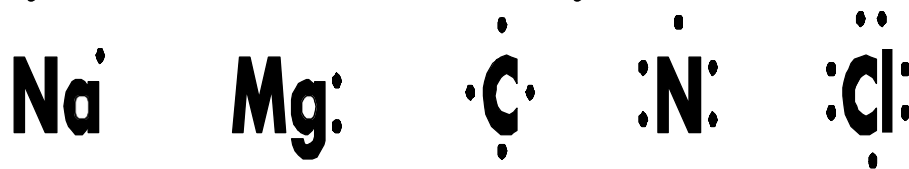


# Chemical Bonding and Shapes of Molecules

## Valence Shell , Valence Electron

The number of electrons present in the outermost shell of an atom determines the valency of the element, these electrons are called **valence electrons** and the corresponding shell is called **valence shell**. Excepting valence electrons, the rest of the electrons present in an atom are called **core electrons**.

G.N. Lewis devised a simple method of representing the electronic symbol of the atom in which the valence electrons are also shown. This type of symbol is often called Lewis electron dot symbol. The electron dot symbols of several atoms are given below.



## Octet Rule

He, Ne, Ar, Kr, Xe and Rn are called inert gases, and these inert gases have a little or no tendency for chemical combination.

ELEMENT	ATOMIC NO.	ELECTRONIC CONFIGURATION					
		K	L	M	N	O	P
He	2	2					
Ne	10	2	8				
Ar	18	2	8	8			
Kr	36	2	8	18	8		
Xe	54	2	8	18	18	8	
Rn	86	2	8	18	32	18	8

Excepting helium, all other inert gases have 8 electrons in their valence shell. This combination of 8 electrons is called **OCTET**. All other elements excepting inert gases do not have octet in their outermost orbit and they try to acquire octet.

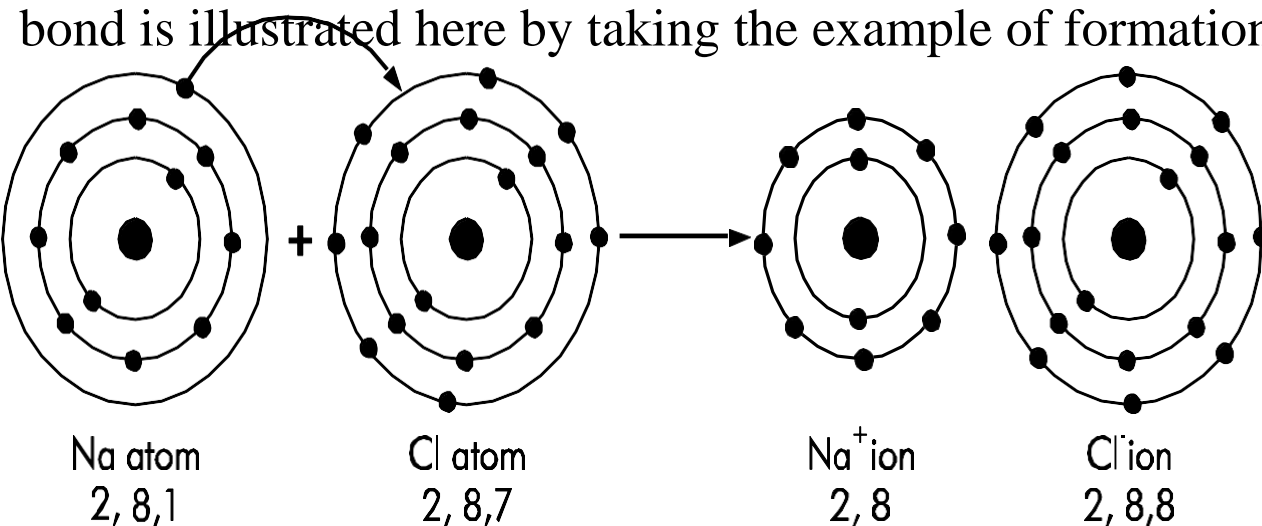
*Atoms can combine either by transfer of valence electrons from one atom to another by gaining or losing or by sharing of valence electrons in order to have an octet in their valence shells is known as OCTET RULE.*

According to the electronic theory of valency, atoms combine to acquire the electronic configuration of nearest inert gas. Three important modes of formation of a chemical bond are :

## Ionic Bond

*The bond formed by the complete transfer of one or more electrons from one atom to the other is called Ionic bond or electrovalent bond, and this type of valency is called electrovalency.*

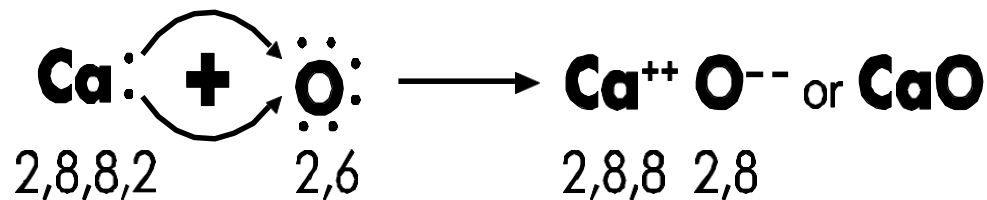
In the formation of electrovalent bond, metal atom loses electron, whereas nonmetal atom gains electrons, and thereby both attain octet. The metal atom which loses electron is called **electropositive element**, and it becomes positively charged after losing electron. The non-metal atom which gains electron is called **electronegative element**, and it becomes negatively charged after gaining electron. The formation of electrovalent bond is illustrated here by taking the example of formation of sodium chloride.



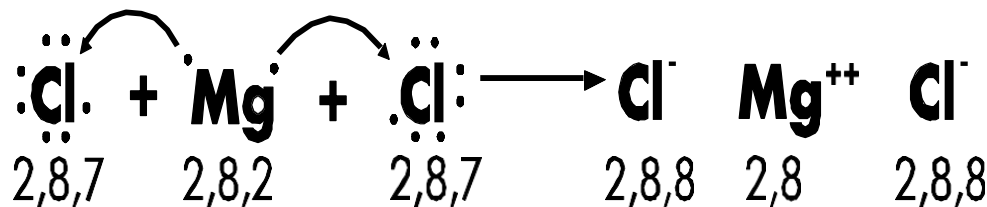
In the above example of formation of NaCl, the electrovalency of sodium is 1, and that of chlorine is also 1. The electrostatic force of attraction which arises due to transference of electron is called **electrovalent bond**.

## Formation of calcium oxide

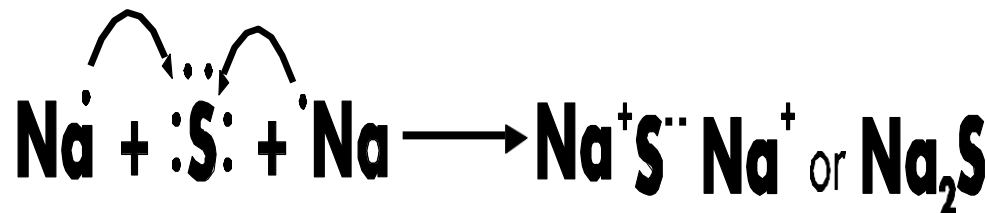
The electronic configuration of calcium is 2,8,8,2 and that of oxygen is 2,6. When calcium combines with oxygen, calcium transfers two electrons to oxygen whereby both acquire octet. Calcium ion with two positive charges and oxygen with two negative charges are then held together by electrovalent bond.



## Formation of magnesium chloride



## Formation of sodium Sulphide



## Characteristics of ionic compounds

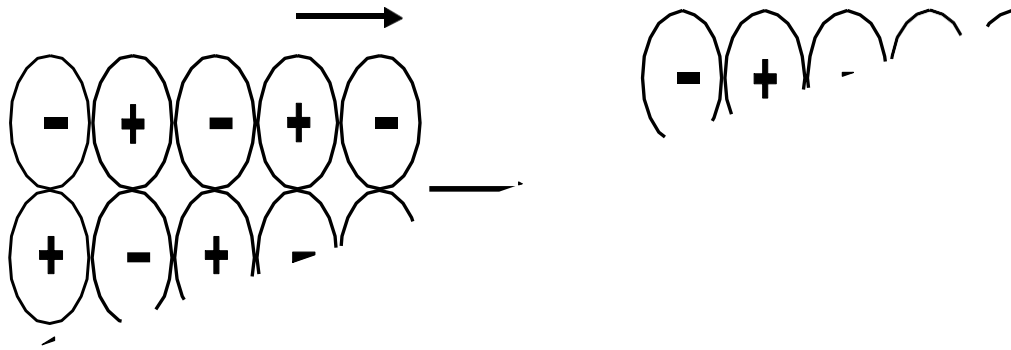
**1. Physical state:** Ionic compounds usually exist as solids and are crystalline in nature.

Even in the solid state, they exist as ions, and the ions are arranged in three dimensional space with regular geometric pattern known as **crystal lattice**.

**2. Solubility:** Ionic compounds are generally soluble in polar solvents like water and insoluble in non-polar solvents like carbon tetrachloride, benzene etc.

**3. Electrical conductivity:** Ionic compounds in molten state or in aqueous solution contain mobile ions. Therefore, they conduct electricity.

**4. Brittleness:** Ionic compounds are usually brittle. Ionic crystal consists of closely packed oppositely charged ions. When a stress is applied to the crystal, similarly charged ions come closer, and because of repulsion between them the crystal breaks into pieces.



**5. Melting and boiling point:** Ionic compounds have high melting and boiling points, because the electrostatic forces of attraction are very strong, and a large amount of energy is required to overcome these forces.

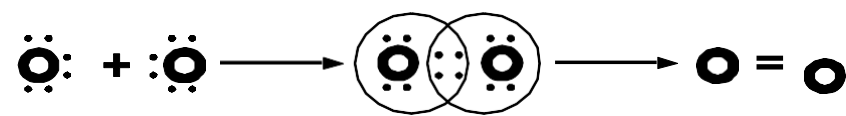
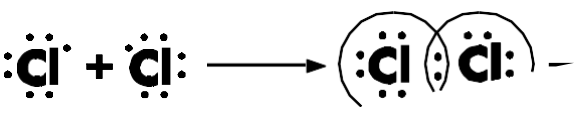
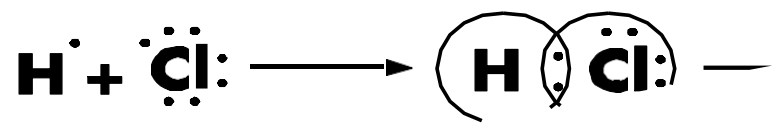
**6. Ionic bond is not directional**

### Covalent Bond

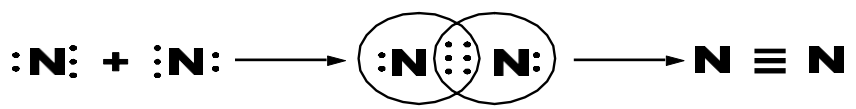
*The bond formed by mutual sharing of electrons between combining atoms of same or different elements is called covalent bond.* In the formation of a covalent bond, each combining atom contributes one electron for each shared pair of electrons.

*Covalency of an element is the number of electrons which its atom contributes for sharing during the covalent bond formation.*

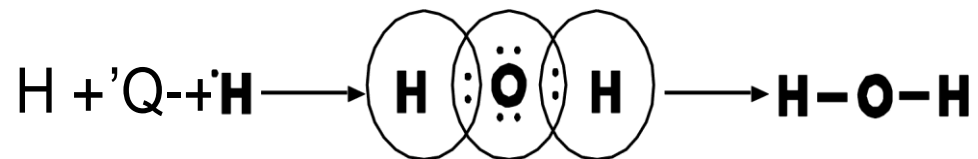
Let us illustrate the covalent bond by taking the example of the formation of hydrochloric acid. The electronic configuration of hydrogen is 1 and that of chlorine is 2,8,7. Hydrogen needs one electron to have a duplet, the electronic configuration of inert gas helium, and chlorine needs one electron to have octet, the electronic configuration of inert gas argon. Thus by mutual sharing of electrons both hydrogen and chlorine acquire the stable electronic configuration as diagrammatically shown below.



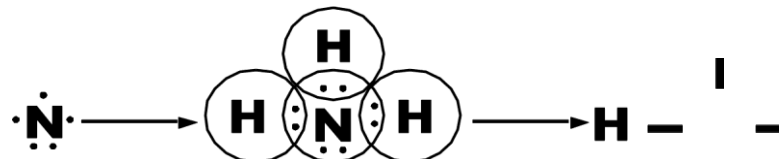
**Formation of oxygen molecule**



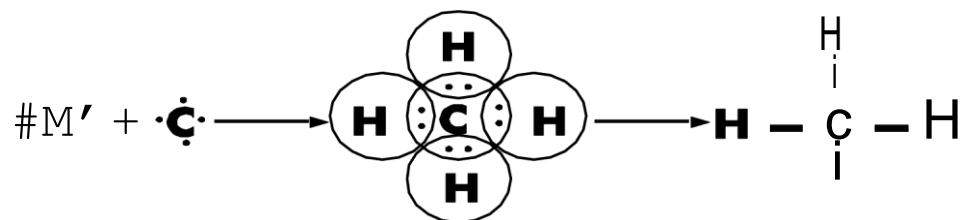
**Formation of nitrogen molecule**



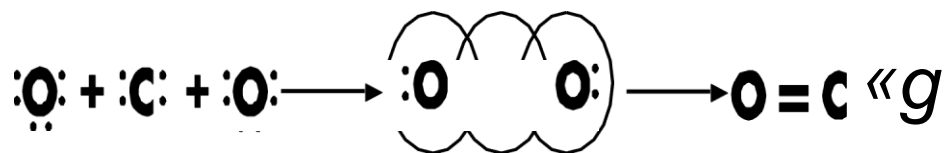
Formation of water molecule



Formations of ammonia



Formation of methane



Formation of carbon dioxide

## Properties of covalent compounds

**1. Physical state, melting and boiling point:** Covalent compounds are made up of molecules and not ions. These molecules are not bound together by strong intermolecular forces. Hence they exist in all the three states (solid, liquid and gas), and if they exist as solid or liquid, they have low melting and boiling points.

**2. Electrical conductivity:** Covalent compounds generally disperse in solution as individual molecules, hence do not give charged particles in solution. Therefore aqueous solutions of such covalent compounds do not conduct electricity. Examples are aqueous solutions of sugar, glucose, urea etc.

**3. Solubility:** Covalent compounds are generally insoluble in polar solvent like water, but soluble in non-polar or weakly polar organic solvents like ether, alcohol, benzene etc.

**4. Directional nature:** Covalent bonds have directional character. Hence covalent

**4. Directional nature:** Covalent bonds have directional character. Hence covalent molecules have particular geometrical shape. For example, water molecule is angular, and ammonia molecule has pyramidal shape as portrayed in the following diagram.



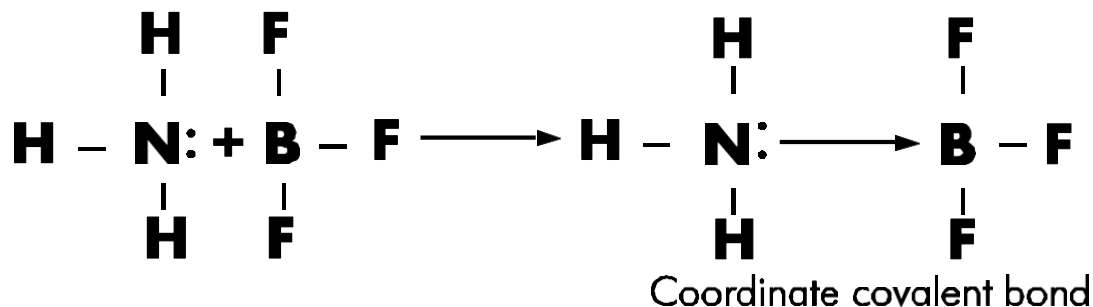
Share

### Coordinate Covalent Bond

*The bond formed by mutual sharing of electrons in which both the shared pair of electrons is contributed by one of the bonded atoms is called coordinate covalent bond.*

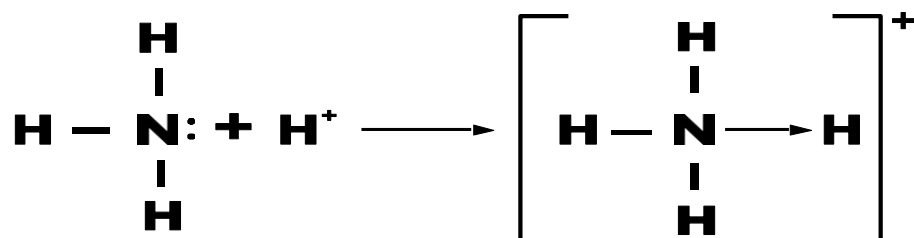
This type of coordinate covalent bond is formed only when there is an atom which is deficient of at least a pair of electrons, while the other atom has acquired the stable octet and contains at least a lone pair of electrons which has not been used for the bond formation.

For example, nitrogen atom of the ammonia molecule has a lone pair of electrons, and can act as a donor atom and the boron atom of boron trifluoride is short of a pair of electrons, and can act as an acceptor atom.

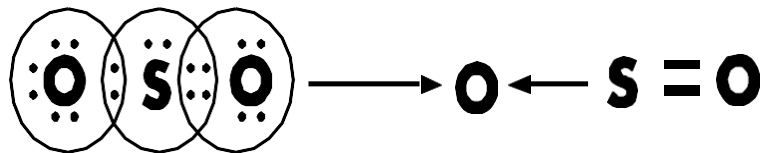


The coordinate covalent bond is represented by an arrow pointing from donor atom to acceptor atom.

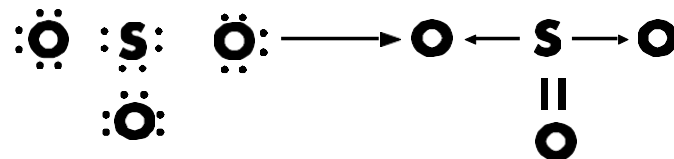
In ammonium ion also there is a coordinate covalent bond. In the formation of ammonium ion, nitrogen atom of ammonia donates its lone pair of electrons to hydrogen ion, and forms coordinate covalent bond.



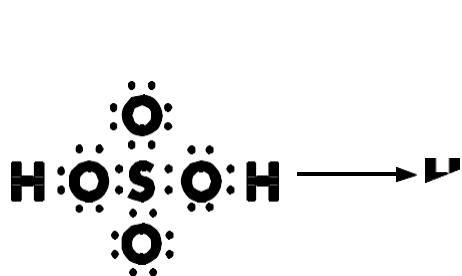
## Some more examples of coordinate covalent bond



Sulphur dioxide



Sulphur trioxide

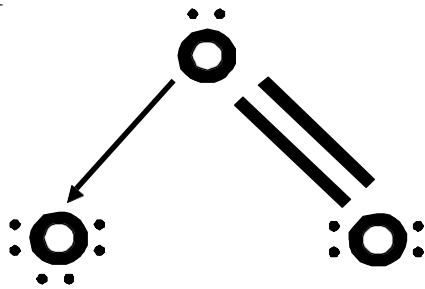


Sulphuric acid

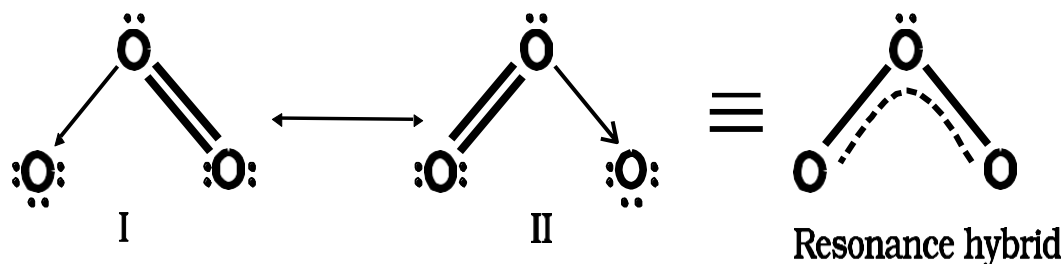
## Resonance as Delocalized Bonding

There are many molecules in which actual arrangement of electrons in the molecule can not be represented by a single Lewis structure.

For example, the following simple Lewis structure can be written for ozone molecule to satisfy the octet rule.

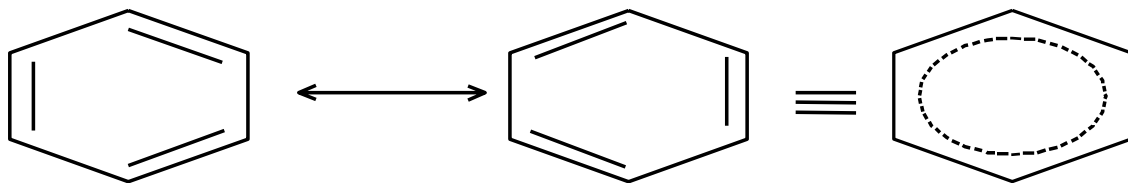
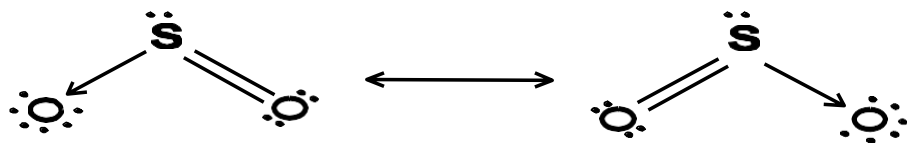
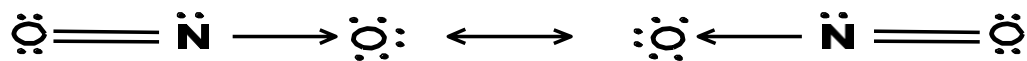
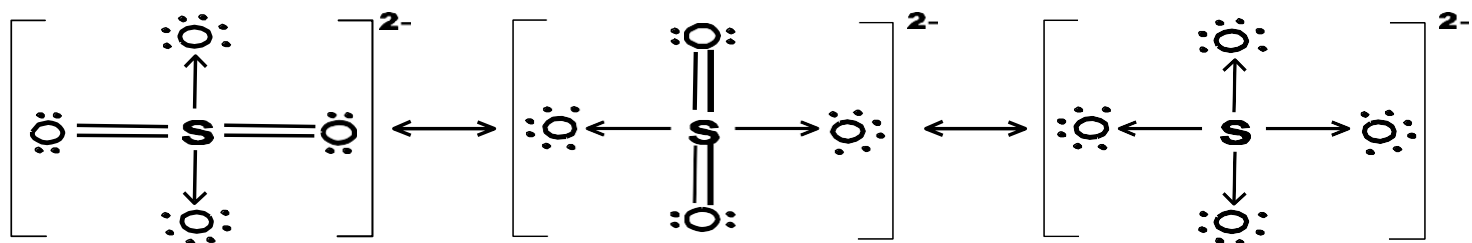
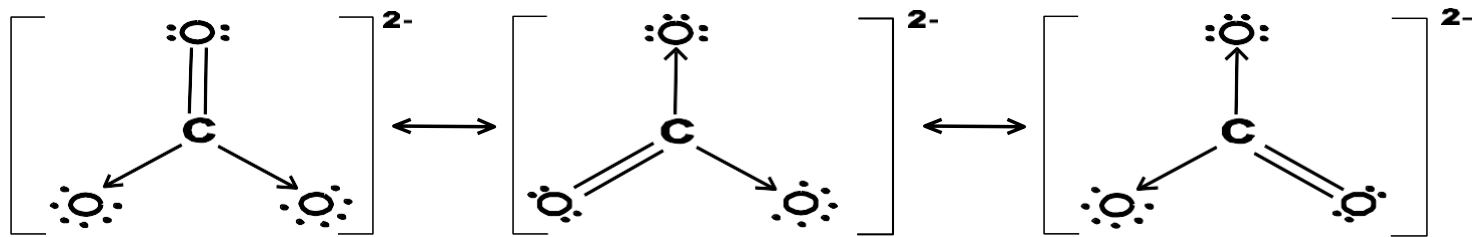


In the above structure, the central oxygen atom is bonded to one oxygen atom by double covalent bond and another oxygen atom by a single co-ordinate covalent bond. The double bonds are shorter than single bonds, hence we would expect the two bond lengths in ozone molecule to be unequal. But actual bond lengths in ozone molecule are found to be equal. To account for this, ozone molecule is considered to be a resonance hybrid of following two structures.



The actual structure of ozone is neither I nor II but is a hybrid of the two. The combination structure is called the resonance hybrid of the contributing structures. The resonance hybrid is more stable than any of the resonating structures. *The term resonance itself means the use of two or more Lewis structures to represent a particular molecule.*

**Resonance structures of some important molecules and ions are given below.**



## **Shapes of molecules**

One simple theory to predict the shapes of molecules is the valence shell (V.S) electron pair (EP) repulsion (R) theory, VSEPR theory, developed by Sidwick and Powel in 1940. Two other modern theories have been also developed One of these is called Valence Bond Theory (VBT) developed by Heitler and London (1927) and later extended by Linus Pauling and Slater (1931). The other is called Molecular Orbital Theory (MOT) developed by Hund and Mulliken.

### **VSEPR Theory**

The shapes of molecules depend upon the number and nature of electron pairs present in the valence shell of the central atom.

The main assumptions of VSEPR theory are:

1. In a covalent molecule there is a central atom to which all other atoms are attached.
2. The valence shell of the central atom contains electrons in pairs which may be lone pairs or bond pairs.

3. The repulsion between electron pairs decreases in the order:  
**lone pairs-lone pairs > lone pairs-bond pairs > bond pairs- bond pairs.**
4. The molecules take the shape that tend to minimize the electrostatic repulsion between electron pairs.

On the basis of VSEPR theory, let us discuss the shapes of simple molecules.

### Shape of BeF<sub>2</sub>

The Lewis electron dot formula for BeF<sub>2</sub> is



The central Be atom has two bond pairs of electrons in its valence shell. Therefore these two bond pairs of electrons stretch at an angle of 180°, and the molecule will have linear shape.



Fig: A linear structure of BeF<sub>2</sub>

## Shape of BF<sub>3</sub>

The Lewis electron dot formula for BF<sub>3</sub> is



The central boron atom has three bond pairs of electrons in its valence shell. To have minimum repulsion among these three electrons pairs the molecule will have a plane triangular geometry with each bond angle equal to 120°.

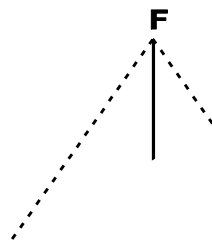
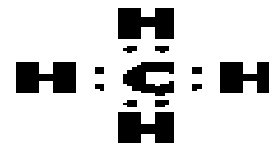


Fig: The trigonal structure of BF<sub>3</sub>

## Shape of CH<sub>4</sub>

The Lewis electron dot formula for methane is



The central carbon atom has four bond pairs of electrons in its valence shell. When these four pairs of electrons are stretched symmetrically in space they form an angle of 109.5° between every two bonds. If the points where hydrogen atoms reside are joined by imaginary lines, it will have a regular tetrahedral geometry which is shown below.

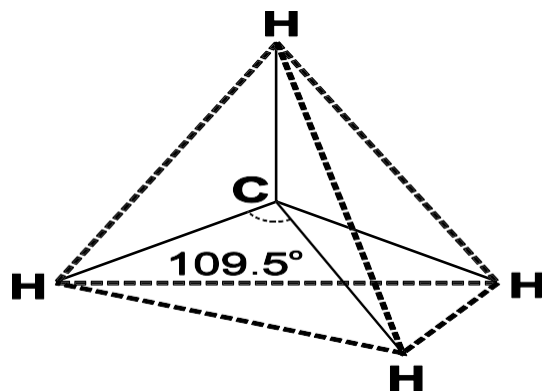
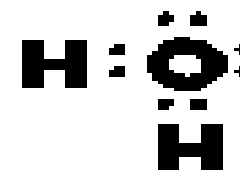


Fig: Tetrahedral structure of methane

## Shape of H<sub>2</sub>O

The electron dot formula of water molecule is given below.



The central oxygen atom of water molecule has four pairs of electrons in its valence shell. Two of them are bond pairs, and the other two are lone pairs. The four pairs of electrons will arrange tetrahedrally, but the repulsion between two lone pairs is stronger than the repulsion between lone pair and bond pair which is in turn stronger than that between two bond pairs. Consequently, the angle between bonds of hydrogen and oxygen reduces from tetrahedral angle of  $109.5^\circ$  to  $104.5^\circ$ . The bond angle in H<sub>2</sub>O molecule is  $104.5^\circ$  and has angular shape as shown below.

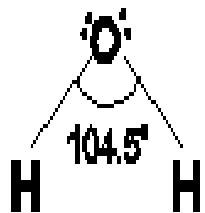
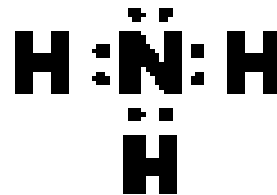


Fig: Angular shape of water molecule.

### Shape of NH<sub>3</sub>

The Lewis electron dot formula for ammonia is



The central nitrogen atom of ammonia molecule has four pairs of electrons in its valence shell. Three are bond pairs and one is lone pair. As a first approximation, these four pairs of electrons should be arranged tetrahedrally to minimize the electrostatic repulsion. The repulsion between lone pair and bond pair is stronger than the mutual repulsion between bond pairs. Hence H-N-H bond angle is squeezed to 107.5° as against the tetrahedral angle 109.5°. It is to be noted that the bond angle in NH<sub>3</sub> is greater than in H<sub>2</sub>O molecule, since NH<sub>3</sub> contains only one lone pair while water has

two lone pairs of electrons.

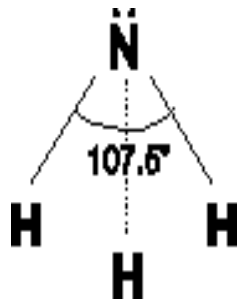


Fig: Pyramidal structure of ammonia.

### Shape of $\text{PF}_5$

The electron dot formula of  $\text{PF}_5$  is given below.

The central phosphorus atom has five bond pairs of electrons in its valence shell. When the electron pairs are stretched out in space so as to have minimum mutual repulsion, three of them are in one plane termed as equatorial plane. The remaining two adjust themselves in opposite directions. The bond angles in the equatorial plane are  $120^\circ$  each while the angle between the equatorial plane and the perpendicular bond is  $90^\circ$ . When the positions of F atoms are joined together by straight lines, we get a space model which is trigonal bipyramid as shown in figure:

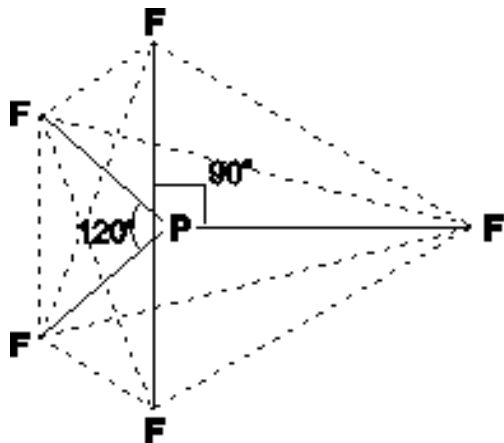


Fig: The trigonal bipyramidal structure of  $\text{PF}_5$ .

### Shape of $\text{SF}_6$

The electron dot formula of  $\text{SF}_6$  is given below.



The central S atom has six pairs of electrons in its valence shell. When these six pairs of electrons are stretched out in space with minimum repulsion between one another, four of them adjust themselves in equatorial plane, and the remaining two adjust themselves perpendicular to the equatorial plane in opposite directions. Each of the bond angles is  $90^\circ$ . When the positions of F atoms are joined by straight lines, we get a space model known as Octahedron. Octahedron contains eight faces each of triangular shape, and has six corners. The geometrical shape of  $\text{SF}_6$  is given below.

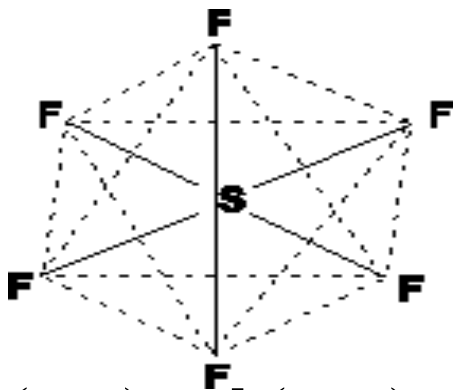


Fig: Octahedral shape of  $\text{SF}_6$ .

Sigma ( ) and ( )

bonds sigma ( )

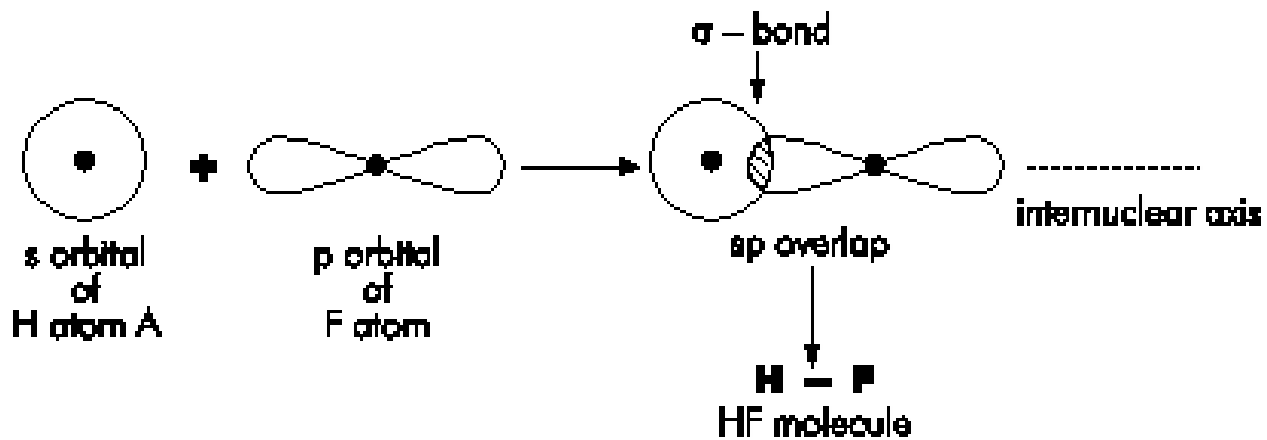
bonds

The  bond is formed by the head-on overlapping of one atomic orbital with another along the internuclear axis. Sigma bonds are formed by the following types of overlapping.

**s-s overlapping:** The overlapping of half filled s-orbital of two atoms always leads to the formation of  -bond. For example, this type of overlapping occurs in the formation of hydrogen molecule

**s-p overlapping:** The overlapping of one s-orbital of one atom with the p orbital of another atom also leads to the formation  -bond. For example this type of overlapping

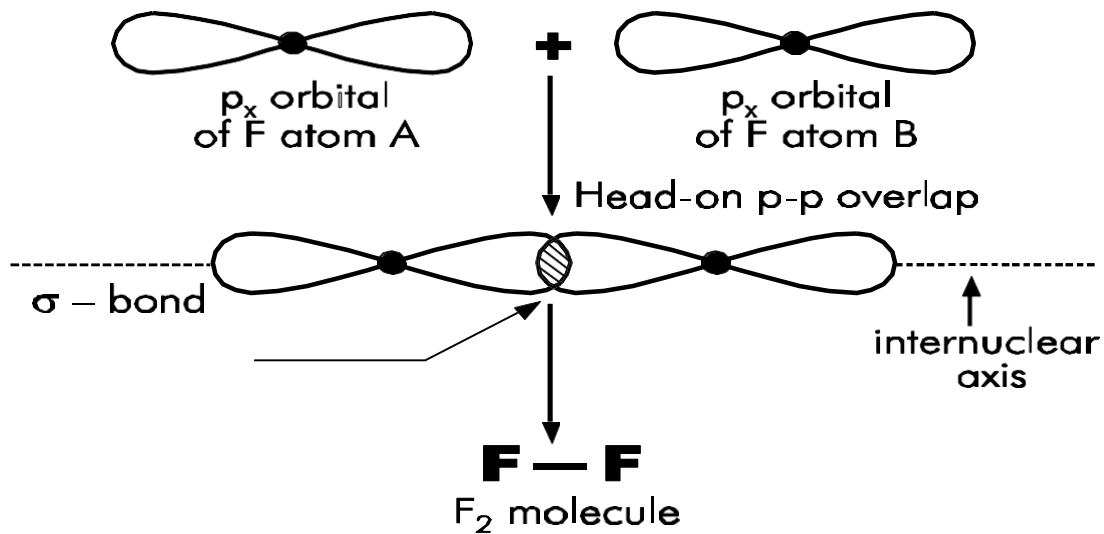
occurs in the formation of hydrogen halides.



## Head-on p-p overlapping

The head-on overlapping of two p orbitals of two atoms also results in the formation of  $\sigma$  -bond. This type of overlapping takes place in the formation of halogen molecules.

( $F_2$ ,  $Cl_2$ ,  $Br_2$ , etc.)

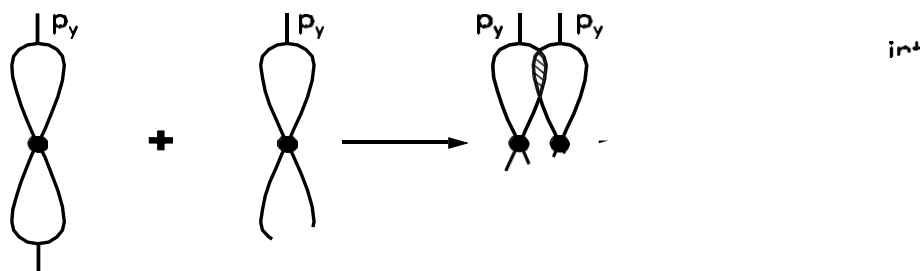


## **Pi ( $\square$ )**

### **bond**

The  $\square$  bond is formed by the lateral overlapping of two p-orbitals. It is evident that here

the overlapping takes place at both the lobes of each of the participating p orbitals of the two atoms, and the overlap is very small. The  $\square$  -bond formed is oriented above and below the inter-nuclear axis.



## **Hybridization involving s and p orbitals**

*Hybridization is the process of mixing of dissimilar atomic orbitals of same atom giving rise to equal number of a new set of orbitals having same energy contents.*

Depending upon the number and the type of orbitals involved, there may be different types of hybridization. s and p orbitals can hybridize in three different ways giving rise to different geometry to hybrid orbitals.

sp hybridization — Linear

$sp^2$  hybridization — Triangular  
 $sp^3$  hybridization — Tetrahedral

**sp – Hybridization:** The mixing of one s-orbital with one p-orbital to give two sp-hybrid orbitals is known as sp hybridization. The sp-hybrid orbitals have linear geometry. This type of hybrid orbitals are involved in the formation of BeF<sub>2</sub> molecule.

**sp<sup>2</sup> – Hybridization:** In sp<sup>2</sup> -hybridization one s-orbital and two p-orbitals mix together to give three sp<sup>2</sup>-hybrid orbitals. The three hybrid orbitals are oriented to the three corners of a triangle having an angle of 120° to one another. sp<sup>2</sup>-hybrid orbitals are involved in the formation of BF<sub>3</sub> molecule, and it has trigonal shape.

**sp<sup>3</sup> – Hybridization:** The mixing of one s-orbital and three p-orbitals to give four sp<sup>3</sup>-hybrid orbitals is known as sp<sup>3</sup> hybridization. The four hybrid orbitals are oriented along the apices of a regular tetrahedron having an angle of 109.5° to one another. In the formation of methane molecule sp<sup>3</sup> hybrid orbitals are involved, and methane molecule has tetrahedral shape.