**By- SHAILENDRA SHUKLA SIR**

# Valency

The term 'valency' has been derived from the Latin word 'valentia' meaning 'combining power' or 'combining capacity'. Thus,

"The combining capacity of an atom is called its valency."

Valency of an element depends upon its electronic configuration especially upon the number of electrons in its outermost shell (valence shell) and is determined using following rules-

(1) If an atom cotains 8 electrons in its outermost shell i.e. has complete octet ($ns^2$, $np^6$), then its valency is zero. For example, inert gases like Ne, Ar, Kr etc.

Ne (10) - $1s^2$, $2s^2$, $2p^6$

Ar (18) - $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

Helium is its exception, where first shell is outermost shell and it can accommodate only a maximum of two electrons. Hence, for He duplet configuration ($1s^2$) is stable configuration and its valency is zero.

(2) If only outermost shell of an atom is incompletely filled, then its valency depends upon the number of electrons in its outermost shell. Here,

(a) If the outermost shell contains 1 - 4 electrons, then its valency is equal to the number of electrons in the outermost shell. For example,

| | |
|---|---|
| Li (3) - $1s^2$, $2s^1$ | Valency = 1 |
| Be (4) - $1s^2$, $2s^2$ | Valency = 2 |
| B (5) - $1s^2$, $2s^2$, $2p^1$ | Valency = 3 |
| C (6) - $1s^2$, $2s^2$, $2p^2$ | Valency = 4 |
| Na (11) - $1s^2$, $2s^2$, $2p^6$, $3s^1$ | Valency = 1 |
| Mg (12) - $1s^2$, $2s^2$, $2p^6$, $3s^2$ | Valency = 2 |
| Al (13) - $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$ | Valency = 3 |

(b) If it contains 4 - 7 electrons, then its valency is equal to (8 - n), where n is number of electrons in the outermost shell of the atom. For example,

| | |
|---|---|
| N (7) - $1s^2$, $2s^2$, $2p^3$ | Valency = (8-5) = 3 |
| O (8) - $1s^2$, $2s^2$, $2p^4$ | Valency = (8-6) = 2 |
| F (9) - $1s^2$, $2s^2$, $2p^5$ | Valency = (8-7) = 1 |

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(3) If outer two shells of an atom are incompletely filled, then valency of the atom depends upon the number of electrons in both of these two shells. These atoms show variable valencies. For example, transition metals.

**Electronic theory of valency**
**or**
**Cause of chemical combination**
**(Octet Theory)**

Electronic theory of valency was for the first time proposed by **Kossel and Lewis**. The main postulates of this theory are as under-

(1) Those elements which contain 8 electrons in their outermost shell i.e. which have complete octet ($ns^2$, $np^6$), are highly stable and do not take part in chemical combination e.g. inert gases like Ne, Ar, Kr etc.

Ne (10) - $1s^2$, $2s^2$, $2p^6$
Ar (18) - $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

Thus, octet configuration ($ns^2$, $np^6$) is the stable electronic configuration of the elements. Helium is its exception, where first shell is outermost shell and it cannot accommodate more than two electrons. Hence, for Helium, duplet configuration ($1s^2$) is the stable configuration.

(2) Those elements which do not contain 8 electrons in their outermost shell i.e. which have incomplete octet, are unstable and therefore, they give, take or share electrons to complete their octet. Hence, they have tendency to take part in chemical combination.

Thus, the tendency of elements to complete their octet i.e. to gain stability by acquiring stable electronic configuration of their nearest inert gas, is the principal cause of chemical combination.

**Types of chemical bonds-**

Chemical bonds are mainly of following three types-

**(1) Electrovalent bonds**

"The bonds formed by transfer of one or more electrons between the atoms are called electrovalent bonds."

The number of electrons given or taken by one atom of an element during the formation of these bonds is called electrovalency of the element."

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Here, the atom which gives electron, becomes positively changed while, that which takes electron, becomes negatively changed. The oppositely changed ions thus formed, get bonded together by strong electrostatic force of attraction.

**Examples -**

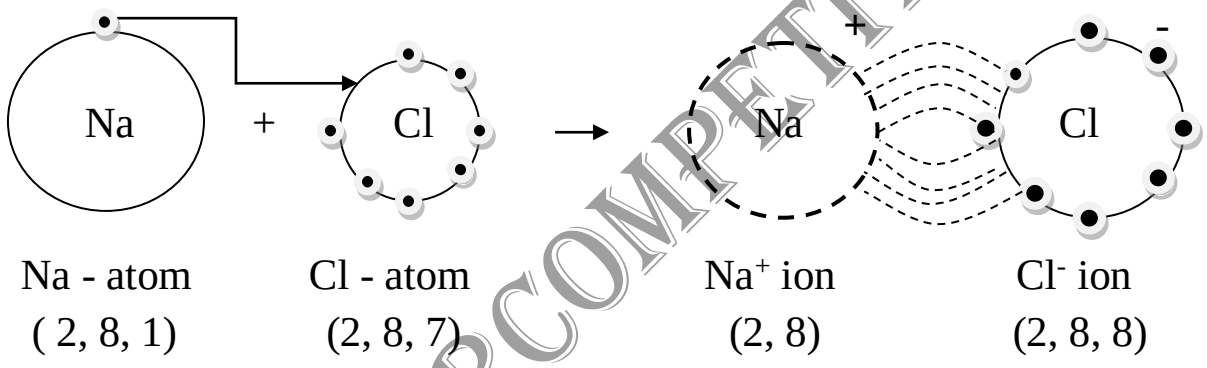
**(1) Formation of Sodium chloride (NaCl) -**

The electronic configuration of sodium and chlorine atoms are as under-

Na (11) - $1s^2$, $2s^2$, $2p^6$, $3s^1$

Cl (17) -$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^5$

During formation of NaCl, sodium atom transfers its valence electron to the outermost shell of chlorine atom. It results in the formation of $Na^+$ and $Cl^-$ ions, which get bonded together by electrostatic force of attraction. Here, the electrovalency of both sodium and chlorine atoms is 1.




| Na - atom | Cl - atom | $Na^+$ ion | $Cl^-$ ion |
|---|---|---|---|
| ( 2, 8, 1) | (2, 8, 7) | (2, 8) | (2, 8, 8) |

**Fig.- Formation of NaCl (diagrammatic)**

Thus, both sodium and chlorine atoms acquire the stable electronic configuration of their nearest inert gas i.e. Ne and Ar respectively.

**(2) Formation of Magnesium oxide (MgO)**

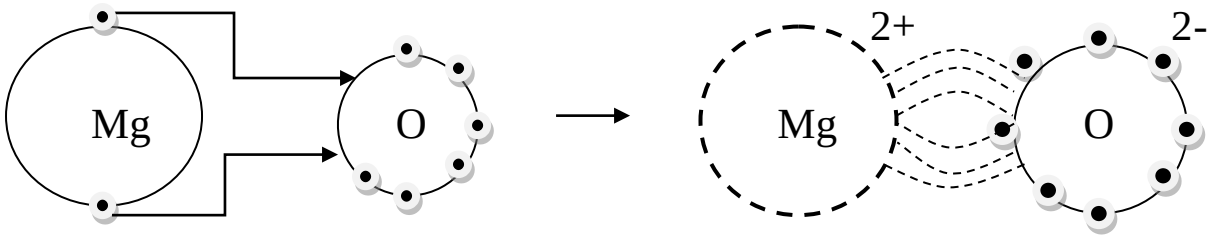
The electronic configuration of magnesium and oxygen atoms are as under-

Mg (12) - $1s^2$, $2s^2$, $2p^6$, $3s^2$

O (8) -$1s^2$, $2s^2$, $2p^4$

During formation of MgO, magnesium atom transfers its both the valence electrons to the outermost shell of oxygen atom. It results in the formation of $Mg^{2+}$ and $O^{2-}$ ions, which get bonded together by electrostatic force of attraction. Here, the electrovalency of both magnesium and oxygen atoms is 2.

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Mg - atom ( 2, 8, 2) | O - atom (2, 6) | $Mg^{2+}$ ion (2, 8) | $O^{2-}$ ion (2, 8)

**Fig.- Formation of MgO (diagrammatic)**

Thus, both magnesium and oxygen atoms acquire the stable electronic configuration of their nearest inert gas i.e. Ne.

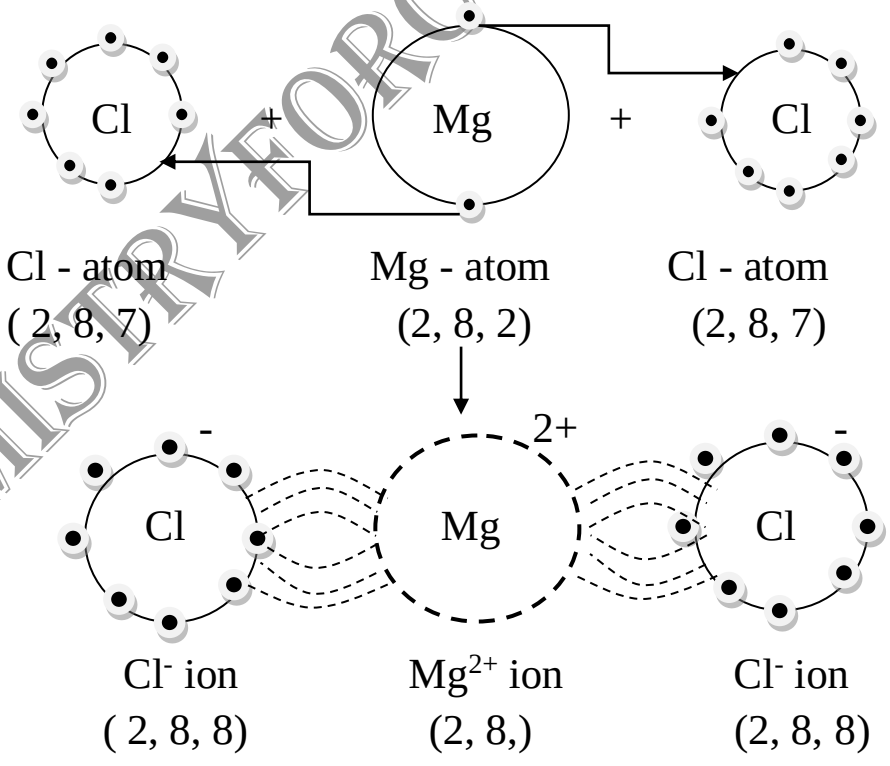
**(3) Formation of Magnesium chloride ($MgCl_2$)**

The electronic configuration of magnesium and chlorine atoms is as under-

Mg (12) - $1s^2$, $2s^2$, $2p^6$, $3s^2$

Cl (17) -$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^5$

During formation of $MgCl_2$, magnesium atom transfers its both the valence electrons to the outermost shell of two chlorine atoms (one each). It results in the formation of $Mg^{2+}$ and $Cl^-$ ions, which get bonded together by electrostatic force of attraction. Here, the electrovalency of magnesium atom is 2 while, that of chlorine atoms is 1.




Cl - atom ( 2, 8, 7) | Mg - atom (2, 8, 2) | Cl - atom (2, 8, 7)

$Cl^-$ ion ( 2, 8, 8) | $Mg^{2+}$ ion (2, 8,) | $Cl^-$ ion (2, 8, 8)

**Fig.- Formation of $MgCl_2$ (diagrammatic)**

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Thus, both magnesium and chlorine atoms acquire the stable electronic configuration of their nearest inert gas.

**Conditions of formation of electrovalent bonds**

(1) When a highly electropositive element (metal) combines with highly electronegative element (nonmetal), then electrovalent bond is formed between them.

(2) If an element can complete its octet by giving one or more electrons and other can do so by gaining one or more electrons, then electrovalent bond is formed between them.

(3) If difference in electronegativities of two elements is more than 1.7, then electrovalent bond is formed between them.

**Properties of Electrovalent compounds**

(1) Electrovalent compounds are ionic in nature i.e. they are consisting of oppositely charged ions bonded together by strong electrostatic force of attraction.

(2) Since, strong electrostatic force of attraction operates between oppositely charged constituent ions, these compounds have very high melting and boiling points.

(3) These compounds have high thermal stability and therefore, do not decompose on heating.

(4) Being ionic in nature, these compounds are highly soluble in polar solvents like water.

(5) When these compounds are dissolved in water or melted, they get dissociated into their constituent ions. For example,

$$NaCl(s) \xrightarrow{Water} Na^{+}(aq.) + Cl^{-}(aq.)$$

This phenomenon is called dissociation.

(6) Due to presence of ions, the aqueous solutions and molten forms of these compounds are good conductor of electricity.

(7) Electrovalent compounds are, in general, solid in nature at room temperature.

(8) Electrovalent bonds are non-directional in nature. Hence, electrovalent compounds do not have a definite geometry.

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**(2) Covalent bond**

"The bonds formed by equal sharing of electrons between the atoms are called covalent bonds."

The number of electrons shared by one atom of an element for the formation of a covalent bond is called covalency of the atom.

Here, shared electron pair lies simultaneously in the outermost shell of both the bonded atoms and provides them stability.

Depending upon the number of shared electron pairs between the bonded atoms, being 1, 2 and 3, these bonds are called single, double and triple bonds respectively and are represented by placing single, double and triple lines between the bonded atoms respectively.

**Examples-**

**(1) Formation of $H_2$ molecule -** The electronic configuration of hydrogen atom is as under-

H (1) - $1s^1$

Thus, it needs one electron to complete its duplet i.e. stable electronic configuration of its nearest inert gas helium. Hence, two hydrogen atoms share one electron each to form a shared electron pair, which lies simultaneously in outermost shell of both the hydrogen atoms and provides them stability.

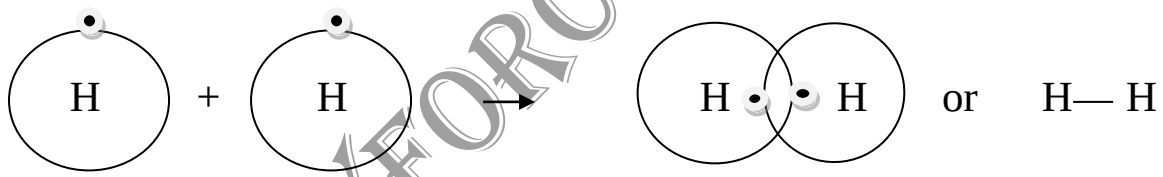



**Fig.- Formation of $H_2$ molecule**

Here since, both the hydrogen atoms give one electron in shared pair, their covalency is 1.

**(2)Formation of HF molecule -** The electronic configuration of hydrogen and fluorine atoms are as under-

H (1) - $1s^1$

F (9) -$1s^2$, $2s^2$, $2p^5$

Here, both hydrogen and fluorine atoms need one electron to acquire the stable electronic configuration of their nearest inert gas. Hence, they share one electron each to form a shared electron pair, which lies simultaneously in outermost shell of both the atoms and provides them stability.

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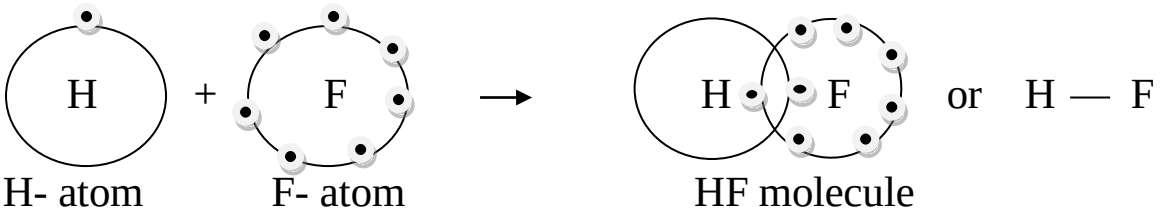



**Fig.- Formation of HF molecule**

Here since, both hydrogen and fluorine atoms give one electron each in shared pair, their covalency is 1.

**(3)Formation of $O_2$ molecule -** The electronic configuration of oxygen atom is as under-

O (8) -$1s^2$, $2s^2$, $2p^4$

Here, both oxygen atoms need two electrons to acquire the stable electronic configuration of their nearest inert gas i.e. neon. Hence, they share two electrons each to form two shared electron pairs, which lie simultaneously in outermost shell of both the atoms and provide them stability.

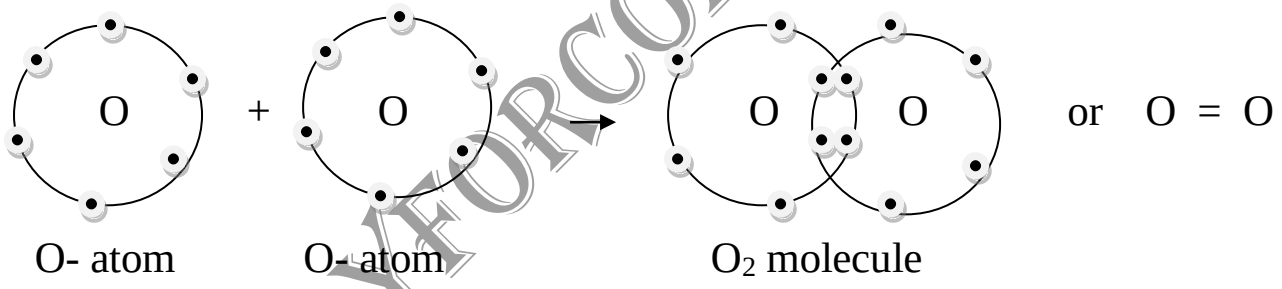



**Fig.- Formation of $O_2$ molecule**

Here since, both the oxygen atoms give two electrons each in shared pairs, their covalency is 2.

**Conditions of formation of covalent bonds**

(1) When two highly electronegative elements (nonmetals) combine together, then covalent bond is formed between them.

(2) If both the atoms require one or more electrons to complete their octet ($ns^2$, $np^6$), then covalent bond is formed between them.

(3) If difference in electronegativities of two elements is less than 1.7, then covalent bond is formed between them.

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**Properties of Covalent compounds**

(1) Covalent compounds are molecular in nature i.e. they are consisting of neutral molecules, bonded together by weak vander Waal forces.

(2) Since, weak vander Waal forces operate amongst constituent molecules, these compounds have relatively low melting and boiling points.

(3) Covalent compounds are usually insoluble in water. However, they are fairly soluble in non-polar solvents like benzene, carbon tetrachloride, chloroform etc.

(4) Due to absence of ions, the aqueous solutions and molten forms of these compounds are in general, bad conductor of electricity.

(5) These compounds are thermally unstable and therefore, get decomposed on heating.

(6) Covalent bonds are directional in nature i.e. they are formed in some definite directions and provide a definite shape to the molecules. Thus, covalent compounds have a definite geometry.

**(3) Co-ordinate bond**

It a special type of covalent bond, where both the electrons of shared pair are given only by one atom and they are simply shared by another atom. Thus, the bonds formed by unequal sharing of electrons between the atoms are called coordinate bonds.

Here, the atom which gives electron pair for sharing is called donor, while that which shares it is called acceptor. Hence, this bond is also called donor – acceptor bonds.

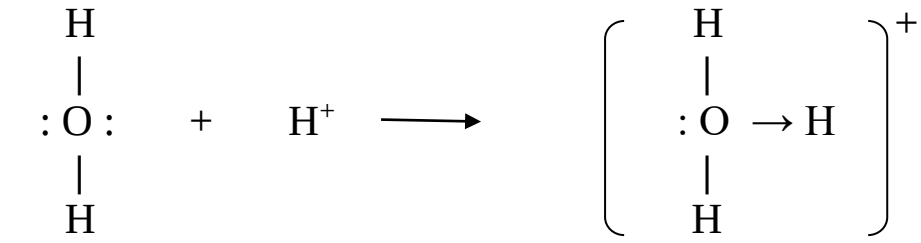
Coordinate bonds are represented by arrow (→) directed from donor to acceptor.

**Examples –**

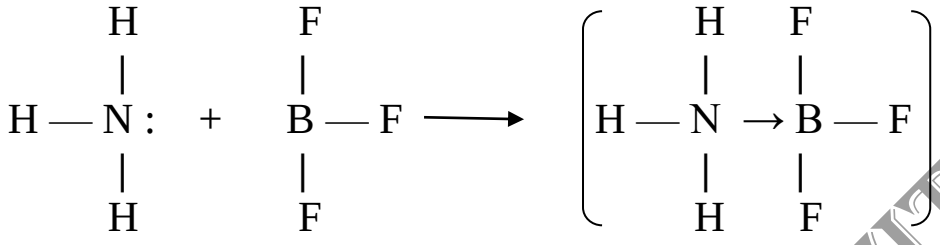
(1) $H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{N}}}}:$ + $H^+$ ⟶ $\left[H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{N}}}}\rightarrow H\right]^+$

Ammonia (Donor) Proton (Acceptor) Ammonium ion

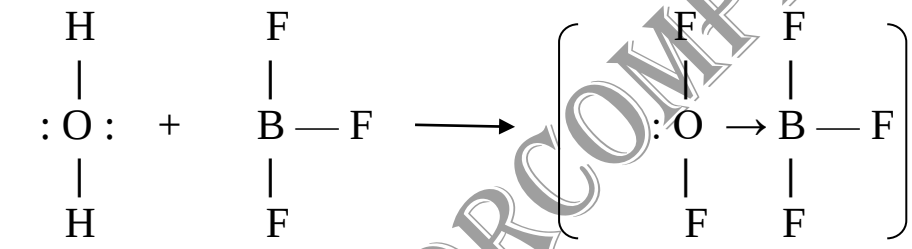
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(2) 

Water (Donor) Proton (Acceptor) Hydronium ion

(3) 

Ammonia (Donor) Boron trifluoride (Acceptor) Addition compound

(4) 

Water (Donor) Boron trifluoride (Acceptor) Addition compound

Co-ordinate bonds are also called semi-polar or dative bonds.

**Conditions of formation of co-ordinate bonds**

If an atom contains one or more lone pair of electrons and can donate it to the other atom, while the other atom is electron deficient and can accept one or more lone pair of electrons, then co-ordinate bond is formed between them.

**Properties of Co-ordinate compounds**

(1) co-ordinate compounds are molecular in nature i.e. they are consisting of neutral molecules, bonded together by weak vander Waal forces.

(2) Since, weak vander Waal forces operate amongst constituent molecules, these compounds have low melting and boiling points. However, it is higher than those of covalent compounds.

(3) These compounds are usually insoluble or sparingly soluble in water.

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(4) Due to absence of ions, the aqueous solutions and molten forms of these compounds are bad conductor of electricity.
(5) These compounds are thermally unstable and therefore, get decomposed on heating.
(6) Co-ordinate bonds are directional in nature i.e. they are formed in some definite directions and provide a definite shape to the molecules. Thus, these compounds have a definite geometry.

## Overlapping

According to modern concept, the covalent bonds are formed by overlapping of atomic orbitals. Here, two half-filled atomic orbitals, having elections with opposite spin, come close together, share some common space and their unpaired elections get paired up in the shared space. Whole this process is called overlapping. Thus,

**"The inter-penetration of atomic orbitals to share common space is called overlapping of the atomic orbitals."**

**Types of Overlapping-**

Depending upon the type of orbitals involved, the overlapping may be of following types-

**(1) s-s Overlapping-** when s-orbital of one atom overlaps with that of another atom, then it is called s-s overlapping.

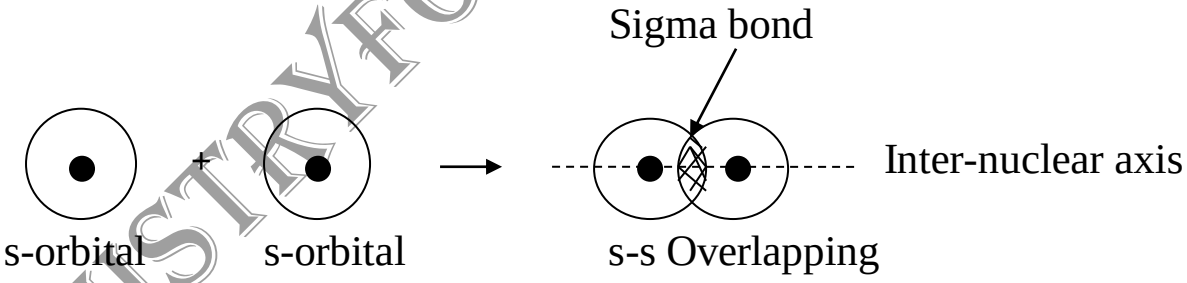



**Fig.- s-s Overlapping**

The covalent bonds formed in s-s overlapping, have maximum election density in between two nuclei and are symmetrical about inter-nuclear axis. Such covalent bonds are called sigma bonds ( σ- bonds).

**Example –Formation of $H_2$ molecule.**

During formation of $H_2$ molecule, half-filled 1s-orbital of both the hydrogen atoms overlap together to form H-H sigma bond. Here, shared election pair lies in shared space and provides stability to both the atoms.

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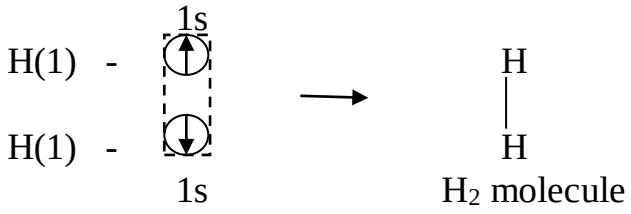



**Fig.-Formation of $H_2$ molecule (schematic)**

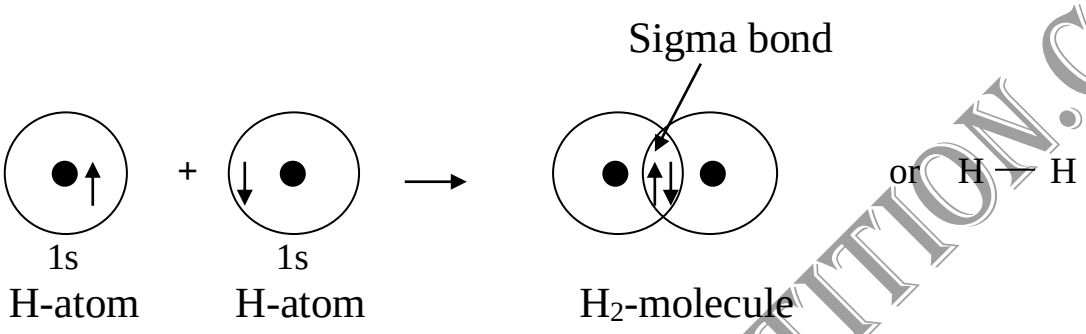



**Fig.- Formation of $H_2$ molecule (diagrammatic)**

**(2) s-p Overlapping-** when s-orbital of one atom overlaps with p-orbital of another atom, then it is called s-p overlapping.

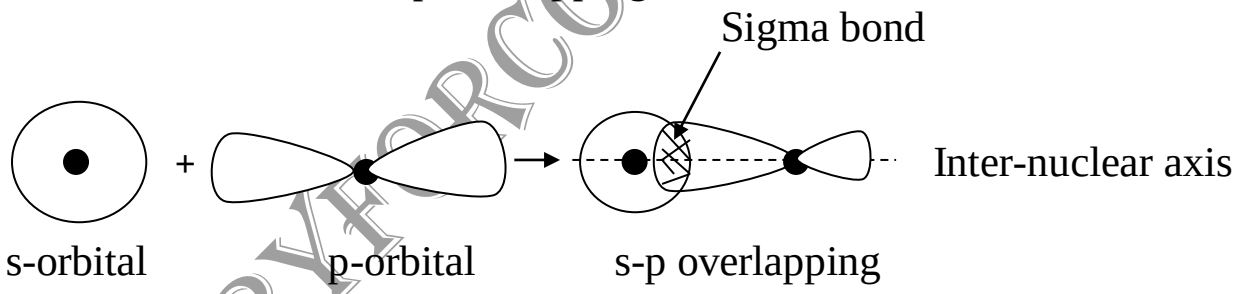



**Fig.- s-p overlapping**

The covalent bonds formed in s-p overlapping, have maximum election density in between two nuclei and are symmetrical about inter-nuclear axis. Such covalent bonds are called sigma bonds (σ - bonds).

**Example-** Formation of HF molecule.

During formation of HF molecule, half-filled 1s-orbital of hydrogen atom overlaps with half-filled $2p_z$ -orbital of fluorine atom to form H-F sigma bond. Here, shared election pair lies in shared space and provides stability to both the atoms.

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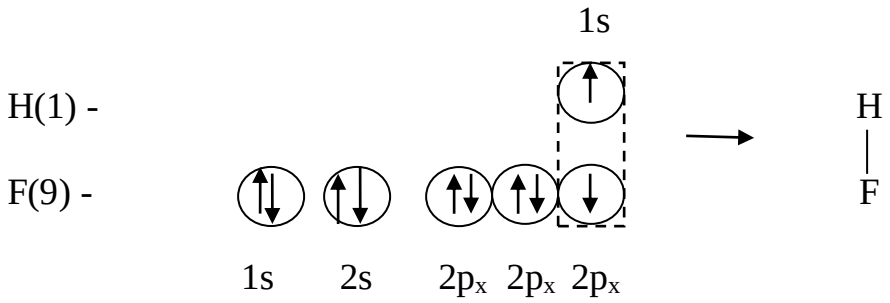



**Fig.-Formation of HF molecule (schematic)**

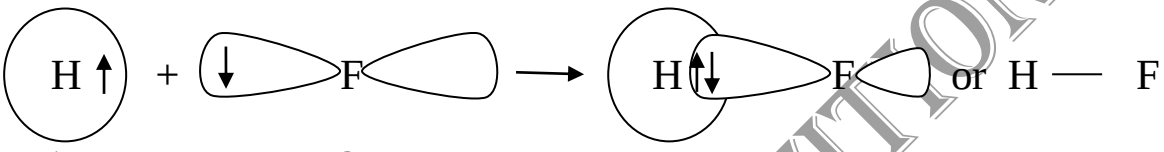



**Fig.- Formation of HF molecule (diagrammatic)**

**(3) p-p Overlapping**- when p-orbital of one atom overlaps with that of another atom, then it is called p-p overlapping.

p-p overlapping may be of following two types-

**(A) Head-wise or axial p-p overlapping-** When two p-orbitals come close together in head-wise manner and overlap, then it is called head-wise or axial p-p overlapping.

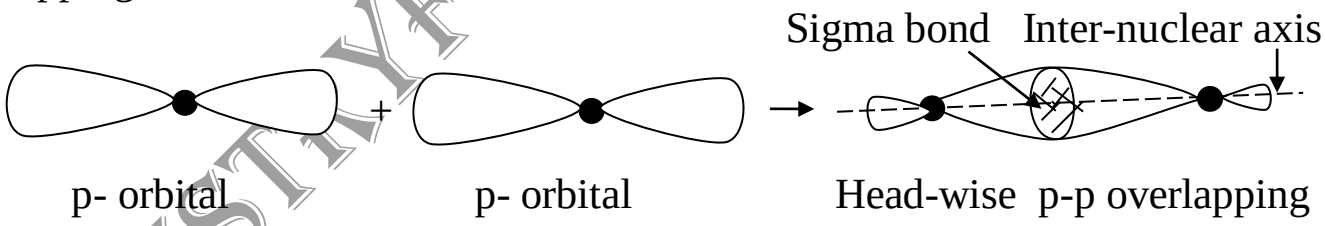



**Fig.- Head-wise or axial p-p overlapping**

The covalent bonds formed in head-wise or axial p-p overlapping have maximum election density in between two nuclei and are symmetrical about inter-nuclear axis. Such covalent bonds are called sigma bonds (σ - bonds).

**Example-** Formation of $F_2$ molecule –

During formation of $F_2$ molecule, half-filled $2p_z$ - orbital of both the fluorine atoms, overlap together in head-wise manner to form F-F sigma bond. Here, shared election pair lies in shared space and provides stability to both the fluorine atoms.

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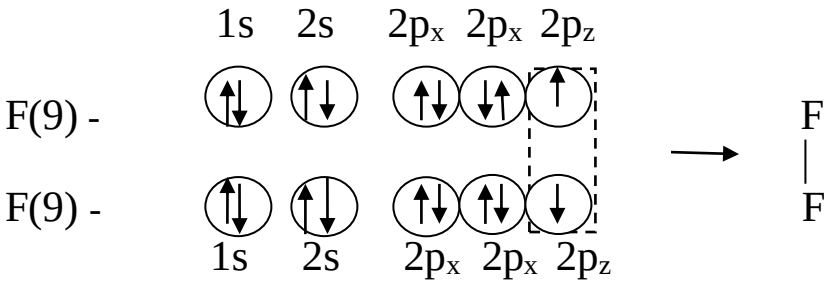



**Fig.-Formation of $F_2$ molecule (schematic)**

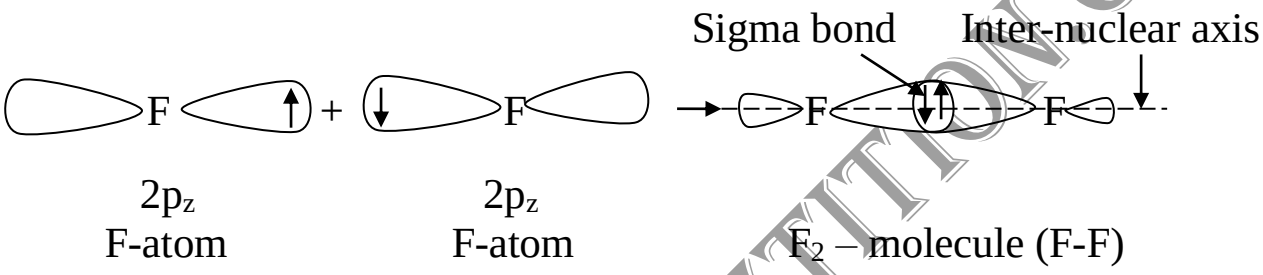



**Fig.- Formation of $F_2$ molecule (diagrammatic)**

**(B) Side-wise or lateral p-p overlapping-** When two p-orbitals come close together in side-wise manner and overlap, then it is called side-wise or lateral p-p overlapping.

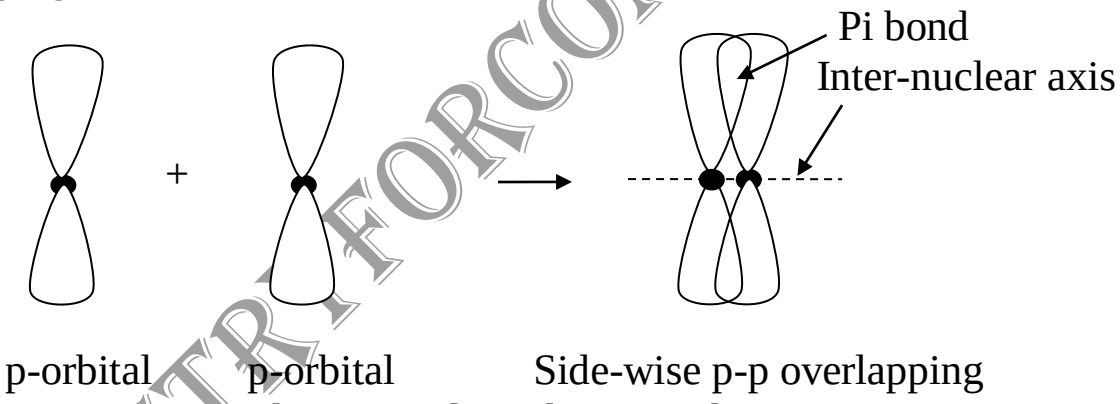



Fig.- Side-wise or lateral p-p overlapping

The covalent bonds formed in side-wise or lateral p-p overlapping, have maximum election density above and below the inter-nuclear axis and are not symmetrical about inter-nuclear axis. Such covalent bonds are called pi bonds ($\pi$- bonds).

Side-wise p-p overlapping never occurs alone, but always occurs along with head-wise p-p overlapping. Thus, pi bonds have no free existence, but are always formed along with sigma bond.

**Example-** Formation of $O_2$ molecule.

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During formation of $O_2$ molecule, half-filled $2p_z$ - orbital of both the oxygen atoms overlap together to form O-O sigma bond while half-filled $2p_y$ - orbital of both the atoms overlap together in side-wise manner to form pi bond.

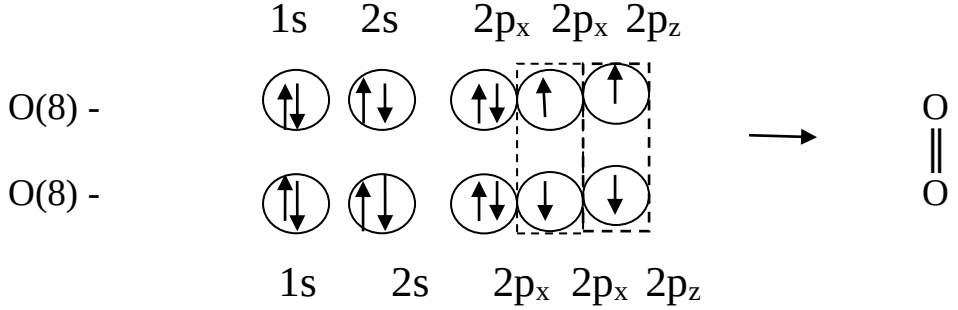



**Fig.-Formation of $O_2$ molecule (schematic)**

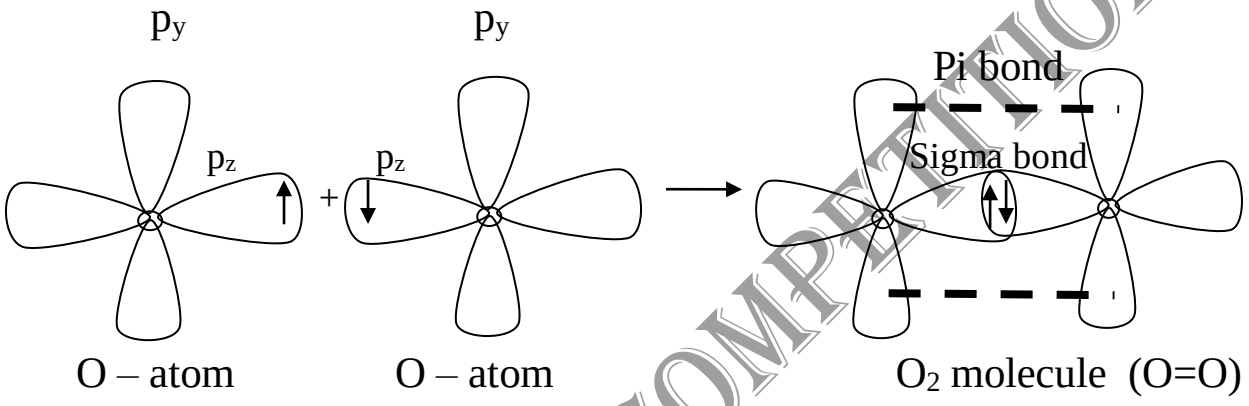



**Fig.- Formation of $O_2$ molecule (diagrammatic)**

## Hybrization

"The process in which two or more atomic orbitals of nearly same energy, mixed together by redistribution of energy and form new orbitals of exactly same energy and same shape in same number, is called hybridization and the new orbitals formed are called hybridized orbitals."

Hybridization is characterized by following rules-

(1) In hybridization only the atomic orbitals having nearly same energy take part.

(2) In hybridization there occurs redistribution of energy and space.

(3) The hybridized orbitals formed in hybridization, have exactly same shape, size and energy.

(4) The number of hybridized orbitals formed in hybridization, is always equal to the number of atomic orbitals involved in hybridization.

(5) The hybridized orbitals formed in hybridization, remain directed in some specified directions in space and provide a definite shape to the molecule. Thus, hybridization decides the geometry of the molecule.

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(6) In hybridization all types of orbitals i.e. half-filled, full-filled and vacant can take part.
(7) Hybridized orbitals form more stronger bonds as compared to unhybridized orbitals.

**Types of Hybrization**

Depending upon the number and type of atomic orbitals involved, hybridization may be of following types-

**(1) sp-Hybridization-**

"The process in which one-s and one-p orbitals of nearly same energy, mixed together by redistribution of energy and form two new orbitals of exactly same energy and same shape is called sp-hybridization and new orbitals formed are called sp-hybridized orbitals."

sp-hybridized orbitals remain arranged linearly at an angle of $180^0$ and provide linear shape to the molecules. Hence, sp-hybridization is also called **linear hybridization**.




**Fig.- sp-hybridization**

Each sp-hybridized orbital contains 50% character each of s and p orbitals.

**Example- Formation of $BeF_2$ molecule.**

The electronic excitation and sp hybridization in central beryllium atom, leading to the formation of $BeF_2$ molecule can be represented as under-

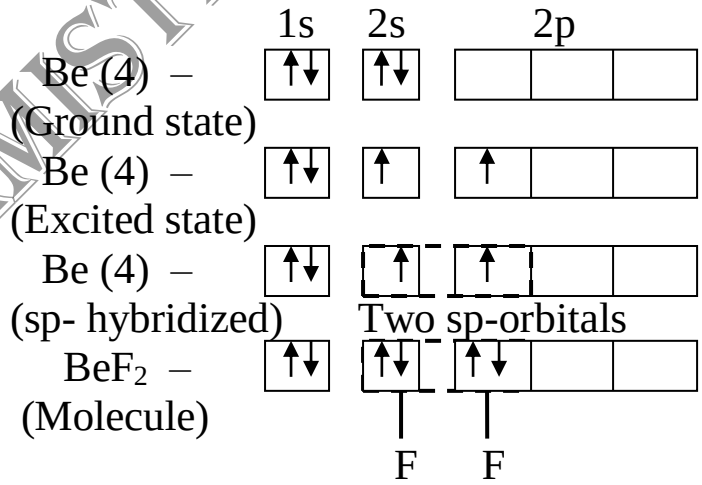
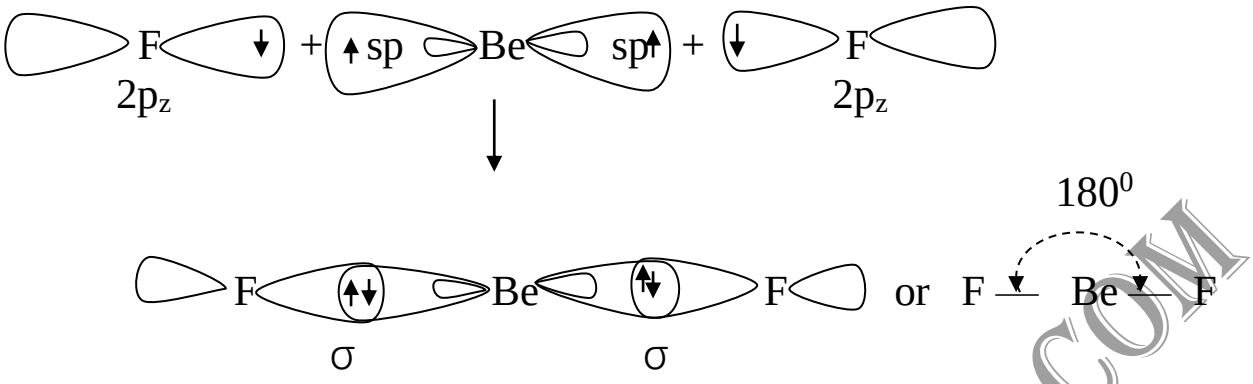



**Fig.- Formation of $BeF_2$ molecule (schematic)**

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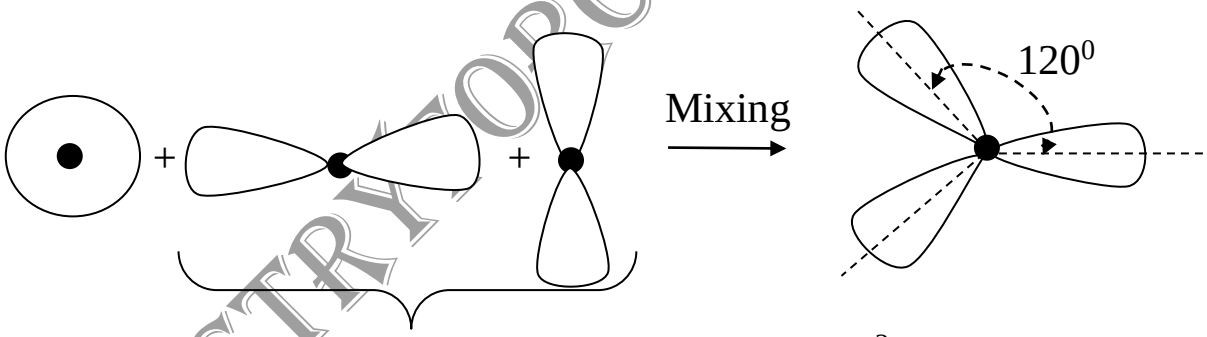

$BeF_2$ molecule (linear)

**Fig.- Formation of $BeF_2$ molecule ( diagrammatic)**

Since, $BeF_2$ involves sp hybridization, it is linear in shape with a bond angle of $180^0$ .

**(2) $sp^2$- Hybridization-**

"The process in which one-s and two-p orbitals of nearly same energy, mixed together by redistribution of energy and form three new orbitals of exactly same energy and same shape is called $sp^2$ hybridization and new orbitals formed are called $sp^2$-hybridized orbitals."




s-orbital two p-orbitals three $sp^2$-orbitals (trigonal planar)

**Fig.- $sp^2$-hybridization**

$sp^2$-hybridized orbitals remain directed towards three corners of an equilateral triangle and lie in same plane at an angle of $120^0$. Thus, $sp^2$-hybridization provides trigonal planer shape to the molecules with a bond angle of $120^0$. Hence, it is also called **trigonal planer hybridization**.

Each $sp^2$-hybridized orbital contains 33.33 % character of s orbital and 66.67 % character of p orbitals.

**Example- Formation of $BF_3$ molecule.**

The electronic excitation and $sp^2$ hybridization in central boron atom, leading to the formation of $BF_3$ molecule, can be represented as under-

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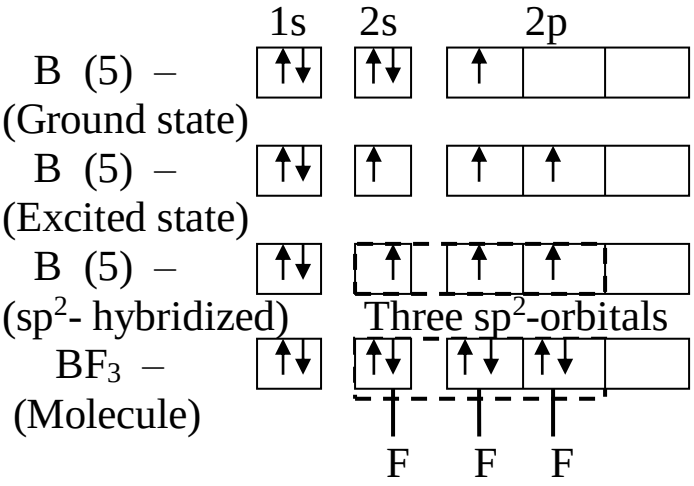



**Fig.- Formation of $BF_3$ molecule (schematic)**

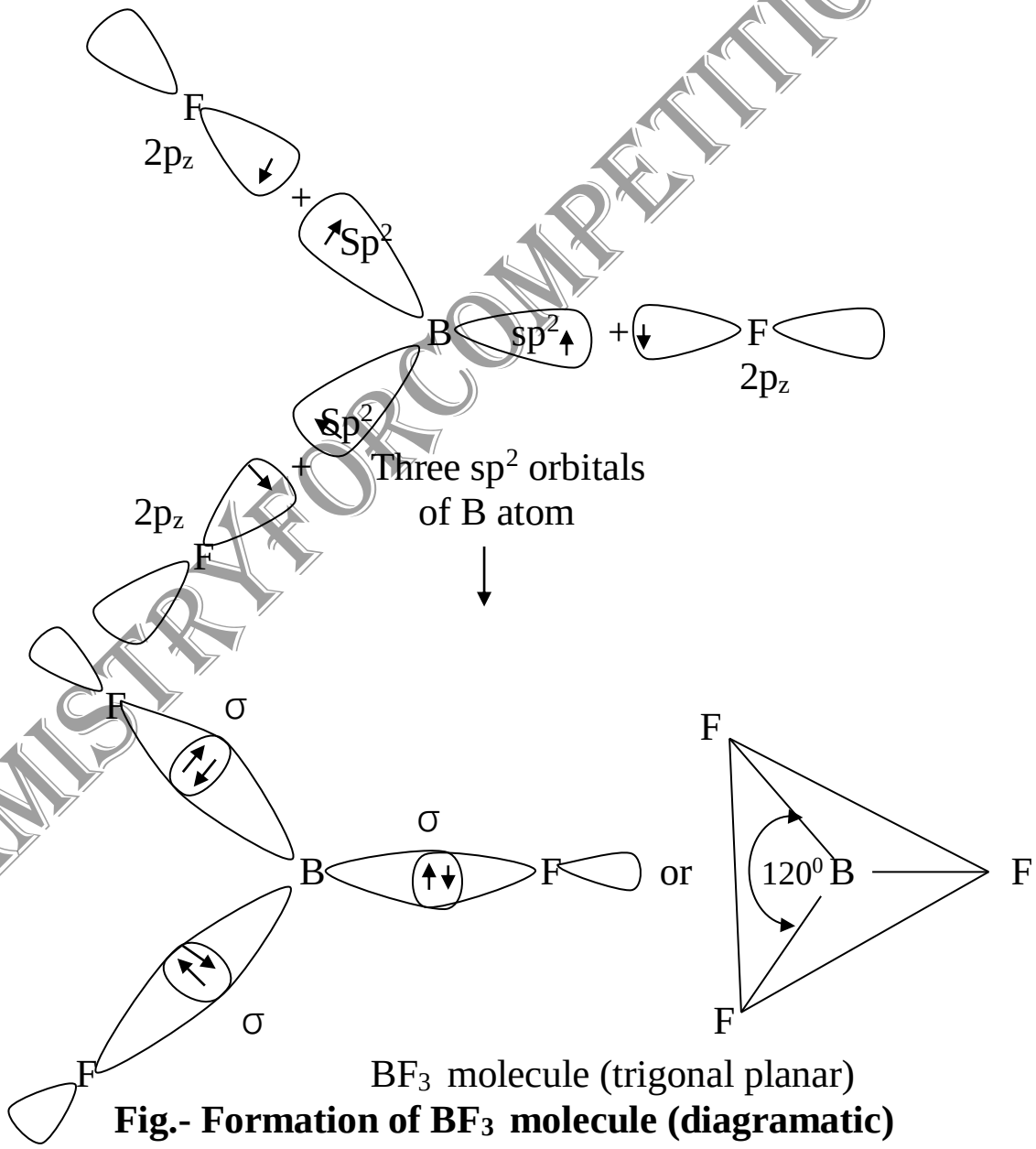


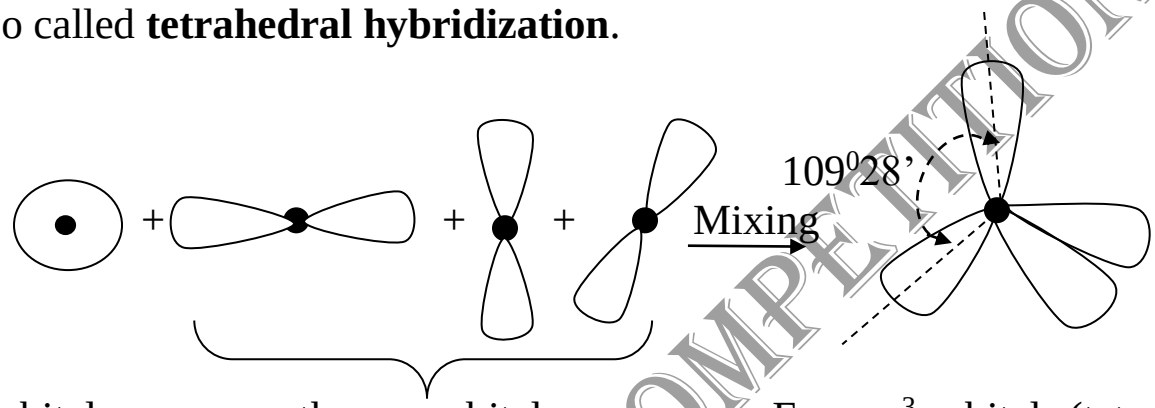

**Fig.- Formation of $BF_3$ molecule (diagramatic)**

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Since, $BF_3$ molecule involves $sp^2$ hybridization, it is trigonal planer in shape with a bond angle of $120^0$.

**(3) $sp^3$- Hybridization-** "The process in which one-s and three-p orbitals of nearly same energy, mixed together by redistribution of energy and form four new orbitals of exactly same energy and same shape is called $sp^3$ hybridization and new orbitals formed are called $sp^3$-hybridized orbitals."

$sp^3$-hybridized orbitals remain directed towards four corners of a regular tetrahedron and lie at an angle of $109^028'$. Thus, it provides tetrahedral shape to the molecules with a bond angle of $109^028'$. Hence, $sp^3$ hybridization is also called **tetrahedral hybridization**.




s-orbital three p-orbitals Four $sp^3$-orbitals (tetrahedral)

**Fig.- $sp^3$-hybridization**

Each $sp^3$-hybridized orbital contains 25 % character of s orbital and 75 % character of p orbitals.

**Example- Formation of $CH_4$ molecule.**

The electronic excitation and $sp^3$ hybridization in central carbon atom, leading to the formation of $CH_4$ molecule can be represented as under-

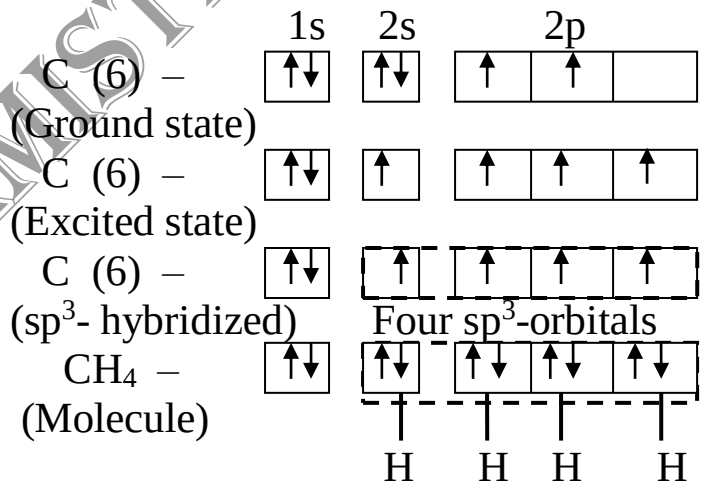



**Fig.- Formation of $CH_4$ molecule (schematic)**

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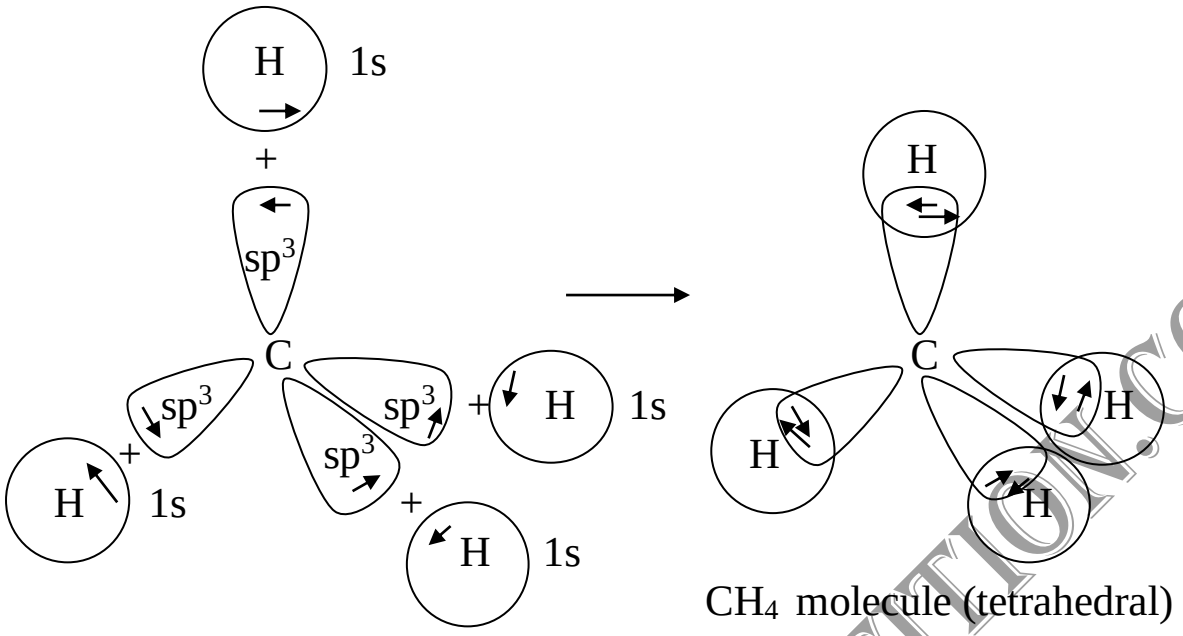



**Fig.- Formation of $CH_4$ molecule (diagrammatic)**

Since, $CH_4$ molecule involves $sp^3$ hybridization, it is **tetrahedral in shape** with a bond angle of **$109^0 28'$**.

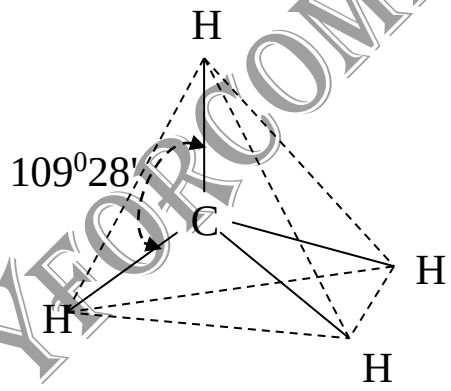
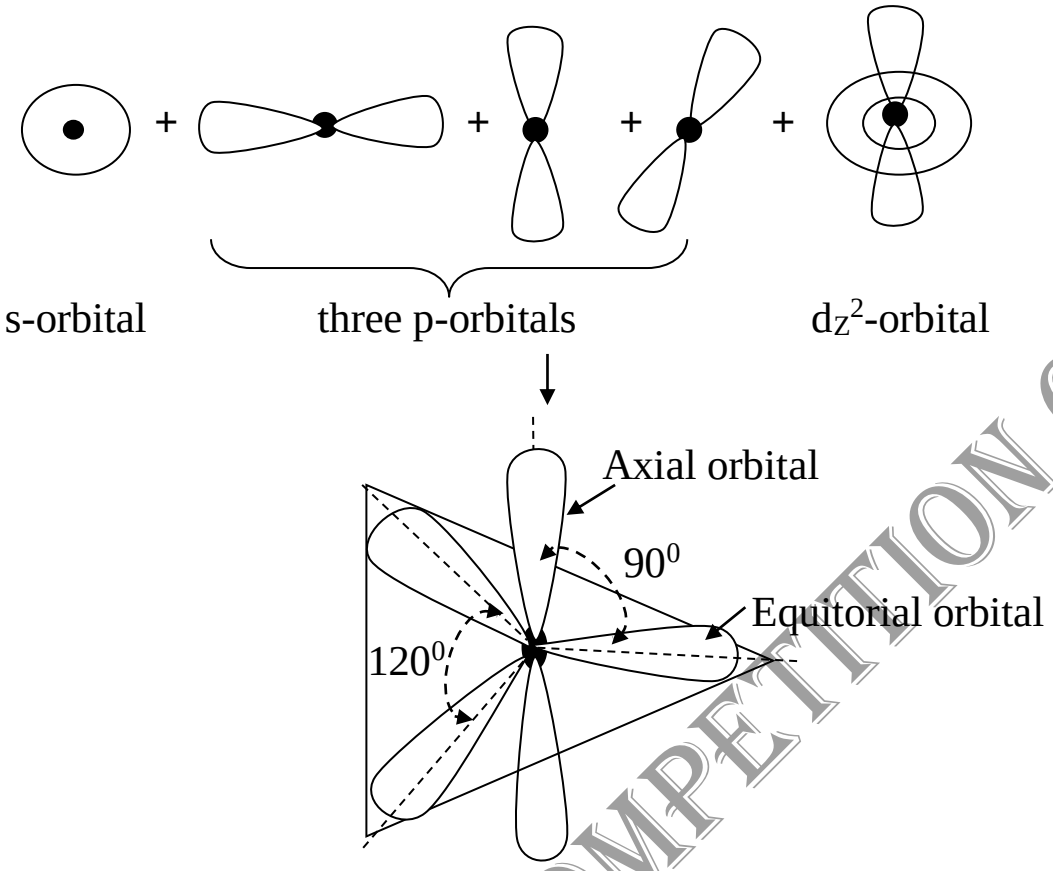



**Fig.- $CH_4$ molecule (tetrahedral)**

(4) **$sp^3d$- Hybridization**- "The process in which one-s, three-p and one-d orbitals of nearly same energy, mixed together by redistribution of energy and form five new orbitals of exactly same energy and same shape is called $sp^3d$ hybridization and new orbitals formed are called $sp^3d$ -hybridized orbitals."

Here, three $sp^3d$ -hybridized orbitals remain directed towards three corners of an equilateral triangle and lie in same plane at an angle of $120^0$. These orbitals are called **equatorial orbitals**. The remaining two $sp^3d$ -orbitals lie perpendicularly above and below the plane formed by equatorial orbitals and are called **axial orbitals**. Thus, $sp^3d$ hybridization provides trigonal bi-pyramidal shape to the molecules with a bond angle of $120^0$ and $90^0$. Hence, it is also called **trigonal bi-pyramidal hybridization**

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Five $sp^3d$-orbitals (trigonal bipyramidal)

**Fig.- $sp^3d$ hybridization**

**Example- Formation of $PCl_5$ molecule.**

The electronic excitation and $sp^3d$ hybridization in central phosphorus atom, leading to the formation of $PCl_5$ molecule can be represented as under-

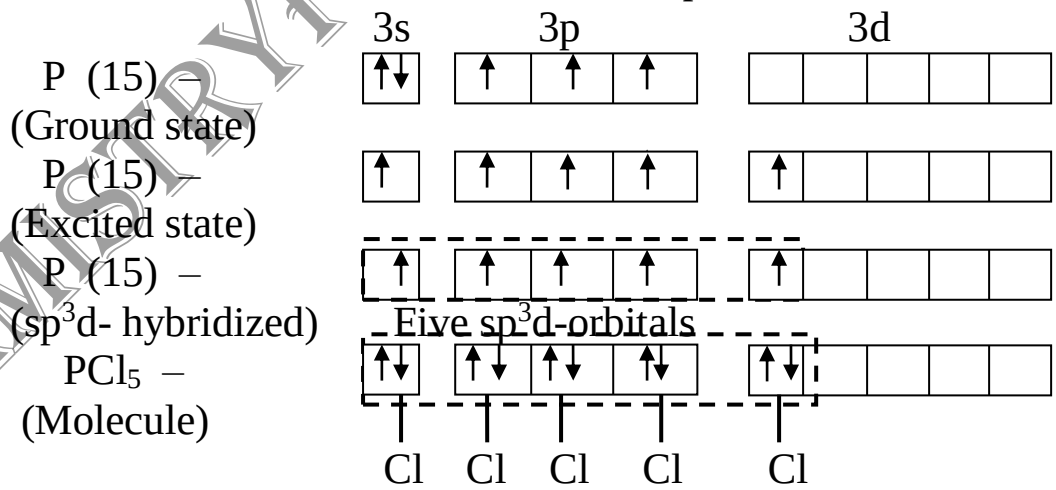



**Fig.- Formation of $PCl_5$ molecule ( schematic)**

Since, $PCl_5$ molecule involves $sp^3d$ hybridization, it is trigonal bi-pyramidal in shape with a bond angle of $120^0$ and $90^0$.

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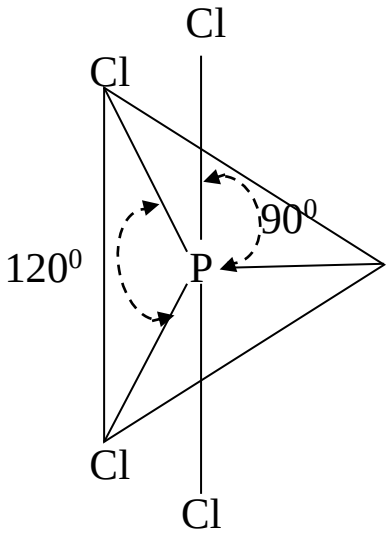



**Fig.- $PCl_5$ molecule (trigonal bi-pyramidal)**

**(5) $sp^3d^2$- Hybridization-** "The process in which one-s, three-p and two-d orbitals of nearly same energy, mixed together by redistribution of energy and form six new orbitals of exactly same energy and same shape is called $sp^3d^2$ hybridization and new orbitals formed are called $sp^3d^2$ -hybridized orbitals."

$sp^3d^2$ -hybridized orbitals remain directed towards six corners of a regular octahedron and lie at an angle of $90^0$ from one another. Thus, $sp^3d^2$ hybridization provides octahedral shape to the molecule with a bond angle of $90^0$. Hence, it is also called **octahedral hybridization.**

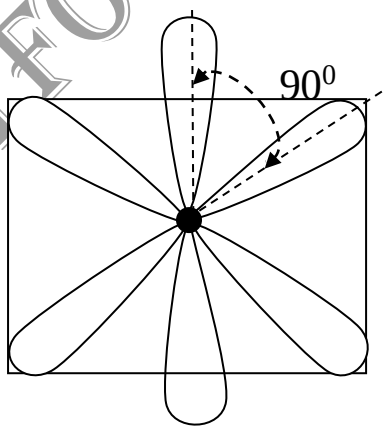



**Fig.- Six $sp^3d^2$ orbitals (octahedral)**

**Example- Formation of $SF_6$ molecule.**

The electronic excitation and $sp^3d^2$ hybridization in central sulphur atom, leading to the formation of $SF_6$ molecule can be represented as under-

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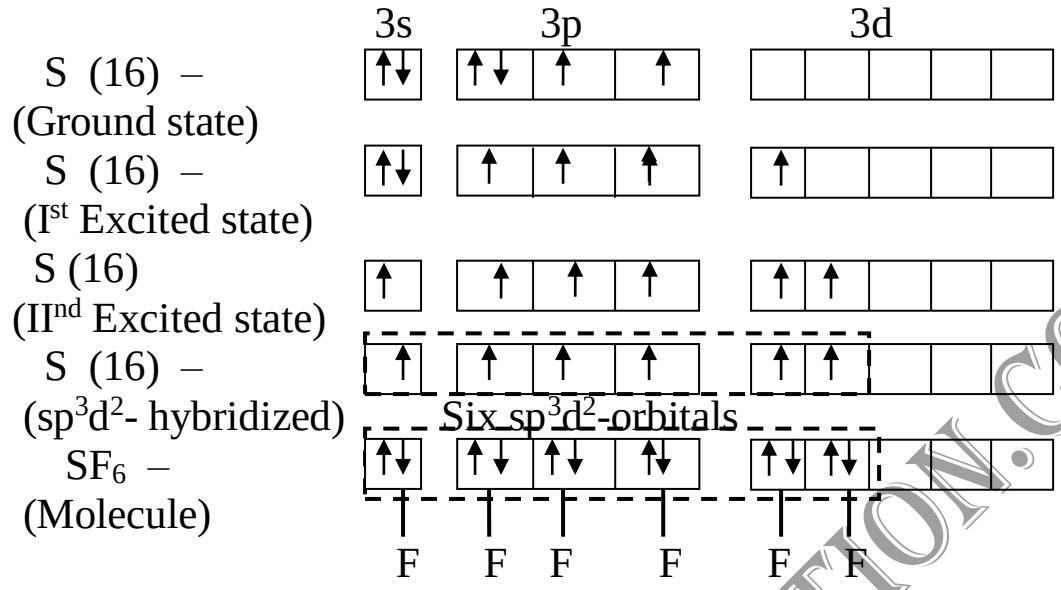



**Fig.- Formation of $SF_6$ molecule (schematic)**

Since, $SF_6$ molecule involves $sp^3d^2$ hybridization, it is octahedral in shape with a bond angle of $90^0$.

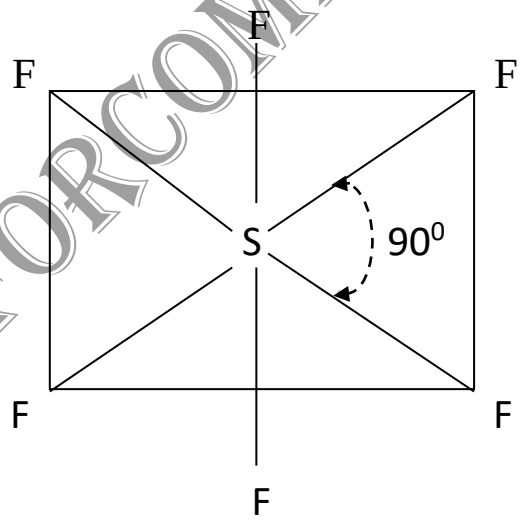



**Fig.- $SF_6$ molecule (octahedral)**

## Valence Shell Elections Pair Repulsion Theory (VSEPR Theory)

This theory was for the first time proposed by Powel and then modified by **Gillispie and Nyholm.** It is useful in deciding the geometry of those polyatomic covalent molecules in which all the atoms or groups remain attached to the central atom only by single bonds, but not by multiple bonds (double or triple bonds).

The main postulates of this theory are as under-

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(1) The geometry of a polyatomic covalent molecule depends upon the total number of election pairs (bond pairs + lone pairs) present in valence shell of its central atom.
(2) The election pairs present in valence shell of central atom repel each other. Hence, they tend to be at maximum distance, which corresponds to the minimum repulsion, minimum energy and therefore, maximum stability.
(3) If valence shell of central atom contains only bond pair of electrons, then these electron pairs repel one another in same extent, so that, the geometry of molecule is regular.
(4) If valence shell of central atom contains lone pairs along with bond pairs of electrons, then different types of repulsions operates amongst different electron pairs. Here, lone pair-lone pair repulsion is stronger than lone pair-bond pair repulsion and it is intern more stronger than bond pair-bond pair repulsion. Thus,

$$lp - lp > lp - bp > bp - bp$$

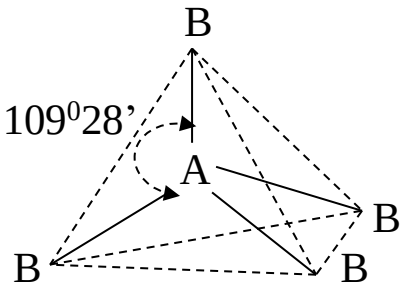
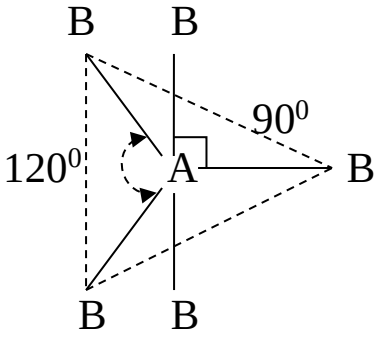
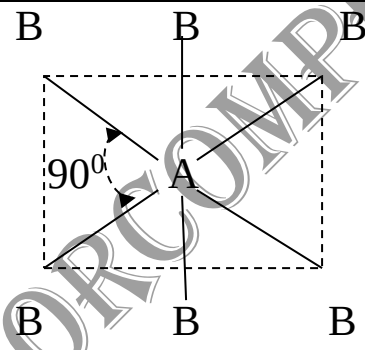
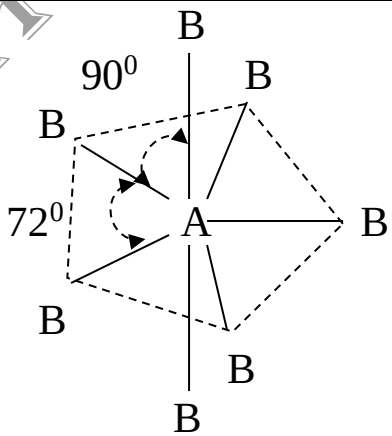
In such cases the geometry of molecules gets distorted.
(5) The electronic repulsion decreases rapidly with increase of bond angle. It is highest for $90^0$, intermediate for $120^0$, and is least for $180^0$.

**Applications of VSEPR Theory-**

Depending upon the number of total bond pairs of electrons present in valence shell of central atom, the regular geometry of different types of molecules with bond angles and examples are listed here-

| Type of Molecule | Number of bond pairs | Geometry | Bond angle | Examples |
|---|---|---|---|---|
| $AB_2$ | 2 | $180^0$<br>B — A — B<br>Linear | $180^0$ | $BeF_2$, $BeCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, |
| $AB_3$ | 3 | B<br>$120^0$ A — B<br>B<br>Trigonal Planar | $120^0$ | $BF_3$, $BCl_3$, $AlCl_3$ |

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| | | | | |
|---|---|---|---|---|
| $AB_4$ | 4 |  Tetrahedral | $109^028'$ | $CH_4$, $CCl_4$, $SiF_4$, $SiCl_4$ |
| $AB_5$ | 5 |  Trigonal bipyramidal | $120^0$, $90^0$ | $PF_5$, $PCl_5$ |
| $AB_6$ | 6 |  Octahedral | $90^0$ | $SF_6$ |
| $AB_7$ | 7 |  Pentagonal bipyramidal | $72^0$, $90^0$ | $IF_7$ |

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**Geometry of Molecules Containing Lone Pairs along with Bond Pairs of Electrons-**

**(1) Geometry of $NH_3$ molecule -** In $NH_3$ molecule, central N atom is $sp^3$ hybridized and contains in all four electron pairs in its valence shell, of which three are bond pairs, while rest one is lone pair. Due to presence of a lone pair, the molecule has **trigonal pyramidal geometry.**

$$N = ½(V + M + A - C)$$
$$= ½ (5 + 3 + 0 - 0)$$
$$= 4 (sp^3)$$

Here, lone pair-bond pair repulsion is more stronger than bond pair-bond pair repulsion.

Hence, N-H bonds come close together and bond angle gets reduced to $107^0$ from $109^028'$(normal bond angle of $sp^3$ hybridization). Thus, the geometry of molecules gets distorted from tetrahedral to **trigonal pyramidal**.

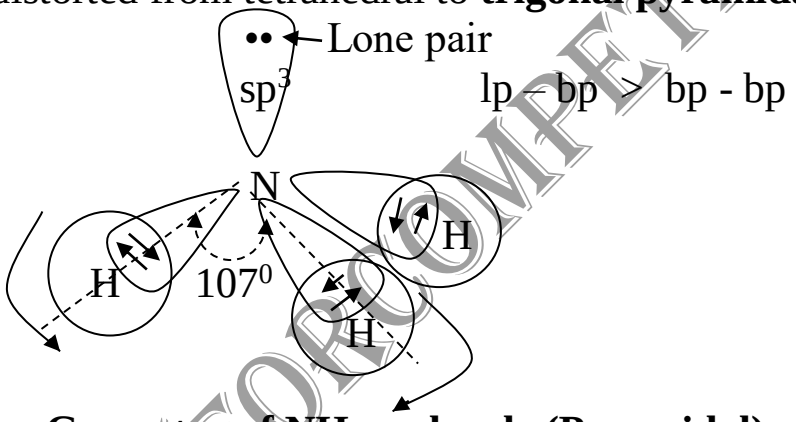



**Fig.- Geometry of $NH_3$ molecule (Pyramidal)**

- The geometry of $PH_3$, $AsH_3$, $PF_3$, $NCl_3$, $PCl_3$ etc. are identical to that of $NH_3$.

**(2) Geometry of $H_2O$ molecule -** In $H_2O$ molecule central O atom is $sp^3$ hybridized and contains in all four electron pairs in its valence shell, of which two are bond pairs, while rest two are lone pairs. Due to presence of two lone pairs, the molecule has **angular, bent or V-shaped geometry.**

$$N = ½(V + M + A - C)$$
$$= ½ (6 + 2 + 0 - 0)$$
$$= 4 (sp^3)$$

Here, the decreasing order of repulsion amongst different electron pairs is as under-

$$lp - lp > lp – bp > bp – bp$$

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Hence, O-H bonds come close together and bond angle gets reduced to $104.5^0$ from $109^028'$(normal bond angle of $sp^3$ hybridization). Thus, the geometry of water molecules becomes angular, bent or V-shaped.

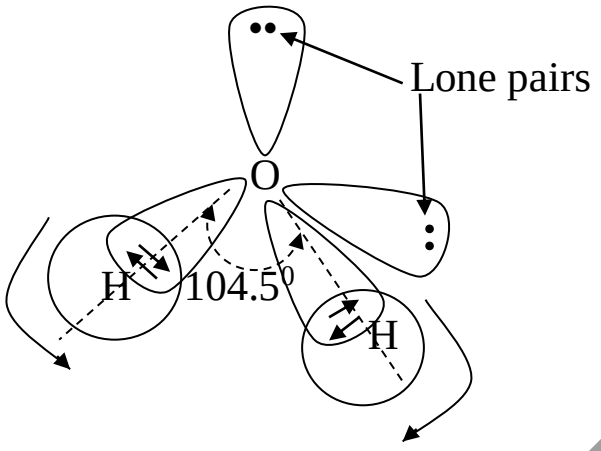



**Fig.- Geometry of $H_2O$ molecule (angular, bent or V-shaped)**

- The geometry of $H_2S$, $H_2Se$, $H_2Te$ etc. are identical to that of $H_2O$.

**(3) Geometry of $SnCl_2$ molecule -** In $SnCl_2$ molecule, central Sn atom is $sp^2$ hybridized and contains in all three electron pairs in its valence shell, of which two are bond pairs, while rest one is lone pair. Due to presence of a lone pair, the molecule has **angular or vent (V-shaped) geometry.**

$$N = ½(V + M + A - C)$$
$$= ½ (4 + 2 + 0 - 0)$$
$$= 3 (sp^2)$$

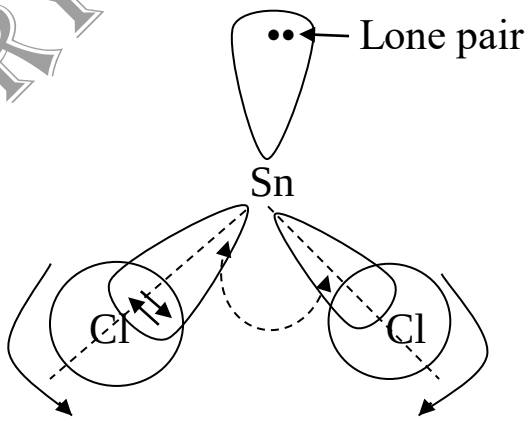



**Fig.- Geometry of $SnCl_2$ molecule (angular, bent or V-shaped)**

- The geometry of $PbCl_2$ is identical to that of $SnCl_2$.

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(4) **Geometry of $SF_4$ molecule-** In $SF_4$ molecule, central S atom is $sp^3d$ hybridized and contains in all five electron pairs in its valence shell, of which four are bond pairs, while rest one is lone pair. Here, lone pair occupies one of the equitorial orbitals, Hence, the molecule has **sea-saw shaped geometry**.

$$N = ½(V + M + A - C)$$
$$= ½ (6 + 4 + 0 - 0)$$
$$= 5 (sp^3d)$$

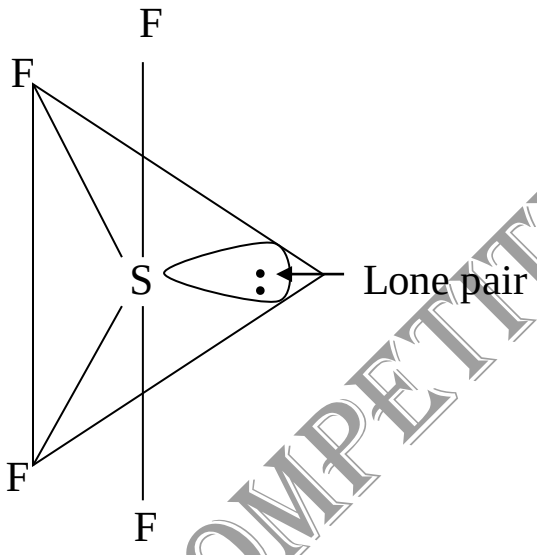



**Fig.- Geometry of $SF_4$ molecule (sea-saw shaped)**

- The geometry of $SCl_4$ is identical to that of $SF_4$.

(5) **Geometry of $ClF_3$ molecule-** In $ClF_3$ molecule, central Cl atom is $sp^3d$ hybridized and contains in all five electron pairs in its valence shell, of which three are bond pairs, while rest two are lone pairs. Here, lone pairs occupy equitorial positions, Hence, the molecule has **T- shaped geometry**.

$$N = ½(V + M + A - C)$$
$$= ½ (7 + 3 + 0 - 0)$$
$$= 5 (sp^3d)$$

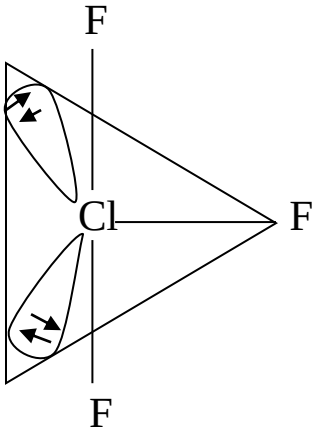



**Fig.- Geometry of $ClF_3$ molecule (T-shaped)**

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- The geometry of $BrF_3$, $BrCl_3$, $ICl_3$ etc. is identical to that of $ClF_3$.

(6) **Geometry of $ClF_5$ molecule-** In $ClF_5$ molecule, central Cl atom is $sp^3d^2$ hybridized and contains in all six electron pairs in its valence shell, of which five are bond pairs, while rest one is lone pair. Here, lone pair occupies one of the axial positions, Hence, the molecule has **square pyramidal geometry**.

$$N = ½(V + M + A - C)$$
$$= ½ (7 + 5 + 0 - 0)$$
$$= 6 (sp^3d^2)$$

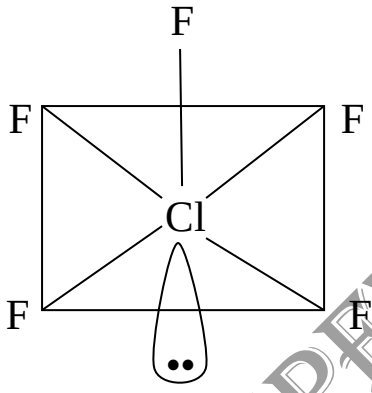



**Fig.- Geometry of $ClF_5$ molecule (square pyramidal)**

- The geometry of $BrF_5$, $BrCl_5$ etc. is identical to that of $ClF_5$.

(7) **Geometry of $XeF_2$ molecule-** In $XeF_2$ molecule, central Xe atom is $sp^3d$ hybridized and contains in all five electron pairs in its valence shell, of which two are bond pairs, while rest three are lone pairs. Here, lone pairs occupy all the equitorial positions, while both the fluorine atoms occupy axial positions. Thus, $XeF_2$ molecule has **linear geometry**.

$$N = ½(V + M + A - C)$$
$$= ½ (8 + 2 + 0 - 0)$$
$$= 5 (sp^3d)$$

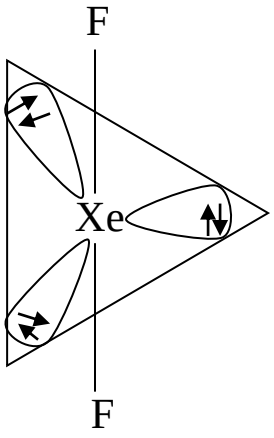



**Fig.- Geometry of $XeF_2$ molecule (linear)**

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(8) **Geometry of $XeF_4$ molecule-** In $XeF_4$ molecule, central Xe atom is $sp^3d^2$ hybridized and contains in all six electron pairs in its valence shell, of which four are bond pairs, while rest two are lone pairs. Here, lone pairs occupy both the axial positions, while fluorine atoms occupy all the equitorial positions. Thus, $XeF_4$ molecule has **square planar geometry**.

$$N = \frac{1}{2}(V + M + A - C)$$
$$= \frac{1}{2}(8 + 4 + 0 - 0)$$
$$= 6\ (sp^3d^2)$$

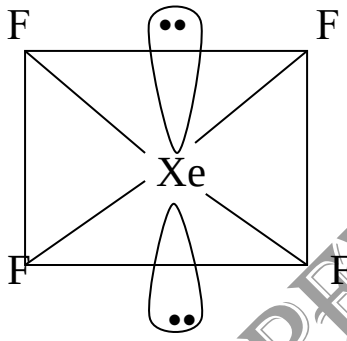



**Fig.- Geometry of $XeF_4$ molecule (square planar)**

(9) **Geometry of $XeF_6$ molecule-** In $XeF_6$ molecule, central Xe atom is $sp^3d^3$ hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs, while rest one is lone pair. Here, lone pair occupies one of the equitorial positions. Thus, $XeF_6$ molecule has **distorted octahedral geometry**.

$$N = \frac{1}{2}(V + M + A - C)$$
$$= \frac{1}{2}(8 + 6 + 0 - 0)$$
$$= 7\ (sp^3d^3)$$

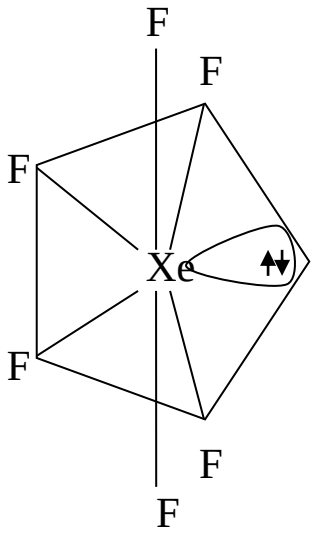



**Fig.- Geometry of $XeF_6$ molecule (distorted octahedral)**

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(10) **Geometry of $XeOF_2$ molecule-** In $XeOF_2$ molecule, central Xe atom is $sp^3d$ hybridized and contains in all six electron pairs in its valence shell, of which four are bond pairs (three sigma + one pi), while rest two are lone pairs. Here, lone pairs and oxygen atom occupy equitorial positions, while both the fluorine atoms occupy axial positions. Thus, $XeOF_2$ molecule has **T-shaped geometry**.

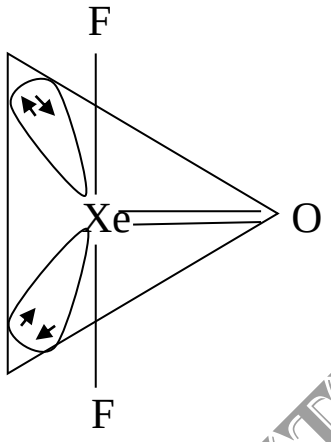



**Fig.- Geometry of $XeOF_2$ molecule (T-shaped)**

(11) **Geometry of $XeOF_4$ molecule-** In $XeOF_4$ molecule, central Xe atom is $sp^3d^2$ hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs (five sigma + one pi), while rest one is lone pair. Here, lone pair and oxygen atom occupy axial positions, while fluorine atoms occupy equitorial positions. Thus, $XeOF_4$ molecule has **square pyramidal geometry**.

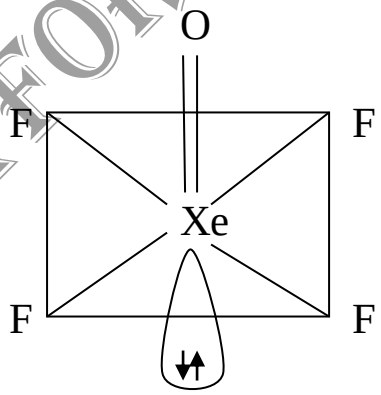



**Fig.- Geometry of $XeOF_4$ molecule (Square pyramidal)**

(12) **Geometry of $XeO_3$ molecule-** In $XeO_3$ molecule, central Xe atom is $sp^3$ hybridized and contains in all seven electron pairs in its valence shell, of which six are bond pairs (three sigma + three pi), while rest one is lone pair. Thus, $XeO_3$ molecule has **trigonal pyramidal (ammonia like) geometry**.

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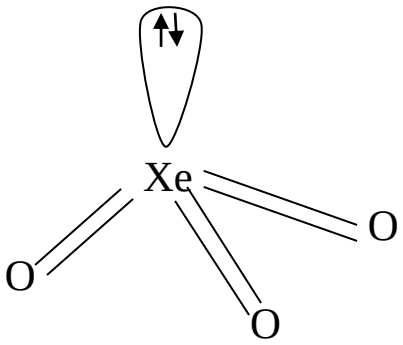



**Fig.- Geometry of $XeO_3$ molecule (Trigonal pyramidal)**

## Dipole Moment

The polarity of a covalent molecule is measured in terms of its dipole moment. By definition,

"The product of the charge present on one pole and the bond length of a bond is called dipole moment (bond moment) of the respective bond."

Mathematically, Dipole moment,

$$\mu = e \times d$$

Where, e = charge on one atom

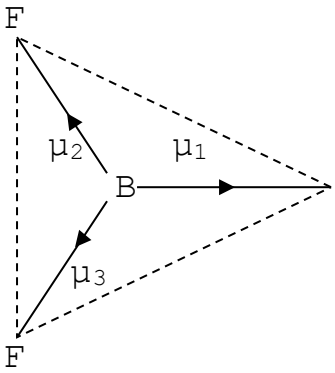
d = bond length

For most of the covalent bonds, charge produced on the bonded atoms is of the order of $10^{-10}$ esu and the bond length is of the order of $10^{-8}$ cm. Hence, dipole moment of most of the covalent bonds is of the order of $10^{-18}$ esu-cm, which is called **1 Debye**. Thus,

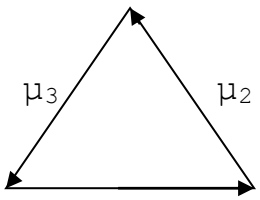
$$\mu = 10^{-10} \text{ esu} \times 10^{-8} \text{ cm}$$
$$= 10^{-18} \text{ esu-cm}$$
$$= 1 \text{ Debye}$$

Dipole moment is a vector quantity. Hence, if a molecule contains a number of polar covalent bonds, then the resultant dipole moment of molecule is obtained from vector sum of the bond moments of different bonds. Thus, a molecule having a number of polar covalent bonds, can have its dipole moment zero.
For example, $BF_3$ has three polar B-F bonds, but its dipole moment is zero.

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$BF_3$ Molecule




$\mu_{resultant} = 0$

Here, vector sum of any two bond moments is equal in magnitude but opposite in direction to the bond moment of third bond. Hence, resultant dipole moment of the molecule is zero.

Similarly, $CCl_4$ has four polar C-Cl bonds, but its dipole moment is zero.

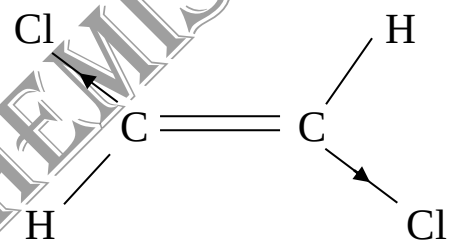
**Applications of Dipole Moment**

**(1) Determination of percentage ionic character-** The percentage ionic character in a polar covalent bond is given by following expression-

$$\%\text{age ionic character} = \frac{\textit{Observed dipole moment}}{\textit{Calculated dipole moment}} \times 100$$

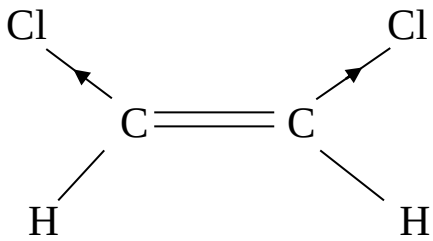
$$= \frac{\textit{Experimental dipole moment}}{e \times d} \times 100$$

**(2) Distinction between cis and trans isomers-** For an alkene of type $_{ab}C = C_{ab}$, cis isomer has a definite non-zero value of its dipole moment, while trans form has its dipole moment zero. For example, dipole moment of trans-1,2-dichloroethene is zero, while that of cis-1,2-dichloroethene is non-zero.




Trans-1,2-dichloroethene

($\mu = 0$)



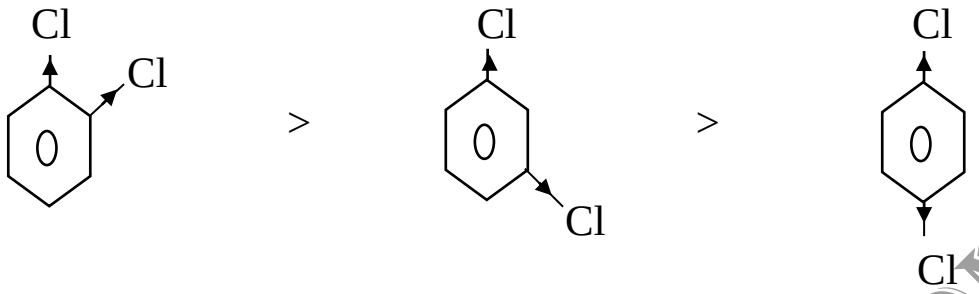

Cis-1,2-dichloroethene

($\mu \neq 0$)

**(3) Distinction amongst ortho, meta and para disubstituted benzene-** Here, ortho disubstituted benzene has highest value of its dipole moment, while para

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isomer has zero dipole moment. Dipole moment of meta isomer is in between ortho and para isomers. For example, the order of dipole moment of ortho, meta and para dichlorobenzene is as under-



Ortho-dichloro benzene  Meta-dichloro benzene  Para-dichloro benzene

**(4) Determination of geometry of molecules-** If a molecule has its dipole moment zero, its geometry is regular. On the other hand, if dipole moment of a molecule has a non-zero value, then its geometry is distorted. For example,

**(a) Geometry of molecules of type $AB_2$-** For molecule of type $AB_2$ following two geometries are possible-



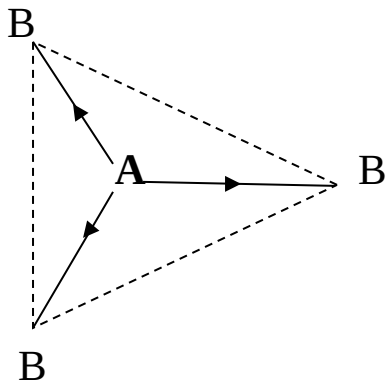
($\mu = 0$)
Linear
e.g. $BeF_2$, $BeCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $CO_2$, $CS_2$ etc.

($\mu \neq 0$)
Angular, Bent or V-shaped
e.g. $NO_2$, $H_2O$, $H_2S$, $H_2Se$ $SO_2$ etc.

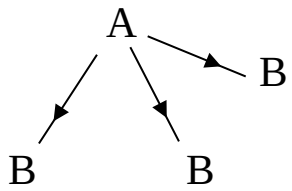
Thus, if a molecule of type $AB_2$, has its dipole moment zero, then the geometry of molecule is linear. On the other hand, if it has a definite non-zero value of its dipole moment, then its geometry is angular, bent or V-shaped.

**(b) Geometry of molecules of type $AB_3$-** For molecule of type $AB_3$ following two geometries are possible-

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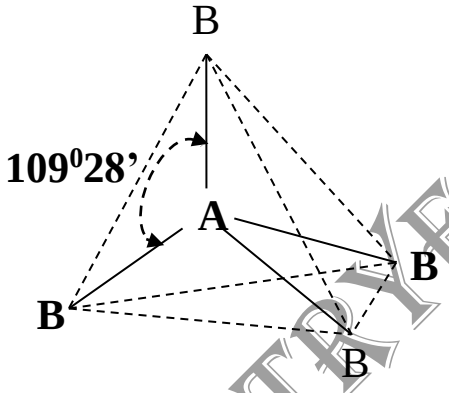

($\mu = 0$)
Trigonal Planar
e.g. $BF_3$, $BCl_3$, $AlCl_3$ etc.



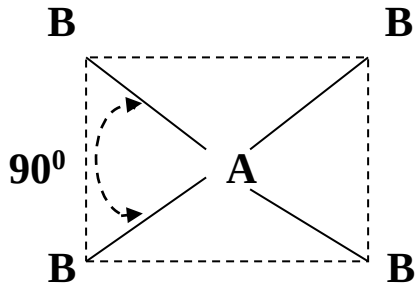

($\mu \neq 0$)
Trigonal pyramidal
e.g. $NH_3$, $PH_3$, $AsH_3$, $NF_3$, $NCl_3$ etc.

Thus, if a molecule of type $AB_3$ has its dipole moment zero, then the geometry of molecule is trigonal Planar. On the other hand, if it has a definite non-zero value of its dipole moment, then its geometry is trigonal pyramidal.

**(c) Geometry of molecules of type $AB_4$-** For molecule of type $AB_4$ following two regular geometries are possible-




($\mu = 0$)
Tetrahedral
e.g. $CH_4$, $CF_4$, $CCl_4$
$NH_4^+$, $NiCl_4$ etc.




($\mu = 0$)
Square planar
e.g. $XeF_4$, $[Ni(CN)_4]^{2-}$etc.

Thus, if a molecule of type $AB_4$ has its dipole moment zero, then the geometry of molecule is either tetrahedral or square planar. On the other hand, if it has a definite non-zero value of its dipole moment, then its geometry is distorted. For example, $SF_4$ has sea-saw shaped geometry.

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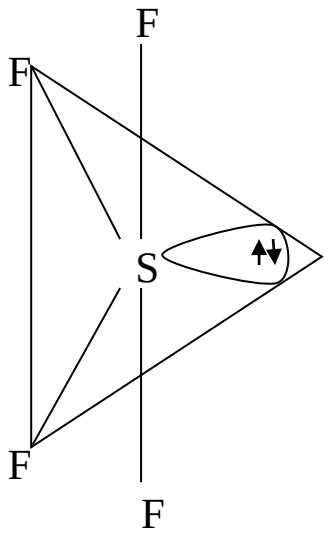
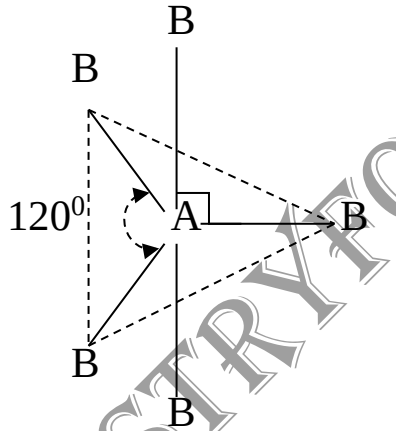
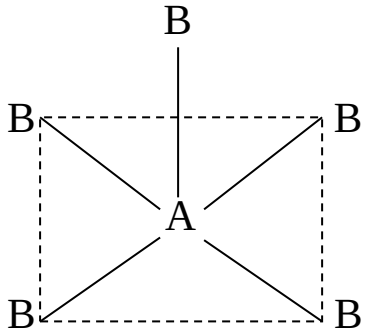



**Fig.- $SF_4$ molecule (Sea-saw shaped)**
**($\mu \neq 0$)**

**(d) Geometry of molecules of type $AB_5$-** For molecule of type $AB_5$ following two geometries are possible-




($\mu = 0$)
Trigonal bipyramidal
e.g. $PF_5$, $PCl_5$




($\mu \neq 0$)
Square pyramidal
e.g. $ClF_5$, $XeOF_2$

**(e) Geometry of molecules of type $AB_6$-** For molecule of type $AB_6$, if dipole moment is zero, then the molecule has octahedral geometry. For example, $SF_6$ molecule.

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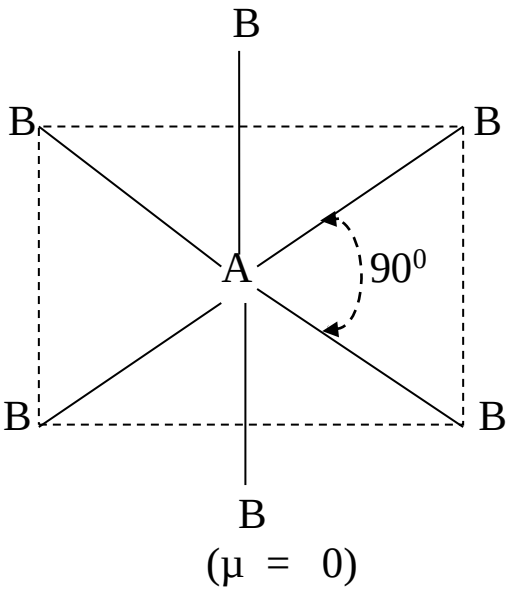



**Fig.- $SF_6$ molecule (octahedral)**

However, if its dipole moment has a definite non-zero value, then its geometry gets distorted. For example, $XeF_6$ has distorted octahedral geometry.

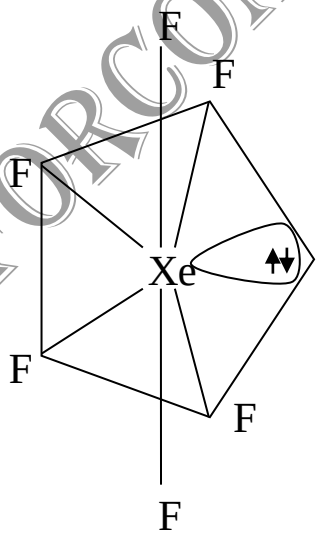
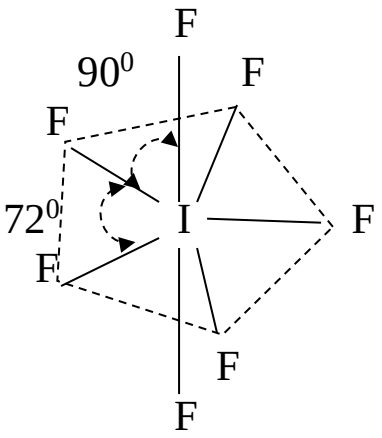



**Fig.- $XeF_6$ molecule (distorted octahedral)**

**(f) Geometry of molecules of type $AB_7$-** For molecule of type $AB_7$, if dipole moment is zero, then the molecule has pentagonal bipyramidal geometry. For example, $IF_7$ molecule.

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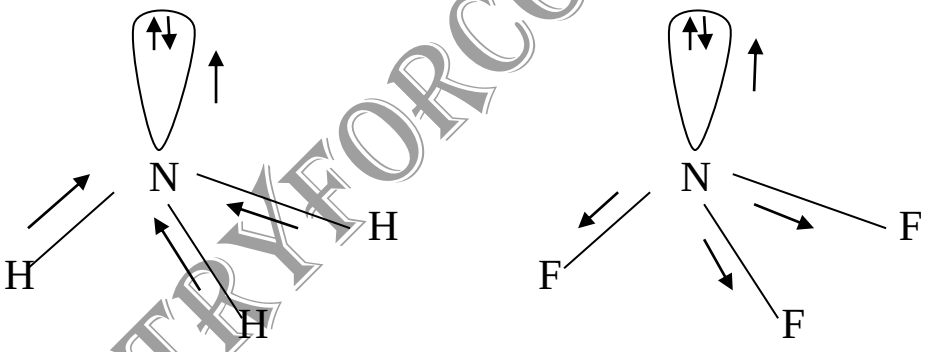

(μ = 0)

**Fig.-$IF_7$ molecule (Pentagonal bipyramidal)**

However, if its dipole moment has a definite non-zero value, then its geometry gets distorted.

**Q.** Amongst $NH_3$ and $NF_3$ which has more dipole moment and why ?

**Ans.** In $NH_3$, resultant dipole moments of three N-H bonds and dipole moment of lone pair operate in same direction, while in $NF_3$, resultant dipole moments of three N-F bonds and dipole moment of lone pair operate in opposite directions.




$NH_3$ molecule $NF_3$ molecule

Thus, resultant dipole moment of $NH_3$ will be more than that of $NF_3$.

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