect square $= \{1, 4, 9, 16, 25, 36, 49\}$

$\therefore$ Number of favourable cases $=7$. Hence, required probability $=\frac{7}{50}$.

Q.7. A card is drawn from a pack of 52 cards. Find the probability of getting :

(i) a jack or a queen **(ii) a king or a diamond**

(iii) a heart or a club **(iv) either a red or a face card**

(v) neither a heart nor a king **(vi) neither an ace nor a jack.**

Sol. Total number of cards $=52$

Number of cards drawn $=1$

(i) $P(\text{a jack or a queen}) = P(\text{a jack}) + P(\text{a queen}) - P(\text{a jack and queen})$

$$= \frac{4}{52} + \frac{4}{52} - 0 = \frac{2}{13}.$$

(ii) $P(\text{a king or a diamond}) = P(\text{a king}) + P(\text{a diamond}) - P(\text{a king and diamond})$

$$= \frac{4}{52} + \frac{13}{52} - \frac{1}{51} = \frac{4}{13}.$$

(iii) $P(\text{a heart or a club}) = P(\text{a heart}) + P(\text{a club}) - P(\text{a heart and club})$

$$= \frac{13}{52} + \frac{13}{52} - 0 = \frac{1}{2}.$$

(iv) $P(\text{either a red or a face card}) = P(\text{a red card}) + P(\text{a face card}) - P(\text{a red and face card})$

$$= \frac{26}{52} + \frac{12}{52} - \frac{6}{52} = \frac{8}{13}.$$

(v) $P(\text{neither a heart nor a king}) = 1 - P(\text{either a heart or a king})$

$$= 1 - [P(\text{a heart}) + P(\text{a king}) - P(\text{a heart and king})]$$

$$= 1 - \left[\frac{13}{52} + \frac{4}{52} - \frac{1}{52}\right] = \frac{9}{13}.$$

(vi) $P(\text{neither an ace nor a jack}) = 1 - P(\text{either an ace or a jack})$

$$= 1 - [P(\text{an ace}) + P(\text{a jack}) - P(\text{an ace and jack})]$$

$$= 1 - \left[\frac{4}{52} + \frac{4}{52} - 0\right] = \frac{11}{13}.$$

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MODEL PAPER

Fundamentals of Chemistry

B.Sc.-I (SEM-I) [M.M. : 75

Note : Attempt all the sections as per instructions.

Section-A : Very Short Answer Type Questions

Instruction : Attempt all **FIVE** questions. Each question carries **3 Marks**. Very Short Answer is required, not exceeding 75 words.

1. Lithium salts are slightly covalent whereas sodium salts are ionic, explain.

2. Why is σ bond stronger than π bond?

3. What are the limitations of slater rules?

4. What are electrophiles?

5. What is number system in computer?

Section-B : Short Answer Type Questions

Instruction : Attempt all **TWO** questions out of the following 3 questions. Each question carries **7.5 Marks**. Short Answer is required not exceeding 200 words.

6. Write a short note on Shanti Swarup Bhatnagar.

Or Discuss in brief the concept of atomic orbitals.

7. What do you mean by periodicity in properties?

Or What do you understand by bond length?

8. What do you mean by centre of symmetry or centre of inversion?

Or Prove that : $\log\frac{26}{51}+\log\frac{119}{91}=\log 2-\log 3$

Section-C : Long Answer Type Questions

Instruction : Attempt all **THREE** questions out of the following 5 questions. Each question carries **15 Marks**. Answer is required in detail, between 500-800 words.

9. Describe the introduction to Indian ancient chemistry in detail.

Or What is dipole moment? Describe its applications.

10. What are sigma (σ) and pi (π) bonds? How they are formed?

Or Describe dsp^2, dsp^3, d^2sp^3 and d^3sp^3 with examples.

11. What do you understand by atomic radii? What are the factors that affects atomic radii? How does the atomic radii change with in a group and in a period of the periodic table?

Or What is hyperconjugation? Describe its applications.

12. What do you understand by curved arrow notations. Describe the detail.

Or What is optical isomerism? Describe in detail.

13. What are input devices? Explain.

Or Find the maximum and minimum values of x^3-3x^2-9x.

❑