Chapter - 3

CHEMICAL BONDING AND MOLECULAR STRUCTURE

UNIT : 1

1. Kossel's Lewis approach to chemical bonding
2. Factors favourable for the formation of ionic bond ; Energy changes in ionic bond formation
3. Crystal lattice energy – calculation lattice energy – Born- Haber cycle
4. Crystal structures of sodium chloride and Caesium chloride
5. Properties of ionic compounds

Very Short Answer Questions :

1. **What are the coordination numbers of NaCl and CsCl crystals ?**

   In NaCl crystal, the coordination number of both Na^+ and Cl^- are 6 and 6 respectively because the limiting radius ratio is 0.52.

   CsCl crystal, has the coordination number of Cs^+ and Cl^- are 8 and 8 respectively because the limiting radius ratio is 0.93

2. **Cl^- has greater stability than chlorine atom. Why ?**

   Cl^- is stable due to [Ar] configuration. Cl atom has one electron lessthan (Ar) configuration. Hence it is unstable and has lesser stability.

Short Answer Questions :

1. **Define "Lattice energy" of crystals. Calculate the number of sodium ions and chloride ions per unit cell of NaCl.**

   Lattice energy :

   "The energy liberated when one mole of crystalline substance is formed from the gaseous ions" is known as lattice energy (U) of the crystal.

   Calculation of number of ions per unit cell of NaCl :

   Number of body centered sodium ions in the lattice = 1

   Number of Na^+ ions present on the edge centre = 12

   $\therefore$ Total number of Na^+ ions present per unit cell = $\left(12\times\frac{1}{4}\right)+1=4$

   Similarly number of Cl^- ions present at the corners of the unit cell = 8

   Number of face centered Cl^- ions = 6

   $\therefore$ Total number of Cl^- ions present per unit cell = $\left(8\times\frac{1}{8}\right)+\left(6\times\frac{1}{2}\right)=4$

Thus there are $4Na^+$ and $4Na^+$ ions present per unit cell of NaCl i.e, the unit cell of NaCl consists of 4 ion pairs.

2. **Which of the two ions Ca^{2+} and Zn^{2+} is more stable ? Why ? For ionic substances which is the proper term to use "Formula weight" or "Molecular weight" ?**

   a) Ca^{2+} ion (2, 8, 8) with noble gas configuration is more stable than Zn^{2+} ion (2, 8, 18) which has pseudo inert gas configuration.

   b) For ionic substances, formula weight is proper term to use, because ionic compounds do not have exact independent molecules as their constituent units. On vapourization of such ionic crystals, only "ion pairs are produced. In such situations as these, it is proper to express their quantities in terms of "formula weights" rather than in terms of molecular weights.

3. **Explain the properties of ionic compounds.**

   i) Physical state : Due to close packing of ions, ionic compounds are crystalline solids.

   ii) Melting and Boiling points : In ionic crystals the oppositely charged ions are bound by strong electrostatic force of attraction. To break these attractive forces between ions, more heat energy is required. Hence the melting and boiling points of ionic compounds are high.

   iii) Solubility : Ionic compounds are soluble in polar solvents like water, liquid ammonia etc, but are insoluble in non – polar solvents like benzene, carbon disulphide, etc

   iv) Reactivity : Reactions between ionic compounds in aqueous solution are very fast due to strong attraction among ions.

   e.g : When $AgNO_3$ solution is added to NaCl solution, a white precipitate of AgCl is formed.

   $$Ag^+NO_{3\,(aq)}^- + Na^+Cl^-_{(aq)} \longrightarrow AgCl_{(ppt)} \downarrow + Na^+NO_{3\,(aq)}^-$$

   v) Isomerism : Ionic compounds do not exhibit isomerism due to non – directional bonds

   vi) Electrical conductivity : Ionic substances conduct electricity in molten state and in aqueous solution, **due to the movement of ions** The ionic compounds act as electrolytes.

   In solid state the ions are not free to move due to regular arrangments and are poor conductors of electricity. In molten state the regular arrangement of ions is destroyed and ions are free to move

LONG ANSWER QUESTIONS :

1. **Explain the formation of ionic bond in terms of atomic orbitals. Discuss the factors that favour the ionic bond formation.**

   "The electrostatic force of attraction between oppositely charged ions is called ionic bond".

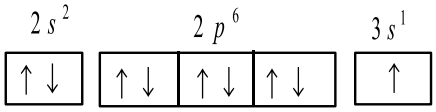
   Ionic bond is formed by the transper of electrons from one atom to another atom.

   Formation of ionic bond is explained by Kossel.

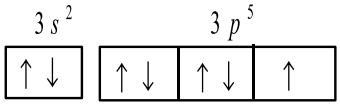
Orbital Concept – Ionic Bond : The formation of ionic bond can be explained by orbital concept by representing each orbital by one square bracket and electron by an arrow.

Ex : 1 Formation of Sodium Chloride

Outer electronic configuration of Na is



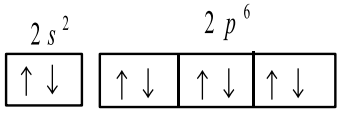
Outer electronic configuration of Cl is



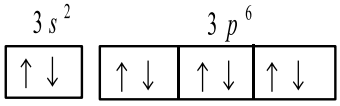
Na contains one electron excess than Neon configuration and Cl contains one electron less than the Argon configuration.

Electron transfer takes place from 3s of Na atom to 3P of Cl atom forming Na^+ and Cl^- ions.

Outer configuration of Na^+



Outer configuration of Cl^-



The Na^+ and Cl^- ions are held by strong electrostatic force known as ionic bond.

Factors favourable for the formation of ionic bond :

1) Factors favourable for the cation formation

2) Factors favourable for the anion formation

FORMATION OF CATION :

i) Low ionization potential :

If the ionization potential is less, the energy required to remove the electron is less and hence cation is formed readily. Since IP of K is less than Na, K^+ is readily formed than Na^+

ii) Low charge on the ion :

As the magnitude of charge on the ion increases, more number of electrons are to be removed. This requires high energy. So ion with lower charge will be formed easily.

order of ease of formation.

$$Na^+ > Mg^{+2} > Al^{+3}$$

iii) Large atomic size :

As the size of atom increases the force of attraction of the nucleus on the outermost electron decreases. Hence it requires less energy to remove electron and cation will be formed easily.

In case of IA group elements the size of elements increases from Li to Cs hence the order of ease of formation of ions also increases.

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

iv) ion with inert gas configuration :

Ions possessing noble gas electronic configuration are more stable and formed more easily than ions **with pseudo inert gas configuration.**

Ex : Ca^{+2} ion (2, 8, 8) with noble gas configuration is more stable than Zn^{+2} ion (2, 8, 18). Ca^{+2} ion is formed from the Calcium atom more easily than Zn^{+2} ion from Zn.

Possing 18 electrons instead of 8 electrons in the outermost shell is called pseudo inert gas configuration or Nickel group configuration.

Ions of IIB $\left(Zn^{+2}, Cd^{+2}, Hg^{+2}\right)$ and ions of IB $\left(Cu^+, Ag^+, Au^+\right)$ have nickel group configuration.

FORMATION OF ANION :

i) High Electron Affinity and Electro negativity :

Higher the value of electron affinity and electro negativity, greater is the tendency of an atom to accept electrons. Hence elements with higher electron affinity and electro negativity forms anions more readily.

Tendency to form anion among Cl_2 and Br_2 is Cl > Br

ii) Charge on the ion :

Ions with lower charge are more easily formed than those with higher charge. Anions with higher charge have greater inter electronic repulsions. Hence they are not formed easily. The order of ease of formation of anions is $F^- > O^{-2} > N^{-3}$

iii) Small atomic size :

Lesser the size of atom, greater will be the nuclear force of attraction. Hence atoms with smaller size form anions more easily.

Ex : $F^- > Br^- > I^-$

2. Discuss Born – Haber cycle with reference to NaCl.

(or)

Calculate theoretically the lattice energy of an ionic solid.

Born Haber Cycle : Lattice energy of an ionic crystal is determined by using Born Haber's cycle which is based on **"Hess's law"**

Hess's law states that "Whether a reaction takes place in a single step or in several steps the total amount of energy change in the same"

Starting from solid sodium and gaseous chlorine, one mole of solid sodium chloride can be obtained in two different paths.

First Path : When chlorine is passed over solid sodium metal, sodium chloride crystals are formed. The energy released in the formation of one gram mole of solid NaCl crystals is called heat of formation, represented by ΔH_f

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \longrightarrow NaCl_{(s)} \;\; \Delta H = -\Delta H_f = -410.5\,KJ/mole$$

Second path : In this path sodium chloride is obtained in 5 stages

1) Formation of gaseous sodium atoms : Solid sodium when heated, changes to gaseous sodium atom. The energy absorbed in this process is called sublimation energy, represented by

$$Na_{(s)} \longrightarrow Na_{(g)}\,;\, \Delta H_1 = S_{Na} = 108.7\,KJ/mole$$

2) Dissociation of chlorine molecule into atoms : The energy required for the dissociation of one gram mole of chlorine molecules into chlorine atoms is called "dissociation energy" represented by

$$\frac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)}\,;\, \Delta H_2 = \frac{1}{2}D_{Cl_2} = 119.55\,KJ/mole$$

3) Ionization of Sodium : When energy equivalent to ionization energy is given to sodium atom in gaseous state. Sodium ions are formed represented by

$$Na_{(g)} \longrightarrow Na^{+}{}_{(g)} + e^{-}\,;\, \Delta H_3 = I.P = 492.82\,KJ/mole$$

4) Formation of chlorine atom : Gaseous chlorine atom gains electrons and forms chloride ion. The energy released in this process is called electron affinity represented by E. It is equal to

$$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}{}_{(g)}\,;\, \Delta H_4 = -E = -361.57\,KJ/mole$$

5) Formation of NaCl crystals : One gram mole of sodium chloride crystal is formed from gaseous Na^{+} and Cl^{-} ions, the energy released in this process is called "Lattice energy" represented by 'U'

$$Na^{+}{}_{(g)} + Cl^{-}{}_{(g)} \longrightarrow NaCl_{(s)}\,;\, \Delta H_5 = -U = -769.96\,KJ/mole$$

Total energy change in the formation of NaCl crystals from Na (s) and $\frac{1}{2}Cl_2(g)$ in the above five steps is

$$S_{Na} + \frac{1}{2}D_{Cl_2} + IP - E - U$$

According to Hess law : Energy changes in single step = energy changes in 5 steps

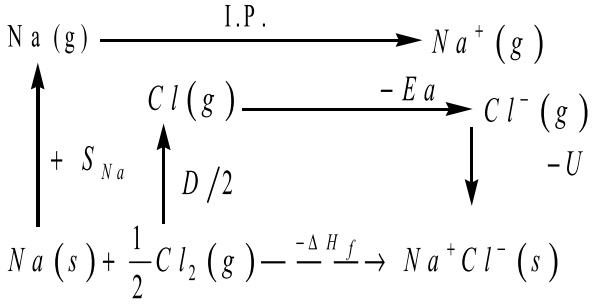
$$-\Delta H_f = S_{Na} + \frac{1}{2}D_{Cl_2} + IP - E - U$$

$$\therefore U = \Delta H_f + S + \frac{D}{2} + I - E$$

= - 410.5 + 108.7 + 119.55 – 492.82 – 361.57

$= -769.96\,KJ/mole$

Formation of NaCl crystals by the two paths can be represented by the following diagram which is known as **Born – Haber cycle.**



Applications of Haber cycle :

1) Lattice energies of ionic crystals can be determined

2) Electron affinities of certain non metals can be determined

3. Write a note on Fajan's rule.

Fajan's Rules : With the help of Fajan's rule, the nature of the chemical bond (ionic or covalent) can be predicted knowing the size, charge, configuration etc of the atoms involved in bonding.

1) ionic nature of the bond increases with increase in size of the cation

Ex : The ionic nature increases with increase in size of the cation

Ex : The ionic nature increases in the order, $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, since the size of the cation increases in the same order

2) Formation of a smaller anion favours the formation of ionic bond

Ex : F^- is smaller than I^-. So CaF_2 is more ionic than CaI_2

3) Anion or cation or both ions, having smaller charges favour the formation of ionic bonds

Ex : Na^+Cl^- is more ionic that $AlCl_3$ (with Al^{3+} ion)

4) Cations with inert gas configurations form ionic compounds while cations with pseudo inert gas configurations favour covalent bond formation.

Ex : $CaCl_2$ is more ionic than $ZnCl_2$

In $Ca^{2+}\left(3s^2 3p^6\right)$ there is inert gas configuration. In $Zn^{2+}\left(3s^2 3p^6 3d^{10}\right)$ there is pseudo inert gas configuration.

5) Highly charged cation and highly charged anion generally form covalent compounds.

4. Define Octet rule. Discuss its significance.

Octet rule: "Every atom must possess 8 electrons in its outermost energy level for its stability".

Atoms combine in two ways to get octet either by transfer of electrons (or) by mutual sharing of electrons. They can attain $ns^2\,np^6$ configuration.

e.g : 1) Na loose one electron to get Ne configuration by possessing 8 electrons

Na : $1s^2\,2s^2\,2p^6\,3s^1$ and $Na^+ : 1s^2\,2s^2\,2p^6$

2) 'Cl' atom take one electron to get "Ar" configuration

Cl^- : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

Here Na^+ and Cl^- ions obey octet rule

3) In H_2O molecule oxygen obey octet rule

It is therefore, concluded that s^2p^6 configuration in the outer energy level constitutes a structure of maximum stability and therefore, of minimum energy.

The atoms of all elements when enter into chemical combination try to attain noble gas configuration (i.e) they attain 8 electrons in their outermost energy level which is of maximum stability and hence of minimum energy.

The tendency of an atoms to achieve eight electrons in their outermost shell is known as OCTET **RULE.**

Octet rule was the basis of electronic theory of valency.

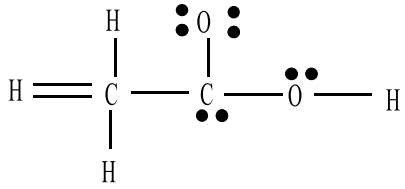
CHEMICAL BONDING AND MOLECULAR STRUCTURE

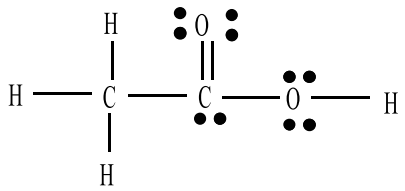
UNIT: 2

1 Covalent bond – VSEPR theory and prediction the geometry of simple molecules
2 The valence bond approach for the formation of covalent bonds
3 Directional properties of covalent bond
4 Properties of covalent bond
5 Hybridization of orbitals and shapes of molecules
6 Definition of coordinate covalent bond with examples

Very Short Answer Questions:

1. **Predict the shape of molecule with four bond pairs on the central atoms.**
   According to VSEPR theory, the molecule with four bond pairs on central atom will have tetrahedral geometry.
2. **Explain what is meant by localized orbitals?**
   The orbitals which are involved in bond formation in a molecule and are present in between the nuclear axis are called localized orbitals.
3. **When does 'AB' molecule become a covalent molecule? (A and B are atoms of elements)**
   When A and B with electronegativity difference less than 1.9 and bond is formed by sharing electron pairs to form a covalent bond ..
4. **Why argon is not represented by Ar_2 ?**
   Ar atom has all paired electrons with stable octet configuration. Thus it cannot form diatomic molecule by sharing the electrons..
5. **What is the valency of element [A(Z) = 15]**
   The element with Z = 15 has its E.C. $[Ne]3s^2\,3p^3$. It can show valency 3 due to three unpaired electrons in psubshell in ground state. Due to the presence of vacant d orbitals, in excited state it can exhibit valency 5 due to 5 unpaired electrons.
6. **Correct the given structure :**





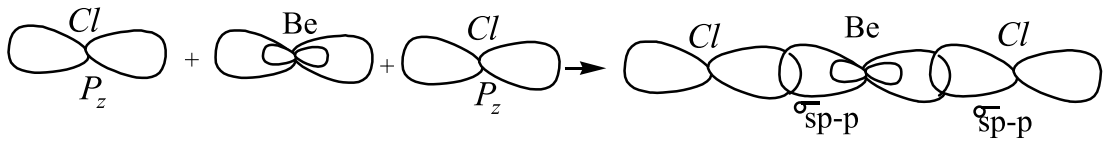
Short Answer Questions:

1. Explain the shape and the bond angle in $BeCl_2$ in terms of VBT.

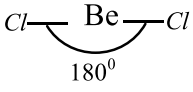
In $BeCl_2$, Be is the central atom. Its atomic number is 4. Therefore its ground state electron configuration is $1s^2 2s^2$. In order to explain the formation of $BeCl_2$. Sp hybridization is to be assumed for Be in its excited state. The excited state configuration of Be is $1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$.

As a result of which two sp hybrid orbitals will form on it. Now the two sp hybrid orbitals overlap Head-Head with $3p_z$ orbitals of two chlorine atoms forming two sigma bonds.

The molecule is linear and the bond angle is 180^0.



(or)

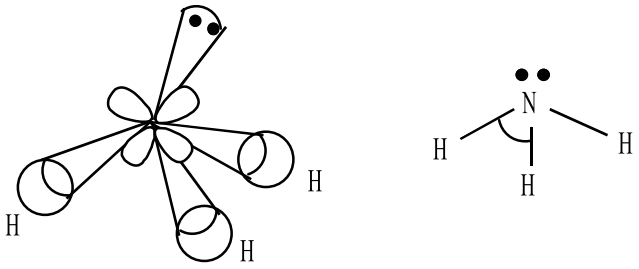


2. Even though nitrogen in ammonia is in sp^3 - hybridization, the bond angle is not $109°28'$. Explain.

Ammonia molecule: (NH_3)

The central atom Nitrogen in ammonia molecule undergoes sp^3 hybridization to form four hybrid orbitals. Out of four one contains a lone pair of electrons and remaining are half filled. These half filled sp^3 hybrid orbitals overlap with 1s orbital of hydrogen to form 3σ $sp^3 - s$ bonds. The bond angle is expected to be$109°28'$.

According to VSEPR theory, due to **repulsions between the lone pair and the bond pair the angle reduces to** $107°$ and the molecule attains **trigonal pyramidal** shape

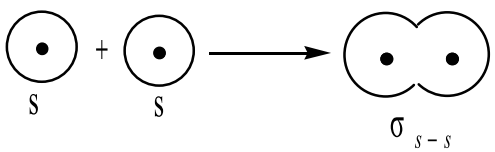


Structure of NH_3

3. Explain the formation of sigma (σ) bonds in molecules with at least two examples.

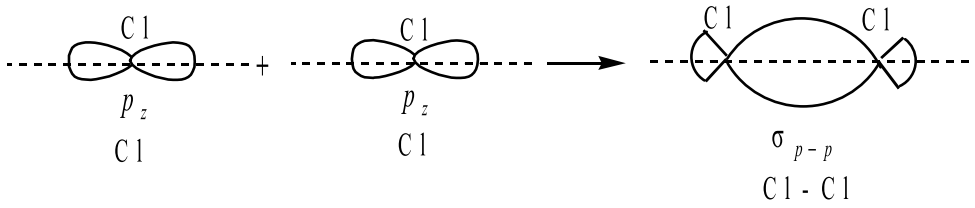
Sigma (σ) bond: "A covalent bond formed between two atoms with the electron clouds concentrated along the internuclear axis or formed by end on overlapping is known as a sigma (σ) bond

Ex : (1) When two hydrogen atoms approach each other, 1s – orbitals of the Hydrogen atoms overlap to form a strong "σ" bond. This bonding orbital includes in it both the nuclei. It is σ_{s-s}



Formation of H_2 molecule overlap of 's' orbitals

2) The electronic configuration of Cl: $[Ne]3s^2\,2p_x^2\;3p_y^2\,3p_z^1$ The $3p_z$ orbital of one chlorine atom overlaps with the $3p_z$. Orbital of anotherchlorine atom along internuclear axis. The two electrons with opposite spins pair up to form covalent bond. resulting in the formation of σ_{p-p} bond.



Formation of chlorine molecule (overlap of 'p' orbitals)

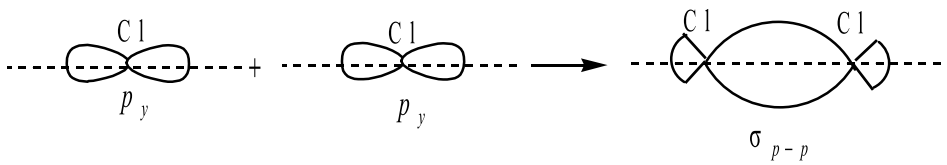
4. What is π bond? Explain with two examples.

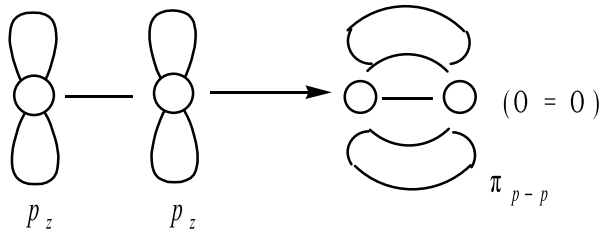
Definition of π - bond : "A covalent bond formed by a side wise overlap of p – orbitals or p - and d - orbitals of atoms in which the electron clouds are present above and below the internuclear axis is known as π - bond"

Pi bond is formed after the formation of sigma bond

e.g : **(1) Formation of O_2 molecule :**

The electronic configuration of oxygen atom is $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$. Then the $2p_y$ orbitals of the two oxygen atoms overlap along the internuclear axis i.e, undergo end – on overlap, to produce a σ - bond. The $2p_z$ orbitals of these atoms are in a perpendicular direction to that of the internuclear axis. . hence they can undergo lateral overlap (i.e. side-wise overlap) to form a second covalent bond. The banana shaped electron clouds of this bond are on either side (above and below) of the internuclear axis. The bond of this type, when formed, is known as π - bond.





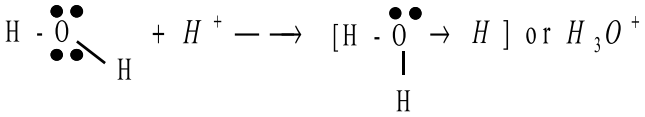
Formation of oxygen molecule $(1\sigma \text{ and } 1\pi \text{ bonds})$

e.g : **(2) Formation of N_2 molecule:**

The electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. There are three half-filled 2p orbitals, by the overlap of p_x orbitals of the two atoms gives a σ_{p-p} bond and by the overlap of the p_y and p_z orbitals two π bonds of the nature π_{p-p} are formed.

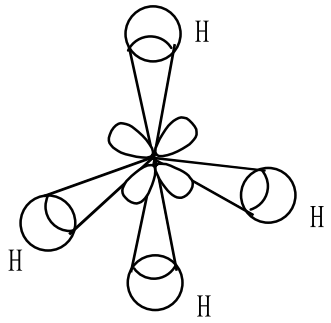
5. Draw a similarity between the bonds in H_3O^+ and those in CH_4 Hydronium ion:

Central atom 'O' undergoes sp^3 hybridization. There are two σ_{sp^3-s} bond and one dative bond.



Methane molecule:

Central atom 'C' undergoes sp^3 hybridization. There are four σ_{sp^3-s} bonds.



Structure of CH_4

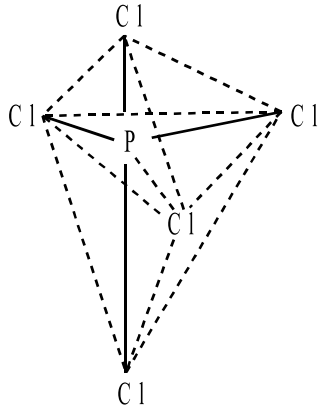
6. Write the order of bond strengths of various bonds formed from's' and 'p' orbitals. When do they hybridize?

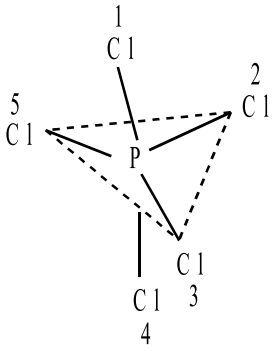
- According to the valence bond theory, the greater the extent of overlapping, the greater will be the bond strength. Because of the shape dumbbell of 'p' orbitals, 'p' orbitals can effectively overlap with each other than other kind of orbitals. The 's' orbitals being spherical they cannot overlap to a greater extent. Hence the order of overlapping is p – p > s – p > s – s
- In case of hydrogen atom the strength of s – s bonds is more. due to of the small size they can overlap strongly. The increasing order of bond energies for hybrid orbitals is $sp < sp^2 < sp^3$
- The orbitals of the same atom only participate in the hybridization. Orbitals of different atoms do not hybridize.
- The energies of the hybridizing orbitals be nearly equal

7. What hybridization is undergone by the central element in PCl? Apply VBT to its structure.

Shape of PCl_5 by using sp^3d hybridization:

- In PCl_5 the central atom is phosphorus
- Ground state outer shell configuration of Phosphorus is $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
- The excited state outer shell configuration of Phosphorus is $3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d_{z2}^1$ In the formation of PCl_5 the central atom phosphorus **undergoes into sp^3d hybridization** to form five half filled sp^3d hybrid orbitals, which are oriented in trigonal bi-pyramidal arrangement. These five orbitals overlap with p_z orbitals of chlorine atoms to form five sigma bonds between phosphorus and chlorine.
- Therefore the shape of the molecule is trigonal **bipyramidal** and **the bond angles are** $90°$ **and** $180°$ **and** $120°$





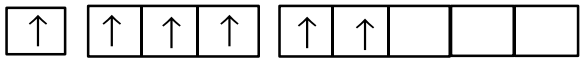
8. Explain sp^3d^2 hybridization with an example.

In this hybridization one 's' orbital, three 'p' orbitals and two 'd' orbitals of the excited atom combine to form six equivalent sp^3d^2 hybrid orbitals.

e.g : SF_6

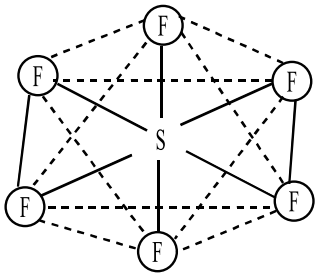
S (Z = 16) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$ (ground state)

$1s^2\,2s^2\,2p^6\,3s^1\,3p_x^1\,3p_y^1\,3p_z^1\,3d^2$ (excited state)

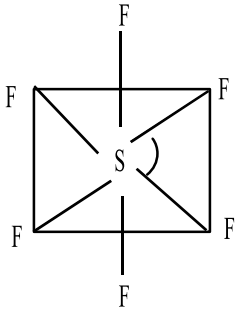


sp^3d^2 hybridisation

These six sp^3d^2 hybrid orbitals overlap six $2p_z$ orbitals of fluorine atoms to form six $\sigma_{sp^3d^2}$ bonds. The directions of the bonds give an octahedral shape to the molecule. The bond angle is $90°$ or $180°$ and $90°$



Structure of SF_6 molecule
(not to scale)



Octahedral
total σ
bonds = 6

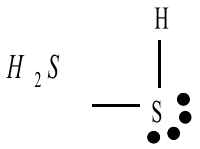
LONG ANSWER QUESTIONS:

1. Draw Lewis structures for the following molecules and ions.

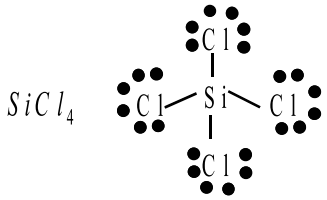
a) H_2S **b)** $SiCl_4$ **c)** CO_3^{2-} **d) HCOOH**

Lewis structures:

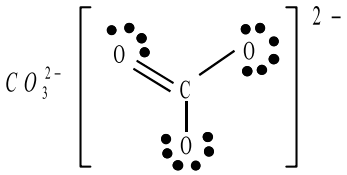
a)



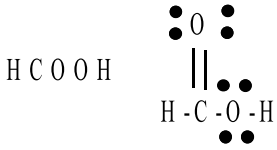
b)



c)



d)



2. Write a note on Fajan's rule.

Fajan's Rules:

Fajan's rules are useful to predict the nature of the bond formed between two atoms. The rules are

- Increase in cationic size increases the ionic nature of the bond

  Ex: Among the alkali metal ions, the ionic nature of the bond follows the sequence $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

- Decrease in anionic size favours the formation of ionic bond

  Ex: Among the calcium halides, (CaX_2) the fluoride is more ionic than iodide.

- Low charged cation or anion or both generally leads to more ionic character

  Ex: Na^+Cl^- is ionic because both ions have low charges. $AlCl_3$ is more covalent due to the presence of highly charged Al^{3+} ions.

- Cations with inert gas configuration form ionic compounds while those cations with pseudo inert gas configuration favour covalent bond formation.

  Na^+ in NaCl has an inert gas configuration. So NaCl is ionic, but CuCl is more covalent because Cu^+ has pseudo inert gas configuration in this compound.

Element – A	**Element – B**	**Name of compound formed**
Larger cation	Smaller anion	Strong ionic bond
Smaller size cation	Larger size anion	Covalent bond
Larger cation with low charge	Smaller cation with low charge	Strong ionic bond
Smaller cation with higher charge	Larger anion with higher charge	Covalent bond

3. Define Octet rule. Discuss its significance.

Octet rule: "Every atom must possess 8 electrons in its outermost energy level for its stability".

Atoms combine in two ways to get octet either by transfer of electrons (or) by mutual sharing of electrons. They can attain $ns^2\,np^6$ configuration.

e.g : 1) Na loose one electron to get Ne configuration by possessing 8 electrons

Na: $1s^2\,2s^2\,2p^6\,3s^1$ and $Na^+ : 1s^2\,2s^2\,2p^6$

2) 'Cl' atom takes one electron to get "Ar" configuration

Cl^- : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

Here Na^+ and Cl^- ions obey octet rule

3) In H_2O molecule oxygen obey octet rule

It is therefore, concluded that s^2p^6 configuration in the outer energy level constitutes a structure of maximum stability and therefore, of minimum energy.

The atoms of all elements when enter into chemical combination try to attain noble gas configuration (i.e) they attain 8 electrons in their outermost energy level which is of maximum stability and hence of minimum energy.

The tendency of atoms to achieve eight electrons in their outermost shell is known as OCTET RULE.

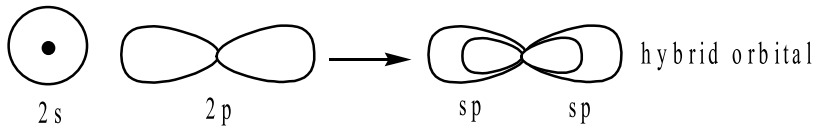
Octet rule was the basis of electronic theory of valency.

4. Discuss Hybridization with suitable examples.

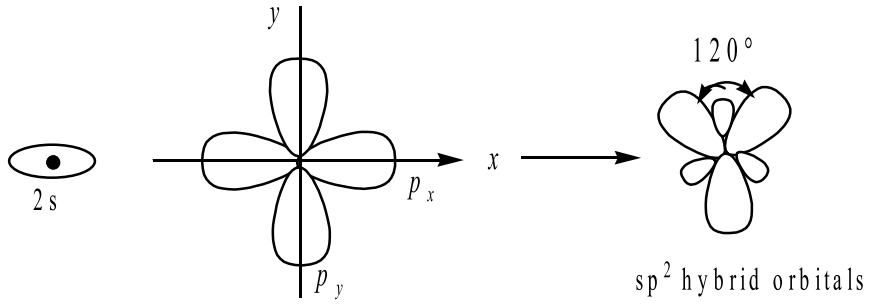
Hybridization of atomic orbitals may be defined as "The intermixing of atomic orbitals of almost equal energies of an atom and their redistribution into an equal number of identical orbitals".

Types of Hybridisation:

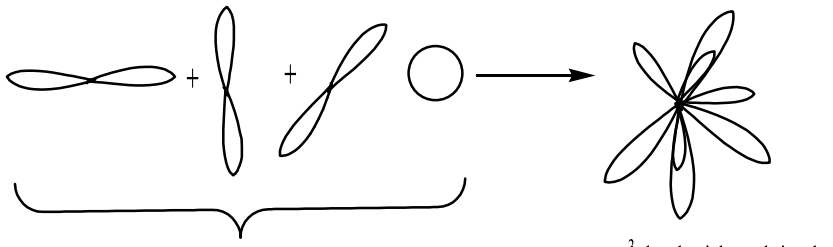
sp hybridization : The mixing of an s and p orbital only leads to formation of two hybrid orbitals. The bond angle between these is $180°$ and each sp orbital has 50 percent s character and 50 percent p character.



sp^2 **hyridisation:** When one s and two p orbitals mix upto hybridize, these results three new orbitals called sp^2 **hybrid orbitals** inclined at a bond angle of $120°$ giving a shape of **trigonal planar**, with % of s = 33.3 and % of p = 66.6



sp^3 **Hybridization:** When one s and three p orbitals mix up and hybridise on total of **four** sp^3 **hybrid orbitals** are formed which orient themselves at a bond angle of $109°28'$ giving the shape **tetrahedral**. % of s = 25% and p = 75%



Examples of sp^3 hybridization:

(i) Formation of Methane molecule:

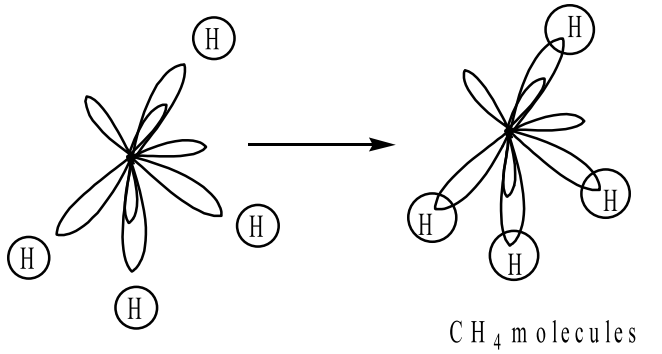
Ground state outer configuration of carbon

$$2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^o$$

Excited state outer configuration of C atom:

$$2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

In the formation of CH_4 carbon undergoes sp^3 **hybridization** to form four half filled sp^3 hybrid orbitals which are oriented themselves in tetrahedral manner. Each of these sp^3 hybrid orbitals overlap with 1s orbital of hydrogen forming methane molecule having **tetrahedral shape** with **bond angle** 109°28'



σ bonds = 4

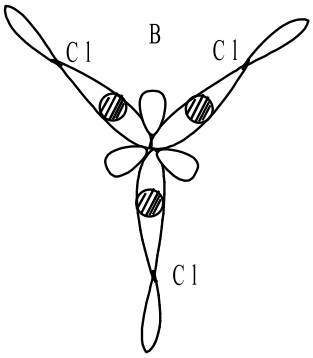
B. = 109°28'

Shape of BF_3 using sp^2 hybridization:

In BF_3 central atom is B

Ground state configuration of B is $1s^2\,2s^2\,2p^1$

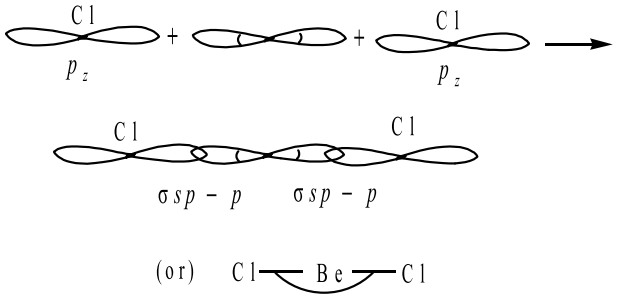
Excited state configuration of B is - $1s^2\,2s^1\;2p_x^{\,1}\,2p_y^{\,1}\;2p_z^{\,o}$. In the formation of BF_3 the **central B** undergoes sp^2 **hybridization** to form 3 half filled sp^2 hybrid orbitals which are oriented themselves in triangular planar manner. These three hybrid orbitals having unpaired electrons overlap with 'p' orbitals of fluorine forming three sigma bonds.



The molecule is **trigonal planar** with **bond angle** of $120°$. Boron can form one dative bond by accepting lone pair into vacant p_z orbital.

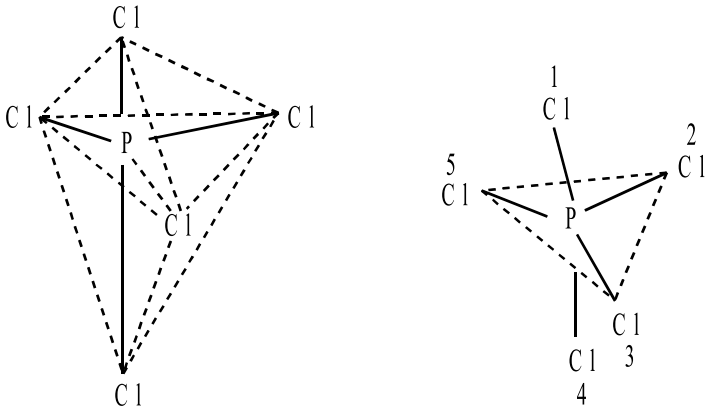
Shape of $BeCl_2$ using sp hybridization:

- In $BeCl_2$ the central atom is Be
- The ground state configuration Be - $1s^2\,2s^2$
- The excited state configuration of Be - $1s^2\,2s^1\;2p_x^{\,1}\,2p_y^{\,o}\;2p_z^{\,o}$
- In the formation of $BeCl_2$ the central **Be atom** undergoes **sp hybridization** to form two half filled sp hybrid orbitals which are oriented themselves in linear manner. Using these orbitals Be forms two bonds with two Cl atoms by overlapping with their half filled p_z orbitals. Hence the molecule is linear with a **bond angle of** $180°$



Shape of PCl_5 by using sp^3d hybridization:

- In PCl_5 the central atom is phosphorus
- Ground state outer shell configuration of Phosphorus is $3s^2\ 3p_x^{\ 1}\ 3p_y^{\ 1}\ 3p_z^{\ 1}$
- The excited state outer shell configuration of Phosphorus is $3s^1\ 3p_x^{\ 1}\ 3p_y^{\ 1}\ 3p_z^{\ 1}.\ 3d^1_{z^2}$
- In the formation of PCl_5 the central atom, phosphorus **undergoes into** sp^3d **hybridization** to form five half-filled sp^3d hybrid orbitals, which are oriented in trigonal bi-pyramidal arrangement. These five orbitals overlap with p_z orbitals of chlorine atoms to form **five sigma bonds** between phosphorus and chlorine.
  Therefore the shape of the molecule is trigonal bipyramidal and the **bond angles are** $90°$ **and** $180°$ **and** $120°$



Shape of SF_6 molecule by using sp^3d^3 hybridization:

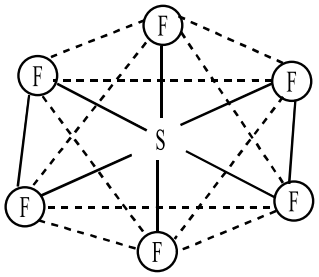
- In SF_6 the central atom is sulphur
- Ground state outer shell configuration of Sulphur is $3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 1}\ 3p_z^{\ 1}$

- The excited state outer shell configuration of sulphur is

  $3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1 . 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

- In the formation of SF_6 the central atom, sulphur **undergoes into** sp^3d^2 **hybridization** to form six half filled sp^3d^2 orbitals, which are oriented in the octahedral arrangements. These six orbitals overlap with p_z orbital of six fluorine atoms to form **sigma bonds** between sulphur and fluorine.

  Therefore, the shape of the molecule is **octahedral** and the **bond angle** is $90°$



Structure of SF_6 molecule
(not to scale)

5. Write an essay on VSEPR theory.

VSEPR theory was proposed by Gillespy and Nyholm. It predicts the shapes of molecules without reference to the hybridization.

The important points in the theory are:

1) The shape of a molecule depends upon the number of electron pairs (bond pairs) present on the central atom. It there are only 'bond pairs' and no ' lone pairs' on the central atom, the molecules assumes a regular geometrical shape.
2) If there are 'lone pairs ' also on the central atom. Then the structure gets distorted and the bond angle changes
3) A 'lone pair of electrons' occupy more space around the central atom than a bond pair is attracted by two nuclei.
4) The electron pairs orient in space so as to have minimum repulsions among them, which determines the 'bond angles'.
5) The order of repulsion between various electron pairs is
   1. p – 1 p> 1.p – b.p > b.p- b.p

6) The magnitude of repulsion between bond pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
7) The order of repulsion between different bonds is : Triple bond > Double bond > Single bond

Shape of molecules based as VSEPR theory

No. of electron pairs	**Type of electron pairs**	**Type of molecule**	**Shape**	**Example**
2	2BP	AB_2	Linear	$BaCl_2$
3	3BP	AB_3	Plane triangular	BCl_3
3	2BP + 1LP	AB_2	V-shaped	SO_2
4	4BP	AB_4	Tetrahedral	CH_4
4	3BP + 1LP	AB_3	Pyramidal	NH_3

6. How does Pauling – Slater's valence bond theory explain the bond directions and molecular geometries?

This theory explains the shapes of covalent molecules as well as directions of the bonds in them.

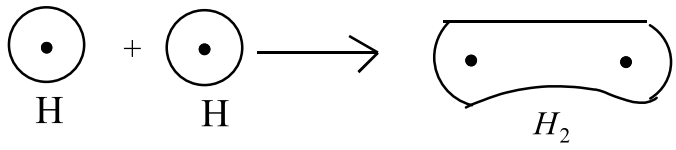
Important postulates:

1) Covalent bond is formed by the overlap of two atomic orbitals.
2) The overlapping orbitals contain upaired electrons with opposite spins.
3) Each of the bonded atoms retains its own atomic orbitals. But the electron pair in the overlapping orbitals is shared by both the atoms.
4) The greater the extent of overlap of orbitals, the stronger is the covalent bond formed.

5) Except ‘s’ orbitals, the remaining all atomic orbitals are directional. So the bonds formed due to their overlap are also directional. This determines the shape of the molecule.
6) When the atomic orbitals of the two atoms overlap, then electron density increases on their internuclear axis. This binds the two atoms, firmly. Thus the molecule is stabilized.

Ex : Formation of Hydrogen molecule (s-s- overlap) :

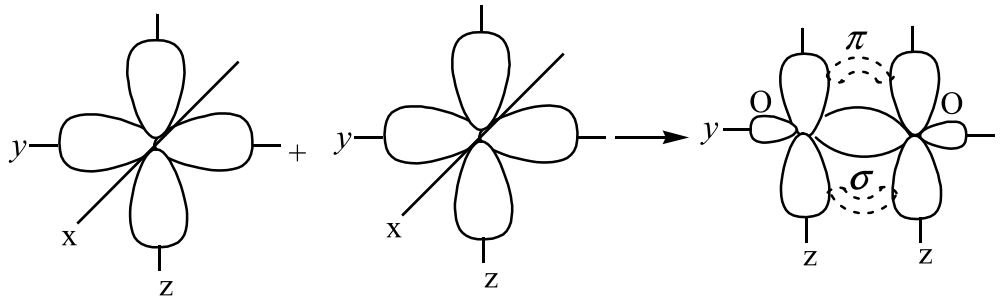
Hydrogen molecule is formed due to overlap of 1 s- orbitals of two hydrogen atoms. The bond formed between the two H- atoms is called sigma bond and the type of overlapping is s-s overlap.



Formation of Hydrogen molecule

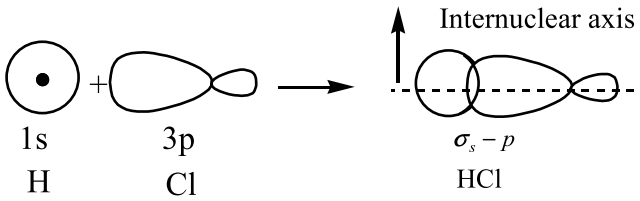
Formation of oxygen molecule (p-p overlap):

Atomic number of oxygen is 8. Therefore, its electron configuration is $Is^2 2s^2 2p_x^2 2p_x^1 2p_z^1$. It has two half- filled 2p orbitals ie., $2p_y \, and \, 2p_z$. In the formation of O_2 molecule, at first, the $2P_y$ orbital of one oxygen atom overlaps Head-Head with $2P_y$ orbital of the second oxygen atom forming a sigma bond between them. Now, the $2p_z$ orbitals of the two oxygen atoms which are at right angles to the $2p_y$ orbitals overlap sidewise forming a pi bond between them. Thus in oxygen molecule there exists a double bond between the two oxygen atoms. Out of them one is σ_{p-p} bond and the other is π_{p-p} bond



Formation of Hydrogen chloride molecule (s – overlap):

In the formation of HCl molecule, Is orbital of H-atom overlaps with half-filled 3p, orbitals of chlorine atom forming a sigma s-p bonds

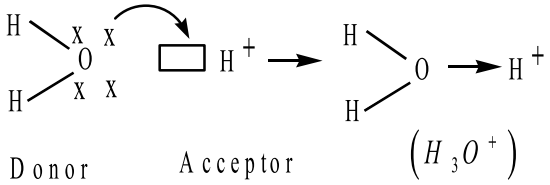


7. Write an essay on Co-ordinate covalent bond.

Co-ordinate covalent bond or Dative bond:

- It was proposed by Sidgwick
- It is a special type of covalent bond in which the shared pair of electrons are contributed by only one of the bonded atoms
- The atom contributing the pair of electrons is known as donor while that atom which does not contribute but shares the pair of electrons is referred to as acceptor. The bond is represented by '$\rightarrow$' from donor atom to acceptor atom

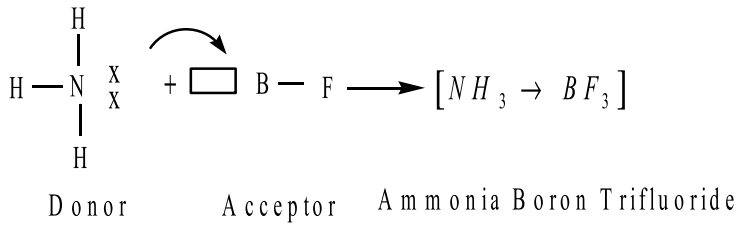
Ex : 1 (i) Hydronium ion formation $\left[H_3O^+\right]$



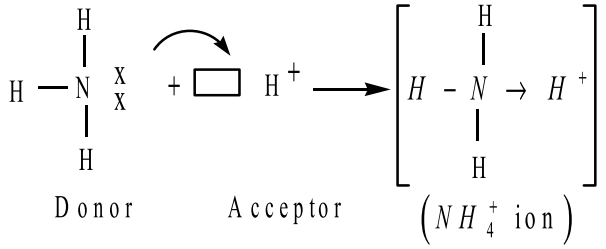
Hence the criteria to form dative bond is, one atom should contain lone pair and the other atom should carry vacant orbital.

1) In Ammonia molecule the nitrogen atom carries a lone pair of electron. However, in BF_3, boron atom contains vacant p_z orbital. Hence nitrogen can donate that lone pair to the vacant orbital of BF_3 to form a dative bond. Hence valency is four for both 'N' and 'B'

Formation of Ammonia Boron Tri fluoride



2) Formation of NH_4^+ ion: Similarly, in the formation of NH_4^+, Ammonia molecule can donate its lone pair to the vacant orbital of H^+ ion to form a dative bond.



Properties:

Since dative bond is also a special type of covalent bond, the properties of these compounds resembles covalent compounds.

1) These compounds are not good conductors

2) They are insoluble in water but soluble in non polar solvents like CCl_4

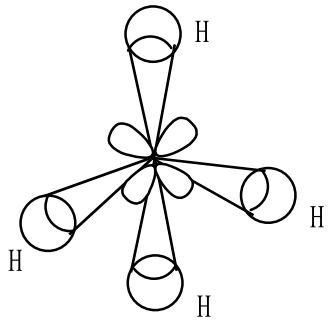
3) Their M.P and B.P's are in between ionic and covalent compounds.

8. CH_4 could have a square planar structure with C at the centre of the square. But it is having tetrahedral structure. Explain. Why?

CH_4 (Methane):

- The central atom of methane is carbon. The electronic configuration of carbon in ground state is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^o$ and on excitation it is $2s^2 2p_x^1 2p_y^1 2p_z^o$.

- The $2s, 2p_x, 2p_y$ and $2p_z$ undergo sp^3 **hybridization** giving four sp^3 hybrid orbitals.
- Each sp^3 hybrid orbital overlaps with the 1s orbitals of hydrogen forming σ_{sp^3-s} bond. In case of methane four σ_{sp^3-s} bonds are formed. The bonds are directed towards the four corners of a regular tetrahedron.



Structure of CH_4

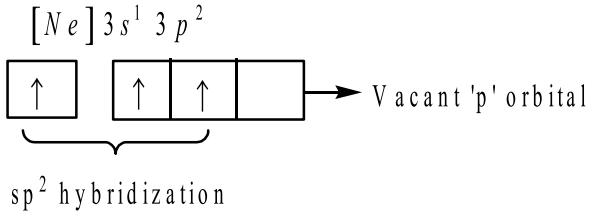
The shape of the molecules is tetrahedral with a bond angle $109°28'$.

9. Predict if there is any change in the hybridization of 'Al' in the following reaction. $AlCl_3 + Cl^- \longrightarrow AlCl_4^-$

$AlCl_3 + Cl^{\odot} \longrightarrow AlCl_4^-$

1) Structure of $AlCl_3$:

Configuration of 'Al' in excited state is $[Ne]2s^1 3p^2$



Central 'Al' undergoes 'sp^2' hybridization are formed three sp^2 hybrid overlap with three p orbital of three 'Cl' atoms leading to the formation three σ_{sp^3-s} bonds. One vacant unhybrid 'p' orbital is remaining on 'Al' atom

2) Effect of 'Cl^-': ion the vacant 'p' orbital on 'Al' atom undergoes hybridization so that the hybridization of 'Al' changes form sp^2 to sp^3. The vacant hybrid orbital is bonded to Cl through dative bond.

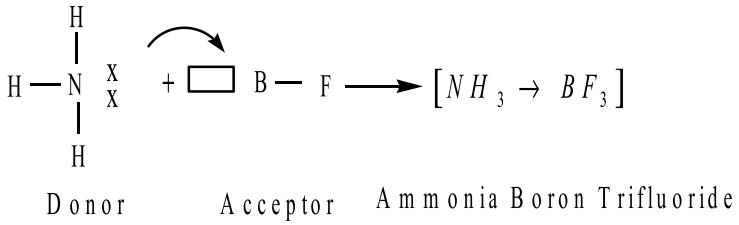
3) Structure of $AlCl_4^-$: Among four bonds between Al and chlorine atoms, three bonds are covalent and one bond dative and central 'Al' undergoes sp^3 hybridization.

$$\underset{\left(sp^3\ hybridized\ 'Al'\right)}{AlCl_4} + Cl^- \longrightarrow \underset{\left(sp^3\ hybridized\ 'Al'\right)}{AlCl_4^-}$$

10. Discuss the formation of $\left[BF_3 \leftarrow NH_3\right]$. Is there any change in the hybridization of B and N in its formation?

Ammonia – Boron trifluoride formation $\left(H_3N \longrightarrow BF_3\right)$:

Ammonia molecule contains Nitrogen atom with a lone pair of electrons (in sp^3 hybrid orbital) BF_3 has atom with an incomplete octet (with P_z orbital). Therefore, nitrogen of ammonia donates it lone pair of Boron and thus forms coordinate covalent bond. During this bond formation, the sp^3 orbital of nitrogen having a lone pair overlaps the vacant 'p' orbital of Boron. The equation corresponding to the reaction is written as follows :



b) Change in hybridized states N and B during $\left[H_3N \rightarrow BF_3\right]$ formation:

Boron in BF_3 undergoes (sp^2 hybridization with one vacant unhybrid 'p' orbital. This orbital also undergoes) hybridization in presence of NH_3 so that the

hybridized state of 'B' changes form sp^2 to sp^3. This vacant hybrid orbital is bonded to NH_3 through dative bond. During this process there is **no change in the hybridized state of Nitrogen in** NH_3

$$[H_3N: \quad + \quad BF_3 \longrightarrow \quad [H_3N: \quad \longrightarrow \quad BF_3]$$

(N - sp^3 hybridized) (B - sp^2 hybridized) (N - sp^3 hybridized) B - sp^3 hybridized)

(No change in hybridization)

11. Distinguish between 'σ' and 'π' bond.

Definition of σ bond: "σ - bond is along inter nuclear axis. It has a cylindrical symmetry".

Definition of π bond: "A covalent bond formed by a sidewise overlap of 'p' orbitals of atoms that they are already bonded through a σ - bond and in which the electron clouds are present above and below inter nuclear axis is known as π - bond".

	Sigma bond (σ)	**Pi bond (π)**
1	This is formed due to the overlap of pure 's' s-s : s-p : p-p (or) hybrid orbitals of two atoms along their internuclear axis	This bond is formed due to lateral or side wise or parallel overlapping of pure 'p' orbitals of two atoms
2	It is a strong bond	It is a weak bond
3	There are less reactive	These are highly reactive
4	The electron cloud is symmetrical to the line joining the nuclei of the two atoms	The electron cloud lies above and below the plane of the line joining the atoms
5	Free rotation of atoms is possible	Free rotation is not possible
6	The lobe participating in the overlapping is stretched and the other lobe is reduced	Both the lobes take part in bonding and remain the same in size
7	It is also called localized bond	It is non – localized bond
8	It has independent existence	It is forms only after the formation of 'π' bonds

CHEMICAL BONDING AND MOLECULAR STRUCTURE

UNIT: 3

1 Description of molecular orbital theory of homonuclear diatomic molecules

2 Bonding, Antibonding molecular orbitals, ∞ , $\prod$ bond orbitals - their symmetry

3 Energy diagrams of molecular orbitals of H_2, N_2, and O_2.

Short Answer Questions:

1. What are the guidelines to be followed to predict the formation of molecular orbitals?

A. 1) The molecules orbitals are formed when the atomic orbitals combine linearly (i.e,) when the atoms approach each other. The number of molecular orbitals resulting is equal to the number of atomic orbitals combining.

2) Only such atomic orbitals which are of similar energies and symmetry with respect to the inter nuclear axis combine to form molecular orbitals.

3) The total number of molecular orbitals produced will be numerically equal to the number of combining orbitals.

4) The order of energies of bonding, anti bonding and non bonding orbitals can be written as bonding orbitals < non bonding orbitals < anti – bonding orbitals.

2. Write the MOED of N_2

A. Molecular orbital energy level diagram (MOED) of 'N_2':

Electronic configuration of nitrogen (z = 7) is $1s^2\,2s^2\,2p^3$. Since nitrogen atom has 7 electrons, the molecular orbitals of nitrogen molecule $\left(N_2\right)$ has 14 electrons which are distributed as below:

$$\sigma\left(1s^2\right),\ \sigma^*1s^2,\sigma 2s^2,\ \sigma^*2s^2 \begin{cases} \pi\, 2p_y^2 & \sigma P_x^2 \\ \pi_2\ p_z^2 & \end{cases}$$

Bond order = $\dfrac{8-2}{2} = 3\left(N \equiv N\right)$

Absence of unpaired electrons showed that N_2 molecule is diamagnetic

MOED of 'O_2' :

Electronic configuration of Oxygen (Z = 8) is $1s^2\,2s^2\,2p^4$. Since oxygen atom has 8 electrons, it molecular orbit of oxygen molecule (O_2) has 16 electrons, which are distributed as below:

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

Bond order = $\frac{10-6}{2} = 2(O=O)$

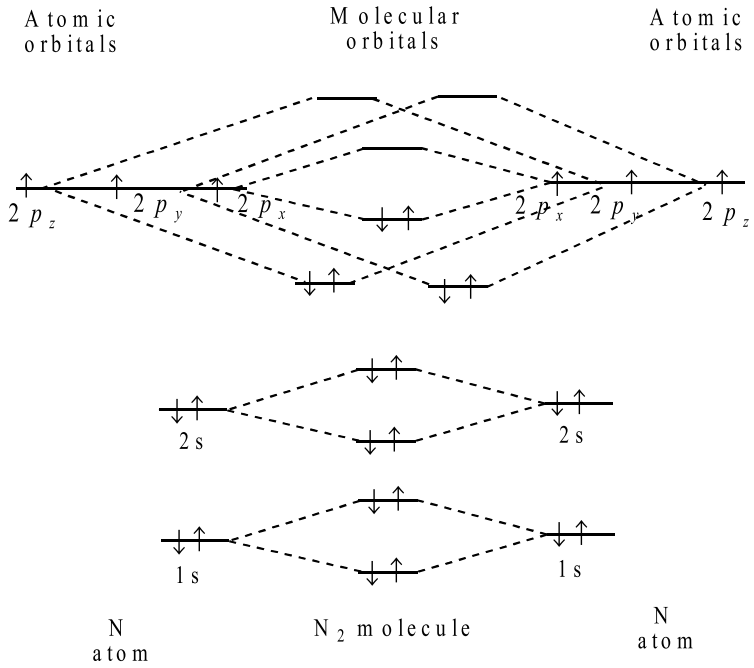
Presence of two unpaired 6 electrons $\left(\pi^* 2p_y^1,\ \pi^* 2p_z^1\right)$ showed that O_2 molecule is paramagnetic.

LONG ANSWER QUESTIONS:

1. Write the MOED's of (a) N_2 (b) O_2

A. **Molecular orbital energy level diagram (MOED) of 'N_2' :**

Electronic configuration of nitrogen (z = 7) is $1s^2\,2s^2\,2p^3$. Since nitrogen atom has 7 electrons, the molecular orbitals of nitrogen molecule (N_2) has 14 electrons which are distributed as below:



$$\sigma\left(1s^2\right),\ \sigma^*1s^2,\sigma 2s^2,\ \sigma^*2s^2\begin{cases}\pi 2p_y^2 & \sigma P_x^2\\ \pi_2\ p_z^2\end{cases}$$

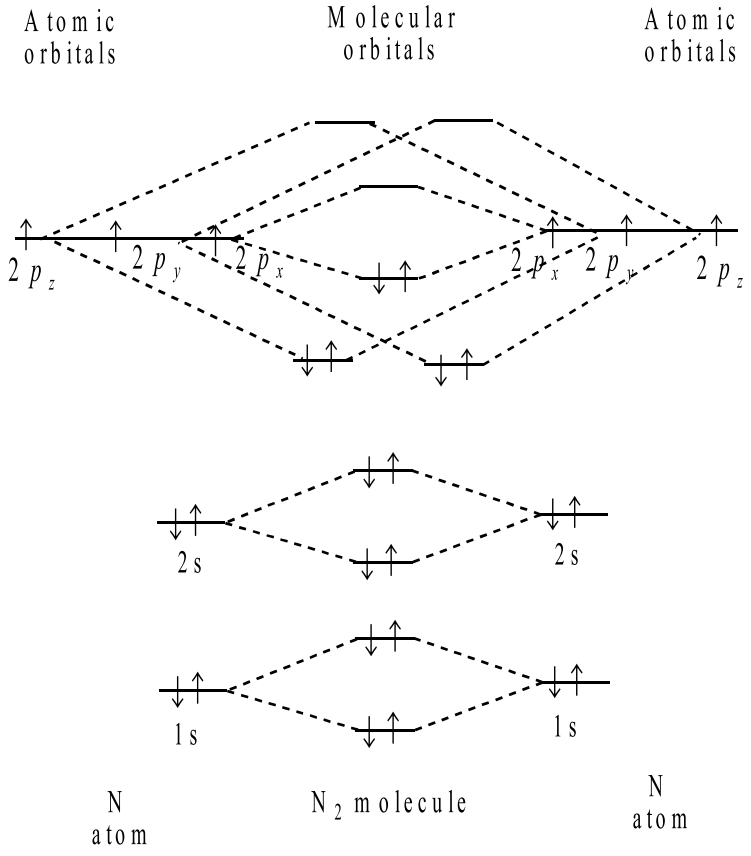
Bond order = $\dfrac{8-2}{2}=3\left(N\equiv N\right)$

Absence of unpaired electrons showed that N_2 molecule is diamagnetic

MOED of 'O_2':

Electronic configuration of Oxygen (Z = 8) is $1s^2\,2s^2\,2p^4$. Since oxygen atom has 8 electrons, it molecular orbit of oxygen molecule $\left(O_2\right)$ has 16 electrons, which are distributed as below:

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



Bond order = $\dfrac{10-6}{2}=2\left(O=O\right)$

Presence of two unpaired 6 electrons $\left(\pi^* 2p_y^1, \pi^* 2p_z^1\right)$ showed that O_2 molecule is paramagnetic.

CHEMICAL BONDING AND MOLECULAR STRUCTURE

UNIT: 4

1. Concept of hydrogen bond – Types of hydrogen bonds, inter and intra molecular hydrogen bonds.
2. Effects of H – bonds on some properties of substances with examples
3. Different states of matter in terms of balance between intermolecular forces, thermal energy of particles.

Very Short Answer Questions:

1. **Write the consequences of hydrogen bonding.**

   Consequences of Hydrogen bonding:

   1) The covalent compounds are usually insoluble in water. Covalent compounds with hydrogen bonding are soluble in water. e.g. glucose and alcohol..

   2) The M.P. and B.P. of compounds increases enormously due to hydrogen bonding. e.g H_2O has high B.P. than any other hydride in the VIA group.

2. **Define hydrogen bond. Is it weaker or stronger than Vander Waal's forces?**

   It is the weak electrostatic force of attraction between a partially positively charged hydrogen atom of a molecule and high electronegative atom of the same or different molecule.

   Hydrogen bond is stronger than the Vander Waal's forces.

Short Answer Questions:

1. **Give reasons for the higher boiling of H_2O than HF and NH_3**

   B.P. of H_2O is higher than that of HF:

   - Water molecule can have a maximum of four H- bonds. As temperature increases, the number of H- bonds decrease. In liquid water, there will be two H-bonds. In water vapour, all the bonds are broken and there would be only individual H_2O molecules. Therefore, water has high b.p.
   - In HF liquid, the H- bonds are strongest than in water. But in vapors of HF, all the H-bonds are not broken. There will be clusters of HF molecules. $(HF)_n$ in vapour ; n= 2 to 6. Hence, HF has lower b.p.

   B.P. of H_2O is higher than that of NH_3 :

- In NH_3 the energy of H- bond (-8 kj mol^{-1}) is less than the energy of H- bond in water $\left(-29\,kJ\,mol^{-1}\right)$ This is due to lower E.N. value of N compared to O. Therefore, less energy is sufficient, vapourise ammonia than water. Hence, B.P of ammonia is less than that of water.

2. **Predict the reason (s) for the observation in boiling points HF > HBr > HCl**

Hydrogen halide	**Physical state**	**B.P.**
HF	Liquid	$19.5°C$
HCl	Gas	$-85°C$
HBr	Gas	$-67°C$

1) Hydrogen fluoride in liquid state exists as $(HF)_2$ due to Hydrogen bond. Hence its boiling point is more than that of HCl and HBr

2) HCl and HBr are gases. Among them as molecular weight increases, the Vander Waal forces of attraction increases. Since the molecular weight of HBr is more than that of HCl, the boiling point of HBr is more than HCl

3) HCl is more volatile gaseous compound. The order of boiling points is HF > HBr > HCl.

LONG ANSWER QUESTIONS:

1. **Define and describe H – bonding?**

Hydrogen Bond:

It is the weak electrostatic force of attraction between a partially positively charged hydrogen atom of a molecule and high electronegative atom of the same or different molecule.

The energy of a hydrogen bond is relatively less (10 – 50 KJ/mole) than energy of the covalent bond (418 KJ/mole) and much stronger than the vanderwaal's forces. It is denoted by dotted lines. (----)

Types of Hydrogen Bonds:

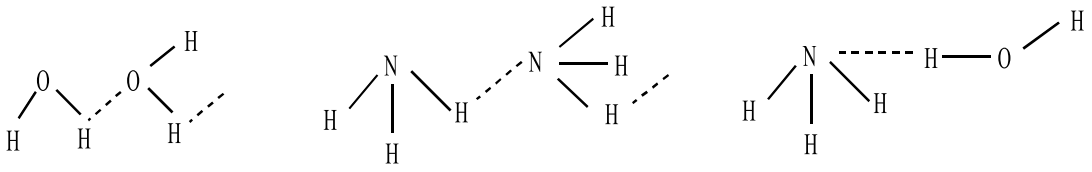
Hydrogen bonding is of two types

1) Inter Molecular Hydrogen Bond: "Hydrogen bond formed between two different polar molecules (of the same substance or of different substances) is known as intermolecular hydrogen bond".

Ex: HF, H_2O, NH_3, alcohols, etc

H – F ------- H – F

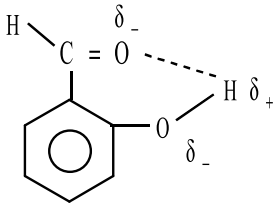
Hydrogen fluoride



Water Ammonia Ammonia in H_2O

2) Intra Molecular Hydrogen Bond: A hydrogen bond formed between hydrogen atom of a molecule and highly electro-negative atom of the same molecule is known as intramolecular hydrogen bond.

Ex: Salicylaldehyde (ortho hydroxyl benzaldehyde) ; Ortho nitro phenol ; Ortho nitro aniline ; Orthofluorophenol, etc



Salicylaldehyde

Conditions for Hydrogen bonding: There are two conditions for an effective hydrogen bond to be formed.

1) The electronegative atom attached to the hydrogen should be small

Ex: Although chlorine has the same electronegativity as nitrogen, NH_3 have hydrogen bonds while HCl does not have. This is because of the smaller size of the nitrogen atom compared to a chlorine atom.

2) The electronegativity of the atom to which hydrogen atom is attached should be high

Ex: F, N, O

Consequences of Hydrogen Bonding:

Substances having hydrogen bonding exhibit certain abnormal characteristics

1) They have different physical state when compared to the similar substances which have no H – bond.

Ex: H_2O is liquid because of H – bonding while other hydrogen hydrides of the remaining elements of the same group are gases.

Eg: H_2S, H_2Se

2) Lower alcohols (eg CH_3OH, C_2H_5OH) are water soluble

3) Their melting points, boiling points enthalpies of vapourisation and sublimation are different from those normally expected.

Ex: In hydrogen halides (HF, HCl, HBr, HI), HF has the highest boiling point due to intermolecular hydrogen bonding

B.P. order

VIIA – Hydrides H-F > HI > HBr > HCl

VIA – Hydrides $H_2O > H_2Te > H_2Se > H_2S$

VA – Hydrides $SbH_3 > NH_3 > AsH_3 > PH_3$

4) Substances with intramolecular hydrogen bonding like salicylaldehyde have lesser solubilities than those with intermolecular hydrogen bonded compounds like para hydroxyl benzaldehyde

Substances with intermolecular hydrogen bonding do not undergo steam distillation

Ex: Para hydroxyl benzaldehyde is more soluble in water than ortho hydroxyl benzaldehyde. Para hydroxyl benzaldehyde can not be purified by steam distillation

5) Substances with intramolecular hydrogen bonding results in lower boiling point i.e, greater volatility. Eg P – Nitro phenol has high boiling point than O – Nitro phenol.

Boiling point of H_2O is higher than that of HF and NH_3 Reason:

i) H_2O contains hydrogen bonds in liquid state only but water vapour contains free molecules where as HF contains hydrogen bonds in liquid and vapour state $\left[(HF)_6\right]$

Therefore vapourisation of HF liquid involves partial breakage of H – bonds and required less energy than required for vapourisation of water as it involves complete breakage of H – bonds. Hence H_2O has high boiling point than HF

ii) Each H_2O is involved in 4H – bonds, but as an average 2H bonds. But each HF is involved in 2H bonds but as an average 1H bond Lesser the number of H – bonds, lesser will be the energy required to break them and boiling point will be less.

iii) In NH_3, the H – bond is very weak. Hence its boiling point is less.