

CHEMICAL BONDING

SESSION – 1

AIM

- **To define Chemical Bond**
- **To understand the reason for chemical bond formation**
- **To introduce Ionic bond**

CHEMICAL BOND is an attractive force which holds various constituents (atoms, molecules or ions) together in different species.

Chemical bonds devided into **two types**:

a) Bonds which constitute **molecules or formula units**. These are ionic bonds, covalent bonds and co-ordinate or dative bonds.

b) Bonds which hold various particles in solid or liquid state of the substances. These are also called **INTERMOLECULER FORCES**. These are: metallic bonds, dipole-dipole forces, van der Waal forces, hydrogen bonds.

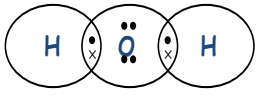
Cause of Chemical Combination: Chemical bonding takes place due

- To **acquire a state of minimum energy and maximum stability**
- **To convert atoms into molecule to acquire stable noble gas configuration.**

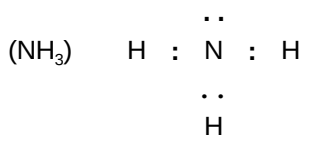
LEWIS THEORY

Lewis theory gave the first explanation of a covalent bond in terms of electrons that was generally accepted. **If two electrons are shared between two atoms, this constitutes a bond and binds the atoms together**. For many light atoms, a **stable arrangement is attained when the atom is surrounded by eight electrons.**

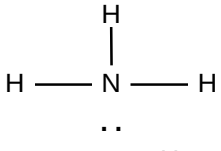
OCTATE RULE- 'Atoms combine with each other either by sharing or by the transfere of electrons to attain stable noble gas configuration I n outer most shell.'

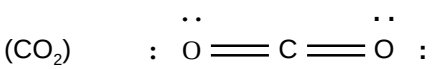


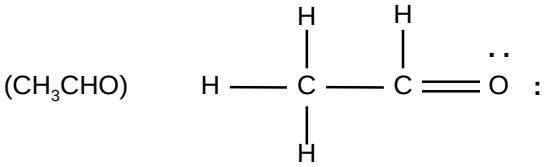
Obeys octet rule



or







LEWIS DOT STRUCTURES - The formula of a molecule shows the number of atoms of each element but does not show the bonding arrangement of the atoms.

For example, F_2 is $:\ddot{F}:\ddot{F}:$ or $:\ddot{F}—\ddot{F}:$ and a molecule of hydrogen fluoride is shown as

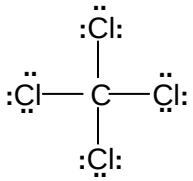
$H:\ddot{F}:$ or $H—\ddot{F}:$

Arrangement of valence electrons and symbol of elements in a molecules are called **Lewis structures**.

(i) In water (H_2O), one $\dot{H}$ and two $\cdot\ddot{O}:$ complete their duet and octet respectively $:\ddot{O}(—H)—H$

(ii) In ammonia (NH_3), three $\dot{H}$ and one $\cdot\ddot{N}\cdot$ fit together and satisfy their duet and octet respectively as $H—\ddot{N}(—H)—H$

(iii) In carbon tetrachloride (CCl_4), four $:\ddot{Cl}\cdot$ and one $\cdot\dot{C}\cdot$ complete their octet as



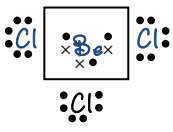
Limitations of Octate rule

- It is failed to explain the **stability of incomplete octate**.

  For example, BH_3, BF_3, BCl_3, $AlCl_3$, $GaCl_3$ etc.

  i.e., contraction of octet < $8e^-$

BeF_2 ↓ (4e) BF_3 ↓ (6e) $AlCl_3$ ↓ (6e) BCl_3 ↓ (6e)



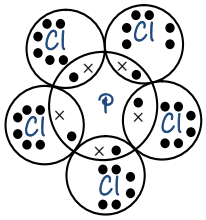
In BCl_3 Boron has only 6 electrons

- It is failed to explain the **stability of extended octate**. It is possible in those **molecules having vacant d–orbitals**.

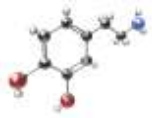
  For example, PCl_5, SF_6 etc.

  i.e., Expansion of octet > $8e^-$

PCl_5 ↓ (10e) SF_6 ↓ (12e) ClF_3 ↓ (10e) ICl_5 ↓ (12e) IF_7 ↓ (14e)

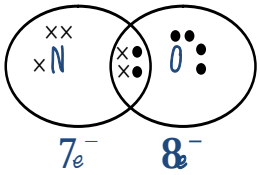


Electron dot formula of PCl_5



- It is failed to explain the **stability of odd electron species**.
  For example, NO, NO_2 and ClO_2.

  NO (11e) NO_2 (17e) ClO_2 (19e)



- It is failed to explain the **stability of duplet structure of Hydrogen atom**.
- It is failed to explain the stability of **Cations of transition metals, which contains 18 electrons in outermost orbit**

  Examples : Ga^{+3}, Cu^{+}, Ag^{+}, Zn^{+2}, Cd^{+2}, Sn^{+4}, Pb^{+4} etc.

  Electronic configuration of Ga - $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^{10}$,$4s^2$ $4p^1$ Electronic configuration of Ga^{+3} - $1s^2$, $2s^2$ $2p^6$,

- Octate rule based on the **chemical inertness of noble gases** but some noble gases able to form compounds like XeF_2 , KrF_2 etc
- Failed to explain the **geometry of molecules**.
- It is failed to explain the **relative stability** of molecules.

METHOD OF DRAWING LEWIS STRCUTURES of polyatomic species

(i) First calculate n_1.
n_1 = Total valence electron of all the atoms of the species $\pm$ net charge on the species.
For anion, electrons are added and for cations electrons are subtracted.

(ii) Then calculate n_2.
n_2 =(8 $\times$ no, of atoms other than H) + (2 $\times$ no, of H atoms)

(iii) Subtract n_1 from n_2, which gives n_3.
$n_3 = n_2 - n_1$ = number of electrons shared between atoms = number of bonding electrons.

$$\frac{n_3}{2} = \frac{n_2 - n_1}{2}$$ = number of shared electron or bps = number of bonds.

(iv) Subtracting n_3 from n_1 gives n_4.
$n_4 = n_1 - n_3$ =number of unshared electrons or nonbonding electrons.

$$\frac{n_4}{2} = \frac{n_1 - n_3}{2}$$ = no, of unshared electron pairs = number of lone pairs.

(v) Identify the least electronegative atom in a molecule as central atom, when the other atoms do not contain hydrogen.
When other atoms are hydrogen only, then the central atom would be the more electronegative atom.



(vi) Now around the central atom, place the other atoms and distribute the required number of bonds (as calculated in step (iii) & required number of lone pairs (as calculated in step (iv), keeping in mind that every atom gets an octet of electrons except hydrogen.

(vii) Calculate the formal charge on each atom.

(ix) Lewis structure should obey like resonance (delocalization), bond length, $p\pi-d\pi$ back bonding etc.

Exp- **Determine Lewis structure of NO_3^- ion.**

(i) $n_1 = 5 + (6 \times 3) + 1 = 24$

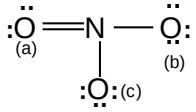
(ii) $n_2 = (4 \times 8) = 32$

(iii) $n_3 = n_2 - n_1 = 32 - 24 = 8$

$\therefore$ Number of bonds = $\frac{8}{2} = 4$

(iv) $n_4 = n_1 - n_3 = 24 - 8 = 16$ $\quad\therefore$ Number of lone pairs = $\frac{16}{2} = 8$

(v) Nitrogen is central atom (less electronegative than O). Arranging three O atoms around it and distributing 4 bonds and 8 lone pairs as



(vi) Calculating formal change on each atom.

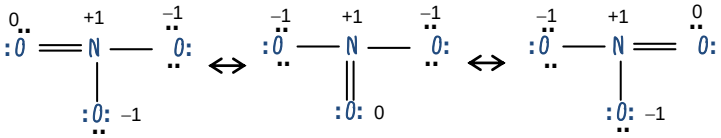
Formal charge on N = 5 – 4 – 0 = + 1

Formal charge on O (a) = 6 – 2 – 4 = 0

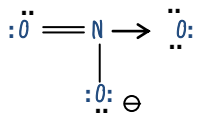
Formal charge on O (b) = 6 – 1 – 6 = –1

Formal charge on O (c) = 6 – 1 – 6 = –1

Thus, the structures can now be shown as

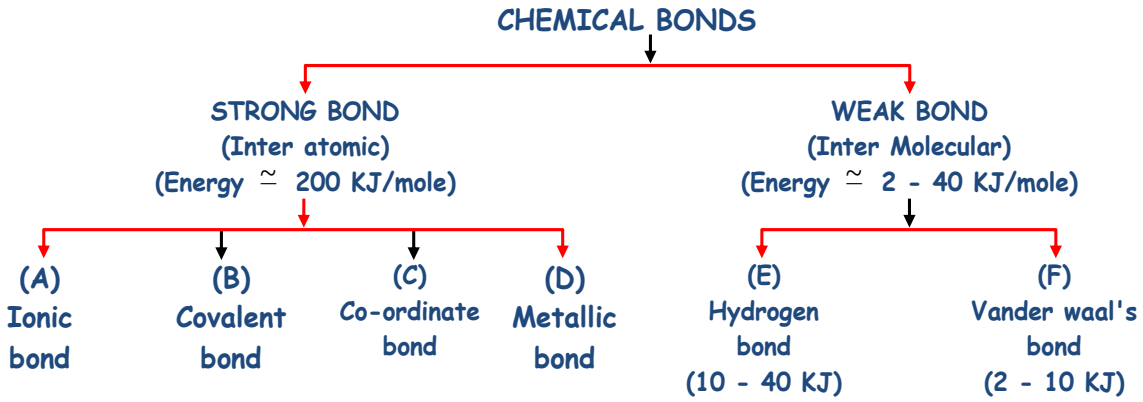


Final structure of NO_3^- is therefore shown as



which even accounts for resonance in NO_3^- ion.

Classification of bonds: -



- **IONIC or ELECTROVALENT BOND**

  Ionic bond is **formed by transference of electrons from electropositive atom to electronegative atom**.

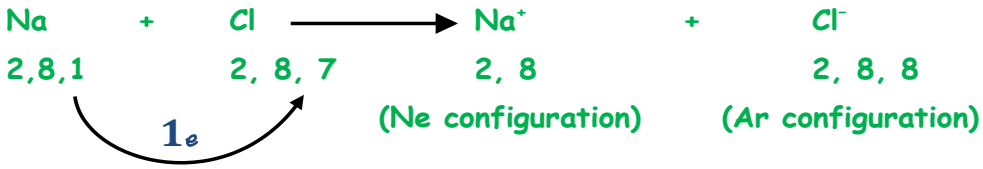
  Atom losing electrons becomes cation while the atom gaining electrons becomes anion.

Electro +ve atom loses electron (group IA to IIIA)

Electro –ve atom gains electron (group VA to VIIA)

'The electrostatic force of attraction holding the oppositely charged ions' is called **electrovalent bond or ionic bond**.

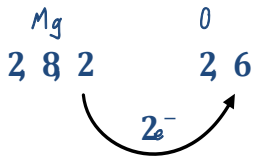
Exp- *IA and VIIA group elements form **maximum ionic** compound.



- More the distance between two elements in periodic table more will be ionic character of bond.
- **Total number of electron lose or gained** by an atom during the formation of ionic bond is called **electrovalency**.

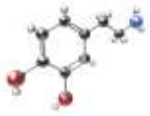
(a) In $MgCl_2$ formation, electovalelency of Mg and Cl are 2 and 1 respectively.

(b)

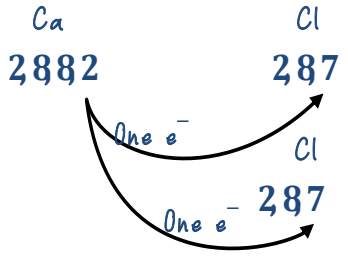


electrovalency of Mg = 2

electrovalency of O = 2



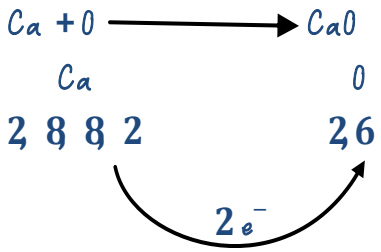
(c)



electrovalency of Ca = 2

electrovalency of Cl = 1

(d)



electrovalency of Ca = 2

electrovalency of O = 2

Factors favouring formation of ionic bond:

- **Atomic Size:** Larger atoms can easily form **cations**.

  i.e., form ionic compounds easily, due to decrease in force of attraction of the nucleus on the valence electrons.

Order of formation of alkali metal cations is: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

Smaller atoms can easily form **anions**.

Ex: The ease of formation of halide ions is: $F^+ > Cl^- > Br^- < I^-$

- **Ionisation Potential:** Atoms with low I.P can easily form cations.

Lesser i e → Greater tendency to form cation.

Ex: The I.P of Na is 117.3 Kcal / mole, while that of K is 100 Kcal/mole. Therefore K^+ ion is formed more easily than Na^+ ion.

e.g $Na^+ > Mg^{+2} > Al^{+3}$

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ } Cation formation tendency

- **Charge of the ion:** Cations with low charge are formed more easily than the cations with high charge.

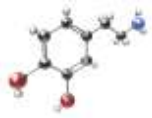
  Ex: Ease of formation: $Na^+ > Mg^{2+} > Mg^{3+}$

- **Electronic Configuration:** Cations with inert gas configuration are formed more easily than the cations with pseudo inert gas configuration. (18 valence electrons).

  Ex: Ca^{2+} ion (2, 8, 8) is formed more easily than Zn^{2+} ion (2, 8, 8).

- **Electron Affinity/Electronegativity:** Atoms with high electron affinity are able to form anion more easily.

  Ex: halogens possess high electron affinity. So the formation of their ions is very common.



Higher electron affinity ~~Greater~~ tendency to form anion

e.g. $Cl^- > F^- > Br^- > I^-$ $F^- > O^{-2} > N^{-3}$

- **Charge of the ion**: Anions with low charge are formed more easily than the anions with high charge.Vice versa for cation.

  Ex: Ease of formation: $F^- > O^{2-} > N^{3-}$

- **Lattice energy** –'**Amount of energy released when one mole of crystal product is formed from gaseous reactants**'. Or

  '**Amount of energy absorbed when one mole of ionic crystal is dissociated into its gaseous reactants**'.

Factors affecting lattice energy :

(i) Magnitude of charge U $\propto z^+ z^-$ (Ionic charge)

High lattice energy ~~Greater~~ stability of ionic compound.

- Lattice energy $\propto$ Magnitude of charge

  $NaCl$ $MgCl_2$ $AlCl_3$

  Na^+ Mg^{+2} Al^+

  → – Lattice energy increases

  – Size of cation decreases.

- Size of Cation : – Lattice energy

  LiCl NaCl KCl RbCl CsCl

  → – Size of cation increasing

  – Size of anion is constant – Lattice energy decreases

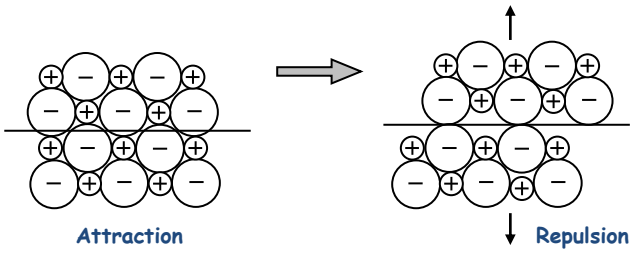
SESSION – 2

AIM

1]To understand the properties of ionic compounds
2]To introduce lattice energy

PROPERTIES OF IONIC COMPOUNDS

- **Physical state-** They are **hard, crystalline** and **brittle solids** due to **strong electrostatic force of attraction.**



(Same charged ions comes nearer. So they repell each other)

- **Isomorphism** Ionic compounds are isomorphous i.e., they have same no. of electrons. (similar configuration of their cation and anion)with same crystal structure.

Example –	Na^+	F^-	Mg^{+2}	O^{-2}
Valency	+ 1,	-1	+ 2,	- 2
electronic configuration	2, 8,	2, 8	2, 8	2, 8

- **Boiling point and melting point** is high due to strong electrostatics force of attraction among oppositely charged ions.
- **Conductivity** depends on ionic mobility.

  In solid state - No free ions - Bad conductor of electricity.

  In fused state or aqueous solution Due to free ions - Good conductor of eletricity.

conductivity order : Solid state > Fused state < Aqueous solution

* **Reactivity:** Ionic compounds undergo ionic reactions which have very high reaction rates. i.e., quite fast

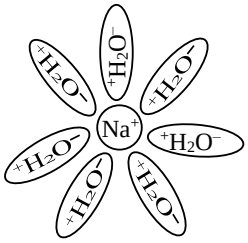
* They **do not exhibit isomerism due to non-directional nature** of the polar bonds present in these compounds.

* **Solubility** Highly soluble in water (Polar solvents) with high value of dielectric constant but insoluble in non-polar solvents due to low dielectric constant. The solubility of ionic compounds decreases with increase in covalent character of ionic compounds.

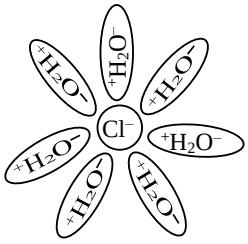
Example : NaCl in water

(I) The Na^+ ions get associates with –vely charged 'O' of water

(II) And Cl^- ions associates with +vely charged 'H' of water.



Oxygen atom of H_2O give its electron to Na^+



H atom of H_2O gain electron from Cl^-

Solubility of Ionic compound is governed by

a)Lattice energy: Larger the lattice energy, the lesser is the solubility.

e.g., sulphates and phosphates of Ba & Sr are insoluble in water due to high lattice energy.

b)Heat of hydration: Larger the heat of hydration, the more is the solubility of ionic compound.

e.g., $AlCl_3$, though covalent in nature is soluble in water due to high

Born - Haber Cycle

(Energy changes involved in the formation of an ionic bond):

The energy changes which take place in the formation of an ionic compound from its component elements can be studied with the help of a thermochemical cycle known as **Born-Haber cycle.**

For example, in the formation of one mole of sodium chloride from sodium and chlorine the following steps are involved.

- **Conversion of metallic sodium (solid) into gaseous sodium atoms:**

$$\underset{1\text{mole}}{Na_{(s)}} + \Delta H_{(sub)} \rightarrow \underset{1\text{mole}}{Na_{(g)}}$$

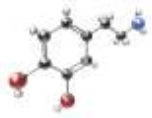
Here ΔH sub = ΔH atomisation

where ΔH_{sub} is the **enthalpy of sublimation** of sodium. It is the amount of energy required for converting one mole of solid sodium into gaseous sodium atoms.

- **Dissociation of chlorine molecules into chlorine atoms:**

$$\underset{\text{Chlorine molecule(1mole)}}{Cl_{2(g)} + D} \rightarrow \underset{\text{Chlorine atom (2moles)}}{2Cl_{(g)}}$$

where **D is dissociation energy (bond energy)** of Cl_2. It is clear that the energy needed for the formation of one mole of chlorine atoms is D/2.



- **Conversion of gaseous sodium atoms into gaseous sodium ions:**

$$\underset{1\text{mole}}{Na_{(g)}} + \underset{(I.E)}{\text{Ionization energy}} \rightarrow \underset{1\text{mole}}{Na^{+}_{(g)}} + e^{-}$$

- **Conversion of gaseous chlorine atoms into gaseous chloride ions:**

$$\underset{1\text{mole}}{Cl_{(g)}} + e^{-} \rightarrow \underset{1\text{mole}}{Cl^{-}_{(g)}} + \underset{(\text{Electron affinity})}{E.A.}$$

- **Combination of gaseous sodium ions, chloride ions** to give **solid crystal.**

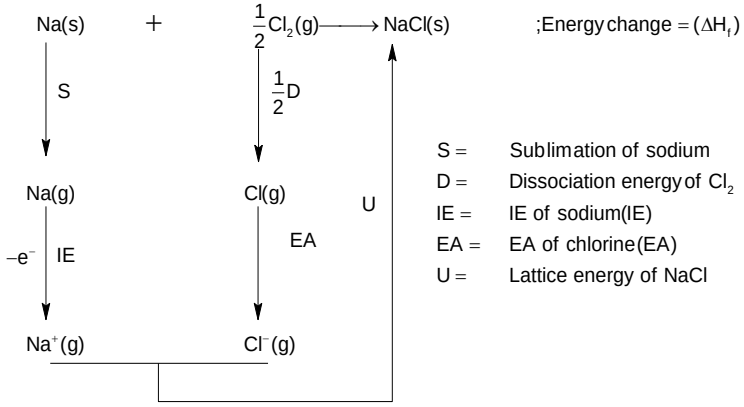
$$\underset{1\text{mole}}{Na^{+}_{(g)}} + \underset{1\text{mole}}{Cl^{-}_{(g)}} \rightarrow \underset{1\text{mole}}{Na^{+}Cl^{-}_{(s)}} + \underset{\text{lattice energy}}{U}$$

The **overall formation of ionic solid** may be represented as below:

$$Na_{(s)} + \tfrac{1}{2}Cl_{2(g)} \rightarrow Na^{+}Cl^{-}_{(s)}; \Delta H_f$$

Where ΔH_f is the heat of formation of 1 mole of $Na^{+}Cl^{-}_{(s)}$.

Steps may be represented in the form of **Born-Haber cycle.**



According to **Hess law of constant heat summation**, the **heat of formation of one mole of $Na^{+}Cl^{-}_{(s)}$ should be the same whether its formation takes place directly in a single step or through a number of steps.**

Hence, $\Delta H_f = \Delta H_{sub} + IE + \frac{1}{2}D + (-EA) + (-U)$

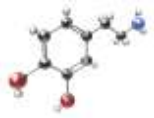
On substituting values in the above expression,

we get: $\Delta H_f = (+108.5) + 495.2 + \frac{1}{2}(243.0) + (-348.3) + (-758.7) = -381.8\,\text{kJ mole}^{-1}$

The **negative sign** in the values shows the **energy released**, while the **positive signs** indicate that the **energy is absorbed.**

Formation of NaCl molecule,involves **net fall** in the energy of the system,hence **$Na^{+}Cl^{-}_{(s)}$ is quite stable.**

Higher the negative values of heat of formation, greater will be the stability of the resulting ionic compound.



SESSION – 3

AIM

1]To introduce covalent bond

2]To explain covalent bond formation and types of covalent bond

3]To explain Lewis -dot structures.

COVALENT BOND-The bond is formed by mutual sharing of electrons between the atoms.

The **atoms** participating in bonding **contribute equal number of electrons for mutual sharing.**

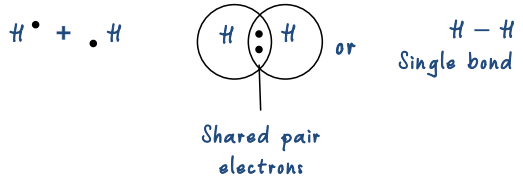
It is of 3 types

a) Single covalent bond: Here covalent bond formed by sharing of two electrons(i.e.,**1** electron pair).

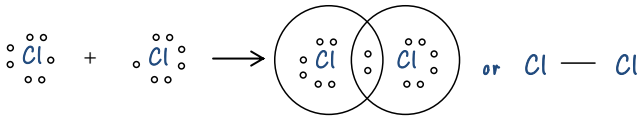
It is represented by a **single line** between two atoms.

Example :

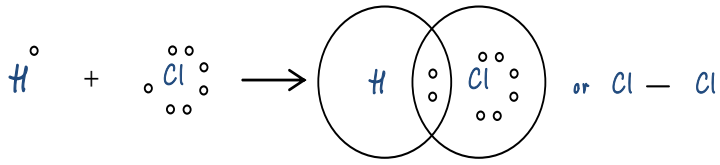
- formation of H_2 molecule



- formation of Cl_2 molecule:

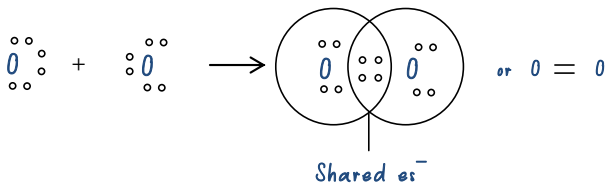


- formation of HCl :



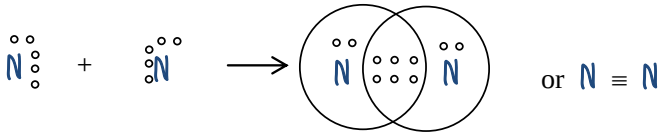
b) Double bond or double covalent bond formed by **sharing of two electron pairs, between two atoms**, it is represented by a double line (=) between two atoms.

Example . Formation of O_2 molecule :



c) Triple covalent bond formed by sharing of three electron pairs. It is represented by a triple line (≡) between two atoms.

Example. Formation of N_2 molecule



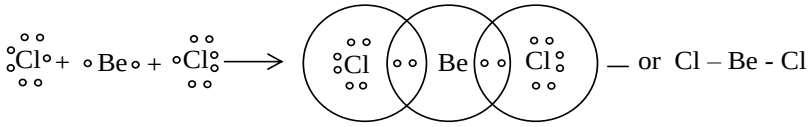
Thus, the **number of covalent bonds formed by an atom depend** on

i) the **number of unpaired electrons in their valency shell.**

ii) the **number of electrons required to attain inert gas configuration.** Generally **p block elements are involved in the covalent bond formation.**

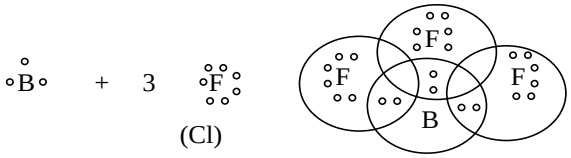
Some more examples of formation of covalent Bonds:

- **$BeCl_2$:**



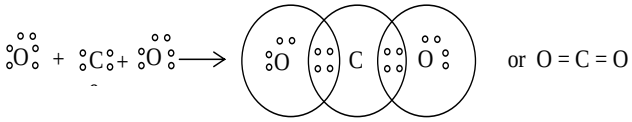
Short of 4 electron pair

- **BF_3 or BCl_3:**

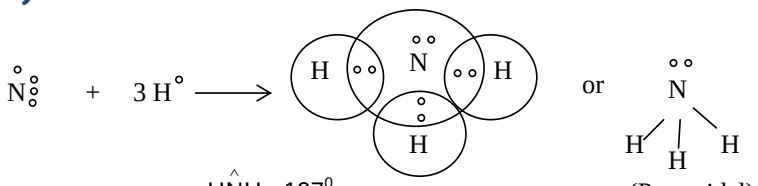


Short of 2-electrons

- **CO_2:**



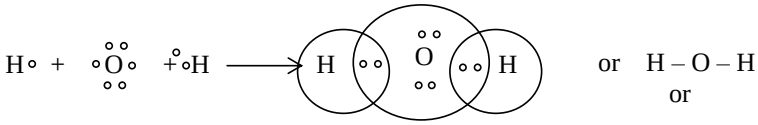
- **NH_3 (Pyramidal):**

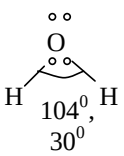


$\hat{HNH} = 107^0$

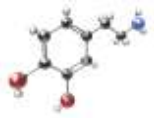
(Pyramidal)

- **H_2O (Angular) :**



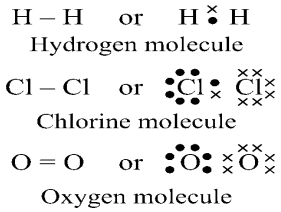


(V-Shaped)



Based on nature of atoms b/w electrons, covelent bonds devided into

1. **Non-Polar Covalent Bonds:** Here **bond is formed between similar atoms, shared pair of electrons lies almost in the centre and electron cloud is uniformly distributed around the two atoms.**



2. **Polar Covalent Bonds bond is formed between dissimilar atoms having different electro negativities**, the bond pair is displaced towards more electronegative atoms creating partial positive charge on the less electronegative atom and partial negative charge on more electronegative atom. Such a bond develops some ionic character.

   Ex: HCl or $H^{\delta+} - Cl^{\delta-}$

SESSION – 4

AIM 1]To introduce properties of covalent compounds

2] To introduce dative bond

3]To introduce Fajan's rules

Characters of Covalent compounds

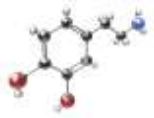
* **Constituents:** They made with discrete molecules and strong bonding forces exist between the atoms of a covalent compound.

* **Physical State:** They occur as liquids or gases or soft solids (e.g., sulphur, phosphorus and iodine).

The various **molecules are held together by weak van der Waal's forces.**

* **Solubility:** They dissolve in non-polar solvents (organic solvents) like ethanol, ether, benzene, chloroform etc. and insoluble in polar solvents. Some of the covalent compounds like alcohols, amines dissolve in water due to hydrogen bonding.

* **Electrical Conductivity:** Covalent compounds contain neither ions nor mobile electrons, so they are **unable to conduct electricity in either the solid, liquid or gaseous state.**



* **Melting and Boiling Points** : is low bcz in covalent compounds, molecules are held together by weak **van der Waal's forces**.

Some giant molecules (eg. diamond,SiC & Silica have high MP and BP.

* **Nature of Reaction:** is **molecular reactions** which are **slow** and complex.

* Covalent compounds show structural and space isomerism because covalent bonds is **rigid and directional**.

Covalency : It is defined as **the number of electrons contributed by an atom of the element for shairing with other atoms to achieve noble gas configuration.**

If the **outermost orbit has empty orbitals then covalent bonds are formed in exicted state.**

Variable valency in covalent bonds :

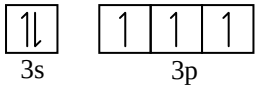
(I) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

(II) Lone pair electrons gets excited in the subshell of the same to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

(III) The energy required for excitation of electrons is called promotion energy.

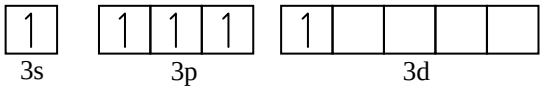
(IV) Promotion rule – Excitation of electrons in the same orbit.

(a) Phosphorus ▯▯▯Ground state



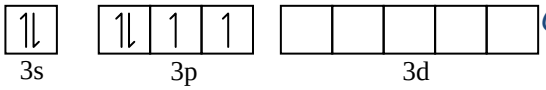
Covalency 3 (PCl_3)

Phosphorus ▯▯▯Excited state



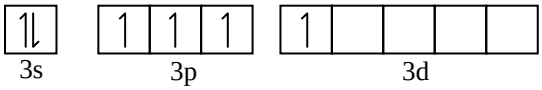
Covalency – 5(PCl_5)

(b) Sulphur ▯▯▯Ground state.



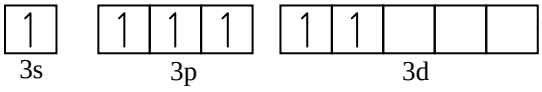
Covalency–2 (SF_2)

Sulphur ▯ Excited state 1st excitedstate



Covalency – 4 (SF_4)

2st excited state



Covalency–6 (SF_6)

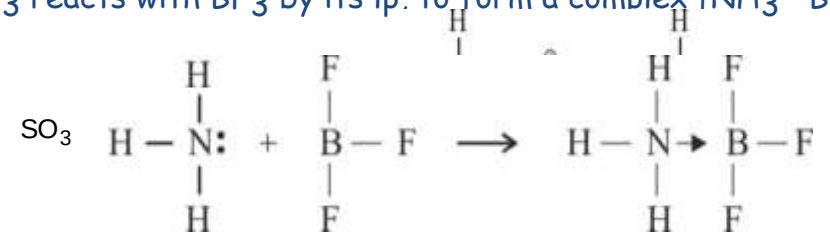
So variable covalency of S is 2, 4 & 6.

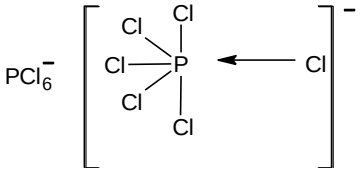
CO-ORDINATE BOND OR DATIVE BOND " **a covalent bond in which both electrons of the shared pair are contributed by one of the two atoms**". It is represented by an arrow (→) pointing its head towards the acceptor atoms.

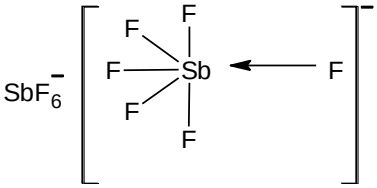
The atom which supplies the electron pair (a lone pair) is called **donor(Lewis base)** and the other atom accepting the share in this lone pair is called the **acceptor(Lewis acid)**.

Ex: Formation of ammonium ion: Even though ammonia molecule has a stable electronic configuration, it can react with a hydrogen ion H^+ by donating a share in the lone pair of electrons, forming the ammonium ion, NH_4^+.

Ex:NH_3 reacts with BF_3 by its lp. to form a complex $[NH_3 \quad BF_3]$.







Comparison of ionic, covalent & coordinate compounds

Property	Ionic	Covalent	Coordinate
binding force	Between ions strong (coulombic)	Between molecules smaller (Vander Waal's)	in between
mp/bp	High	less than ionic	in between
condition	conductor of electricity in fused state & in aqueous solution	bad conductor	Greater than covalent
solubility in polar solvent (H_2O)	High	Less	in between
Solubility in non polar solvent (ether)	Low	High	in between
6. Physical state	generally solid	liquid & gaseous	solid, liquid gas

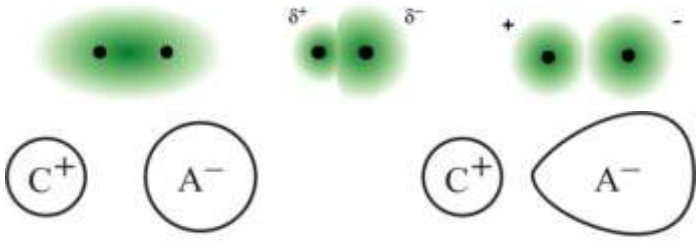
POLARISATION OF IONS

(Fajan's Rule) (Covalent nature in ionic bond)

In ionic compound,**cation approaches an anion** closely,**positive charge on the cation attract the electron cloud of the anion** towards itself due to electrostatic force of attraction.

At the same time the cation also tends to repel the positively charged nucleus of the anion.As a result electron cloud of the anion no longer remains symmetrical and elongated towards the cation is called deformation or **Polarization of the anion by the cation and the anion is said to be polarised.**

The ability of a cation to polarise a nearby anion is called its **polarization power**.



(a) No Polarisation (b) Polarised anion

Polarizability is the al n.

- **Polarisation** of anion causes some **sharing of electron between the ions so ionic bond acquires certain covalent character.**

i.e., Polarisation Covalent character

Factors affecting the polarisation of an ion: (Fajan's Rule)

- **Charge on the ions: Charge on the cation increases, its tendency to polarize the anion increases and covalent nature increases in ionic compound.**

  Whereas with the increasing charge of anion, its ability to get polarized, by the cation, also increases.

i.e., Polarisation ∝ charge on cation anion

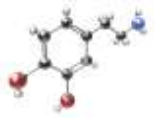
Charge on cation ∝ Polarisation (covalent character)

eg. $NaCl$ $MgCl_2$ $AlCl_3$ $SiCl_4$

Na^+ Mg^{++} Al^{+++} Si^{++++}

→

- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)



Charge on anion ∝ polarisation ∝ covalent nature ∝ $\frac{1}{M.P.}$

- Among **$PbCl_2$** and **$PbCl_4$** having charges +2 and +4 respectively. $PbCl_4$ shows covalent nature.
- Among NaCl, Na_2S, Na_3P, the charge of the anions are increasing,so order of covalent character is NaCl < Na_2S < Na_3P
  - **Size of the cation: Smaller the size of cation more will be the polarizing power and higher is its covalent nature.**

Polarisation $\propto \frac{1}{\text{size of cation}}$

- In a group –

$BeCl_2$
$MgCl_2$ — Size of cation increases
$CaCl_2$ — Covalent character decreases
$SrCl_2$ — Ionic character increases
$BaCl_2$ ↓

Greatest polarising power of Be^{2+}, shows its maximum covalent character.

- In a period – Na^+, Mg^{+2}, Al^{+3}, Si^{+4}

→
- Size of cation decreases
- Covalent charater increases

  - **Size of anion:Larger the size of the anion,polarized by the cation and covalent character increases.**

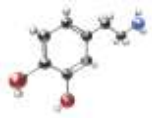
Polarisation ∝ size of anion

For example, in the case of halides of calcium, the covalent character increases from F^- anion to I^- anion i.e.

CaF_2
$CaCl_2$ — Size of anion increases
$CaBr_2$ — Covalent character increases
CaI_2 ↓ — Ionic character decreases

Similarly, AlF_3 $AlCl_3$ $AlBr_3$ AlI_3 →

Covalent character increases as the size of the halide ion increases



- **Nature or Electronic configuration of cation : -**

  Polarization capacity of cation having pseudo inert gas configuration is high. If the size of cations is same than that of cation having inert gas configuration.

  CuCl (M.P. 442°C) $Cu^+ \Longrightarrow$ 2, 8, 18(Covalent)

  NaCl (M.P. 800°C) $Na^+ \longrightarrow$ 2, 8(Ionic)

  Cu^+ and Na^+ both the cation (Pseudo & inert) have same charge and size but polarizing power of Cu^+ is more than Na^+ .

  So CuCl has more covalent character than NaCl.

SESSION – 5

AIM - To introduce VBT

Valency Bond Theory: VBT was proposed by **Heitler** and **London**. It was modified by **Pauling and Slater**. **(According to this theory, a covalent bond is formed by overlapping of atomic orbitals].**

- A covalent bond is formed by overlapping of unpaired atomic orbitals of two atoms. After overlapping both orbitals got **common region of electron density**.
- Overlapping of orbitals causes delocalization of electrons which in turn, lowers the energy and increases the stability.

  Resulting bond acquires a pair of electrons with opposite spins to get stability.
- The strength of the bond depends on the extent of overlapping. Overlapping of orbitals is higher, the bond formed is stronger.

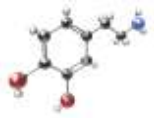
  Order of overlapping s-s > s-p > p-p

  The direction of the bond formed is the direction in which the bonding orbitals are oriented.
- As the value of n increases, bond strength decreases.

  1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3

  If n is same 2p - 2p > 2s - 2p > 2s - 2s

  1s - 2p > 2s - 2p > 3s - 3p
- Orbitals can overlap in 2 ways,



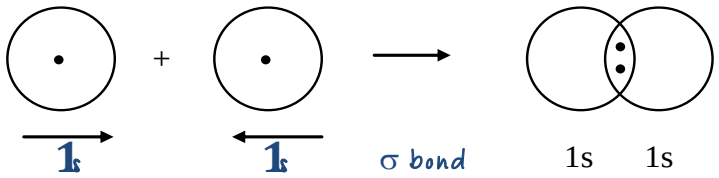
- **Axial overlapping** results in **sigma (σ) bond** here **atomic orbitals overlap along the inter-nuclear axis** and involve end to end or head on overlap.Here electron cloud is cylindrically symmetrical about inter-nuclear axis. **The electrons constituting sigma bond are called sigma electrons.**

Three types of axial overlapping

- **s-s overlapping** - Overlapping of two half-filled s-orbitals of the atoms approaching to form a bond **s-s σbond**.

Formation of H_2 molecule:

Hydrogen atom has one electron in 1s orbital. H → (1) $1s^1$. This orbital having unpaired electron overlaps axially with 1s orbital of another H atom to form a sigma bond. H-H molecule is thus formed.



(Formation of H_2 molecule)

- **s-p overlapping**. involves overlapping of half-filled s-orbital of the one atom with half-filled p-orbital of the other, bond formed is called **s-p bond**.

Formation of HCl molecule:

Electronic configuration of H is $1s^1$ with 1s orbital.

Electronic configuration of chlorine is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ with unpaired electron in $3p_z$ orbital.

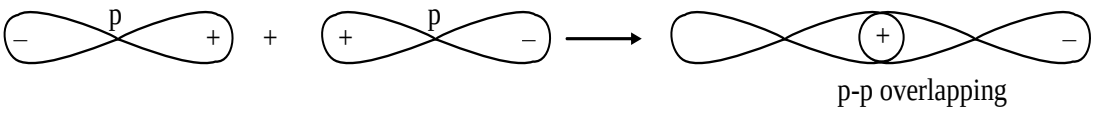
- Hydrogen's 1s orbital and chlorine's $3P_z$ orbital overlap with each other axially to form a sigma bond.



- **p-p overlapping**.involves overlapping of half-filled p-orbitals of the two atoms. The bond so formed is called p-p bond.

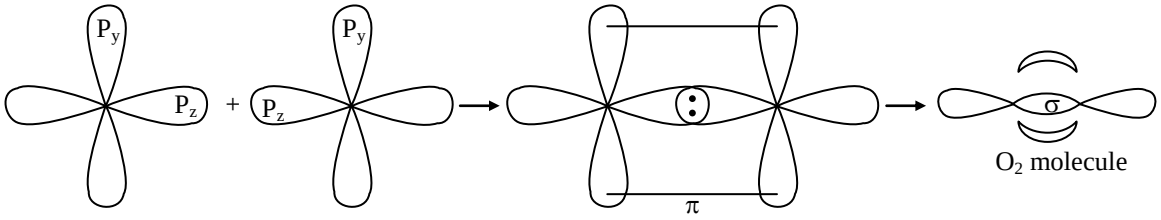
Formation of Cl_2 molecule:

The electronic configuration of chlorine atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ with an unpaired electron in $3P_z$ orbital.$3P_z$ orbital of two chlorine atoms overlap with each other axially to form a sigma bond.



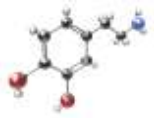
- **Side ways overlapping** of orbital is called **π (Pi) bond**. Here electrons are oriented **above and below the inter nuclear axis.**

  - **Formation of O_2molecule**:Electronic configuration of oxygen $1s^2\ 2s^2\ 2p^4$. It has 2 unpaired electrons in 2Py and 2Pz orbitals.
    $2p_x$ orbitals of each oxygen atoms overlap each other axially to form a sigma bond, 2Py orbitals of the oxygen atoms are perpendicular to the axis.So they overlap laterally to form π bond. Thus O = O is formed.



- σ bond stronger than π bond due to higher overlapping of orbitals.
- In a σ bond, the electrons are oriented along the inter nuclear axis but in a π bond,.
- Free rotation of molecule about σ bond is possible but free rotation of molecule about π bond is not possible.

Sigma Bond	Pi Bond
It is a stronger bond.	It is a weaker bond.
It can exist independently.	It exists along with bond
It allows the free rotation of bonded atoms.	It restricts the free rotation of bonded atoms.
The electron cloud of sigma bond is along theinter nuclear axis of the bonded atoms.	The electron cloud of the bond liesaboveand below this axis.
All orbitals s, p, d..... can form sigma bond.	Except 's' orbital, all other orbitals can form bond
Both pure and hybrid orbitals can form bond.	Hybrid orbitals cannot form bond
This bond is formed by the axial overlappingof orbitals.	This is formed by the lateral overlappingof orbitals.



SESSION – 6

AIM - To introduce VSEPR Theory

VALENCE SHELL ELECTRON PAIR REPULSION THEORY:

VSEPR theory was proposed by **Gillespie and Nyholm**. This theory helps us to predict the **shape of covalent molecules** based on the **repulsive interactions of valence electrons**.

- The **shape of the molecule depends upon the number and nature of electron pairs** present in the valency shell of the central atom.
- Electron pairs around the central atom of a molecule repell one another bcz negative charge on the electron cloud.
- In order to minimise the repulsion and to maximise the stability, **valence electron pairs arranged away from each other around the central atom in a space**.
- Central atom in a molecule surrounded with 2 types of electrons.
  - **Bonding or shared electrons(bond pair)**
  - **Non-bonding electrons(lone pair)**
- Bond pair of electrons are under the influence of two nuclei but the lone pairs are under the influence of only one nucleus. Hence lone pairs are spread around the central atom and occupy more space
- If central atom surrounded with **only bond pair electrons**,molecules shows **definite geometry**.

If central atom surrounded by **atleast one lone pair electrons**, molecules shows **altered or distorted or indefinite geometrty**.

ie. the original bond angle will disturbed due to repulsion between lone pair of electrons. Bond

$$\text{angle} \propto \frac{1}{\text{No. of lone pair of electron}}$$

- The various repulsive forces experienced by these electron pairs is of the order **l.p - l.p > l.p - b.p > b.p - b.p repulsions**

Shape of molecule having only bond pairs

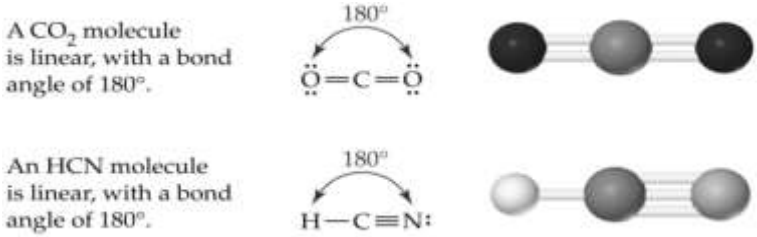
No. of bp es⁻	Shape	Molecule
2	Linear	BeF_2, $BeCl_2$, CO_2
3	Triangular	BF_3,BCl_3,SO_3, CO_3^{2-}
4	Tetrahedral	CH_4, CCl_4 etc
5	Trigonal bipyramidal	PF_5, PCl_5 etc
6	Octahedral	SF_6, SiF_6^{-2}
7	Pentagonal bipyramidal	IF_7

Shape of molecule having bond pairs as well as lone pair electrons.

bond pairs	lone pairs	Total No.	Shape of Molecule		Example
			basic shape	actual shape	
2	1	3	Triangular	Angular	$SnCl_2$, SO_2
3	1	4	Tetrahedral	Pyramidal	NH_3, H_3O^+
2	2	4	Tetrahedral	Angular	H_2O
4	1	5	Folded square	See Saw	SF_4
3	2	5	Trigonal bipyramidal	T-shaped	ClF_3
2	3	5	Trigonal bipyramidal	Linear	XeF_2
5	1	6	Octahedral	Squarepyramidal	IF_5, BrF_5
4	2	6	Octahedral	Square planar	XeF_4

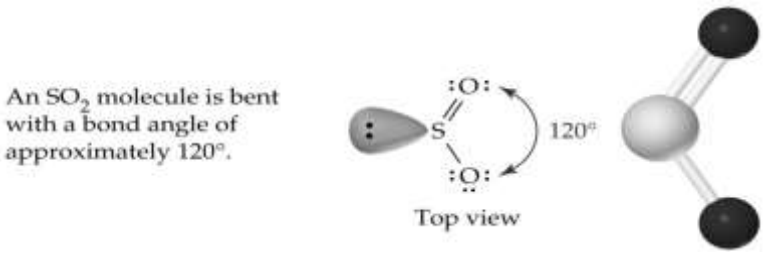
GEOMETRY OF MOLECULES

- **Two Charge Clouds**: When there are two charge clouds, as in carbon atoms(two double bonds) and HCN (one single bond and one triple bond), the clouds are far apart or in opposite directions. Thus, CO_2 and HCN are linear molecules with bond angles of 180°.



- **Three Charge Clouds**: When 3 charge clouds, as in carbon atom of formaldehyde (two single bonds and one double bond) and the sulfur atom of SO_2(one single bond, one double bond, and one lp), the clouds are farthest aptwhen they lie in the same plane and point to the corners of an **equilateral triangle** with bond angle 120° ratherthan180°.

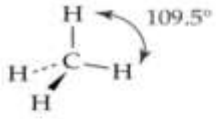
- **Four Charge Clouds**: is occurs on the central atoms CH_4 (four single bonds), NH_3 (three single bonds and one lone pair), and H_2O (two single bonds and two lone pairs), the clouds are farthest apart if they extend toward the corners of a **regular tetrahedron** with bond angle **109.5°**.



in

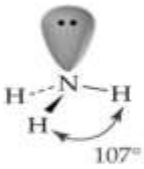


A methane molecule is tetrahedral, with bond angles of 109.5°.



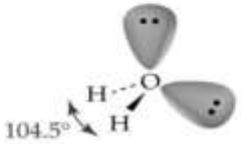


An ammonia molecule is trigonal pyramidal, with bond angles of 107°.



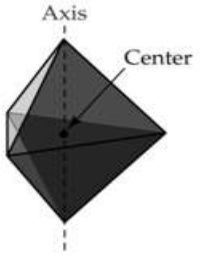


A water molecule is bent, with a bond angle of 104.5°.

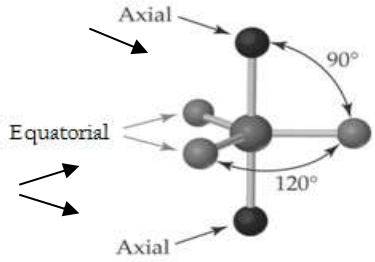




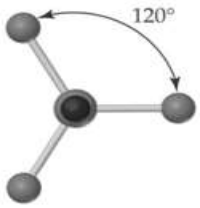
- **Five Charge Clouds**:found in central atoms in PCl_5, SF_4 and ClF_3 are oriented toward the corners of **trigonalbipyramidal.** Three clouds lie in a plane and point toward the corners of an equilateral triangle,the fourth cloud points directly up, and the fifth cloud points down:



A trigonal bipyramid



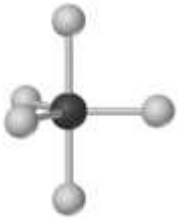
Side view



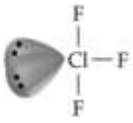
Top view

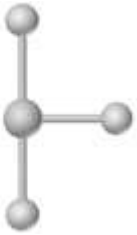
A PCl_5 molecule is trigonal bipyramidal.



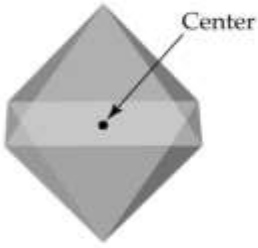


A ClF_3 molecule is T-shaped (turn 90° to see it).

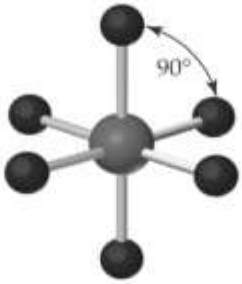




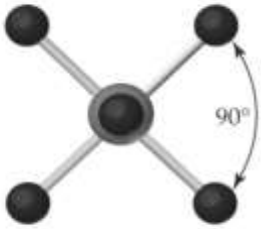
- **Six Charge Clouds**: shows **regular octahedron**,



A regular octahedron



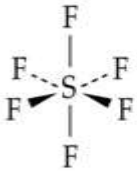
Side view

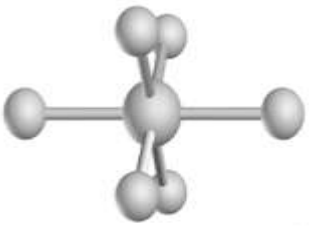


Top view

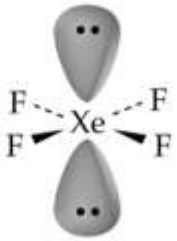


An SF_6 molecule is octahedral.



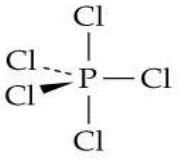
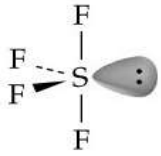
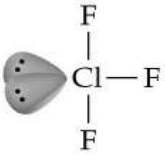
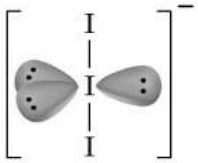


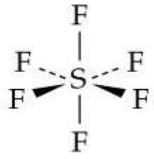
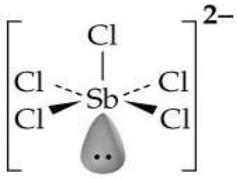
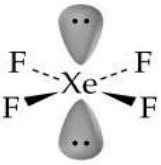
An XeF_4 molecule has a square planar shape.

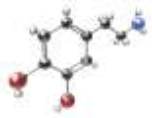




Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	Linear	O=C=O
3	0	3	Trigonal planar	H, H, C=O
2	1		Bent	O, O, S:
4	0	4	Tetrahedral	H, H, C, H, H
3	1		Trigonal pyramidal	H, H, N, H
2	2		Bent	H, H, O:

5	0	5	Trigonal bipyramidal	
4	1		Seesaw	
3	2		T-shaped	
2	3		Linear	

6	0	6	Octahedral	
5	1		Square pyramidal	
4	2		Square planar	



SESSION - 7 AND 8

AIM - To introduce hybridization

HYBRIDIZATION

The intermixing up of pure atomic orbitals of an atom having nearing energies to give a set of equal number of identical hybrid orbitals of same energy is called **Hybridization**.

This is a hypothetical concept and was proposed by **Pauling** and **Slater**

Rules for Hybridization:

- Atomic orbitals of an atom can intermix
- Atomic orbitals having nearing energy can intermix
- Vacant, half-filled or completely filled atomic orbitals can intermix to form hybrid orbitals
- No. of hybrid orbitals formed is equal to number of atomic orbitals intermixing
- Hybrid orbitals are identical in shape and have same energies but differ in orientation in space.
- The electrons are redistributed in these hybrid orbitals following Hund's rule and Pauli's exclusion principle
- Atomic orbitals only participating in Hybridization but not electrons.
- Hybrid orbitals form σ bonds, unhybridized orbitals form π bonds. Molecule has a regular geometry, when hybrid orbitals contain shared pair of electrons if one or more lone pairs of electrons in the valence shell,molecule shows **distorted geometry**.
- Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- The hybrid orbitals are oriented in space as far apart as possible. Thus, they help in determining the shape or geometry of a molecule.

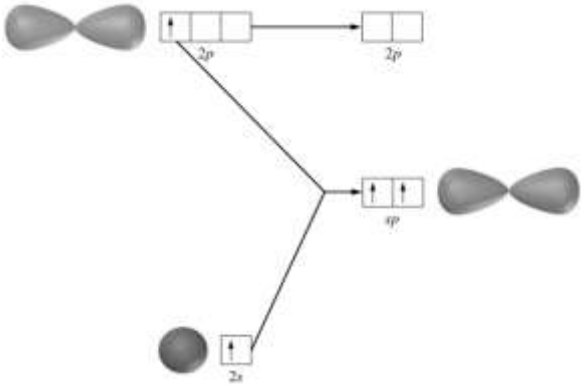
Difference between hybridization & overlapping

Overlapping	Hybridisation
• It occurs between orbitals of two atoms	• **It** occurs among orbitals of the same atom
• Only half filled orbitals takes part inoverlapping	• Any type of orbital can participates
• It occurs during bond formation bond formed after hybridization	• Process, just before overlapping.
• Orbital of different energies may participatesin excited states.	• It may takes place in ground or in excited state Inground state- NH_3, NCl_3, PH_3, PCl_3,
• Molecular orbitals are formed	• Hybridised orbitals are formed

TYPES OF HYBRIDISATION:

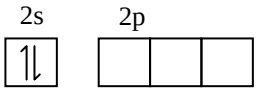
- **sp Hybridization:**

  One s & one p orbital intermix to form two sp hybrid orbitals. This process is called **sp hybridization**.*sp*-hybridised orbitals of **equivalent shapes and energies** and arrange in **straight line(linear shape)** with angle of 180°. Each *sp* hybrid orbital having **50% s - character and 50% p –character**

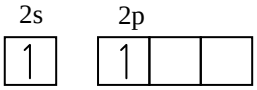


Example: BeH_2 - central atom is Be.

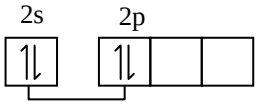
Be (ground state)



Be (excited state)

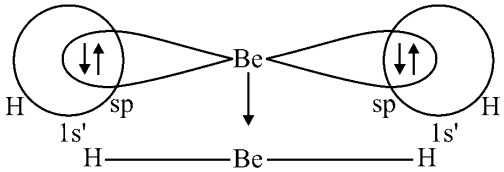


Be-atom accepts 2 electrons from H in BeH_2,



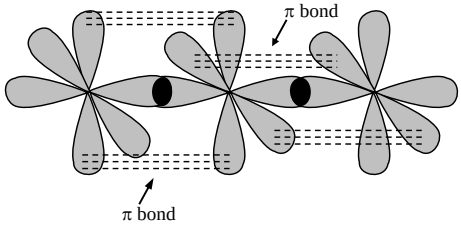


These two sp hybrid orbitals of Be overlap axially with the $1S^1$ orbitals of 2 H atoms to form 2 sigma bonds with **linear in shape and** bond angle 180°



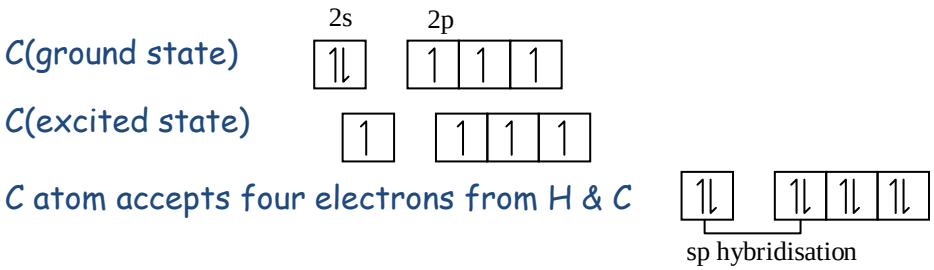
Beryllium Hydride
—Linear Molecule
—Bond Angle 180°

CO_2 Molecule (O = C = O) : Here C has two sp hybrid orbitals & two unhybridized p orbitals. It shows linear in shape with 180° bond angle .



Molecular orbital picture of CO_2

CHΞCH [H–C_AΞC_B–H] Here each C atom contains two sp hybrid orbitals & two unhybridized p orbitals



- sp hybrid orbital of each C overlaps to give sigma bond C – C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bonds between C – H.
- The two unhybridized p orbitals of each C atom (p_y and p_x) overlap laterally or sideways to form two pibonds.

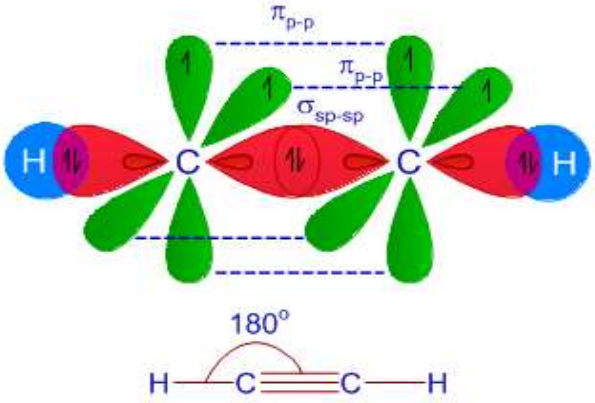
  Therefore in **H–C_A Ξ C_B–H**

  sigma bond between C_A – C_B is formed sp – sp overlapping

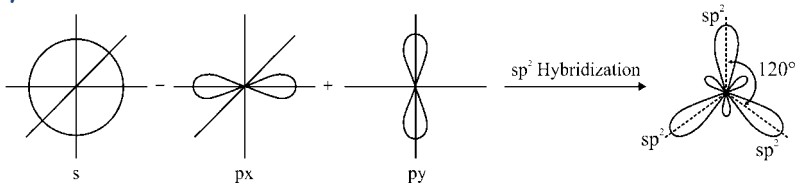
  sigma bond between C_A – H is formed sp – s overlapping

  sigma bond between C_B – H is formed sp – s overlapping

  pi bond between C_A – C_B is formed : p_y–p_y,p_x–p_x overlapping
- Each C atom forms two sigma bonds but in C_2H_2 3 sigma bonds
- Each C atom forms two sigma bonds. Total sigma bonds in C_2H_2 are two
- Total number of bonds in acetylene are : 3sigma + 2pi bond = 5 bonds



- **sp^2 Hybridisation: is** intermixing of one s and two p orbitals to give 3 sp^2 hybrid orbitals is called sp^2 hybridisation.

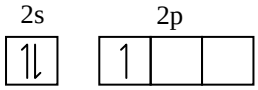


3 sp^2-hybrid orbitals lie in the same plane, directed towards corners of **equilateral triangle** with is 120° bond angle between them. sp^2 hybrid orbitals shows 33.3% of s –character , 66.7 % of p –character.

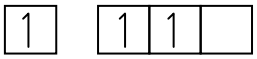
Example: - BF_3

In BF_3 molecule the central atom is B electronic configuration is in

B (ground state)

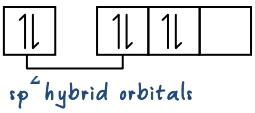


B (excited state)

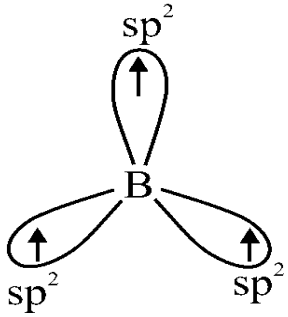


B atom accepts 3 electrons

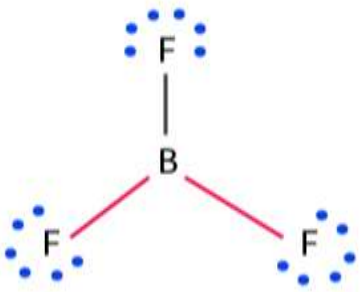
From 3 F atom in BF_3

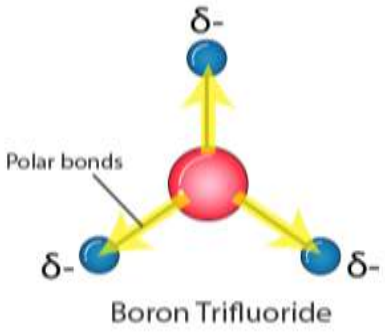


One S orbital and two P orbitals of B atom intermix to form 3 sp^{2}hybrids orbital. These 3 hybrid orbitals orient in space in a **planar triangular** manner with bond angle 120°



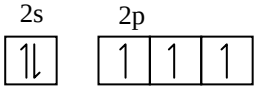
These three hybrid orbitals overlap axially with $2p_z$ orbitals of 3F atoms to form 3 sigma bonds





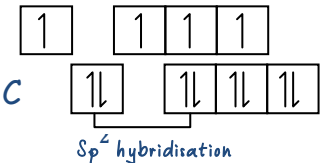


Ethylene (C_2H_4). Here each C atom contains three sp^2 hybrid orbitals & one unhybridised p orbitals arranged in trigonal manner with bomd angle 120^0 C(ground state)

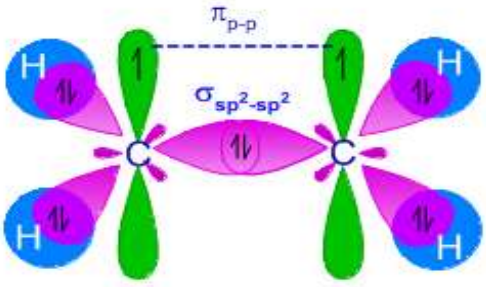


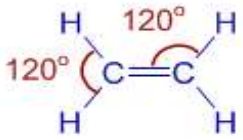
C(excited state)

C atom accepts four electrons from H & C

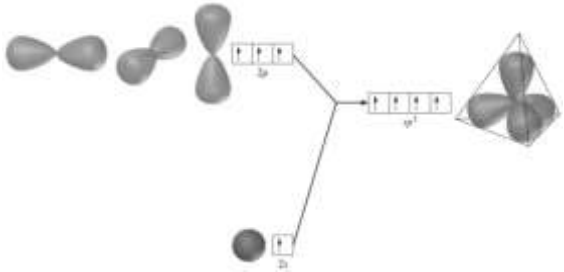


- sp^2 hybrid orbital of each C overlaps to give sigma bond C – C.
- The remaining two sp^2 hybrid orbital of each C atom overlaps with s-orbital of two H atoms, forming 2 sigma bonds between C – H.
- The one unhybridised p orbital of each C atom (p_x) overlap laterally or sideways to form one pi(π)bonds.
- Each C atom forms 3 sigma bonds but in C_2H_4 5 sigma bonds
- Each C atom forms one π bond. Total π bonds in C_2H_2 are two
- Total number of bonds in ethene are : 5σ + 1π bond = 6 bonds





- **sp^3 Hybridisation**: is intermixing of one s and 3 p orbitals to form 4 sp^3 hybrid orbitals is called sp^3 hybridisation. Formed hybrid orbitals Oriented in **tetrahedral manner** with angle between them is 109^0 28'.sp^3 hybrid orbital shows 50% of **s** and 50% of p characters.

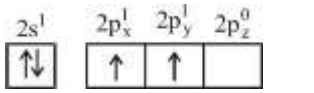


Example: CH_4 (methane)

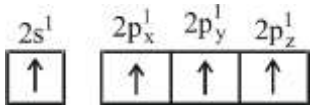
In CH_4 , the central atom is C. Electronic configuration of

$_6C = 1s^2, 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

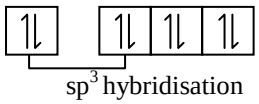
C (ground state)



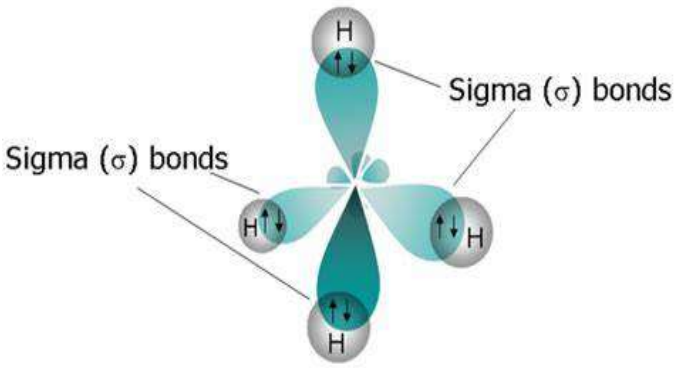
C (excited state)

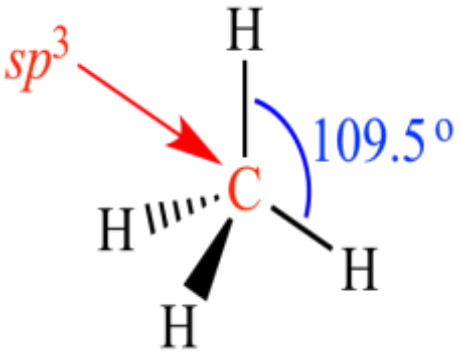


C atom share four electrons with 4 hydrogen atoms



- One 's' orbital and three p orbitals of C intermix to form 4 sp^3 hybrid orbitals. The hybrid orbitals orient in pace tetrahedrally with bond angle 109^0 28'
- These 4 sp^3 hybrid orbitals overlap with 1s orbitals of four H atom to form 4 sigma bonds





Note:

- In organic compounds, wherever C forms 4 sigma and zero pi bonds, it is sp^3 hybridised.

- When C forms 1 π bond, it is sp^2hybridized.
- When C forms 2π bonds, it is sp hyrbridised.

Find the hybridization of all c atoms in the following

- $CH_2 = CH - CH_2 - CH_3$

  SP^2 SP^2 SP^3 SP^3

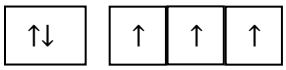
- CCl_4 - All carbon atoms shows SP^3
- $CH_2 = C = CH_2$

  SP^2 SP SP^2

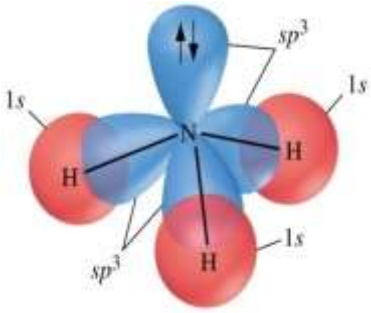
- $CH_2 = CH - CH = CH_2$

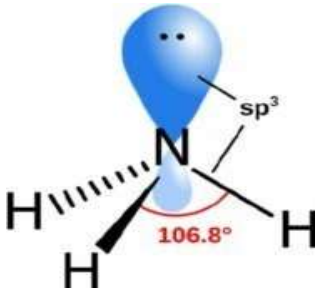
  SP^2 SP^2 SP^2 SP^2

Ammonia (NH_3) molecule In NH_3 the central atom is N.

It's G.E.C = $2s^2\ 2p^3$ 

- One fully filled s and three half filled p orbitals intermix to form 4 sp^3 hybrid orbitals
- After hybridization Nitrogen with 5 valence electrons has 3 unpaired e- in $3sp^3$ hybrid orbitals and a lone pair in the fourth one.
- The three H s - orbitals each are having an unpaired electron overlap with the 3 sp^3 hybrid orbitals of N-atom. Thus 3 N — H electron pair bonds are formed
- Due to the **presence of lone pair, the bond angle decreases to 107° due to 1p - bp and bp - bp interactions and shows pyramidal shape.**

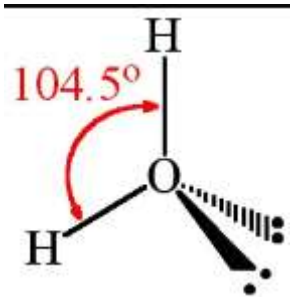


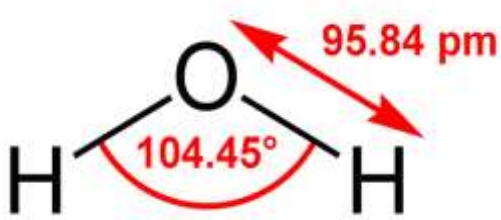


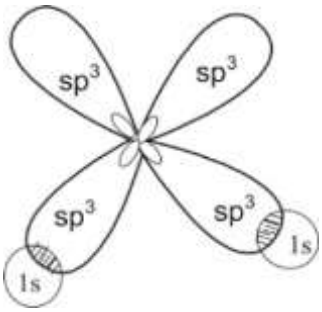
- **H_2O molecule:** In H_2O the central atom is O.

Its G.E.C is $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

- One s and three p orbitals intermix to form 4 sp^3hybrid orbitals Oxygen with 6 valence electrons has 2 unpaired e^- in two sp^3 hybrid orbital and two lone pair in remaining two.
- The two 1s orbitals of H each are having an unpaired e- overlap with sp^3 hybrid orbitals of Oxygen atom. Thus two O–H sigma bonds are formed.
- Due to the presence of two lps ,the shape is distorted to **angular or bent-V** shape and bond angle is decreased from 109° 28^1 to 104° 30′





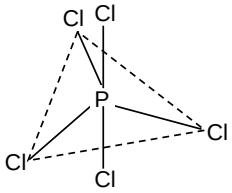




- **sp^3d Hybridisation :**

- Here one s orb three p and one d orbital are mixed to give **five** new hybrid orbitals which are equivalent in shape and energy called as **sp^3d hybrid orbitals**.
- Out of these five orbitals, three hybrid orbitals are at 120° angle present on the plane and two hybrid orbitals are perpendicular to the plane, shape of molecule becomes is **trigonal bipyrmaidal**.

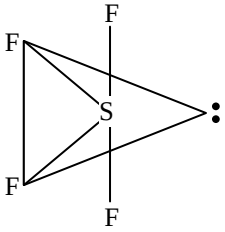
(a) Five sigma and zero lp electron : trigonal bipyramidal PF_5, PCl_5, PBr_5, Pl_5, AsF_5, $AsCl_5$, $SbCl_5$, SbF_5 etc.



(b) Four sigma bonds and one lone pair of electron :

SF_4, SeF_4, TeF_4, PoF_4, PF_4^-, SbF_4^-, SCl_4, $SeCl_4$, $TeCl_4$ etc.

The shape of all above examples will be **irregular tetrahedron**.



Structure of SF_4

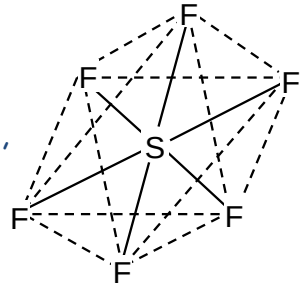
(c) Three sigma bonds & two lone pair of electrons - ClF_3, BrF_3, IF_3, $BrCl_3$, ICI_3 etc. The shape of all above compounds is **'T' shape**

(d) Two sigma bonds & three lone pair of electrons : ICl_2^-, IBr_2^-, ClF_2^-, IF_2^-, BrF_2^-, XeF_2^-, I_3^-, Br_3^- shows **linear shape**.

- **sp^3d^2 Hybridisation :**

- one s-orbitals, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.
- The shape of molecule obtained from above six hybrid orbitals will be symmetrical **octahedral**.
- The angle between all hybrid orbitals will be 90°.

Example : SF_6, AlF_6^{-2}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,





Shape of molecules or ions involving hybridization with bond pair electrons

Hybridization	Bond angle	Shape of molecules	Example
sp	180°	Linear	BeF_2, $BeCl_2$, CO_2 CS_2, $HgCl_2$ $MgCl_2$, C_2H_2
sp^2	120°	Trigonal Coplanar	BF_3, BCl_3, BH_3, $AlCl_3$,SO_2 SO_3, C_2H_4, NO_3^-, CO_3^{2-}
sp^3	109°28′	Tetrahedral	$SiCl_4$,CH_4,$SnCl4$,SO_4^{2-}, ClO_4^-
sp^3d	120°,90°	Trigonal bipyramid	PCl_5, PF_5, $SbCl_5$
sp^3d^2	90°	Octahedral	SF_6,$SnCl_6^{2-}$, PF_6^-, SeF_6
sp^3d^3	90°,72°	Pentagonal bipyramid	IF_7
dsp^2	90°	Square planar	$[Ni(CN)_4]^{2-}$,$[PtCl_4]^{2-}$,

Geometry of molecules or ions involving hybridization with lone pair of electrons

Hybridization	No. of lone pair of electrons	Bond angle	Shape of molecule	Examples
sp^2	1	< 120°	Angular or V shape	$SnCl_2$, SO_2, NO_2^-
sp^3	1	<109°28′	Pyramidal	NH_3, PH_3, PCl_3, AsH_3, ClO_3^-
sp^3	2	<109°28′	V Shaped	H_2,H_2S,I_3^+
sp^3d	3	180°	Linear	XeF_2, I_3^-
sp^3d	2	180°, 90°	T shape	ICl_3, ClF_3
sp^3d	1	186°, 116°	See saw	SF_4, $TeCl_4$
sp^3d^2	2	90°	Square planar	XeF_4
sp^3d^2	1	90°, 180°	Squarepyramidal	IF_5, $XeOF_4$
sp^3d^3	1	72° & 90°	Pentagonal pyramid	XeF_6

Method of predicting the Hybrid state of the central atom

Simple Molecule	Polyatomic Anion	Poyatomic Cation
$X = \frac{1}{2}[V + G]$	$X = \frac{1}{2}[V + G + a]$	$X = \frac{1}{2}[V + G - c]$

Hybridisation or X = $\frac{1}{2}$ [Total number of valence e^- in the central atom + total number of monovalent atoms – charge on cation + charge on anion]

In the above formulae,

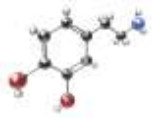
V = No, of monovalent atoms or groups attached to the central atom

G = No, of outer shell electrons in ground state of the central atom

a = Magnitude of charge on anion

c = Magnitude of charge on cation

X	2	3	4	5	6	7
Hybrid state	sp	sp^2	Sp^3	sp^3d	sp^3d^2	sp^3d^3



Calculate the value of X and decide the hybrid state of central atom as follows

For Example:

PF_5	$COCl_2$	NH_4^+	ClO_4^-
$X = \frac{1}{2}[5+5]$	$X = \frac{1}{2}[2+4]$	$X = \frac{1}{2}[4+5-1]$	$X = \frac{1}{2}[0+7+1]$
= 5	= 3	= 4	= 4
Hybrid state of P is sp^3d	Hybrid state of C is sp^2	Hybrid state of N is sp^3	Hybrid state of Cl is sp^3
NO_3^-	IF_5	CO_2	XeF_4
$X = \frac{1}{2}[0+5+1]$	$X = \frac{1}{2}[5+7]$	$X = \frac{1}{2}[0+4]$	$X = \frac{1}{2}[4+8]$
= 3	= 6	= 2	= 6
sp^2	sp^3d^2	sp	sp^3d^2
PCl_6^-	PH_3	SF_3^+	SF_4
$X = \frac{1}{2}[6+5+1]$	$X = \frac{1}{2}[3+5]$	$X = \frac{1}{2}[3+6-1]$	$X = \frac{1}{2}[4+6]$
= 6	= 4	= 4	= 5
Hybrid state	Hybrid state	Hybrid state	Hybrid state
sp^3d^2	sp^3	sp^3	sp^3d

SESSION – 9

AIM

- **To introduce dipole moment.**
- **To introduce resonance**

DIPOLE MOMENT (μ)

A polar covalent molecule behaves like a **dipole**.degree of polarity of a bond or molecule is expressed in dipole moment.

The product of magnitude of negative or positive charge (e) on either atom and the distance between them is called dipole moment

Mathematically,

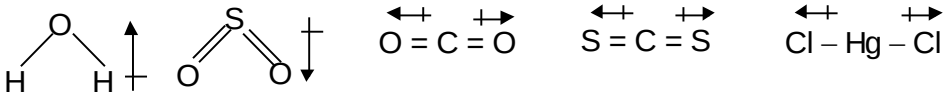
μ = electric charge X bond length = q x d.

Special Unit of dipole moment is **Debye** (D).

1D = 1 x 10^{-18} e.s.u x cm

or 1D = 3.335 x 10^{-30} **coulomb meter (SI unit)**

- Dipole moment is a **vector quantity and is indicated by an arrow having a symbol ($+\longrightarrow$) pointing towards the negative end.**



1.84D 1.63D 0 D 0 D 0 D

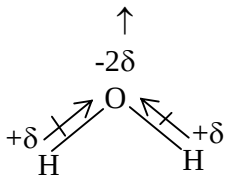
- Greater the dipole moment, greater is the polarity of the bond.
- In case of polar diatomic molecules there is one polar bond so, dipole moment of molecule = dipole moment of the polar bond.

$$\mu_{bond} = \mu_{molecule}$$

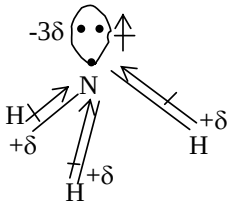
- In case of polyatomic molecules, there are more than one polar bonds, so, μ = Resultant dipole moment of all individual polar bonds.

Resultant dipole moment may be calculated by the vectorial addition of the bond moments, as $\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

e.g.(i)**Dipole moment of water** is 1.84D, which is equal to the resultant dipole moment of two O – H bonds.



μ = 1.84 D



μ = 1.49 D

Dipole moment of unsymmetrical molecules.

e.g. (ii)Dipole moment of Ammonia is 1.49D, which is equal to the resultant of dipole moments of there N – H bonds.

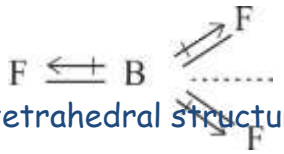
- The molecule having zero resultant dipole moment are said to be **non-polar molecules like** CO_2, $BeCl_2$, BeF_2, CS_2, BF_3, BCl_3, CH_4, CCl_4 having zero dipole moment but contain polar bond.

The molecules having certain dipole moments are said to be polar molecules like H_2O (μ = 1.84D), NH_3 (μ = 1.40D), NF_3 (0.24D) CH_3Cl (1.86D), $CHCl_3$, PCl_3, SO_2 etc.

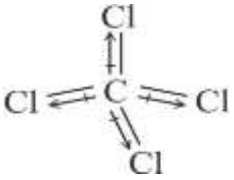
Molecule has zero dipole moment under the following conditions:

(a) If it has sp hybridisation (linear geometry) because $\mu_1 = \mu_2$ and $\alpha = 180^o$
e.g., CO_2, $BeCl_2$, HgF_2 etc O ⇌ C ⇌ O

(b) If it has sp^2 hybridization(trigonal planar geometry) and the atomic number of the central atom is less than 21:
e.g., BF_3, BCl_3, SO_3 etc.

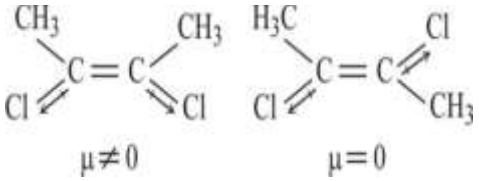


(c) Molecules which have symmetrical tetrahedral structure:
e.g, CCl_4, CH_4, $SiCl_4$ etc



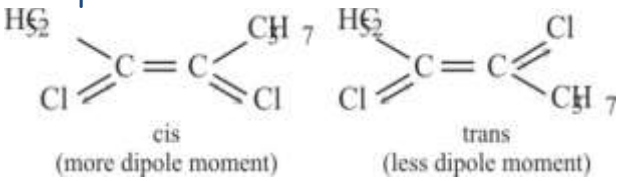
(d) If it is a Trans isomer:

e.g., Trans 1, 2, dichloro butene -2



If there are 3 different groups around the double bond, then both cis and trans isomers show dipole moment but. $\mu_{trans} < \mu_{cis}$

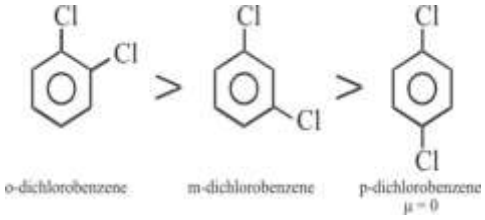
e.g., 3, 4 dichloro heptene – 3



(e) A para isomer has no dipole moment.

e.g., p-dichloro benzene.

Dipole moment follows the order o > m > p.



Applications of Dipole moment

Dipole moment used to predict

(a) **Geometry of the molecule**

If □□= 0 compound is non polar and symmetrical

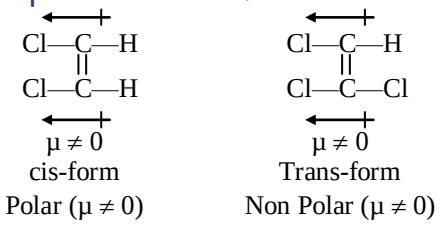
eg. CO_2, BF_3, CCl_4, CH_4. BeF_2 etc.

If □□□□0 compound will be polar and unsymmetrical.

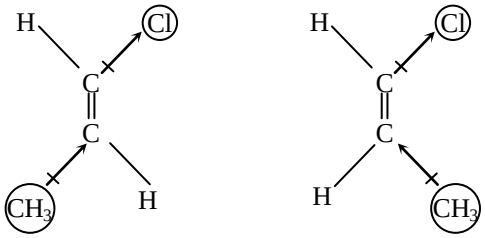
H_2O, SO_2, NH_3, Cl_2O, CH_3Cl, $CHCl_3$ etc.

(b) **cis or trans form of a geometrical isomer**.

- Dipole moment of cis isomers is normally higher than trans isomers

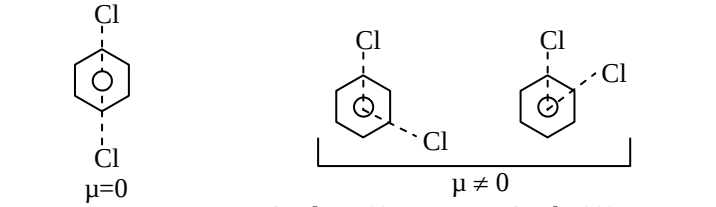


- If two groups have opposite inductive effect than trans-isomer will have greater dipole moment



(c) **Orientation in benzene derivatives** or **to locate position of substituents in aromatic compounds**. $\mu \propto \frac{1}{\text{Bond angle}}$

- If same substituents are preset in the symmetrical position of benzene ring compounds will be zero



- As angle between subtituents decrease value of increase

(d) **% ionic character of a bond.**

$$\text{Percent ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

$$\%\text{Ioniccharacter} = \frac{\text{Experimentalvalueof}\mu}{\text{Theoriticalvalueof}\mu} \times 100$$

e.g. Experimental dipole moment for HCl = 1.03

Suppose charge on H^+ or Cl^-, $q = 4.8 \times 10^{-10}$ esu

$d = 1.27A^0$

$\therefore$ theoretical value of $\mu = q \times d = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8}$

$= 6.09$ D

Thus, **% ionic character** in H – Cl bond or HCl molecule $= \frac{1.03}{6.09} x100 \approx 16.9$

(e)**Extent of polarity**

Molecules having zero dipole moment (μ_R) are nonpolar molecules and those having $\mu_R \neq 0$ are polar in nature.

e.g., H_2, N_2, O_2 etc are nonpolar (μ=0) and HF, HCl, HBr, HI, etc are polar molecules ($\mu_R \neq 0$).

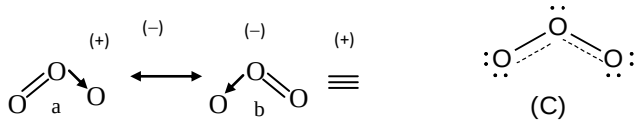
Thus, dipolemoment can also be used to **distinguish between polar and nonpolar molecules.**

RESONANCE

In certain molecules, a simple Lewis structure cannot explain all the properties of the molecule. The molecule is then supposed to have many structures.

The actual structure is in between of all the contributing structures and is called **resonance hybrid**. The different individual structures are called **resonating structures or canonical forms**. This phenomenon is called **resonance**. In representing resonance, a double headed arrow (↔) is put between different contributing structures.

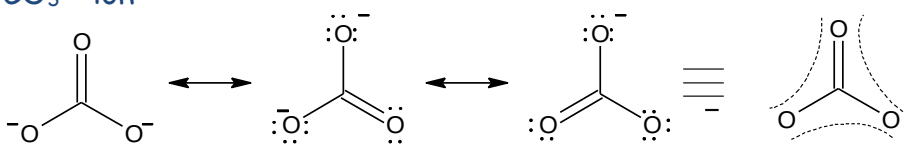
For example we can write two electronic structures of O_3



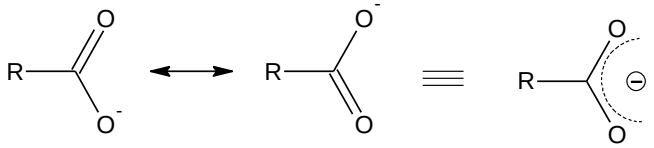
Structures (A) and (B) are called **resonating or canonical structures** and C is the **resonance hybrid**. This phenomenon is called **resonanc**

Some other examples

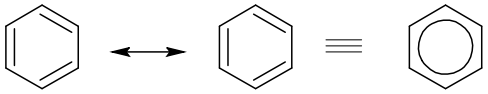
(i) CO_3^{2-} ion



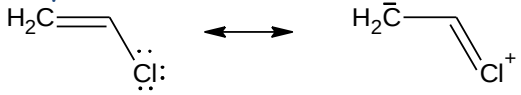
(ii) Carbon–oxygen bond lengths in carboxylate ion are equal due to resonance.

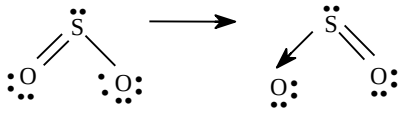


(iii) Benzene

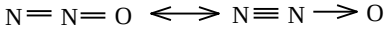


(iv) Vinyl Chloride

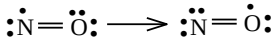




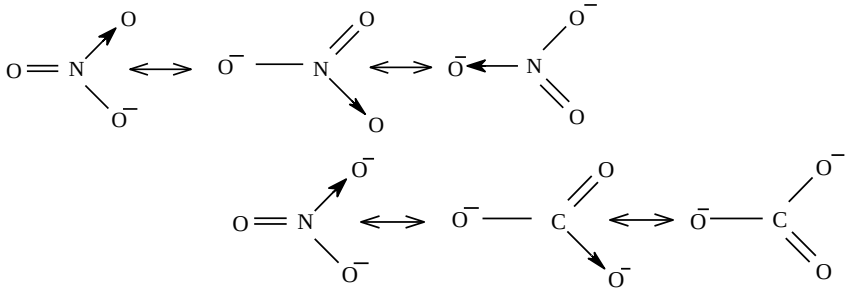
- Sulphur dioxide SO_2
- Nitrous oxide (dinitrogen oxide), H_2O



- Nitric oxide, NO



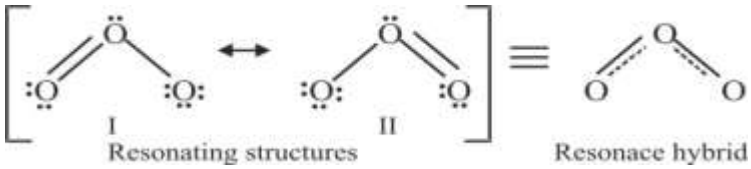
- Nitrate ion, NO_3^- (planar, triangular)



$$\text{BondOrder} = \frac{\text{No. of bonds between the same two atoms in all the structures}}{\text{total no. of resonating structures}}$$

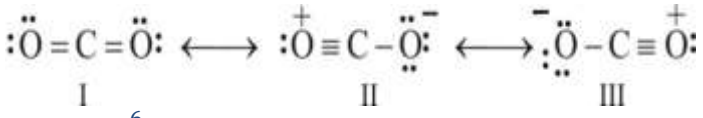
Examples of Resonance:

(i) Ozone (O_3)



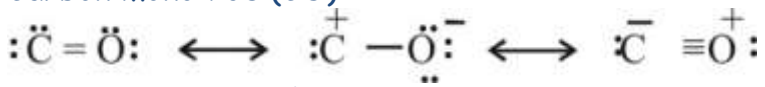
Bond Order = $\frac{3}{2}$ = 1.5

(ii) Carbon dioxide (CO_2)



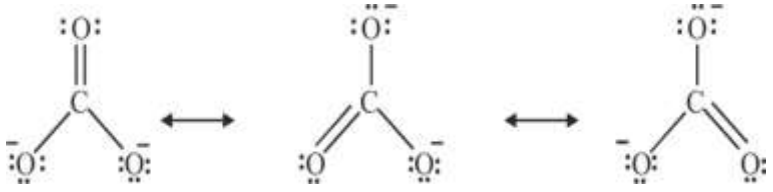
Bond Order = $\frac{6}{3} = 2$

(iii) Carbon monoxide (CO)



Bond Order = $\frac{6}{3} = 2$

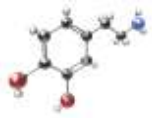
(iv) Carbonate ion (CO_3^{2-})



Resonance explain why all bonds are equivalent in length, energy.

Resonance energy: Difference in the energies of the canonical forms and resonance hybrid is called **resonance stabilization energy**.

The resonance hybrid is more stable than any of the resonating structure. **Greater the resonance energy more will be the stability to species.**



Rules for writing Resonating Structures:

(i) The various resonating structures differ in the position of electrons and not in the relative positions of atoms.

(ii) All the contributing structures should have the same number of unpaired electrons.

(iii) The various canonical structures shows same energy.

(iv) Resonance structures in which the negative charge resides on electronegative atom and positive charge resides on electropositive atom in resonance hybrid

(v) Resonance structures should be so written that unlike charges reside on adjacent atoms.

(vi) Resonance structure with greater number of covalent bonds contributes more towards the resonance hybrid.

SESSION - 10

AIM

1] To introduce bond parameters

2] To introduce formal charge

BOND PARAMETERS

- **Bond Length: The average distance between the nucleus of two bonded atoms** is known as bond lenght, normally it is represented in Å or pm (10^{-10} cm) or A^0 (10^{-8} cm).
- For the same atoms, **bond length decreases with the multiplicity of bonds.** Bond length $\propto \frac{1}{\text{Number of bond or bond order}}$

  C——C > C = C > C≡C

  Ex: C_2H_6 (1.54Å) > C_2H_4 (1.34Å) > C_2H_2 (1.20Å)
- **Bond length decreases with increase in s-characters** of the hybrid orbital used in bonding.

  sp^3-sσ> sp^2-sσ> sp- sσ
- **Polar bonds are shorter than theoretical non-polar** bonds.

  Actual H-Cl distance < theoretical H-Cl distance.
- When the **size of the atom increases, the bond length increases**

  Ex: F - F < Cl -Cl < Br - Br < I – I

- **Bond Energy or bond strength:** It is **amount of energy required to break one mole of the bonds to separate the bonded atoms in gaseous state.**

Factors affecting bond energy:

- **Size of the atoms**: Larger the size of the bonded atoms, larger is the bond length and lesser is the bond energy.

  Bond energy $\propto \frac{1}{\text{Atomic size}}$

  Ex: HF > HCl > HBr > HI
- **Multiplicity of bonds**: For the bond between the same two atoms, bond energy increases with the multiplicity of the bond.

  Bond energy ∝ Bond order

  Ex: C ≡C> C = C > C - C
- The **energy required for homolytic cleavage is more than that required for heterolytic**.
- **Number of lone pairs of electrons:**

  Greater the number of lone pair of electrons present on the bonded atoms, greater is the repulsive interactions between them and **smaller is the bond energy**
- **Bond Polarity :-** Bond energy ∝ polarity

  eg. H-F > H-Cl > H-Br > H-I
- **Hybridisation :- Bond energy ∝ s-character in hybrid orbitals.**

  eg. Sp-sp > sp^2-sp^2 > sp^3-sp^3

  s -character- 50% 33.3% 25%

  - **Bond Angle :- The angle between any two adjacent bond** is known as bond angle.

    It is represented in degree (°), min (') and second (")

    Factors affecting the bond angle

Following factors can affect bond angle:

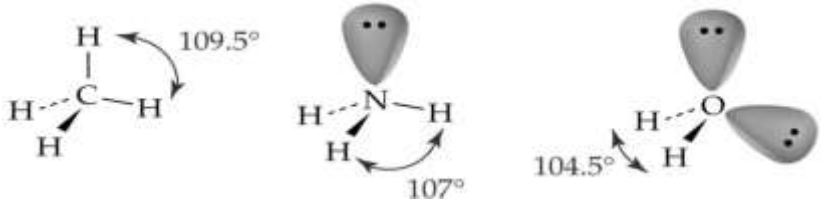
- **Hybridization of central atom:% of s character increases bond angle also increases**

  sp 180°

  sp^2 120°

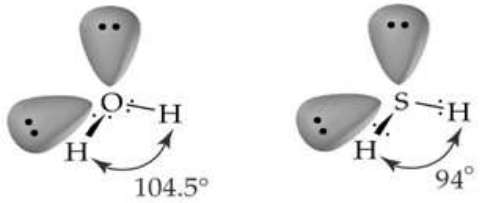
  sp^3 109.5°
- **Presence of lone pair:** Then bond angle $\propto \frac{1}{\text{No.of lone pair}}$

  bcz lp—bp repulsion is more than bp—bp



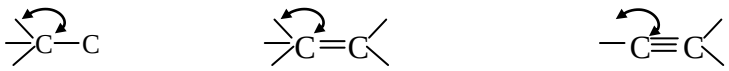
- **Electronegativity of central atom**: Due to more electronegativity of central atom bond pair get shifted toward it and distance between them decrease thus further bp—bp repulsion increases.

- bond angle ∝ electrongativity of central atom



- **Multiple bonds**:Electron density for double bond is more than in single bond, so repulsion in double bond is more than single bond.
  Bond angle ∝ Number of bonds (Bond order)

109° 120° 180°



FORMAL CHARGE

In a molecule,no charge on the molecule as a whole or in a polyatomic ion (e.g.,CO_3^{2-} or NH_4^+ ion etc.)but charge present on the ion is the charge on the ion as a whole and not on the individual atoms,

Formal charge is **the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis Structure**. or

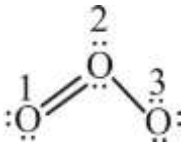
Individual charge possessed by an atom in a molecule.

Formal charge = Valence electrons of the atom – (Shared electrons of that atom + Unshared electrons of that atom).

Formal charge = Valence electrons of the atom – total number of lp electrons – ½ total number of bondind or shared electrons of that atom.

Ex. 1] Calculate formal charge on each O – atom of O_3 molecule.

Sol: Lewis structure of O_3 is:



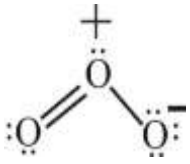
The atoms have been numbered as 1, 2 and 3.

Formal charge on end O – atom numbered 1 = 6 – 4 - $\frac{1}{2}$(4) = 0

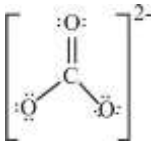
Formal charge on end O – atom numbered 2 = 6 – 2 - $\frac{1}{2}$(6) = +1

Formal charge on end O – atom numbered 3 = 6 – 6 - $\frac{1}{2}$(2) = -1

Hence, we represent O_3 along with formal charges as:

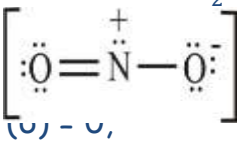


Ex. 2] Write the formal charges on atoms in (i) carbonate ion (ii) nitrite ion.

Sol:(i) Lewis structure of CO_3^{2-} ion is 

Formal charge on C atom = 4 – 0 – $\frac{1}{2}$(8) = 0, Formal charge on double bonded O atom = 6 – 4 – $\frac{1}{2}$ (4) = 0

Formal charge on single bonded O atoms = 6 – 6 – $\frac{1}{2}$(2) = –1

ii) Lewis structure of NO_2^- ion is 

Formal charge on N atom = 5 – 2 – $\frac{1}{2}$(6) – 0,

Formal charge on double bonded O atom = 6 – 4 – $\frac{1}{2}$(4) = 0

Formal charge on single bonded O atom = 6 – 6 – $\frac{1}{2}$(2) = –1

SESSION – 11

AIM To introduce hydrogen bonding

HYDROGEN BONDING is **electrostatic force of attraction existing between covalently bonded H atom of one molecule and the electronegative atom of the other molecule.**

This bond comes into existence when H atom is directly bonded to highly electronegative atom such as N, O or F.

Properties and conditions of HYDROGEN BOND

- H should be covalently bonded with high electro-ve element like F,O,N.
- Atomic size of electro-ve element should be small.

  Decreasing order of atomic size is N > O > F

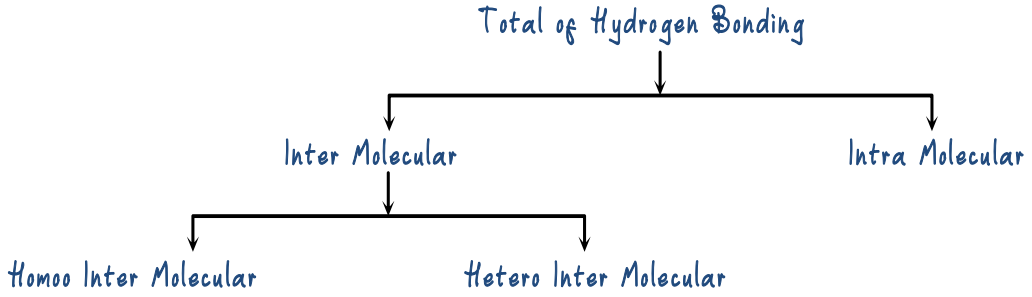
  Strength of H-bond ∝ Electronegativity of Z (element) ∝ $\frac{1}{\text{atomic size of Z}}$

- Hydrogen bonding occurs in HCN,due to (-C≡N)triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

  H—C≡N.....H—C≡N.....H—C≡N

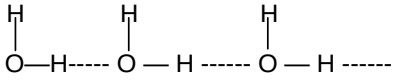
- A hydrogen bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms.
- Hydrogen bond is very weak compared to a covalent bond. The bond energy is in the range of 3-10 kcal/mole.
- Formation of H-bond does not involve sharing of electrons.

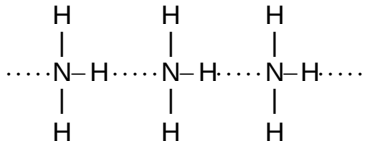
Types of hydrogen bonding

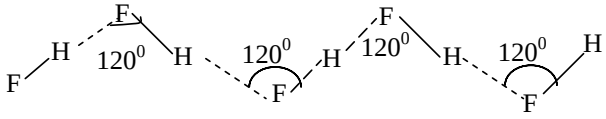


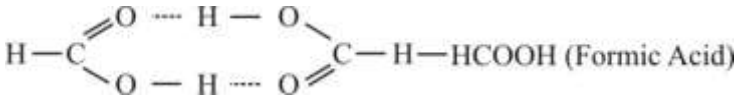
(a) Inter-molecular H-bonding present between two or more molecules (similar or different)

Example: (i) In H_2O, NH_3 and HF molecules:









No. of H-bonds in a molecule = No. of H-atoms attached to electro-negative element + No. of lp electrons on electronegative element.

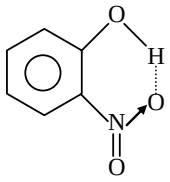
e.g.,**NH_3**, No. of H-bonds = 3 + 1 = 4

in H_2O, No. of H-bonds = 2 + 2 = 4

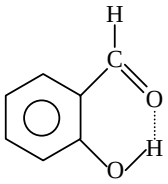
Effect of Intermolecular H-bonding:

- It **increases the boiling point** of the compound.
  E.g. BP of ethanol is higher than that of diethyl ether.
- With increase in intermolecular H-bonding the **physical state changes from gaseous to liquid and to solid.** Ex: HF, H_2O and NH_3 are associated liquids.
- Intermolecular hydrogen bonding **increases the solubility of the substance in water.** Ex: organic compounds like alcohols,amines are soluble in water
- **Ice has less density than water** In ice H-bonding absent so density decreases thats y **ice floats on water**
- **It increases the acidity of an acid**

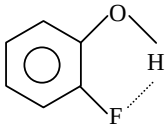
b)Intra-molecular Hydrogen Bonding here H - bonding takes place when hydrogen and the electronegative atom are present in the same molecule.



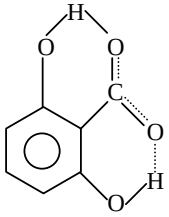
O-nitrophenol



Salicyladehyde



O-fluorophenol



2-6 dihydroxgyl benzoate

Conditions for formation of intramolecular hydrogen bonding:

- The ring formed should be planar
- Position of the interacting atoms should be such that there is minimum strain in ring formation.

e.g.,Intramolecular H-bonding not possible in m- & p- isomers of nitrophenol.

Effect of intramolecular H-bonding

- It decreases the boiling point of the compound.
- It increases the steam volatile nature of the compound.

  e.g., o-nitrophenol is steam volatile but p-nitrophenol is not.
- It increases the acid strength.

  e.g., salicyclic acid is stronger than p- Hydroxybenzoic acid.

SESSION – 12

AIM **To introduce MOT**

MOLECULAR ORBITAL THEORY (MOT) put forward by **Hund & Mulliken**, to overcome the limitations of VBT (Valence bond theory) was unable to explain

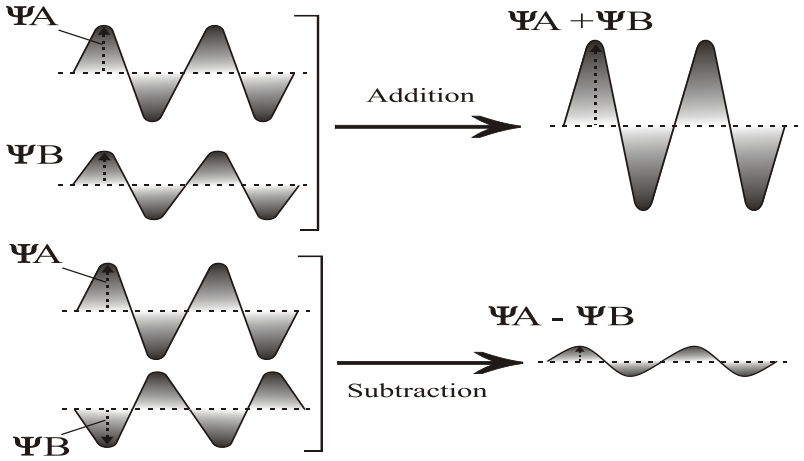
eg. Paramagniic nature Of O_2 molecule, as per VBT (:O: :O:) it should be diamagnetic.

According to this theory,all the atomic orbitals of the atoms participating in molecule formation.They all get mixed up to an equivalent number of new orbitals that belong to the molecule now. These are called **Molecular Orbitals**.

This theory is based on principal of

Linear combination of atomic orbitals (LCAO).

- Electron waves nothing but **atomic orbitals have positive and negative phase**. When waves are combined, they may interact either **constructively or destrcuctively**.
- If **two identical waves are added**, they combine constructively to produce the wave with **double the amplitude and same wavelength** and form two new orbitals called 'bonding molecular orbital' (BMO)
- Conversely, if **they are subtracted**, they combine destructively to produce the **wave with less or zero amplitude** gives **antibonding molecular orbital' (ABMO)**.



Suppose ψ_A and ψ_B **represents the amplitude of electron waves** of the 2 atomic orbitals of the atoms A and B respectively, then the situation may be represented as follows:

Case I: When the two waves are **in phase (constructive interface)**, so that they **add up** and the **amplitude** of the new wave is:

$$\phi = \psi_A + \psi_B$$

The **probability pf electron density** is given by the **square of the amplitude**, therefore, we have

$$\phi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\text{i.e.,} \quad \phi^2 > \psi_A^2 + \psi_B^2$$

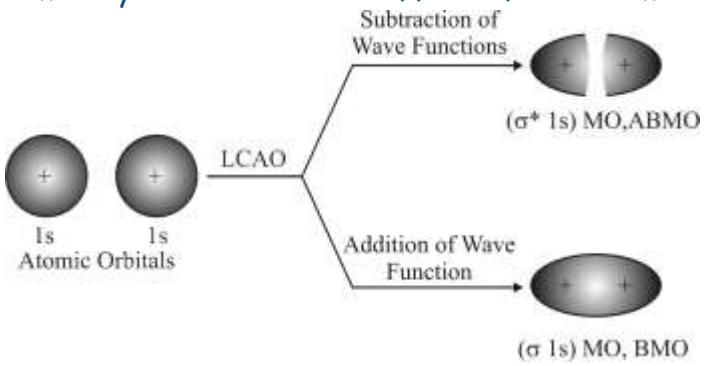
The molecular orbital formed by the additive effect or constructive interference of the atomic orbitals are called **BMO**.

Case I: When the two waves are **out of phase (destructive interface)**, the waves are **subtracted** from each other so that the **amplitude** of the new wave is: $\phi = \psi_A - \psi_B$

The **probability pf electron density** is given by the **square of the amplitude**, therefore, we have

$$\phi^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$
$$\text{i.e. } \phi_1^2 < \psi_A^2 + \psi_B^2$$

The molecular orbital formed by the subtractive effect of the atomic orbitals is called **ABMO**.



Combination of 1s atomic orbital of both atoms

Energy of BMO is always less than the energy of the atomic orbitals. But energy of the ABMO is higher than the energy of atomic orbitals.

Bcz in the BMO, **electron density in the intern clear region is high** so the nuclei are shielded from each other and the between the nuclei are very small.

In ABMO, the **electron density in the internuclear region is very low**. As a result, the **nuclei are directly exposed to each other** i.e., there is very less shielding. Hence the repulsions between the nuclei are very large.

- **Electrons present in BMO contribute towards the stability** of molecule where **electrons present in ABMO destabilize** the molecule
- Atomic orbitals participating in combination must have comparable energies.

  Ex: For homogeneous diatomic molecule, 1s atomic orbital of one atom can combine with 1s atomic orbital of another atom or 2s can combine with 2s and 2p with 2p and so on.

- Combining atomic orbitals must have proper orientation.

  I.e. same symmetry about the molecular axis.

  Ex: Taking 2-axis as the molecular axis, $2P_z$ orbital of one atom can combine with $2p_z$ of another atom but not with $2p_x$ or $2p_y$ orbitals because of their different symmetry.

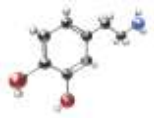
- BMO's are represented as σ, π, δ etc. While ABMO's are represented as $\sigma^*, \pi^*, \delta^*$ etc.

  Thus, 1s atomic orbitals of two atoms combine to form two MO's labeled as σ**1s**(BMO) and σ^***1s**(ABMO).

  Similarly ,2**s** atomic orbitals combine to form σ2**s** and σ^***2s** of the 2p-orbitals.

  If z-axis is taken as molecular axis,

Combination of two $2p_x$ or two $2p_y$ atomic orbitals to form $\pi(2p_x)$ and $\pi^*(2p_x)$ or $\pi(2p_y)$ and $\pi^*(2p_y)$ molecular orbitals



- Filling of electrons in Molecular Orbitals occurs according to Aufbau principle, Pauli's exclusion principle and Hund's rule.
- The shape of the molecular orbitals depends upon the shapes of combining orbitals.
- The presence of one or more unpaired electrons in a molecule shows **paramagnetic nature**. Electronic configuration having all the electrons paired suggests its **diamagnetic nature**.

Comparision of Bonding molecular orbital & Antibonding molecular orbital

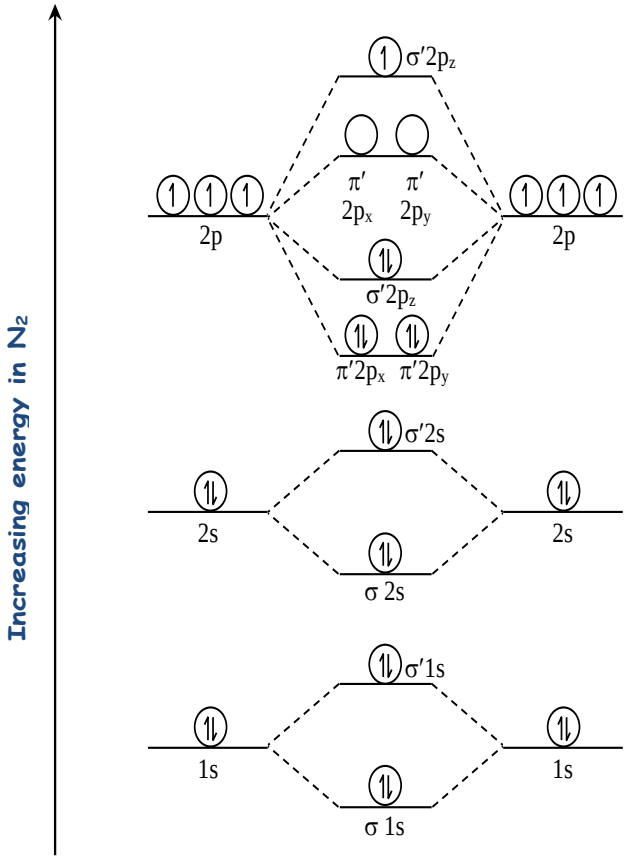
Bonding molecular orbital (BMO)	Antibonding Molecular orbital
• Bonding MO is the result of the linear combination of AO when their wave function are added $\phi = \psi_A + \psi_B$	• ABMO is resulting of linear combination of AO when their wave function are subtracted $\phi = \psi_A - \psi_B$
• It does not have node	• It always have a node between two nuclei of bonded atom
• Charge density increase between two nuclei resulting between two atoms	• Charge density decrease in between two nuclei, leads to repulsion between two atoms.
• Energy of BMO is less, hence stable	• Energy of ABMO is high, hence unstable

Energy Level Diagram of molecular orbital :

- For diatomic homonuclear molecules such as Li_2, Be_2, B_2, C_2, N_2 is (where the energy difference between 2 s and 2 p-orbitals is large and hence they cannot interact)

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

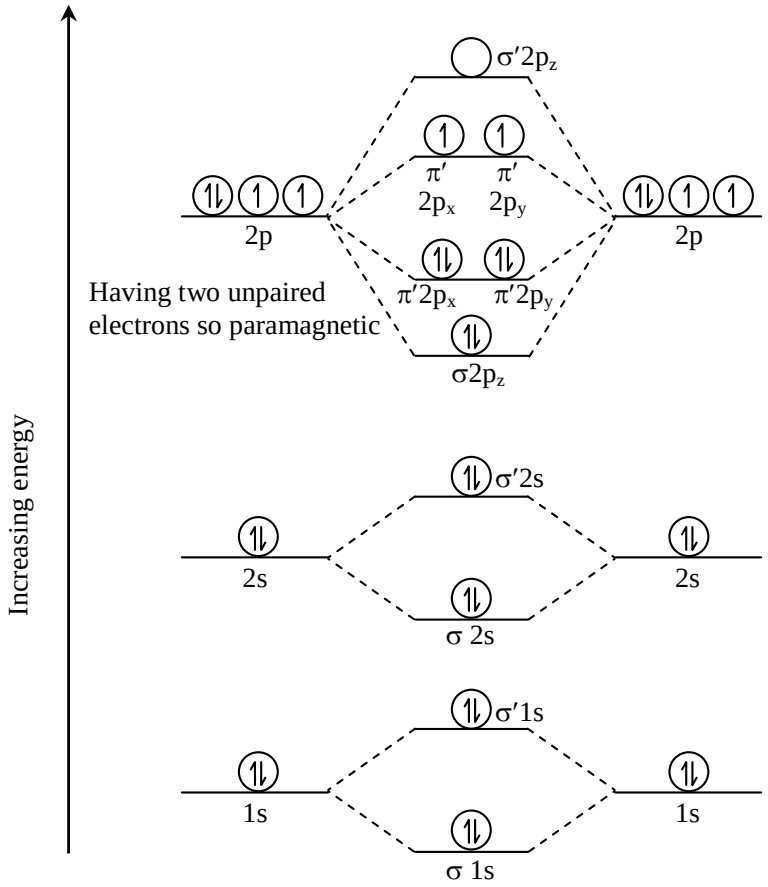
For N_2 type molecule



- For homogeneous diatomic molecules such as O_2, F_2, Ne_2, (where the difference in energies between 2**s** and 2p-orbitals is small and hence they can interact)the energy diagram is

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$

For O_2 type molecule-



Bond order $\frac{1}{2}(8-4) = 2$

Bond order	$O_2 = 1/2\,[8-4] = 2$
	$O_2^+ = 1/2\,[8-4] = 2.5$
	$O_2^- = 1/2\,[8-5] = 1.5$
	$O_2^{2-} = 1/2\,[8-5] = 1.5$
	$O_2^{+2} = 3$
Stability order -	
	$O_2^{+2} > O_2^+ > O_2 > O_2^- > O_2^{2-}$
Bond length –	
	$O_2^{2-} > O_2^- > O_2 > O_2^+ > O_2^{+2}$

INFORMATION FROM MO CONFIGURATIONS

(a) Bond order (B.O.) = $\frac{1}{2}$ (N_b - N_a) or it is defined as **half of the difference between the number of electrons present in the bonding and the antibonding orbitals.**

Where N_b = no. of electrons in the bonding MO's

N_a= no. of electrons in the antibonding MO's.

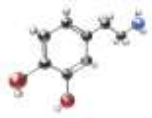
If bond order is more than zero, the molecule/ion exists, otherwise not.

- **Bond dissociation energy** - Higher the bond order, higher is the bond dissociation energy.
- **Stability** - Higher the bond order, greater is the bond stability.

If $N_b > N_a$ the molecule is stable .bcz greater number of bonding orbitals are occupied than antibonding orbitals, resulting in a net force of attraction.

If $N_b < N_a$, the molecule is unstable. Bcz the antibonding influence is greater than the bonding influence, resulting in a net force of repulsion.

If $N_b = N_a$, the molecule is again unstable.Bcz the numbers of electrons are equal, the antibonding influence of the electrons in the antibonding molecular orbitals is greater than the bonding influence of the electrons in the bonding molecular orbitals.



- **Bond length**- Higher the bond order, shorter is the bond length.

(b) **Magnetic properties**: Molecule/molecular ion are **paramagnetic** (atleast one electrons is unpaired) or **diamagnetic**(if all the electrons are paired).

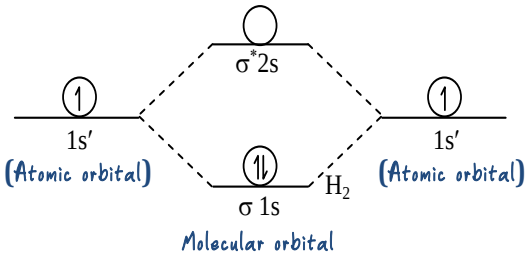
Bonding in molecules :-

(I) H_2 molecule- Having two H atoms with one electron(1s')

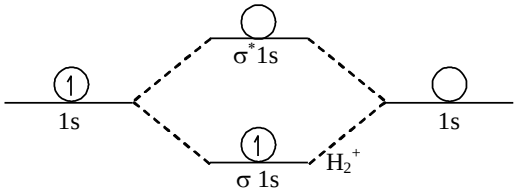
M.O. configuration of H_2 = $(\sigma 1s)^2$ $(\sigma^* 1s)^0$

Bond order = $\frac{1}{2}$ [N_b – N_a] = $\frac{1}{2}$ [2 – 0] = 1 i.e. **single bond**

Having paired electron so **diamagnetic**.



(II)H_2^+ ion –



M O Configuration of H_2^+ = $(\sigma 1s)^1$ $(\sigma 1s)^0$

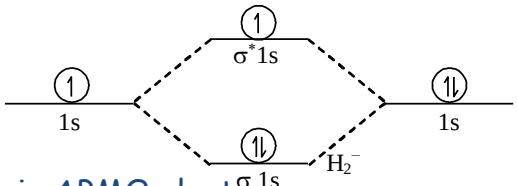
One electron in bonding molecular orbital - paramagnetic

Bond order = $\frac{1}{2}$ [1– 0] = $\frac{1}{2}$

Less stable

(III) H_2^- anion –

M.O. configuration - $(\sigma 1s)^1$ $(\sigma 1s)^1$



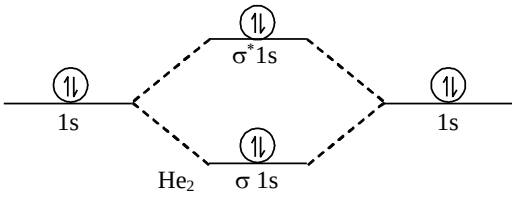
Paramagnetic

Bond order = $\frac{1}{2}$ [2 – 1] = $\frac{1}{2}$

Stability is less than [H_2^+] because H_2^- Contain ABMO electron

(IV) Helium molecule (He_2) :

M.O. configuration (□□1s)^2 (□□□1s)^2



Diamagnetic

Bond order = $\frac{1}{2}$ [2 – 2] = 0 (zero)

Bond order is zero shows no bond between He atoms.So **He_2 molecule does not exist**

Stability (He_2) Highly unstable molecule



(V) (He_2^+)

EC of He = $1s^2$, He^+ = $1s^1$.

MOC = $(\sigma 1s)^2 < (*1s)^1$

Bond order = $\frac{1}{2}$,

Nature – paramagnetic (stable).

(V)Lithium molecule (Li_2): ECofLi $- 1s^2, 2s^1$

MOC = $(\sigma 1s)^2 < (\sigma *1s)^2 < (\sigma 2s)^2$, Bond order = 1

Nature = diamagnetic.

(VI)Beryllium molecule (Be_2) : Be – $1s^2$, $2s^2$

$\mathrm{MOC} = (\sigma 1s)^2 < (\sigma * 1s)^2 < (\sigma 2s)^2 < (\sigma * 1s)^2$

Bond order = 0, nature – diamagnetic (does not exist)

(VII)Boron molecule (B_2) : $\mathrm{B} - 1s^2 2s^2 2p^1$

$\mathrm{MOC} = (\sigma 1s)^2 < (\sigma * 1s)^2 < (\sigma 2s)^2 < (\sigma * 2s)^2 < (\pi 2p_x)^1 = (\pi 2p_y)^1$

BO = 1, Nature = paramagnetic

x) Carbon molecule (C_2) : $6\mathrm{C} - 1s^2 2s^2 2p^2$

$\mathrm{MOC} = (\sigma 1s)^2 < (\sigma * 1s)^2 < (\sigma 2s)^2 < (\sigma * 2s)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\sigma 2p_z)^0$,

Bond order = 2, Nature = diamagnetic

xi) Nitrogen molecule (N_2):

$\mathrm{MOC} = (\sigma 1s)^2 < (\sigma * 1s)^2 < (\sigma 2s)^2 < (\sigma * 2s)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\sigma 2p_z)^2$

Nature – diamagnetic.

BO = 3,

Order of bond order of N_2, N_2^+, N_2^-, N_2^{2-} is $N_2 > N_2^+ = N_2^- > N_2^{2-}$

xi) Oxygen molecule (O_2) : O – $1s^2$ $2s^2$ $2p^4$

Molecular orbital energy level diagram for O_2

$\mathrm{MOC} = \mathrm{KK} < (\sigma 2s)^2 < (\sigma * 2s)^2 < (\sigma 2p_z)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\pi * 2p_x)^1 = (\pi * 2p_y)^1$

BO = 2, Nature – paramagnetic

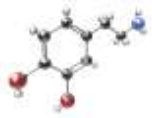
Order of bond order of O_2, O_2^+, O_2^+, O_2^-, O_2^{2-} is $O_2^{2+} > O_2^+ > O_2 > O_2^- > O_2^{--}$

xii) Fluorine molecule (F_2) : F – $1S^2$ $2S^2$ $2P^5$

$\mathrm{MOC} = (\sigma 1s)^2 < (\sigma * 1s)^2 < (\sigma 2s)^2 < (\sigma * 2s)^2 < (\sigma 2p_z)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\pi * 2p_x)^2 = (\pi * 2p_y)^2$

BO = 1, Nature diamagnetic (Stable, BDE = 151 kJ mol^{-1})

xii) **Neon molecular does not exists because Bond order is zero.**



MO CONFIGURATIONS OF HETERONUCLEAR DIATOMIC SPECIES:

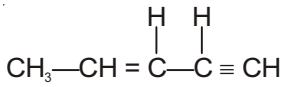
Molecule or ion	Molecular orbitalConfiguration	Bondorder	upaired Electrons	Magentic character
CN($13e^-$)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2(\sigma 2p_z)^1$	$\frac{7-2}{2}2.5$	1	Paramagnetic
CN^-($14e^-$)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $(\pi 2p_y)^2\sigma(2p_z)^2$	$=3.0$	Nil	Diamagnetic
NO ($15e^-$)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2\sigma(2p_z)^2\pi^*(2p_x)^1$	$\frac{8-3}{2}$ $=2.5$	1	Paramagnetic
NO^+ ($14e^-$)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2\sigma(2p_z)^2\pi^*(2p_x)^0$	$\frac{8-2}{2}$ $=3.0$	Nil	Diamagnetic
NO^{2+}($13e^-$)	$KK\sigma(2s)^2\sigma^*(1s)^2\sigma(2p_z)^2$ $\pi(2p_x)^2)\pi(2p_y)^1\pi^*(2p_x)^0$	$\frac{7-2}{2}$ $=2.5$	1	Paramagnetic
CO ($14e^-$)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2\sigma(2p_z)^2$	$\frac{8-2}{2}$ $=3.0$	Nil	Diamagnetic

SECTION - A

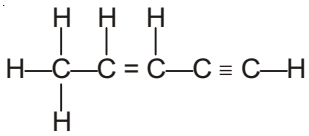
School/Board Exam. Type Questions

Very Short Answer Type Questions :

1. What is total number of sigma and pi bonds in the following structure?



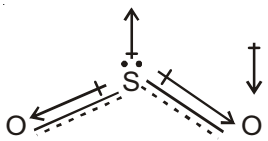
Sol.



It contains 10 sigma (σ) bonds and 3 pi (π) bonds.

2. Sketch the bond moments and resultant dipole moment in SO_2.

Sol.



3. Define ionic bond.

Sol. An ionic bond is a link formed as a result of the electrostatic attraction between the positive and negative ions.

4. Define a covalent bond.

Sol. A covalent bond is a chemical bond which is formed by the sharing of a pair of electrons between atoms.

5. Give reason, sucrose is a covalent compound but it is quite soluble in water.

Sol. The molecule of sucrose contains many –OH groups and hence are capable of forming H–bond with water.

6. Why hydrogen bonding does not exist in HCl though chlorine is quite electronegative?

Sol. This is due to large size of Cl–atom.

7. Why o-nitrophenol has lower boiling point than p-nitrophenol?

Sol. *p*-nitrophenol has higher boiling point due to intermolecular H-bonding.

8. Which *d*-orbital is involved in dsp^2 hybridisation?

Sol. $d_{x^2-y^2}$. This is because its four lobes lie along the x-axis and y-axis. The two *p*-orbitals can combine along these axes.

9. Define electrovalency.

Sol. The electrovalency is defined as the number of electron lost or gained by an atom. It is equal to the number of unit charge on the ion.

10. Write the electronic configuration and Lewis symbol for N^{3-}.

Sol. The electronic configuration of the N^{3-} ion is $1s^2\ 2s^2\ 2p^6$ and its Lewis symbol is $\left[\cdot\dot{\underset{\cdot}{\overset{\cdot}{N}}}\cdot\right]^{3-}$.

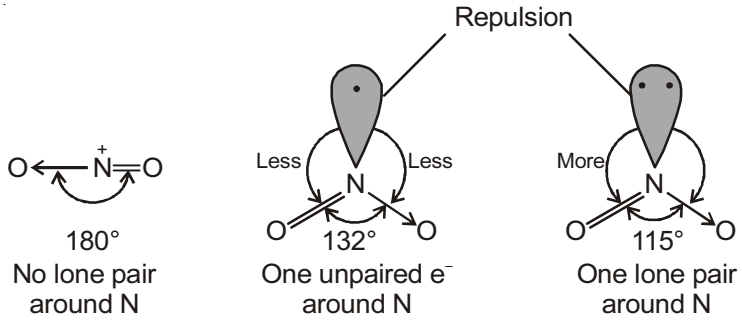
Short Answer Type Questions :

11. How do bond length of C–H bond differ in C_2H_6, C_2H_4 and C_2H_2?

Sol. Hybrid states of C atom in C_2H_6, C_2H_4 and C_2H_2 are respectively sp^3, sp^2 and sp. C–H bonds in C_2H_6, C_2H_4 and C_2H_2 are respectively $sp^3 - s\sigma$, $sp^2 - s\sigma$ and $sp - s\sigma$ bond. Since size of hybrid orbitals varies as $sp^3 > sp^2 > sp$. Therefore, $(sp^3 - s)\ \sigma > (sp^2 - s)\ \sigma > (sp - s)\ \sigma$ bond.

12. Arrange the following in order of decreasing bond angle around N atom, NO_2, NO_2^+, NO_2^-.

Sol. NO_2^+ is linear as there is no lone pair on N atom. NO_2 and NO_2^-, both have bent shape. In NO_2, there is one odd electron on N atom but in NO_2^- there is one lone pair of electron on N atom.



Bond angle around N decreases

13. How is VB theory different from Lewis concept in regard to the formation of covalent bond?

Sol. (i) Lewis concept considers the formation of covalent bond by mutual sharing of electrons. VB theory considers the formation of covalent bond by overlap of half filled atomic orbitals.

(ii) Lewis concept does not provide explanation for different shapes of molecules but VB theory does explain molecular shapes.

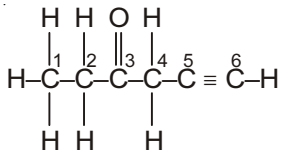
(iii) Lewis concept does not explain the bond strength but VB theory is able to explain it.

14. Consider the structure $\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}O\overset{4}{C}H_2\overset{5}{C}\equiv\overset{6}{C}H$ and answer the following:

(i) Which atoms in the structure have same hybrid state?

(ii) Arrange the atoms C_2, C_3, C_5 in decreasing order of s-character of bonding orbitals.

Sol. The given structure is



The hybrid states of various carbon atoms is

C_1 (sp^3) ; C_2 (sp^3) ; C_3 (sp^2) ; C_4 (sp^3) ; C_5 (sp) ; C_6 (sp)

(i) C_1, C_2, C_4 atoms have sp^3 hybrid state; C_5, C_6 atoms have sp hybrid state.

(ii) Decreasing order of s-character is $C_5 > C_3 > C_2$.

15. Arrange the following species in order of decreasing bond angles around the central atom in each set

(i) CH_4, NH_3, H_2O, BCl_3, C_2H_2

(ii) NH_3, NH_2^-, NH_4^+

(iii) H_2O, H_2Se, H_2Te, H_2S, $ZnCl_2$, CO_2.

Sol. (i) C_2H_2 (180°) > BCl_3 (120°) > CH_4 (109°.28′) > NH_3 (107°) > H_2O (104.5°).

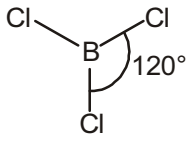
(ii) NH_4^+ (109°.28′) > NH_3 (107°) > NH_2^- (≈ 105°).

(iii) CO_2 (180°) > H_2O (104.5°) > H_2S (92°) > H_2Se (90.5°) > H_2Te (≈ 90°).

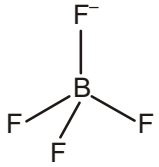
16. BF_3 is planar but anhydrous BF_4^- is tetrahedral. Explain.

Sol. In BF_3 molecule, B atom assumes sp^2 hybrid state. The three sp^2 hybrid orbitals are used to form sigma bonds with 3 fluorine atoms to give trigonal planar structure.

In anhydrous BF_4^-, boron atom is sp^3 hybridised, so it is tetrahedral.



Trigonal planar structure of BCl_3



Dimer of $AlCl_3$

17. (i) How bond energy varies from N_2^- to N_2^+ and why?

(ii) On the basis of molecular orbital theory what is similar between

(a) F_2, O_2^{--}

(b) CO, N_2, NO^+

Sol. (i) Bond energy of N_2^+ ≈ bond energy of N_2^-. This is because they have the same bond order (N_2^- is slightly less stable and hence has less bond energy than N_2^+ due to presence of greater number of electrons in the antibonding molecular orbitals).

(ii) (a) Same bond order and bond length.

(b) Same bond order and bond length.

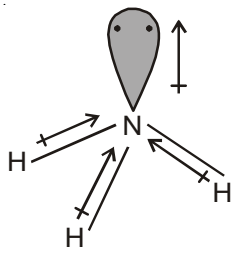
18. What is the hybrid state and shape of $BeCl_2$?

Sol. In the vapour state at high temperature, $BeCl_2$ exists as linear molecule, Cl–Be–Cl. The hybridization of the central atom is sp.

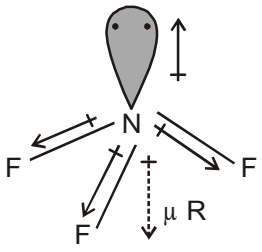


19. Out of NH_3 and NF_3 which has more polarity. Give reasons using diagram of bond moments.

Sol. NH_3 is more reactive than NF_3 because NH_3 is more polar as compared to NF_3. The higher dipole moment of NH_3 is because of the fact that in NH_3 the three N–H bond moments reinforce the lone pair moment while in NF_3, the three N–F bond moments oppose the lone pair moment.



$\mu = 4.9 \times 10^{-30}$ Cm



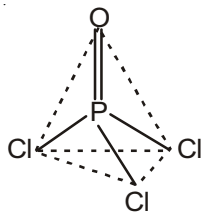
$\mu = 0.8 \times 10^{-30}$ Cm

20. Draw the structure of :

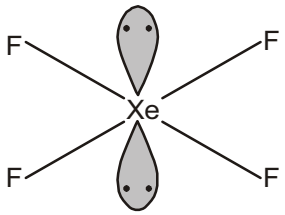
(i) $POCl_3$

(ii) XeF_4

Sol.



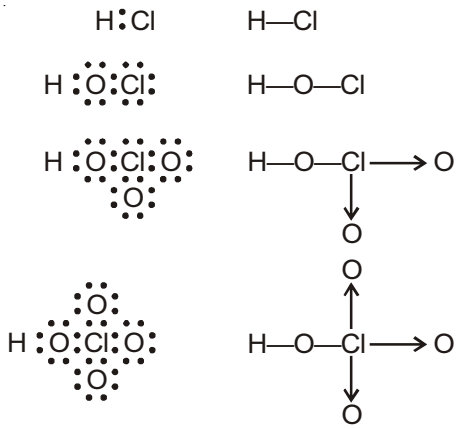
Tetrahedral



Square planar

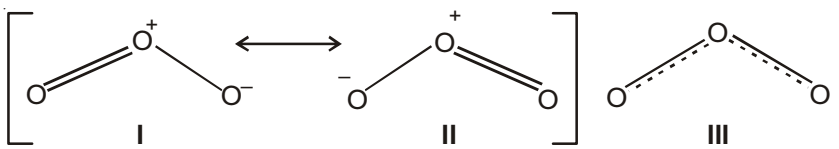
21. Represent the bonding in HCl (hydrochloric acid), HClO (hypochlorous acid); $HClO_3$ (Chloric acid) and $HClO_4$ (Perchloric acid) in terms of Lewis dot representation.

Sol.



22. Give two resonating structures of ozone which satisfy octet rule? Also give the probable hybrid structure.

Sol. The resonating structure of O_3 molecule which satisfy the octet rule are structure **I** and structure **II**. The probable hybrid structure is represented by **III**.



Resonating structure **Hybrid structure**

23. (i) Why melting point of MgO (2800°C) is much higher than that of BaO (1920°C)?

(ii) Why solubility of $MgCl_2$ much greater than that of MgF_2?

(iii) Why AlF_3 is a high melting solid whereas SiF_4 is a gas?

Sol. (i) Lattice enthalpy of MgO is higher than that of BaO due to relatively larger size of Ba^{2+} ion.

(ii) Size of Cl^- ions is larger than F^- ions consequently, Lattice enthalpy of $MgCl_2$ is smaller than that of MgF_2. Due to smaller value of $\Delta_L H°$ of $MgCl_2$, its solubility in water is relatively more.

(iii) AlF_3 is ionic compound while SiF_4 is a non polar covalent compound. Hence interparticle forces in AlF_3 are quite strong.

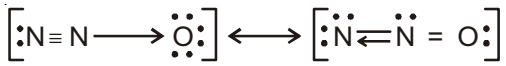
24. (i) Arrange the following in order of increasing bond strength F_2, N_2, O_2, Cl_2.

(ii) Give two resonating structures of N_2O which satisfy octet rule.

Sol. (i) $F_2 > Cl_2 < O_2 < N_2$.

O_2 has double bond while N_2 has triple bond. The bond strength of F_2 is smaller because the presence of three lone pairs around each F atom cause repulsive interactions. It is because of very small size of F atom.

(ii) The two resonating structure of N_2O are



25. Using VSEPR theory identify the type of hybridisation and draw the structure of OF_2.

Sol. The Lewis dot structure of OF_2 is



Since O is surrounded by 2 bond pair and 2 lone pair. Hence, arrangement of lone pair and bond pair should be tetrahedral. Therefore hybrid state of O should be sp^3.

26. (i) Why $BeCl_2$ is linear molecule while $SnCl_2$ is angular?

(ii) What type of ionic species constitute the compound $CsBr_3$?

Sol. (i) Be is surrounded by only two bond pairs while in $SnCl_2$, Sn is surrounded by two bond pairs as well as one lone pairs.

(ii) The ionic species constituting $CsBr_3$ and Cs^+ and tribromide ions (Br_3^-).

27. (i) KHF_2 is known but $KHCl_2$ is not known. Explain.

(ii) Which of the following has highest bond angle?

H_2O, CO_2, NH_3, CH_4

(iii) Among N_2O, SO_2, I_3^+ and I_3^-, which are linear species?

Sol. (i) In KHF_2, the ions present are K^+ and HF_2^-. The HF_2^- ion is formed by combination of H–F and F^- ions due to H-bonding. $[F\ldots\ldots H–F]^-$. The corresponding $[HCl_2]^-$ ion is not possible because Cl^- ion cannot form effective H-bonding with HCl.

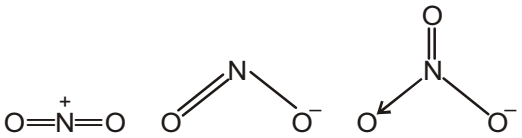
(ii) Highest bond angle is in CO_2 *i.e.*, 180°.

(iii) N_2O and I_3^- are linear species.

28. Arrange the following in order of (i) increasing N–O bond length (ii) Increasing bond angles. Also Give reasons: NO_2^+, NO_2^-, NO_3^-.

Sol. Type of hybridisation of central atom, *i.e.*, N atom in NO_2^+ is sp hybridised while in NO_2^- and NO_3^-, it is sp^2 hybridized.

Their structures are :



Bond angle	180°	>	132°	>	120°
Bond order	2		$\frac{2+1}{2} = 1.5$		$\frac{2+1+1}{3} = 1.33$
Bond angle	NO_2^+	<	NO_2^-	<	NO_3^-

29. Which of the two, peroxide ion or superoxide ion has larger bond length?

Sol. The bond length in a molecule is dependent on bond order. The higher is the bond order, smaller will be the bond length.

Peroxide ion, O_2^{2-}

$O_2^{2-} : K\,K\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_y)^2(\pi 2p_x)^2(\pi^* 2p_y)^2(\pi^* 2p_x)^2$

Bond order = $\frac{8-6}{2} = 1$

Superoxide ion, O_2^-

$O_2^- : K\,K\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_y)^2(\pi 2p_x)^2(\pi^* 2p_y)^2(\pi^* 2p_x)^1$

Bond order = $\frac{8-5}{2} = 1.5$

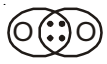
Bond order of superoxide ion is higher than peroxide ion, hence bond length of peroxide ion is larger.

30. Define a single covalent bond and double covalent bond.

Sol. A single covalent bond has only one shared pair of electrons between the two atoms.

For example : 

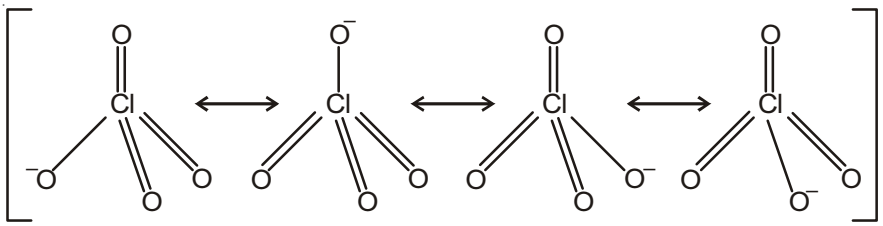
If two atoms share two pairs of electrons, the covalent bond between them is called a double covalent bond.

For example : 

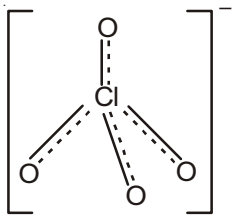
Long Answer Type Questions :

31. All the chlorine-oxygen bond distances in ClO_4^- are 144 pm. What explanation can be given for this?

Sol. ClO_4^- ion is resonance hybrid of the following structures:



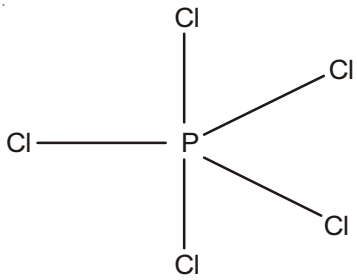
The probable hybrid structure is



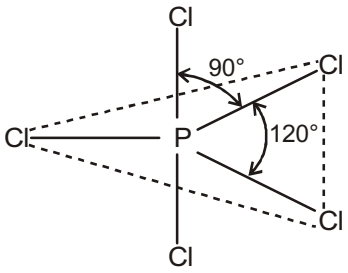
All the Cl–O bonds are equivalent having bond order = 1.75.

32. Using VSEPR theory draw molecular structure of PCl_5 and BrF_5 molecules.

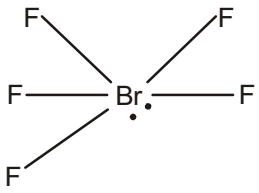
Sol.



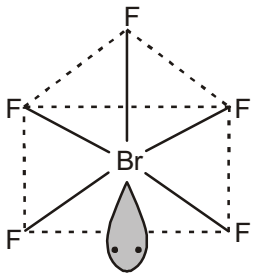
P atom has five bond pairs around it which assume trigonal bipyramidal arrangement.



Trigonal bipyramidal geometry angle around P = 90° and 120°. Axial P—Cl bonds are longer than equatorial bonds.



Br atom has 5 bond pairs and 1 lone pair around it. Hence five F atoms and one lone pair assume octahedral arrangement giving square pyramidal shape.



Square pyramidal shape

33. Arrange the following compound in the increasing order of bond length of O–O bond. O_2, $O_2(AsF_6)$, KO_2. Explain on the basis of ground state electronic configuration of dioxygen in these molecules.

Sol. In $O_2(AsF_6)$, oxygen is present as O_2^+ while in KO_2 it is present as O_2^- ions. Now M.O. electronic configuration of O_2, O_2^+ and O_2^- are

$$O_2 : K\,K\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$$

Bond order = $(8 - 4) \times \frac{1}{2} = 2$

$$O_2^+ : K\,K\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1$$

Bond order = $(8 - 3) \times \frac{1}{2} = 2.5$

$$O_2^- : K\,K\,(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^1$$

Bond order = $(8 - 5) \times \frac{1}{2} = 1.5$

Thus, increasing order of O–O bond length is

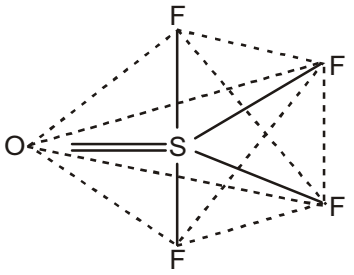
$KO_2 > O_2(AsF_6) > O_2$.

34. Using VSEPR theory draw the molecular structure of

(i) SOF_4

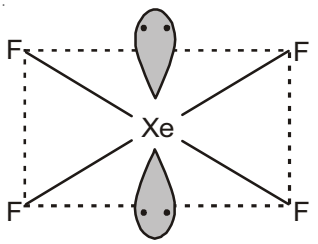
(ii) XeF_4 molecules

Sol. (i) In OSF_4, there are four F atoms bonded to sulphur by σ bonds while O atom is bonded to sulphur by double bond. Thus the molecule adopts trigonal bipyramidal arrangement with S = O bond taking the equatorial position because of the relatively smaller repulsive interactions.



Trigonal bipyramidal arrangement

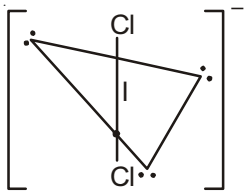
(ii) In XeF_4, Xe atom is surrounded by four bond pairs and two lone pairs. These four F atoms and two lone pairs adopt octahedral arrangement giving square, planar shape to the molecule. The lone pairs occupy diagonally opposite arrangement.



Square planar shape

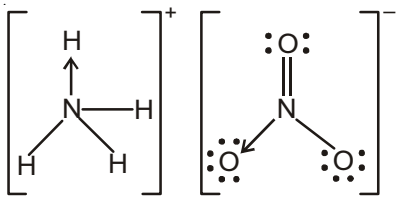
35. Explain the shape of ICl_2^- ion.

Sol. Type of hybridisation, H = $\frac{1}{2}$ [7 + 2 – 0 + 1] = 5, *i.e.*, sp^3d hybridisation. The central atom I undergoes sp^3d hybridization. The electronic configuration of I atom in ground state is $5s^2\ 5p_x^2\ 5p_y^2\ 5p_z^1\ 5d^0$. It undergoes hybridization giving 5 hybrid orbitals. Three hybrid orbitals contain lone pair of electrons each and occupy equatorial positions of the trigonal bipyramid. One hybrid orbital is half filled, it overlaps with an orbital of chlorine atom and forms a covalent bond. One hybrid empty orbital accepts an electron pair from Cl ion to form a co-ordinate bond. The Cl atoms are present on axial positions.



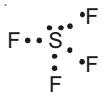
36. Indicate the type of bonds present in NH_4NO_3 and state mode of hybridization of two N-atoms in it.

Sol. NH_4NO_3 is an ionic compound in which cation is NH_4^+ ion and anion is NO_3^- ion. In NH_4^+ ion, three covalent bonds and one co-ordinate bond is present. The nitrogen is in sp^3 hybrid state, *i.e.*, the species is tetrahedral. In NO_3^-, nitrogen is in sp^3 hybrid state, *i.e.*, the species is trigonal planar. One oxygen is linked by a double bond, other by a covalent bond and third by a co-ordinate bond.



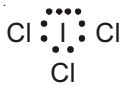
37. Apply VSEPR theory to predict the shapes of SF_4, ICl_3, $PbCl_2$ and NH_4^+.

Sol. The Lewis structure of SF_4 is :

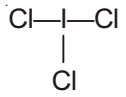


S atom is surrounded by five electron pairs (4 bonded and one lone pair) thus, the geometry is trigonal bipyramidal. The actual shape is see-saw.

The Lewis structure of ICl_3 is :



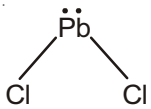
Iodine is surrounded by five electron pairs (3 bonded and two lone pairs). Thus, the geometry is trigonal bipyramidal. The actual shape is T-shape.



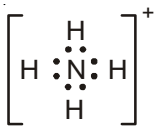
The Lewis structure of $PbCl_2$ is :



Pb is surrounded by three electron pairs (2 bonded and one lone pairs). Thus, the geometry is trigonal planar. The actual shape is V-shape, *i.e.*, bent structure.



The Lewis structure of NH_4^+ ion is :



Nitrogen is surrounded by four bonded pairs. The shape is thus tetrahedral.

38. Draw Lewis structures for

(i) H_2CO_3

(ii) SF_6

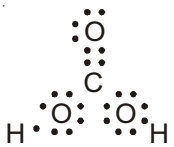
(iii) PF_5

(iv) IF_7

(v) CS_2

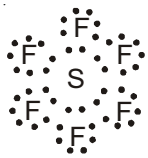
Is the octet rule obeyed in these cases?

Sol. (i) H_2CO_3



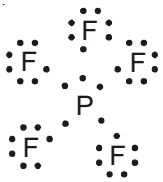
C and all three O atoms obeying octet rule. Only H-atom has two valence electrons.

(ii) SF_6



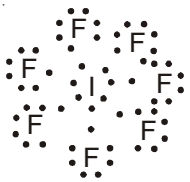
S-atom is not obeying the octet rule. S atom has 12 valence electrons.

(iii) PF_5



Phosphorus has an expanded octet and tatal 10 electrons.

(iv) IF_7



Iodine is not obeying the octet rule. It has total 14 electrons.

(v) CS_2



CS_2 is obeying the Lewis octet rule.

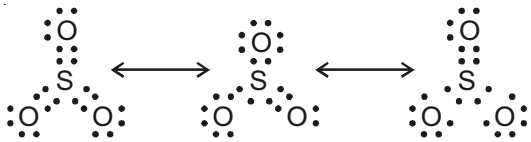
39. Write resonance structures for

(i) SO_3

(ii) NO_2

(iii) NO_3

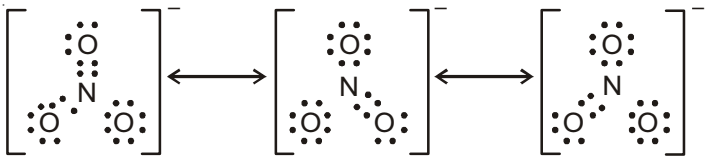
Sol. (i) SO_3



(ii) NO_2



(iii) NO_3^-



40. What do you understand by dipole moment? Give its SI units.

Sol. A dipole consists of a positive and negative charge (equal in magnitude) separated by a distance within a molecule. Dipole moment is defined as the product of the magnitude of charge on any one of the atoms and the distance between them.

Dipole moment is represented by μ (mu).

μ = charge (q) × distance of separation (r)

Dipole moment is usually expressed in debye units (D). The conversion factor is

$1D = 3.33564 \times 10^{-30}$ Cm

where C is coulomb and m is metre.

Dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as :



The shift in electron density is symbolised by crossed arrow ($\overset{+}{\longrightarrow}$) above the Lewis structure to indicate the direction of the shift.

41. Predict whether each of the following molecule is polar or non-polar.

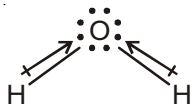
(i) H_2O

(ii) CCl_4

(iii) PCl_5

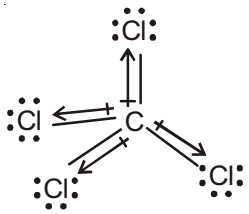
(iv) BF_3

Sol. (i) **H_2O**



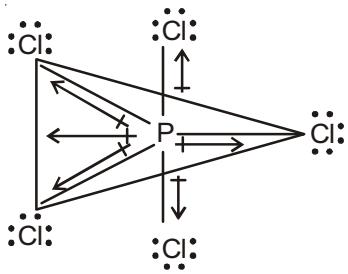
The bond dipole point from the H atoms towards the more electronegative O atom. The H_2O molecule has a non zero dipole moment, hence water molecule is polar.

(ii) **CCl_4 :** Tetrahedral in shape. The Lewis diagram is



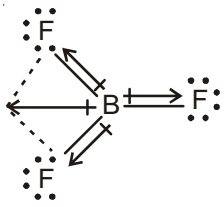
The molecule has a zero dipole moment and hence is a non-polar molecule.

(iii) **PCl_5 :** Trigonal bipyramid. The Lewis structure is



The net dipole moment is zero. So, the molecule is non-polar.

(iv) **BF_3 :** Trigonal planar

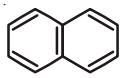


The net dipole moment is zero. So, the molecule is non-polar.

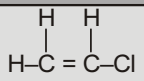
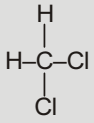
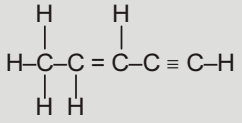
42. What is the total number of sigma bonds and pi-bonds in the following molecules?

(i) C_2H_3Cl

(ii) CH_2Cl_2

(iii) 

Sol.

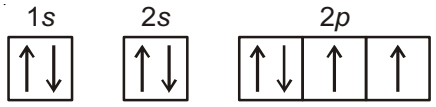
Molecule	Structure bonds	Sigma bonds	pi bonds
(i) C_2H_3Cl		5	1
(ii) CH_2Cl_2		4	0
(iii) $H_3C–CH = CH–C \equiv CH$		10	3

43. Draw orbital representation of the following molecules.

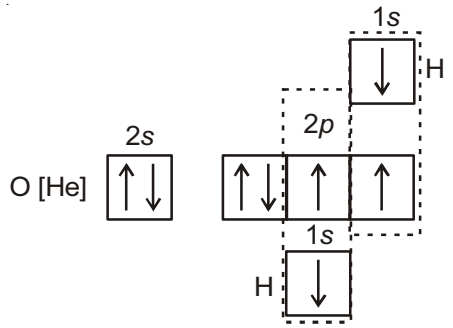
(i) Water

(ii) Nitrogen molecule.

Sol. (i) **Water molecule :** The electronic configuration of an O atom is $1s^2\ 2s^2\ 2p^4$. There are six electrons in the valence orbitals of oxygen.

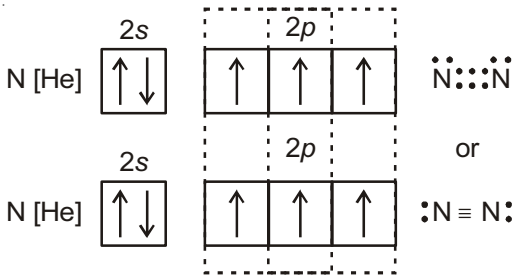


An oxygen atom can complete its octet by sharing two electron pairs. The overlap in H_2O molecule is between the 2*p* orbital of O and the 1*s* orbital of H.





(ii) Nitrogen molecule, N_2. The N atom has the configuration $1s^2\ 2s^2\ 2p^3$. Each of *p*-orbital is half filled. An N-atom join with another N-atom though the overlap of the six half filled 2*p*-orbitals resulting in sharing of three electron pairs.



44. Explain the following:

(i) CCl_4 and $SiCl_4$ both are tetrahedral.

(ii) BF_3 and NF_3 are not isostructural.

(iii) The HSH angle in H_2S is close to 90° while HOH angle in H_2O is 104.5°.

Sol. (i) In both CCl_4 and $SiCl_4$, the central atom is sp^3 hybridised. Both are AX_4 type molecules without any lone pair of electrons present on the central atom. Hence CCl_4 and $SiCl_4$, both are tetrahedral is shape.

(ii) In BF_3, the B atom is sp^2 hybridised (AX_3). The shape is trigonal planar. In NF_3, N atom is sp^3 hybridised due to the presence of one lone pair of electron on N atom, the shape is reduced from tetrahedral to trigonal pyramidal.

(iii) In H_2O, O atom is sp^3 hybridised. But due to the repulsion between lone pair-lone pair of electron on O-atom, the angle is reduced to 104.5° from 109°. In H_2S, S is less electronegative than O atom, so bond pair-bond pair repulsion is less than H_2O.

45. Why in case of polyatomic molecules, the measurement of bond strength is complicated?

Sol. In case of polyatomic molecules, the measurement of bond strength is more complicated. For example in case of H_2O molecule, the enthalpy needed to break the two O–H bonds is not the same.

$$H_2O(g) \longrightarrow H(g) + OH(g) \; ; \; \Delta_a H_1^\circ = 502 \text{ kJ mol}^{-1}$$

$$OH(g) \longrightarrow H(g) + O(g) \; ; \; \Delta_a H_2^\circ = 427 \text{ kJ mol}^{-1}$$

The difference in the $\Delta_a H^\ominus$ value shows that the second O–H bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same O–H bond in different molecules like C_2H_5OH (ethanol) and water. Therefore in polyatomic molecules the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule.

Average bond enthalpy = $\frac{502 + 427}{2}$ = 464.5 kJ mol^{-1}.

Due to these reasons the measurement of bond strength is complicated in polyatomic molecules.

SECTION - B

Model Test Paper

Very Short Answer Type Questions :

1. Who proposed the valence shell electron pair repulsion theory and who developed and refined the theory?

Sol. The VSEPR theory was proposed by Sidgwick and Powell and later developed and refined by Gillespie and Nyholm.

2. Explain why BeH_2 molecule has a zero dipole moment although the Be–H bonds are polar.

Sol. BeH_2 has a zero dipole moment as it is linear in shape. The two bond dipole cancel each other.

$$H \overleftarrow{\longrightarrow} Be \overrightarrow{\longrightarrow} H$$
$$\mu = 0$$

3. What is the decreasing order of repulsion of various electron pairs?

Sol. The decreasing order of repulsion is

Lone pair - Lone pair > Lone pair - Bond pair > Bond pair - Bond pair.

4. Name the molecular shapes associated with the following hybridisation:

   (i) sp^3d

   (ii) sp^3d^2

Sol. (i) $sp^3d \longrightarrow$ Trigonal bipyramidal.

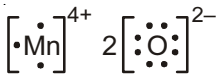
(ii) $sp^3d^2 \longrightarrow$ Octahedral.

5. How are bond order and bond length related to each other?

Sol. Bond order and bond length are inversely related.

$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$

6. Write the Lewis formula of manganese dioxide (MnO_2).

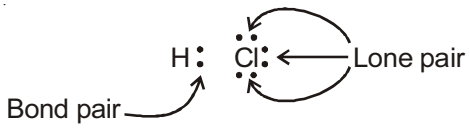
Sol. The Lewis formula of manganese dioxide is 

7. How will you differentiate between the lone pair and a bond pair of electrons?

Sol. A lone pair of electrons is a pair of valence electrons that is not used in bonding.

A bond pair is an electron pair shared between the two atoms.

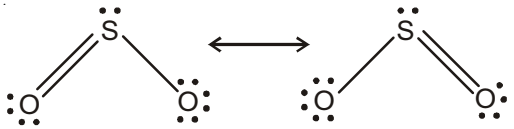
For example :



8. What is meant by resonance in molecules?

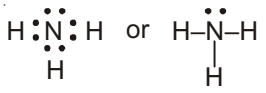
Sol. Resonance is a phenomenon in which we describe the electron structure of a molecule, having delocalised bonding by writing all possible electron dot formula.

For example :



Short Answer Type Questions :

9. Predict the shape of the ammonia molecule according to VSEPR theory.

Sol. The Lewis structure of NH_3 is  or

Because one of the electron pair is lone pair, the NH_3 molecule is pyramidal.

10. What do you understand by covalent radius and van der Waals radius?

Sol. The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The van der Waals radius represents the overall size of the atom which includes its valence shell in a non-bonded situation.

11. Define formal charge.

Sol. Formal charge (F.C.) of an atom in a polyatomic ion/molecule is defined as

Formal charge on an atom in a lewis structure =

$$\left[\begin{array}{l}\text{Total number of}\\ \text{valence electrons}\\ \text{to the free atoms}\end{array}\right] - \left[\begin{array}{l}\text{Total number of}\\ \text{non bonding}\\ \text{electrons}\end{array}\right] - \frac{1}{2}\left[\begin{array}{l}\text{Total number of}\\ \text{bonding electrons}\end{array}\right]$$

12. What are the important consequences of lattice enthalpy?

Sol. The important consequences of Lattice enthalpy are:

(i) The greater the Lattice enthalpy, more the stability of ionic compound.

(ii) The Lattice enthalpy is greater, for ions of higher charge and smaller radii higher m.p. and b.p.

(iii) The Lattice enthalpies affect the solubilities of ionic compounds.

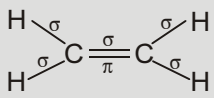
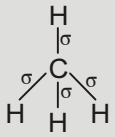
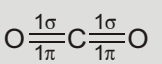
13. How many sigma (σ) and pi (π) bonds are present in each of the following molecules?

(i) C_2H_4

(ii) CH_4

(iii) CO_2.

Sol.

Molecule	Structure	No. of σ bonds	No. of π bonds
(i) C_2H_4		5	1
(ii) CH_4		4	0
(iii) CO_2		2	2

14. Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strengths of chemical bonds?

Sol. Bond order is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals.

Bond order = $\frac{N_b - N_a}{2}$

(i) A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.

(ii) Integral bond order values of 1, 2 or 3 corresponds to single, double or triple bonds respectively.

15. Account for the following

(i) He_2 is not found to exist in nature.

(ii) N_2^+ is not a diamagnetic substance.

Sol. (i) In He_2, total 4 electrons are present. Its MO electron configuration is $\sigma 1s^2\ \sigma^*1s^2$. As $N_b = N_a$, the bond order is zero. He_2 does not exist.

(ii) The MO electron configuration of N_2^+ (total electrons = 13) is $\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2 \begin{bmatrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{bmatrix} \sigma 2p_z^1$.

As one unpaired electron is present in $\sigma 2p_z$ MO. N_2^+ cannot be diamagnetic, it is paramagnetic in nature.

Short Answer Type Questions :

16. What do you mean by intermolecular hydrogen bond and intramolecular hydrogen bond?

Sol. Intermolecular hydrogen bond is formed between two different molecules of the same or different compounds for example, H–bond in case of HF molecule, alcohol or water molecules etc.

Intramolecular hydrogen bond is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitro phenol the hydrogen is in between the two oxygen atoms.

17. Explain diamagnetic character of fluorine molecule by molecular orbital theory.

Sol. Fluorine atom contains 9 electrons. So, fluorine molecule contains 18 electrons. The electronic configuration of F_2 molecule is

$$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2 \begin{bmatrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{bmatrix} \begin{bmatrix} \pi^* 2p_x^2 \\ \pi^* 2p_y^2 \end{bmatrix}$$

As all MO are fully filled, there is no unpaired electron present. Therefore F_2 molecule is diamagnetic.

18. Account for the following

(i) N_2 has a higher bond dissociation energy than NO.

(ii) N_2 and CO both have the same bond order but CO is more reactive than N_2.

Sol. (i) N_2 molecule has total 14 electrons and the bond order is 3, while in NO, the bond order is 2.5. Due to higher bond order, N_2 has higher bond dissociation energy.

(ii) N_2 and CO both are isoelectronic and have the same bond order. CO is more reactive than N_2 because of high electronegativity difference CO is more polar than N_2.

19. Write formal charges of the atoms in the nitrite ion.

Sol. The nitrite ion structure is

$$\left[\overset{\text{(i)}}{\ddot{O}} - \ddot{N} = \overset{\text{(ii)}}{\ddot{O}} \right]^-$$

The formal charge on oxygen atom.

(i) is $6 - 6 - \frac{1}{2} \times 2 = -1$

This is the formal charge on oxygen atom.

(ii) is $6 - 4 - \frac{1}{2} \times 4 = 0$

The formal charge on nitrogen atom is

$5 - 2 - \frac{1}{2} \times 6 = 0$

Long Answer Type Questions :

20. Write the electron dot structure for

(i) CO_2

(ii) PH_3

(iii) CCl_4

(iv) H_2O

(v) BCl_3

Is the octet rule obeyed in these structures?

Or

Write the electron dot structures for:

(i) CN^-

(ii) SO_3^{2-}

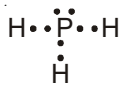
(iii) ClO_2^-

Sol. (i) **CO_2 :** The total number of valence electron is 4 + 2 × 6 = 16. There are 8e^- pairs to be accommodated. The more electropositive atom C is the central atom while O atoms are bonded to it. Both C and O form double bond. The electron- dot structure of CO_2 is



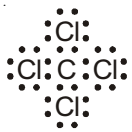
Each atom is obeying the octet rule.

(ii) **PH_3 :** The Lewis electron- dot structure is



Phosphorus has a complete octet but H–atom has only two electrons.

(iii) **CCl_4 :** The Lewis electron dot structure is



Each and every atom has a complete octet.

(iv) **H_2O :** The Lewis dot structure is



Here H atom is not satisfying the Lewis octet rule.

(v) **BCl_3 :**



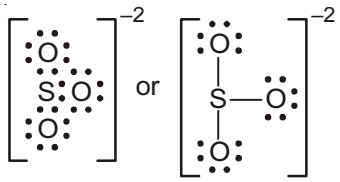
Each chlorine atom is obeying the octet rule while B atom has only six electrons (incomplete octet).

Or

(i) CN^- ion has 4 + 5 + 1 = 10 electron (4 from the C atom, 5 from the N atom, and 1 for the additional negative charge). Therefore, the lewis structure is



(ii) SO_3^{-2} : Total number of electrons = 6 + 3 × 6 + 2 = 26. The Lewis structure is



The –2 charge is present on the entire ion.

(iii) ClO_2^- : The total number of electrons = 7 + 2 × 6 + 1 = 20. The Cl is the central atom and O atoms are bonded to it. The Lewis structure is



21. Describe the main features of the VSEPR theory.

Or

Using valence bond theory, explain the formation of hydrogen molecule from hydrogen atoms.

Sol. Main features of the VSEPR (Valence Shell Electron Pair Repulsion) theory:

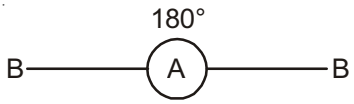
(i) The VSEPR model is used for predicting the shapes of molecules and ions.

(ii) The shape of a molecule is related to the number of electron pairs in the outer shell of the central atom.

(iii) Electron pair occupy orbitals and since the occupied orbitals repel each other, they are oriented in space as far apart as possible. This applies irrespective of whether the electron pair is a bond pair or a non bonding electron pair.

(iv) If the distribution of orbitals about the central atom can be predicted, the shape of the molecule and bond angle can also be predicted.

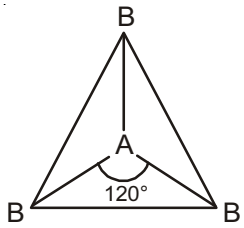
(v) The presence of two electron pairs in the valence shell of an atom gives a linear arrangement with a bond angle of



Example : BeF_2, $MgCl_2$

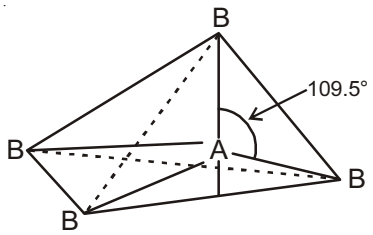
(vi) If three electron pairs are in the valence shell of an atom, they tend to be arranged in a plane directed towards the corners of a triangle of equal sides. This arrangement is called trigonal planar, with a bond angle of 120°.

Example : BF_3.



(vii) Four electron pairs in the valence shell of an atom tend to have a tetrahedral arrangement.

For example : CH_4, CCl_4



Or

Hydrogen atom has one electron which is present in its 1*s*-orbital. Suppose we have two hydrogen atom H_A and H_B with their corresponding electrons e_A and e_B respectively. When the two H atoms are present at large distance from each other, there is practically no interaction between the two atoms. When the two atoms come closer, they begin to interact with each other. As a result, the following new forces of attraction and repulsion come into operation.

(i) Attractive forces between :

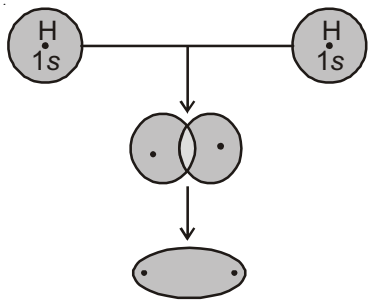
(a) e_A and nucleus H_B

(b) e_B and nucleus H_A

(ii) Repulsive forces between :

(a) e_A and e_B

(b) Nucleus H_A and nucleus H_B

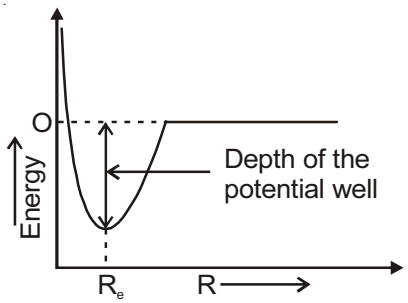


(i) separated hydrogen atoms

(ii) Overlap of two 1*s* atomic orbitals

(iii) Hydrogen molecule

The attractive forces tend to bring the two atoms closer whereas repulsive forces tend to push them apart. The magnitude of attractive forces is greater than the repulsive forces. Therefore, the atoms go on approaching each other and the potential energy of the system continuously decreases. Ultimately, a point is reached where forces of attraction exactly cancel the repulsive forces. This point is reached when the atoms are held up at critical distance R_e. At a distance greater than R_e, the forces of attraction dominate whereas at a distances less than R_e the repulsive forces are dominant. Energy is minimum at critical distance R_e. This critical distance is called bond length or the internuclear distance.



The potential energy curve for two H–atoms as a function of distance, R, between them is given above. The equilibrium internuclear distance, R_e is 0.74 Å (74 pm).

❑ ❑ ❑

SECTION - A

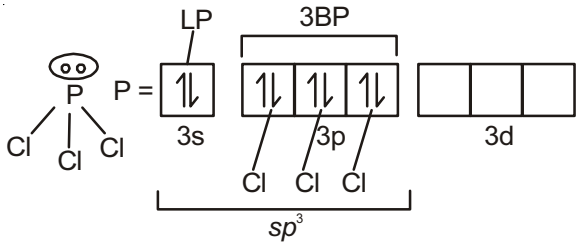
Objective Type Questions

1. Which of the following species contains three bond pairs and one lone pair around the central atom?

(1) NH_2^- (2) PCl_3 (3) H_2O (4) BF_3

Sol. Answer (2)

PCl_3 have 3BP and 1LP



2. Which one of the following pairs of chemical species contains the ions having same hybridisation of the central atoms?

(1) NO_2^- and NH_2^- (2) NO_2^- and NO_3^- (3) NH_4^+ and NO_3^- (4) SCN^- and NH_2^-

Sol. Answer (2)

$$H = \frac{1}{2}[V + M - C + A]$$

where H = hybridisation, V = valence e^-, M = monovalent, A = Negative charge, C = Positive charge

For NO_2^- : $H = \frac{1}{2}[5 + 0 - 0 + 1] = \frac{6}{2} = 3$ $\boxed{sp^2}$

For NO_3^- : $H = \frac{1}{2}[5 + 0 - 0 + 1] = \frac{6}{2} = 3$

same hybridisation sp^2

3. The geometry of electron pairs around S in SF_6 is

(1) Octahedral (2) Trigonal bipyramidal (3) Square pyramidal (4) Pentagonal planar

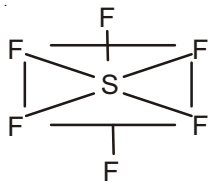
Sol. Answer (1)

SF_6 : $H = \frac{1}{2}[6 + 6 - 0 + 0] = \frac{12}{2} = 6$

sp^3d^2

↓

Octahedral geometry



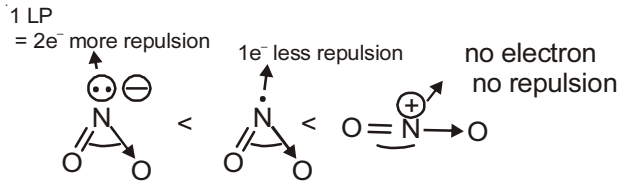
Octahedral

4. The correct order of increasing bond angles in the following triatomic species is

(1) $NO_2^+ < NO_2^- < NO_2$ (2) $NO_2^- < NO_2^+ < NO_2$

(3) $NO_2^- < NO_2 < NO_2^+$ (4) $NO_2^+ < NO_2 < NO_2^-$

Sol. Answer (3)



[More the e^- present more will be the repulsion smaller will be the bond angle]

$[NO_3^- < NO_2 < NO_2]$

5. In the hydrocarbon

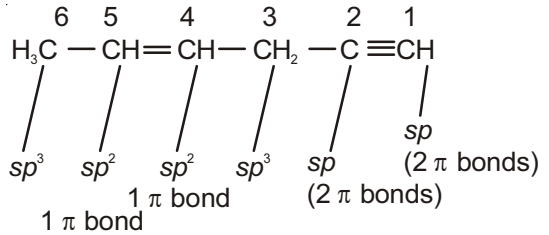
$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{C}\equiv\underset{1}{CH}$$

The state of hybridization of carbons 1, 3 and 5 are in the following sequence

(1) sp^3, sp^2, sp (2) sp^2, sp, sp^3 (3) sp, sp^3, sp^2 (4) sp, sp^2, sp^3

Sol. Answer (3)

For 'C' compounds hybridisation H = $sp^{(3\text{-no. of } \pi \text{ bond})}$



$$\begin{Bmatrix} C\ 1 & sp \\ C\ 3 & sp^3 \\ C\ 5 & sp^2 \end{Bmatrix}$$

6. The BCl_3 is a planar molecule whereas NCl_3 is pyramidal because

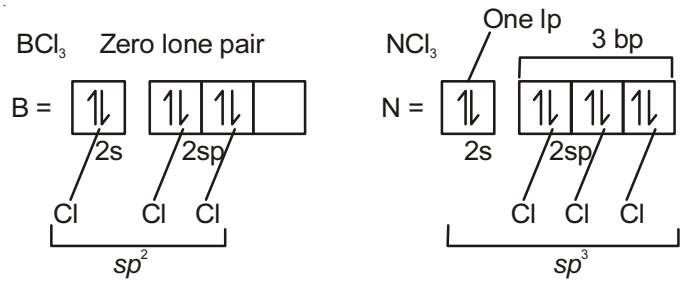
(1) Nitrogen atom is smaller than boron atom

(2) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons

(3) B – Cl bond is more polar than N – Cl bond

(4) N – Cl bond is more covalent than B – Cl bond

Sol. Answer (2)



$\therefore$ BCl_3 have planar structure NCl_3 have pyramidal structure

7. Which of the following bonds has the highest bond energy?

(1) S–S (2) O–O (3) Se–Se (4) Te–Te

Sol. Answer (1)

Expected high bond energy is in O–O due to high electron-negativity but due to smaller size $\therefore$ will be repulsion and bond energy will be low

$\therefore$ [(S – S) have more bond energy than O–O bond].

8. The low density of ice compared to water is due to

(1) Dipole-induced dipole interactions

(2) Induced dipole induced dipole interactions

(3) Hydrogen bonding interactions

(4) Dipole-dipole interactions

Sol. Answer (3)

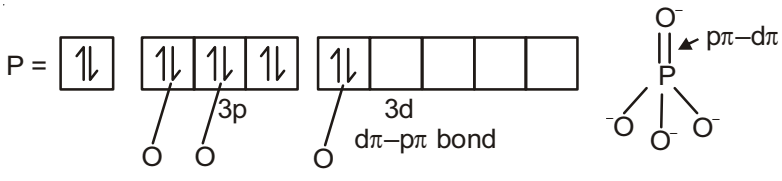
H_2O have more density because on increases the temperature 'H' bonding interaction increases volume decreases and density increases. [Density of H_2O > density of ice]

9. $d\pi - p\pi$ bond present in

(1) CO_3^{2-} (2) PO_4^{3-} (3) NO_3^- (4) NO_2^-

Sol. Answer (2)

$d\pi - p\pi$ bond *i.e.* PO_4^{3-} because P have d-orbital



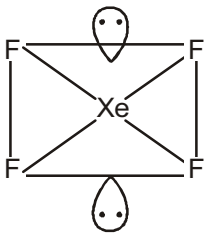
10. Which compound has planar structure?

(1) XeF_4 (2) $XeOF_2$ (3) XeO_2F_2 (4) XeO_4

Sol. Answer (1)

XeF_4 have $H = \frac{1}{2}[8+4-0+0] = \frac{12}{2} = 6 = sp^3d^2$ octahedral geometry

but due to two lone pair have planar shape



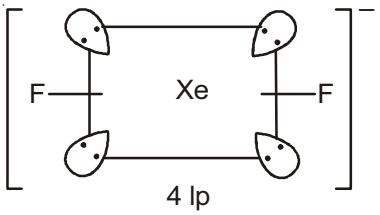
11. Which of the following pairs are isostructural?

(1) XeF_2, IF_2^- (2) NH_3, BF_3 (3) CO_3^{-2}, SO_3^{-2} (4) PCl_5, ICl_5

Sol. Answer (1)

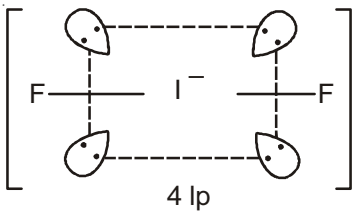
XeF_2

$H = \frac{1}{2}[8+2-0+0] = \frac{10}{2} = 5\ sp^3d$



IF_2^-

$H = \frac{1}{2}[7+2-0+1] = \frac{10}{2} = 5\ sp^3d$



12. In which of the following bond angle is maximum?

(1) NH_3 (2) NH_4^+ (3) PCl_3 (4) SCl_2

Sol. Answer (2)

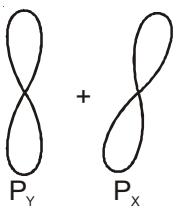
NH_4^+ have no lone pair $\therefore$ no repulsion between lp and bp and have maximum bond angle.

13. Main axis of a diatomic molecule is z, orbital p_x and p_y overlap with each other to form which of the following molecular orbitals?

(1) π molecular orbital (2) σ molecular orbital (3) δ molecular orbital (4) No bond will form

Sol. Answer (4)

No overlapping



= no overlapping

Overlapping will only possible when lobers are symmetrical about the axis $\left\{\begin{matrix} i.e\ p_z - p_z \\ p_y - p_y \\ p_x - p_x \end{matrix}\right\}$

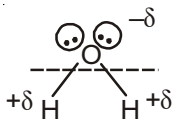
14. Which one of the following statements is not correct for sigma- and pi-bonds formed between two carbon atoms?
    (1) Sigma-bond is stronger than a pi-bond
    (2) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively
    (3) Free rotation of atoms about a sigma-bond is allowed but not in case of a pi-bond
    (4) Sigma-bond determines the direction between carbon atoms but a pi-bond has no effect in this regard

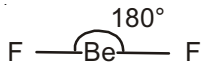
Sol. Answer (2)

σ bond is stronger than π bond $\therefore$ B.E. of σ bond is more than π bond.

15. H_2O is polar, whereas BeF_2 is not. It is because
    (1) The electronegativity of F is greater than that of O
    (2) H_2O involves hydrogen bonding whereas BeF_2 is a discrete molecule
    (3) H_2O is linear and BeF_2 is angular
    (4) H_2O is angular and BeF_2 is linear

Sol. Answer (4)

H_2O have angular shape because of two lone pair 

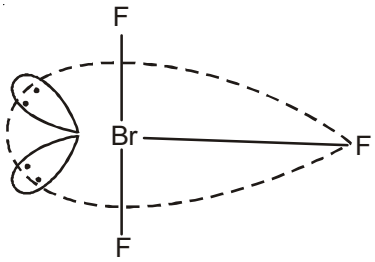
BeF_2 have linear shape 

$\therefore$ H_2O is polar BeF_2 is linear

16. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimize
    (1) Lone pair-bond pair repulsion only
    (2) Bond pair-bond pair repulsion only
    (3) Lone pair-lone pair repulsion and lone pair-bond pair repulsion
    (4) Lone pair-lone pair repulsion only

Sol. Answer (3)

lp–lp repulsion and lp–bp repulsion will be minimum when lp occupy equatorial positions.



17. The correct sequence of increasing covalent character is represented by
    (1) $LiCl < NaCl < BeCl_2$
    (2) $BeCl_2 < LiCl < NaCl$
    (3) $NaCl < LiCl < BeCl_2$
    (4) $BeCl_2 < NaCl < LiCl$

Sol. Answer (3)

According to Fajan's Rule smaller the size of cation; larger the size of anion more will be the covalent character.

$Be^{2+} < Li^+ < Na^+$ size of cation.

$\therefore$ Order of covalent character will be $BeCl_2 > LiCl > NaCl$

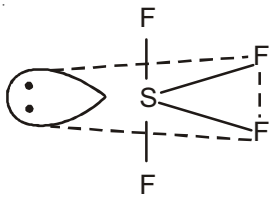
18. Which of the following would have a permanent dipole moment?

(1) SiF_4 (2) SF_4 (3) XeF_4 (4) BF_3

Sol. Answer (2)

SF_4 have sea-saw shape *i.e.* distorted geometry $\therefore$ it will have permanent dipole moments.

[SiF_4 = BF_3 = XeF_4 = Planar = $\mu = 0$]



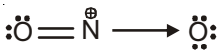
$\mu \neq 0$

19. Which of the following species has a linear shape?

(1) O_3 (2) NO_2^- (3) SO_2 (4) NO_2^+

Sol. Answer (4)

NO_2^+ have linear geometry because of no lone pair. No repulsion



20. The correct order regarding the electronegativity of hybrid orbitals of carbon is

(1) $sp < sp^2 < sp^3$ (2) $sp > sp^2 < sp^3$ (3) $sp > sp^2 > sp^3$ (4) $sp < sp^2 > sp^3$

Sol. Answer (3)

More then s-character more closer towards the nucleus more will be the electronegativity

$sp > sp^2 > sp^3$

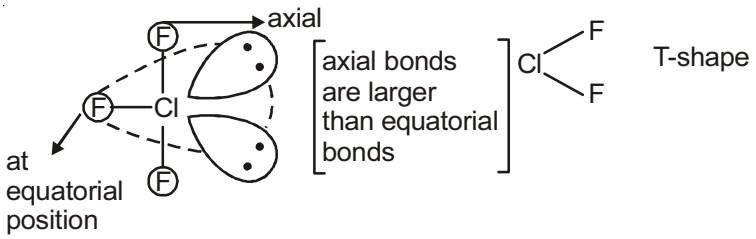
(50%s) (33%s) (25%s)

21. In which of the following molecules all the bonds are not equal?

(1) NF_3 (2) ClF_3 (3) BF_3 (4) PF_3

Sol. Answer (2)

ClF_3 have sp^3d hybridisation and have 3bp and 2lp.



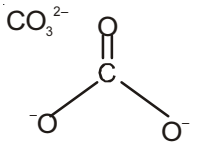
T-shape

22. The correct order of C — O bond order among CO, CO_3^{2-}, CO_2 is

(1) $CO < CO_3^{2-} < CO_2$ (2) $CO_3^{2-} < CO_2 < CO$

(3) $CO < CO_2 < CO_3^{2-}$ (4) $CO_2 < CO_3^{2-} < CO$

Sol. Answer (2)



$<$ O = C = O $<$ C $\equiv$ O

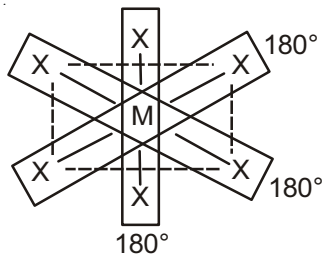
B.O = 2 B.O = 3

B.O = $\frac{4}{3}$ = 1.33

23. In a regular octahedral molecule, MX_6 the number of X – M – X bonds at 180º is

(1) Three (2) Two (3) Six (4) Four

Sol. Answer (1)



X— M— X bonds at 180° = 3.

24. The table shown below gives the bond dissociation energies (E_{diss}) for single covalent bonds of carbon(C) atoms with element A, B, Z and D. Which element has the smallest atoms?

Bond	**E_{diss}(kJ mol^{-1})**
C–A	240
C–B	328
C–Z	276
C–D	485

(1) Z (2) D (3) A (4) B

Sol. Answer (2)

More the dissociation energy *i.e*. stronger the (C–D) bond. ∴ D atoms have smaller size.

25. Which one of the following has the strongest O – O bond?

(1) O_2^+ (2) O_2 (3) O_2^- (4) O_2^{2-}

Sol. Answer (1)

More the bond order more will the bond strength [Bond strength ∝ bond order]

$O_2 = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$

$$B.O = \frac{10-6}{2} = 2$$

$O_2^+ =$ $$B.O = \frac{10-5}{2} = 2.5$$

$O_2^- =$ $$B.O = \frac{10-7}{2} = 1.5$$

$O_2^{2-} =$ $$B.O = \frac{10-8}{2} = 1$$

O_2^+ have maximum bond order and have strongest O–O bond.

26. N_2 and O_2 are converted into monoanions N_2^- and O_2^- respectively, which of the following statements is wrong?

(1) In O_2^-, bond length increases (2) N_2^- becomes diamagnetic

(3) In N_2^-, the N–N bond weakens (4) In O_2^-, the O–O bond order decreases

Sol. Answer (2)

$O_2 = \pi^*2p_x^1 = \pi^*2p_y^1$ $O_2^- = \pi^*2p_x^2 = \pi^*2p_y^1$

$N_2 = \pi2p_x^2 = \pi2p_y^1$ $N_2^- = \pi2p_x^2 = \pi2p_y^2, \pi2p_y^1$

[N_2^- have compound electrons *i.e.* paramagnetic]

27. Which species does not exhibit paramagnetism?

(1) N_2^+ (2) O_2^- (3) CO (4) NO

Sol. Answer (3)

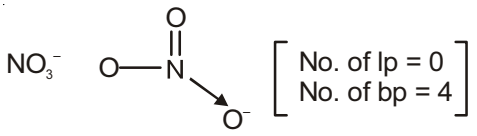
CO have 14 e^- i.e. even no. and also have filled molecular orbitals.

CO = $\sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \sigma2p_x^2 = \pi2p_y^2, \sigma2p_z^2$ all paired e^-

28. In NO_3^- ion number of bond pair and lone pair of electrons on nitrogen atom are

(1) 2, 2 (2) 3, 1 (3) 1, 3 (4) 4, 0

Sol. Answer (4)



29. In an octahedral structure, the pair of *d* orbitals involved in sp^3d^2 hybridisation is

(1) $d_{x^2-y^2}, d_{z^2}$ (2) $d_{xz}, d_{x^2-y^2}$ (3) d_{z^2}, d_{xz} (4) d_{xy}, d_{yz}

Sol. Answer (1)

d^2sp^3 have $d_{x^2-y^2}$ and d_{z^2}

30. Which one of the following species does not exist under normal conditions?

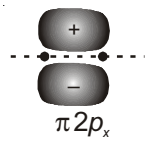
(1) Li_2 (2) Be_2^+ (3) Be_2 (4) B_2

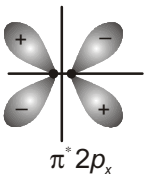
Sol. Answer (3)

Be_2 does not exist because [$N_b = N_a$]

$Be_2 = 8 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2$

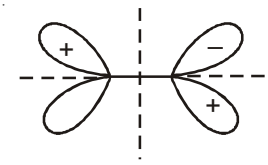
31. The molecular orbital shown below can be described respectively as



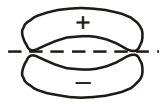


(1) σ, σ^* (2) π, π^* (3) π^*, π (4) π^*, σ^*

Sol. Answer (3)



[π^* two nodal planes]



[π molecular orbital]

32. The hybrid orbital having only 20% d character

(1) CCl_4 (2) SF_6 (3) SF_4 (4) Cl_2O

Sol. Answer (3)

SF_4 have hybridisation sp^3d i.e. five orbital total

$\therefore$ have 20% d character. 20% s and 60% p-character.

33. Which of the following molecule stabilizes by removal of electron?

(1) C_2 (2) O_2 (3) N_2 (4) H_2

Sol. Answer (2)

On removing e^- from O_2 its bond order increases from 2 to 2.5 $\therefore$ stability increases.

$$\left\{\begin{matrix} O_2 = \sigma 1s^2 ... {}^*2p_x{}^1 = {}^*2p_y{}^1 \\ O_2^+ = \sigma 1s^2 ... \pi 2p_x{}^1 = {}^*2p_y{}^0 \end{matrix}\right\}$$

34. Which of the following statement is correct?

(1) The hybridisation of Cl in ClF_3 is sp^2

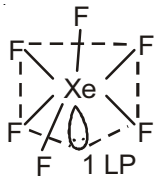
(2) The number of lone pairs and bond pairs in I_3^- are 2 and 2 respectively

(3) The shape of XeF_6 is distorted square bipyramidal

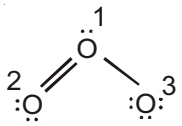
(4) Hybridisation of S is sp^3 in SO_2

Sol. Answer (3)

XeF_6 $H = \frac{1}{2}[8+6-0+0] = \frac{14}{7} = 7$ sp^3d^3 i.e. distorted square pyramidal because of one lone pair



35. The formal charges of oxygen labelled 3,2,1 in ozone respectively are

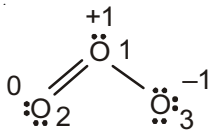


(1) –1, +1, 0 (2) 0, 0, –1 (3) –1, 0, +1 (4) 0, +1, –1

Sol. Answer (3)

$$\text{Formal charge} = \left[V - L - \frac{1}{2}S\right]$$

$$\begin{bmatrix} V = \text{valence } e^- \\ L = \text{lone pair} \\ S = \text{shared pair} \end{bmatrix}$$



$$\text{F.C on } O_1 = 6 - 2 - \frac{1}{2}\times 6 = +1$$

$$\text{F.C on } O_2 = 6 - 4 - \frac{1}{2}\times 2 = 0$$

$$\text{F.C on } O_3 = 6 - 6 - \frac{1}{2}\times 2 = -1$$

36. Number of nodal planes in π^*2p_x are

(1) Zero (2) One (3) Two (4) Three

Sol. Answer (3)

SECTION - B

Objective Type Questions

1. Which of the following is not a correct statement?

(1) Multiple bonds are always shorter than corresponding single bonds

(2) The electron-deficient molecules can act as Lewis acids

(3) The canonical structures have no real existence

(4) Every AB_5 molecules does in fact have square pyramid structure

Sol. Answer (4)

AB_5 molecule geometry also depends upon the no. of lone pair

$\therefore$ always AB_5 will not have square pyramid structure.

AB_5 = trigonal bipyramid, or square pyramid

2. Some of the properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct?

(1) Dissimilar hybridization for the central atom with different structures

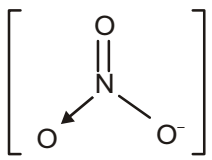
(2) Isostructural with same hybridization for the central atom

(3) Isostructural with different hybridization for the central atom

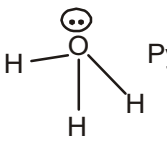
(4) Similar hybridization for the central atom with different structures

Sol. Answer (1)

Hybridisation $NO_3^- = sp^2$

Structure 

$H_3O^+ = sp^3$



Pyramidal

[Different hydridisation and different structural arrangement]

3. The ground state electronic configuration of valence shell electrons in nitrogen molecule (N_2) is written as kk, $\sigma 2s^2$, $\sigma^* 2s^2$, $\begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}$, $\sigma 2p_x^2$. Hence the bond order in nitrogen molecule is

(1) 2 (2) 3 (3) 0 (4) 1

Sol. Answer (2)

$$\text{Bond order} = \frac{\text{No. of bonding} - \text{No. of antibonding}}{2} = \frac{8-2}{2} = 3$$

Bond order of N_2 = 3

4. A certain diatomic molecule, AB has dipole moment 1.6 D and the internuclear distance is 100 pm. The percentage of electronic charge existing on more electronegative atom is

(1) 33% (2) 25% (3) 50% (4) 10%

Sol. Answer (1)

$$\% \text{ ionic} = \frac{\mu \text{ obsc}}{\mu \text{ cal}} = \frac{1.6 \times 10^{-18} \text{esu-cm}}{100 \times 10^{-18} \times 4.8 \times 10^{-10} \text{esu-cm}} = 33\%$$

5. Which of the following is correct for XeO_2F_2 and PCl_5?

(1) Both have same hybridisation and shape

(2) Both have same hybridisation but different geometry

(3) Both have different hybridisation but same shape

(4) Both have same hybridisation but different shape

Sol. Answer (4)

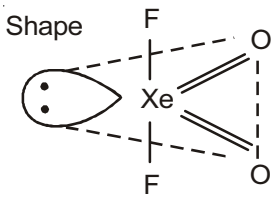
XeO_2F_2

$$\text{Hybridisation} = \frac{1}{2}[V + M - C + A]$$

$$H = \frac{1}{2}[8 + 2 - 0 + 0]$$

$$\frac{10}{2} = 5 \ [sp^3d]$$

Shape



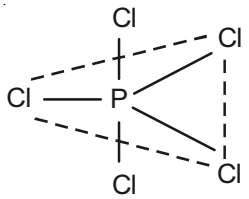
See-saw shape

PCl_5

$$H = \frac{1}{2}[V + M - C + A]$$

$$H = \frac{1}{2}[5 + 5 - 0 + 0]$$

$H = 5$ sp^3d

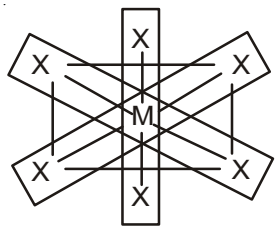


Trigonal bipyramidal

6. The maximum number of 180° angle possible between X-M-X bond for compounds with sp^3d^2 and sp^3d hybridisation respectively are

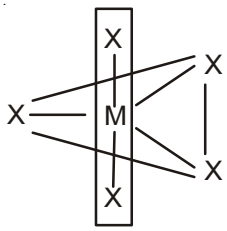
(1) 3, 3 (2) 3, 1 (3) 1, 3 (4) 3, 0

Sol. Answer (2)



X—M—X
180° =3.

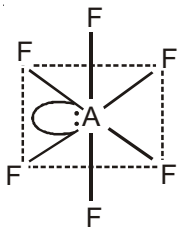
sp^3d^2 octahedral

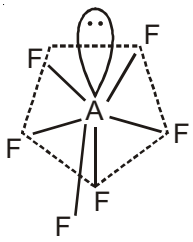


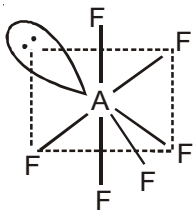
X—M—X
180°

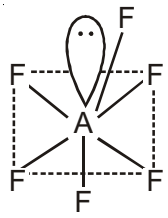
sp^3d trigonal bipyramidal

7. The shape for the molecule with general formula AF_6 with one lone pair can be represented as

(1) 

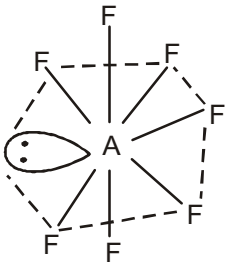
(2) 

(3) 

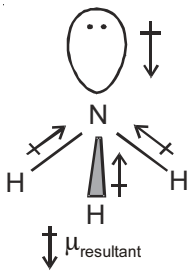
(4) 

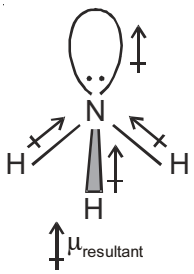
Sol. Answer (4)

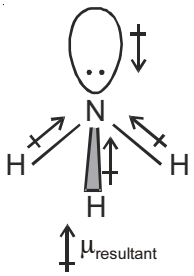
one lp and 6 bp
distorted pentagonal bipyramidal



8. Which of the following is correct representation of dipole moment of NH_3 molecule?

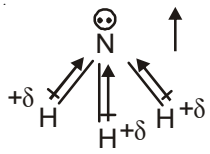
(1) 

(2) 

(3) 

(4) NH_3 being symmetrical will not show dipole moment

Sol. Answer (2)



[H is less electromagnetic than N
∴ Net dipole moment will be toward 'N' atom]

9. Incorrect statement regarding hybridization is

(1) It is not possible for isolated atoms

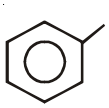
(2) Number of hybrid orbital formed is same as the number of orbitals combining

(3) Only the half filled orbitals and fully filled orbitals can participate not the empty orbital

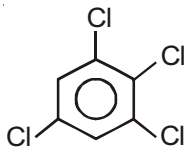
(4) It is not a real physical process

Sol. Answer (3)

Fully filled, half filled, empty orbitals participate in 'H' in excited state e– excited to empty orbital.

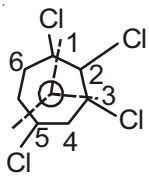
10. Dipole moment of 

is 1.1 D hence dipole moment of given compound will be

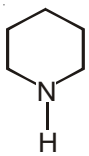


(1) 1.1 D (2) 4.4 D (3) 3.3 D (4) 2.56 D

Sol. Answer (1)



[dipole moment of 1, 3, 5 chlorine will be cancelled due to symmetry
∴ dipole moment exist only due to C–2. i.e. 1.1 D]

11. In 

hybrid state of N atom is

(1) sp^2 (2) sp^3 (3) sp^3d^2 (4) sp

Sol. Answer (2)

N have three bond pair and one lone pair

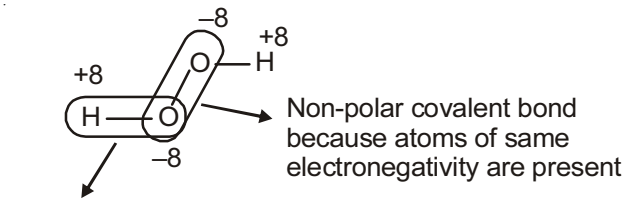
∴ its hybridisation will be sp^3

12. Which molecule contains both polar and nonpolar covalent bond?

(1) NH_4^+ (2) HCl (3) CH_4 (4) H_2O_2

Sol. Answer (4)

H_2O_2 have open book structure



13. The shape of I_3^- is

(1) Linear (2) Bent (3) Pyramidal (4) See saw

Sol. Answer (1)

$I_3^- = [I^- . I_2]$



I_2

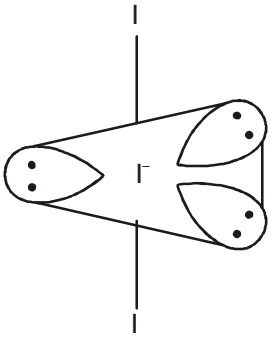
$H = \frac{1}{2}[V + M - C + A]$

I^- have 8 e^-

$= \frac{1}{2}[7 + 2 - 0 + 1] = \frac{10}{2} = sp^3d$

$\therefore$ by combining with two I_2, I^- have 3 LP and 2 BP

Structure of I_3^-



I_3^- have linear structure

14. Which of the following statements are correct?

I. Bond order of NO is 2.5

II. Bond order of NO^+ is 3.0

III. Bond order of O_2 is 1.5

IV. Bond order of CO is 3.0

(1) I, II, III (2) II, III, IV (3) I, II, IV (4) II, IV

Sol. Answer (3)

NO = 15 = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \sigma 2p_x^2 = \pi 2p_y^2, \pi 2p_x^1$

$B.O = \frac{10-5}{2} = 2.5$

NO^+ = 14 = $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \sigma 2p_x^2 = \pi 2p_y^2, \pi 2p_x^2, \pi^* 2p_x^0$

$B.O = \frac{10-4}{2} = 3$

$O_2 = 16 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \sigma2p_z^2, \pi2p_x^2 = \pi2p_y^2, \pi2p_x^0$ B.O $= \frac{10-6}{2} = 2$

$CO = 14 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \pi^*2_x^2 = \pi2p_y^2, \sigma2p_z^2, \sigma^*2ps^2$ B.O $= \frac{10-4}{2} = 3$

$$\therefore \begin{matrix} & 3.0 \\ \left\{\begin{matrix} NO & 2.5 \\ NO^+ & 3 \\ CO & 3 \end{matrix}\right. & \end{matrix}$$

15. Arrange the following species in increasing order of bond angle

NF_3 , NCl_3, NBr_3, NI_3

(1) $NF_3 < NCl_3 < NBr_3 < NI_3$ (2) $NF_3 < NBr_3 < NI_3 < NCl_3$

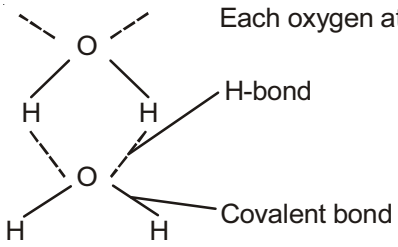
(3) $NI_3 < NBr_3 < NCl_3 < NF_3$ (4) $NBr_3 < NI_3 < NF_3 < NCl_3$

Sol. Answer (1)

16. How many bonds are formed by each oxygen atom in ice?

(1) 4 (2) 2 (3) 3 (4) May be 1 or 2

Sol. Answer (1)



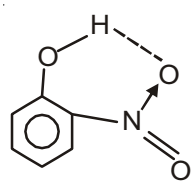
Each oxygen atom will form 4 bonds i.e.

17. o-nitrophenol is

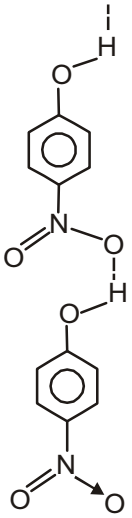
(1) More volatile than p-nitrophenol (2) Less volatile than p-nitrophenol

(3) Equally volatile as p-nitrophenol (4) Non-volatile

Sol. Answer (1)



Intramolecular H-bonding (weaker bonding) as it is in the same molecule.



Intermolecular H-bonding (stronger bonding) as it is with in two molecules.

$\therefore$ o-nitrophenol will easily evaporated compared to p-nitrophenol

18. Which of the following pair consists of only paramagnetic species?

(1) H_2, O_2^+ (2) N_2, O_2 (3) CO, N_2 (4) H_2^+, O_2^-

Sol. Answer (4)

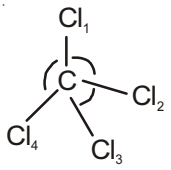
$H_2^+ = \sigma 1s^1$ ↓ 1 unpaired electron in $\sigma 1s$

$O_2^- = \sigma 1s^2 ... \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$ ↓ 1 unpaired electron in $\pi^* 2p_y^1$

19. Number of angles of 109°28′ is present in CCl_4

(1) 2 (2) 4 (3) 6 (4) 8

Sol. Answer (3)

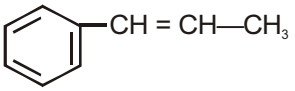


109.28° will be in

Total '6'

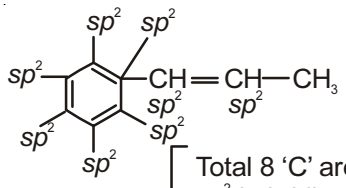
$_1Cl - C - Cl_2$
$_1Cl - C - Cl_3$
$_1Cl - C - Cl_4$
$_2Cl - C - Cl_3$
$_2Cl - C - Cl_4$
$_3Cl - C - Cl_4$

20. Number of carbon atoms present in sp^2 hybrid state of given molecule?



(1) 9 (2) 8 (3) 3 (4) 2

Sol. Answer (2)

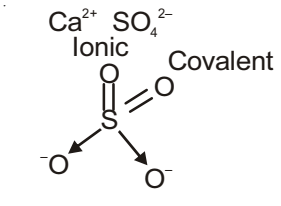


[Total 8 'C' are present and have sp^2 hybridisation]

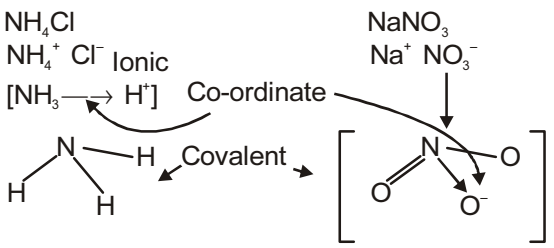
21. According to octet rule the compound which contain ionic, covalent and coordinate bonds

(1) $CaSO_4$ (2) NH_4Cl (3) $NaNO_3$ (4) All of these

Sol. Answer (4)



Co-ordinate covalent



All have ionic, covalent and co-ordinate covalent bond

22. Which of the following molecule is having least ionic character?

(1) $FeCl_2$ (2) $ZnCl_2$ (3) $MgCl_2$ (4) NaCl

Sol. Answer (2)

Full filled and half filled have maximum covalent character $\therefore$ $ZnCl_2$ have $3d^{10}$ configuration have maximum polarising power.

23. The number of antibonding electron pairs in O_2^-

(1) 2 (2) 3 (3) 1 (4) 4

Sol. Answer (2)

$O_2^- = 17 = \sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi 2p_x^2 = \pi^* 2p_y^1$

Number of antibonding electron pairs are 3.

24. In the given structure of a compound, the correct various bond moments direction involving atoms are shown as

(1) $Br \leftarrow N \leftarrow CH_2 \rightarrow SiH_2 \leftarrow CH_2 \rightarrow O \leftarrow CH_3$ (2) $Br \leftarrow N \leftarrow CH_2 \leftarrow SiH_2 \leftarrow CH_2 \rightarrow O \leftarrow CH_3$

(3) $Br \rightarrow N \leftarrow CH_2 \leftarrow SiH_2 \rightarrow CH_2 \rightarrow O \leftarrow CH_3$ (4) $Br \leftarrow N \rightarrow CH_2 \rightarrow SiH_2 \leftarrow CH_2 \rightarrow O \rightarrow CH_3$

Sol. Answer (3)

Electronegativity $\boxed{N > Br > C}$

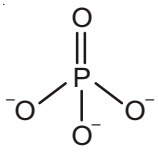
25. In PO_4^{3-} ion, the effective charge on each oxygen atom and P–O bond order respectively are

(1) –0.75, 1.25 (2) –0.75, 1.0 (3) –0.75, 0.6 (4) –3, 1.25

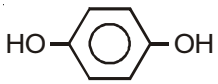
Sol. Answer (1)

Effective charge = $\frac{-3}{4}$

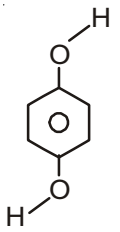
B.O. = $1+\frac{1}{4} = \frac{5}{4} = 1.25$



26. Which of the following is a polar molecule?

(1) Para dichlorobenzene (2) Carbon tetrachloride (3) Tetrachloroethene (4) 

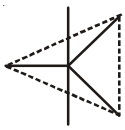
Sol. Answer (4)



27. In a regular trigonal bipyramidal MX_5, the number of X – M – X bonds at 180º is

(1) One (2) Two (3) Six (4) Four

Sol. Answer (1)



SECTION - C

Previous Years Questions

1. Which **one** of the following pairs is isostructural (*i.e.* having the same shape and hybridization)?

(1) [NF_3 and BF_3] (2) [BF_4^- and NH_4^+] (3) [BCl_3 and $BrCl_3$] (4) [NH_3 and NO_3^-]

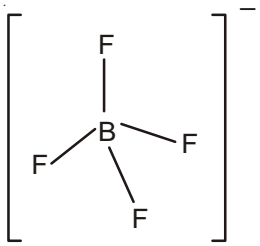
Sol. Answer (2)

BF_4^-

$H = \frac{1}{2}[3+4-0+1]$

$= \frac{8}{2} = 4 = sp^3$

Tetrahedral shape

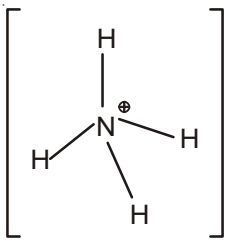


NH_4^+

$H = \frac{1}{2}[5+4-1+0]$

$= \frac{8}{2} = 4 = sp^3$

Tetrahedral shape



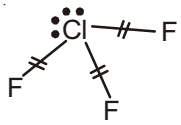
[Both are having tetrahedral shape and same hybridisation]

2. Which of the following species contains three bond pairs and two lone pairs around the central atom?

(1) NH_2^- (2) ClF_3 (3) H_2O (4) BF_3

Sol. Answer (2)

ClF_3



[3 bond pairs and 2 lone pairs]

3. The pair of species with the same bond order is

(1) NO, CO (2) N_2, O_2 (3) O_2^{2-}, B_2 (4) O_2^+, NO^+

Sol. Answer (3)

$O_2^{2-} = 18 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \sigma2p_z^2, \pi2p_x^2 = \pi2p_y^2, \pi2p_x^2 = \pi^*2p_y^2$ $\quad B.O = \frac{10-8}{2} = 1$

$B_2 = 10 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \pi2p_x^1 = \pi2p_y^1$ $\quad B.O = \frac{6-4}{2} = 1$

O_2^{2-} and B_2 have same bond order

4. Bond order of 2.5 is shown by

(1) O_2^{2-} (2) O_2 (3) O_2^+ (4) O_2^-

Sol. Answer (3)

$O_2^+ = 15 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \sigma2p_z^2, \pi2p_x^2 = \pi2p_y^2, \pi^*2p_x^1 = \pi^*2p_y^0$

$$B.O = \frac{10-5}{2} = 2.5$$

5. During change of O_2 to O_2^{2-} ion, the electron adds on which one of the following orbitals?

(1) π^* orbitals (2) π orbitals (3) σ^* orbitals (4) σ orbitals

Sol. Answer (1)

$O_2 = 16 = \sigma 1s^2, \sigma^* 1s^2 ..... * 2p_x^1 = \pi^* 2p_y^1$

$\downarrow$

$O_2^{2-} = 18 = \sigma 1s^2, \sigma^* 1s^2 ..... * 2p_x^2 = \pi^x 2p_y^2$

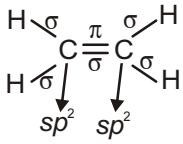
e^- added in π^* orbital

6. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent sp^2 orbitals. The total number of sigma (σ) and pi (π) bonds in ethene molecule is

(1) 1 sigma (σ) and 2 pi (π) bonds (2) 3 sigma (σ) and 2 pi (π) bonds

(3) 4 sigma (σ) and 1 pi (π) bonds (4) 5 sigma (σ) and 1 pi (π) bonds

Sol. Answer (4)

Ethene = 

Total no. of σ bond = 5
π bond = 1

7. Which of the following has the minimum bond length?

(1) O_2 (2) O_2^+ (3) O_2^- (4) O_2^{2-}

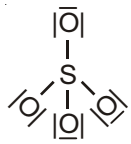
Sol. Answer (2)

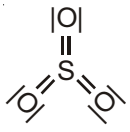
$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

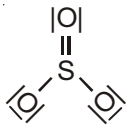
Bond order $O_2 = 2$, $O_2^+ = 2.5$, $O_2^- = 1.5$, $O_2^- = 1$ by molecular orbital theory

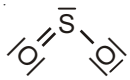
$\therefore$ [O_2^+ have minimum bond length]

8. Which of the following structures is the most preferred and hence of lowest energy for SO_3?

(1) 

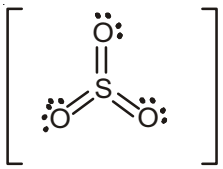
(2) 

(3) 

(4) 

Sol. Answer (2)

Molecule having covalent bond. Without resonance have maximum stability; minimum energy



9. Which of the following is paramagnetic?

(1) C_2^{2-} (2) Na_2O_2 (3) NO_2 (4) CO

Sol. Answer (3)

C_2^{2-}, O_2^{2-}, CO have even number of electron will be diamagnetic, NO_2 have unpaired electron will be paramagnetic.

10. The geometry of electron pairs around I in IF_5 is

(1) Octahedral (2) Trigonal bipyramidal (3) Square pyramidal (4) Pentagonal planar

Sol. Answer (1)

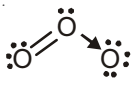
IF_5 $H = \frac{1}{2}[7+5-0+0] = \frac{12}{2} = 6$ sp^3d^2 Geometry = octahedral

11. The angular shape of molecule (O_3) consists of

(1) 2 sigma and 1 pi bond (2) 1 sigma and 2 pi bonds

(3) 2 sigma and 2 pi bonds (4) 1 sigma and 1 pi bond

Sol. Answer (1)



[O_3 have angular shape have two σ bond and 1 π bond]

12. In which of the following pair both the species have sp^3 hybridization?

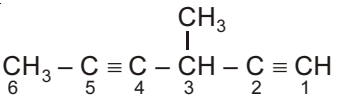
(1) H_2S, BF_3 (2) SiF_4, BeH_2 (3) NF_3, H_2O (4) NF_3, BF_3

Sol. Answer (3)

NH_3 $H = \frac{1}{2}[5+3-0+0] = \frac{8}{2} = sp^3$ H_2O $H = \frac{1}{2}[6+2-0+0] = \frac{8}{2} = sp^3$

[NH_3 and H_2O have same hybridisation but have different shape.]

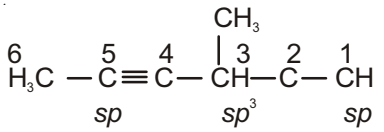
13. In the hydrocarbon



The state of hybridization of carbons 1, 3 and 5 are in the following sequence

(1) sp^3, sp^2, sp (2) sp^2, sp, sp^3 (3) sp, sp^3, sp (4) sp, sp^2, sp^3

Sol. Answer (3)



Hybridisation = $sp^{(3\text{-no. of } \pi \text{ bonds})}$

14. Which of the following molecule does not possess a permanent dipole moment?

(1) CS_2 (2) SO_3^{2-} (3) H_2S (4) SO_2

Sol. Answer (1)

$\mu = 0$ for CS_2 $\overset{-8}{S} = C = \overset{-8}{S}$ linear geometry

sp hybridisation

15. In which of the following compound there is more than one kind of hybridization (*sp*, sp^2, sp^3) for carbon?

(1) $CH_2 = CH–CH = CH_2$ (2) $H–C \equiv C–H$ (3) $CH_3CH_2CH_2CH_3$ (4) $CH_3–CH = CH–CH_3$

Sol. Answer (4)

$H_3C \overset{\sigma}{—} CH \overset{\pi}{=} CH \overset{\sigma}{—} CH_3$ contain both $sp \propto sp^3$

$sp^3 \quad sp^2 \quad sp^2 \quad sp^3$

16. The correct order of the O—O bond length in O_2, H_2O_2 and O_3 is

(1) $O_2 > H_2O_2 > O_3$ (2) $H_2O_2 > O_3 > O_2$ (3) $O_2 > O_3 > H_2O_2$ (4) $O_3 > H_2O_2 > O_2$

Sol. Answer (2)

$H_2O_2 > O_3 > O_2$

$O_2^{2-} \quad O_3 \quad O_2$

$\text{Bond length} \propto \frac{1}{\text{Bond order}}$

B.O = 1 1.5 2

17. Which of the following bonds has the highest energy?

(1) C–C (2) C≡C (3) C=C (4) C–H

Sol. Answer (2)

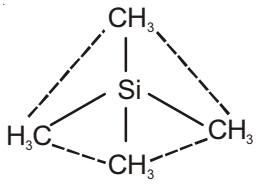
C ≡ C have two π bond and one σ bond, therefore will be more stronger.

18. The structure and hybridization of $Si(CH_3)_4$ is

(1) Octahedral, sp^3d (2) Tetrahedral, sp^3 (3) Bent, *sp* (4) Trigonal, sp^2

Sol. Answer (2)

$\left[Si(CH_3)_4\right] \qquad H = \frac{1}{2}[4 + 4 - 0 + 0] = \frac{8}{2} = 4\ sp^3$



Tetrahedral and sp^3

19. The number of bonding electron pairs in N_2 on the basis of molecular orbital theory is

(1) 3 (2) 2 (3) 5 (4) 4

Sol. Answer (3)

$N_2 = 14 = \sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \pi2p_x^2 = \pi2p_y^2, \sigma^*2p_z^2$

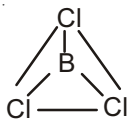
B B B B B

[No. of bonding pair = 5]

20. Which compound is electron deficient?

(1) NCl_3 (2) BCl_3 (3) CCl_4 (4) PCl_5

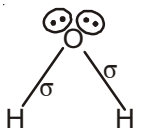
Sol. Answer (2)

BCl_3 is electron deficient molecule  Planar sp^2

21. Which one of the following molecules contains no π bond?

(1) H_2O (2) SO_2 (3) NO_2 (4) CO_2

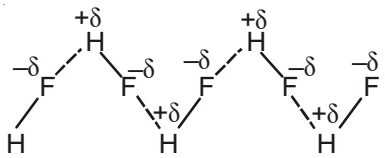
Sol. Answer (1)

H_2O have only sigma bond 

22. Which compound form polymer due to H-bond?

(1) H_2S (2) NF_3 (3) HF (4) HCl

Sol. Answer (3)

 [Polymeric due to H-bond]

23. Cation and anion combines in a crystal to form following type of compound

(1) Ionic (2) Metallic (3) Covalent (4) Dipole-dipole

Sol. Answer (1)

Cation and anion form ionic bond in crystal.

24. Which compound has tetrahedral structure?

(1) XeF_4 (2) $XeOF_2$ (3) XeO_2F_2 (4) XeO_4

Sol. Answer (4)

XeO_4 $\quad H = \frac{1}{2}[8+0-0+0]$

$\frac{8}{2} = 4\ sp^3$ tetrahedral structure

25. In which of the following bond angle is maximum?

(1) NH_3 (2) PCl_4^+ (3) BCl_3 (4) PCl_6^-

Sol. Answer (4)

$[PCl_6]^- \quad H = \frac{1}{2}[5+6-0+1] = \frac{12}{2} = 6\ sp^3d^2 = 180°$

As the bond angle is asked which is maximum in PCl_6^- i.e. 180° between linear pair.

26. In X – H ... Y, X and Y both are electronegative elements. Then

(1) Electron density on X will increase and on H will decrease

(2) In both electron density will increase

(3) In both electron density will decrease

(4) On X electron density will decrease and on H increases

Sol. Answer (1)

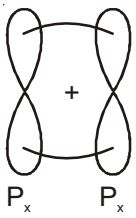
$\overset{-\delta}{X} - H \text{-------} \overset{-\delta}{Y}$ Electron density on X will increase and on H will decrease.

27. Main axis of a diatomic molecule is *z*, molecular orbital p_x and p_x overlap to form which of the following orbitals?

(1) π molecular orbital (2) σ molecular orbital (3) δ molecular orbital (4) No bond will form

Sol. Answer (1)

π molecular orbital $P_x - P_x$



$(P_x - P_x)$

28. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because

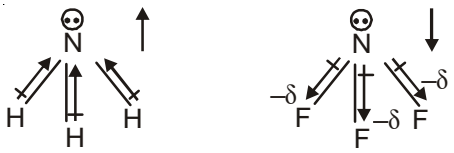
(1) In NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in the same direction

(2) In NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction

(3) In NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions

(4) In NH_3 as well as in NF_3 the atomic dipole and bond dipole are in opposite directions

Sol. Answer (3)



29. In the case of alkali metals, the covalent character decreases in the order

(1) MI > MBr > MCl > MF (2) MCl > MI > MBr > MF

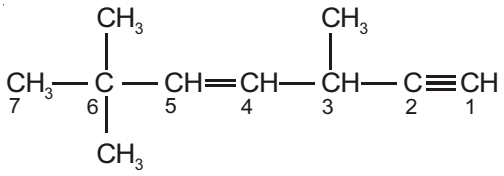
(3) MF > MCl > MBr > MI (4) MF > MCl > MI > MBr

Sol. Answer (1)

For same cation larger anion more will be covalent character

$\therefore$ MI > MBr > MCl > MF

30. The state of hybridization of C_2, C_3, C_5 and C_6 of the hydrocarbon,

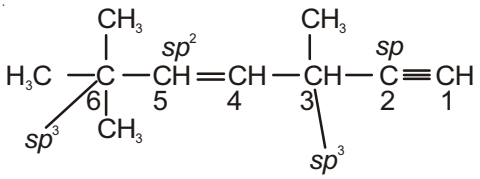


is in the following sequence

(1) sp, sp^2, sp^3 and sp^2 (2) sp, sp^3, sp^2 and sp^3

(3) sp^3, sp^2, sp^2 and sp (4) sp, sp^2, sp^2 and sp^3

Sol. Answer (2)



31. For two ionics solids CaO and KI, identify the wrong statement among the following.

(1) CaO has high melting point

(2) Lattice energy of CaO is much larger than that of KI

(3) KI has high melting point

(4) KI is soluble in benzene

Sol. Answer (4)

32. Which of the following molecules has the maximum dipole moment?

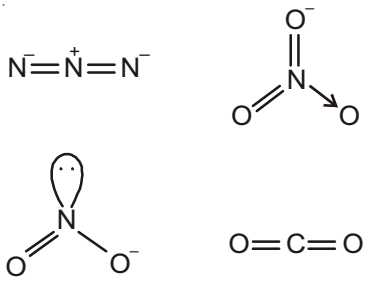
(1) CO_2 (2) CH_4 (3) NH_3 (4) NF_3

Sol. Answer (3)

33. Which one of the following species has plane triangular shape?

(1) N_3 (2) NO_3^- (3) NO_2^- (4) CO_2

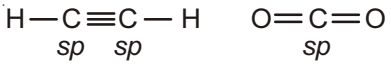
Sol. Answer (3)



34. Which of the following organic compounds has same hybridization as its combustion product –(CO_2)?

(1) Ethane (2) Ethyne (3) Ethene (4) Ethanol

Sol. Answer (2)



SECTION - D

Assertion - Reason Type Questions

1. A : N_2, CO and CN^- are having same bond order.
   R : Isoelectronic species always have same bond order.

Sol. Answer (3)

2. A : Bond angle of BF_3 and NF_3 are different.
   R : Both the molecules are having different shape.

Sol. Answer (2)

3. A : CO_2 is resonance stabilized molecule.
   R : Bond length of C–O in CO_2 is intermediate of single and double bond length.

Sol. Answer (3)

4. A : $BeCl_2$ in vapour phase is electron deficient molecule.
   R : Any molecule in which central atom is having incomplete octet is known as electron deficient molecule.

Sol. Answer (1)

5. A : H–F forms stronger hydrogen bond than H_2O.
   R : F is more electronegative than oxygen.

Sol. Answer (1)

6. A : Each molecule of H_2O forms four H-bond in the form of ice.
   R : Ice is solid state of H_2O.

Sol. Answer (2)

7. A : Both methane and tetrachloromethane are nonpolar.
   R : C–Cl bond is polar bond.

Sol. Answer (2)

8. A : N_2 is more stable than N_2^+.
   R : Bond order of N_2 is 3 while N_2^+ is 2.5.

Sol. Answer (1)

9. A : Lattice energy of CaO is higher than LiCl.
   R : Lattice energy of ionic compound is directly proportional to the product of charges of ion.

Sol. Answer (1)

10. A : All P–Cl bond lengths are equal in PCl_3 but different in PCl_5
    R : Hybrid state of central atom is different in both molecules.

Sol. Answer (2)

11. A : Equal number of sigma and π bonds are present in ethyne.

R : π bond is stronger than σ bond.

Sol. Answer (4)

12. A : Bond order of H_2^+ is 0.5.

R : Electrons are removed from the antibonding molecular orbital from H_2.

Sol. Answer (3)

13. A : LiCl is more covalent than $BeCl_2$.

R : Li^+ ion is smaller than Be^{2+}.

Sol. Answer (4)

14. A : O_2 is paramagnetic.

R : N_2 is paramagnetic.

Sol. Answer (3)

15. A : PCl_5 exist but NCl_5 does not.

R : Nitrogen is highly inert.

Sol. Answer (2)

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