

## 1. LEWIS OCTET THEORY

Atoms of most elements in nature do not exist in single atomic state rather exist in groups of same or different atoms. **The force that holds the atoms together in a group is called chemical bond.** It was observed that the noble gases generally exist in single atomic state and rarely form groups in nature. We know that the noble gases contain 8 electrons in their valence shell (last shell) except helium which contains only two electrons in its last and only shell. This observation helped the American chemist Gilbert Newton Lewis to propose Octet Theory of bonding.

**Octet Theory states that atoms have tendency to have 8 electrons in their valence shell (tendency to complete octet).** In order to complete their octet, atoms can lose, gain or share electrons among themselves or with other type of atoms.

### 1.1 TYPES OF BONDS

Atom may attain a stable electronic configuration in three different ways by losing electron, by gaining or by sharing electron.

Elements may be divided into following three types as:

1. Electropositive elements: Their atoms give up one or more electron fairly readily.
2. Electronegative elements: Their atoms give up one or more electron fairly readily.
3. Elements which have little tendency to lose or gain electrons.

Three different types of bond may be formed depending on the electropositive or electronegative character of atom involved.

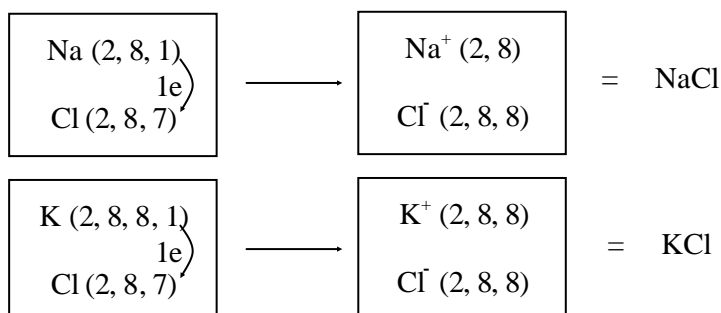
Electropositive element + Electronegative element  $\rightarrow$  Ionic bond

Electronegative element + Electronegative element  $\rightarrow$  Covalent bond

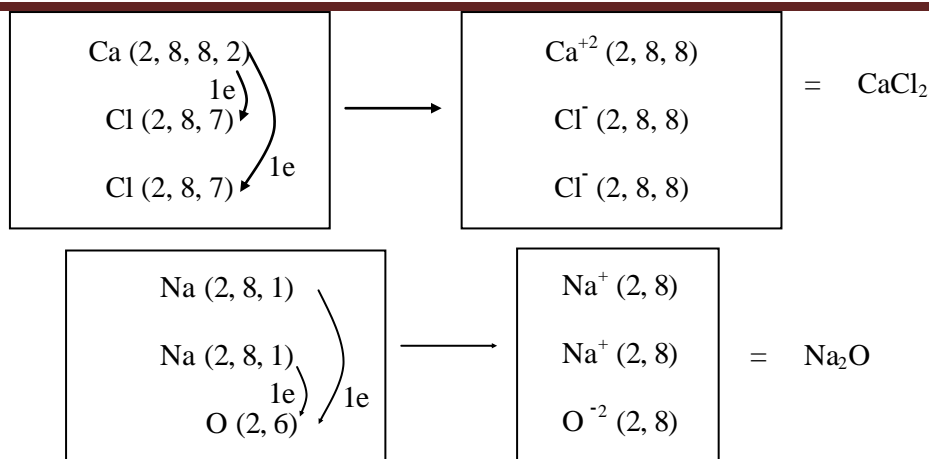
Electropositive element + Electropositive element  $\rightarrow$  Metallic bond

### 1.2 IONIC BOND

The electrostatic force of attraction between oppositely charged ions formed by electron transfer is called ionic bond. An ionic bond is formed between atoms of less ionization potential (on lower left portion of periodic table) and atoms of high electron affinity (on upper right portion of periodic table). During ionic bond formation, some atoms lose electrons after absorbing energy (ionization energy or ionization potential) where as others gain electrons and lose energy (electron affinity). Illustration, given below, suggests how the ionic bond is formed between the atoms of low ionization potential and atoms of high electron affinity (when one type of atom is willing to lose electrons and the other type of atom is willing to gain electrons).



## CHEMICAL BONDING and MOLECULAR STRUCTURE



Above illustrations make it very clear that during ionic bond formation, number of electrons lost by each particular type of atom may and may not be equal to the number of electrons gained by each other type of atom. However, it must be noted that total electrons lost are always equal to total electrons gained during the process.

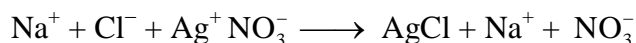
### 1.3 CONDITIONS FOR THE FORMATION OF IONIC BOND

- (i) **High Electronegativity difference:** The difference between the electronegativity of two combining atoms must be greater than two.
- (ii) **Low ionization energy of the metal:** Low ionization energy means that the metal atom requires only a small amount of energy to release its valence electron. For example, sodium, which has a low I.E. readily gives up its loosely held electron and forms  $\text{Na}^+$  ion. Metals of s-block have low ionization energies and so readily form the corresponding cations.
  - ☛ Ionization energy of an element with a single electron in its valence shell is less than that with two electrons. In going across a period of the periodic table from left to right, I.E. increases and the formation of the cation is less likely. On going down a group, the outermost electron gets further away from the nucleus, and hence is more easily removed i.e., I.E. decreases; the formation of the cation becomes more likely.
- (iii) **High electron affinity of the non-metal:** An atom with a high electron affinity releases a lot of energy when it takes up an electron and forms an anion. For example, chlorine which has a high electron affinity, readily takes up an electron from the Na atom and forms  $\text{Cl}^-$  ion. Non-metals of groups VI A and VII A have high electron affinity and can form ionic bonds.
  - ☛ In going across a period from left to right, electron affinity (energy released) increases and so the formation of the negative ion becomes more likely. On going down a group, electron affinity decreases and so the formation of anion becomes less likely.
- (iv) **High Lattice Energy of the crystal:** In the formation of sodium chloride crystal, the  $\text{Na}^+$  ion attracts the  $\text{Cl}^-$  ion to form an ion-pair  $\text{Na}^+\text{Cl}^-$ . Since the electrostatic force of attraction is present in all directions, this ion-pair will attract other ion-pairs and build up into a crystal lattice. A crystal lattice is three dimensional basic pattern of points, in which each point corresponds to a unit of the crystal, say an ion (atom or molecule). As the lattice builds up, energy is released. The energy released when sufficient number of cations and anions come together to form 1 mole of the compound is called the lattice energy of the compound.

Therefore, an ionic compound is formed when the energy released in (iii) and (iv) exceeds the energy absorbed in (ii).

### 1.4 GENERAL CHARACTERISTICS OF IONIC COMPOUNDS

- (i) Generally ionic compounds are hard solids. As single ions of a metal are not associated in the solid with single ions of a non-metal, separate units of ionic compounds do not exist. It is, therefore, wrong to talk of a molecule of an ionic compound. The formula only indicates the ratio of number of ions and the crystal consists of a very large number of oppositely charged ions. Thus in NaCl crystal each  $\text{Na}^+$  ion is surrounded by  $6\text{Cl}^-$  ions and vice versa (in an octahedral arrangement). The attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions is quite large.
- (ii) As a good deal of thermal energy is required to overcome the large electrostatic forces of attraction in an ionic crystal, ionic compounds have high melting and boiling points.
- (iii) Ionic compounds are commonly soluble in water and other polar solvents (which separate the ions). They are practically insoluble in organic solvents such as benzene, carbon tetrachloride, etc., as there is no attraction between ions and the molecules of the non-polar liquids.
- (iv) Ionic compounds are electrolytes. In the presence of an ionizing solvent such as water, the electrostatic forces between the ions are so greatly reduced that the ions get separated. (This is due to the electrostatic attraction between the ions and the polar molecules of the solvent.) The free ions in solution conduct electricity and on passing a current, the ionic compound undergoes chemical decomposition (called electrolysis). When an ionic compound is melted, the crystal lattice structure is broken and free ions are produced. It is the free movement of ions, which makes an ionic compound a conductor and to undergo electrolysis in the molten condition.
- (v) When an ionic compound dissolves in water, the ions get solvated (in this case hydrated). The energy released is called solvation energy. This energy counters wholly or in part the high lattice energy of the ionic compound. Insoluble ionic compounds (eg., sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and the solvation energy of the constituent ions is insufficient to counteract the high lattice energies and make them soluble.
- (vi) The chemical properties of an ionic compound are the properties of its constituent ions. Thus all chlorides give the characteristic reactions of the chloride ion (reactions with conc.  $\text{H}_2\text{SO}_4$ ,  $\text{AgNO}_3$  solution, etc). All acids, which contain  $\text{H}^+$  ions give the same reactions (change blue litmus to red, effervesce with a carbonate, etc).
- (vii) Reactions between solutions of ionic compounds are almost instantaneous, because they are reactions between ions (and do not involve the breaking up of bonds as in covalent compounds, q.v.). For example, when silver nitrate solution is added to sodium chloride solution, silver chloride is immediately precipitated. The reaction may be represented thus:



## 1.5 COVALENT BOND

A covalent bond is formed by *the sharing of a pair of electrons between two atoms, each atom contributing one electron to the shared pair*. The shared pair of electrons should have opposite spins and they are localized between the two nuclei concerned. A covalent bond is usually represented by a short line between the two atoms. Note that the covalent bond consists of a pair of electrons shared between two atoms, and occupying a combination of two stable orbitals, one of each atom; the shared electrons of each covalent bond are counted for each of the two atoms connected by the covalent bond. The difference between the electronegativity of the combining atoms is less than two.

### (i) Formation of the hydrogen molecule

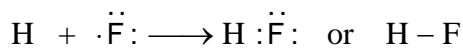
Each hydrogen atom requires 1 electron to become isoelectronic with helium, the nearest inert gas. The hydrogen atoms share their electrons thus:



Once the covalent bond is formed the two bonding electrons are attracted by the two nuclei (instead of one) and the bonded state is more stable than the non-bonded state. The resultant attraction is responsible for the strength of the covalent bond.

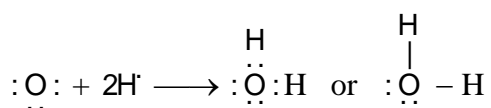
### (ii) Formation of hydrogen fluoride

The hydrogen atom has in its orbital 1 electron. It can achieve the helium configuration by forming a single covalent bond with another atom. Fluorine has 7 electrons in its outer, i.e., L shell. F can acquire the Neon configuration by forming a single covalent bond using its unpaired electron. This may be represented as follows.



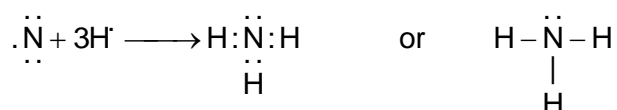
The single covalent bond holds the H and F atoms firmly together. Similarly we can explain the formation of HCl, HBr and HI.

### (iii) Formation of water, H<sub>2</sub>O



Similarly we can explain the formation of H<sub>2</sub>S (hydrogen sulphide), H<sub>2</sub>Se (hydrogen selenide) and H<sub>2</sub>Te (hydrogen telluride).

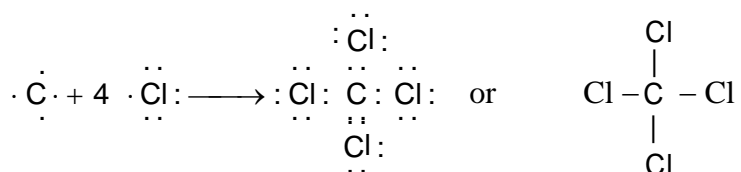
### (iv) Formation of ammonia, NH<sub>3</sub>



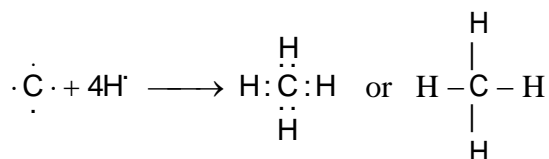
The structures of phosphine (PH<sub>3</sub>), arsine (AsH<sub>3</sub>) and stibine (SbH<sub>3</sub>) are similar to that of ammonia.

## CHEMICAL BONDING and MOLECULAR STRUCTURE

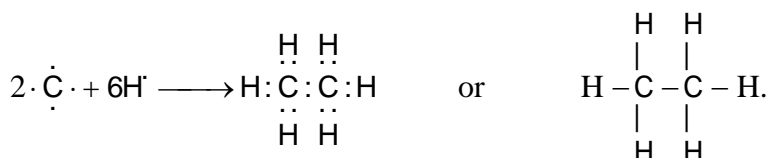
### (v) Formation of carbon tetrachloride, $\text{CCl}_4$



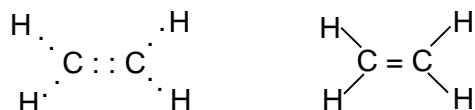
### (vi) Formation of methane, $\text{CH}_4$



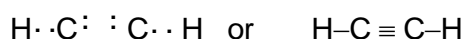
### (vii) Formation of ethane, $\text{C}_2\text{H}_6$



- ☛ (a) The number of electrons needed by an atom to acquire its octet (C-4, N-3, O-2, Cl-1) is equal to the number of covalent bonds commonly formed.
- (b) When two pairs of electrons are shared between two atoms, there is a double bond (represented by double line) as in ethylene,  $\text{C}_2\text{H}_4$ .



- (c) When three pairs of electrons are shared between two atoms, there is a triple bond (represented by triple line) as in acetylene,  $\text{C}_2\text{H}_2$ .



- (d) Generally all atoms involved in covalent bonding have completed octets (except hydrogen, which has a duplet of electrons). Sometimes an atom forms more than 4 covalent bonds.

## 1.6 EXCEPTIONS TO OCTET RULE (LEWIS THEORY)

Lewis theory can explain bonding in most of the covalent compound but some covalent compounds do not obey octet rule as illustrated with the help of following examples:

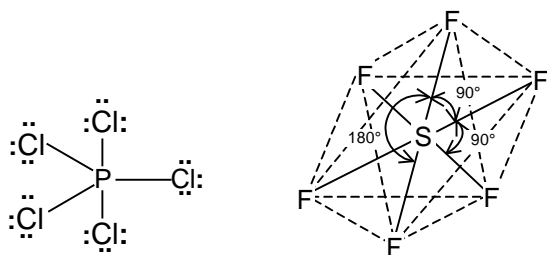
(a) **Electron Deficient Compounds:** Octet of many atoms is not completed even after sharing of electrons. E.g.  $\text{BeCl}_2$ ,  $\text{BH}_3$ ,  $\text{BCl}_3$ ,  $\text{AlCl}_3$  etc.



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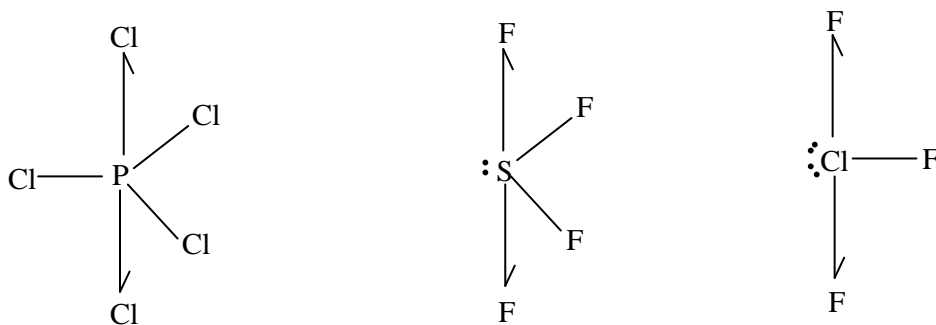
## (b) Formation of bonds even after completion of octet:

Many elements form covalent bonds more than required to complete octet. For example Phosphorus (2, 8, 5) should share only three electrons, Sulphur (2, 8, 6) should share only two electrons, Chlorine (2, 8, 7) should share only one electron but we know that  $\text{PCl}_5$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ ,  $\text{ClF}_3$  etc. also exist in nature.



## 1.7 SUGDEN'S CONCEPT OF SINGLET LINKAGE:

According to Sugden, maximum number of electrons in the outermost shell of any atom can not exceed eight. But an atom can form bonds with other atoms using single electrons also if available. He represented such bonds by a half arrow ( $\rightarrow$ ) with the head pointing from donor atom towards the acceptor atom. He further claimed that the strength of such bonds will be lesser than normal bonds and such bonds will be longer than normal covalent bonds as shown below:



However, later it was found that the strength of such bonds are not different from normal bonds in many cases like  $\text{SF}_6$  etc.

## Sidgwick's concept of maximum covalency:

Sidgwick, later, suggested that the covalency of an element may exceed four and maximum number of electrons in the outer most shell may also exceed eight depending on the period of the periodic table to which the element belongs. According to Sidgwick, maximum number of electrons in the outermost shell of an element can be 4 ( $\text{I}^{\text{st}}$  period), 8 ( $\text{II}^{\text{nd}}$  period), 12 ( $\text{III}^{\text{rd}}$  and  $\text{IV}^{\text{th}}$  period) and 16 ( $5^{\text{th}}$ ,  $6^{\text{th}}$  and  $7^{\text{th}}$  period).

This concept can explain existence of  $\text{PCl}_5$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ ,  $\text{XeF}_6$  and also non existence of  $\text{NCl}_5$ ,  $\text{OF}_4$ ,  $\text{OF}_6$  etc.

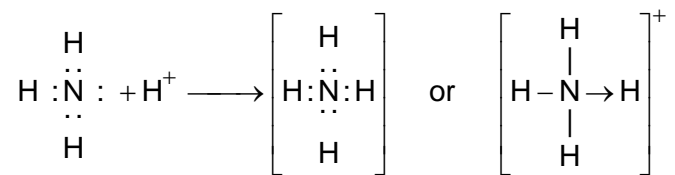
## 1.8 Co-ordinate Covalent Bond:

We have seen that in the formation of a covalent bond between two atoms, each atom contributes one electron to the shared pair. Sometimes **both the electrons of the shared pair may come from one of the atoms. The covalent bond thus formed is a co-ordinate bond or dative bond.**

## CHEMICAL BONDING and MOLECULAR STRUCTURE

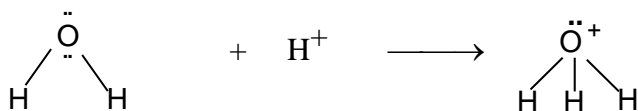
### (i) Formation of ammonium ion

The ammonia molecule has a lone pair of electrons i.e., an unshared pair. The hydrogen ion  $H^+$ , has an empty s orbital. The lone pair comes to be shared between the nitrogen and hydrogen atoms:

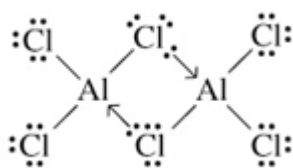


Nitrogen atom is called the donor and  $H^+$ , the acceptor. The arrow-head in  $\text{N} \longrightarrow \text{H}$  shows the acceptor.  $\text{NH}_3$  is a neutral molecule.  $H^+$  carries a unit positive charge; so  $\text{NH}_4^+$  ion carries a unit positive charge. Once the  $\text{NH}_4^+$  ion is formed, all the N–H bonds are identical.

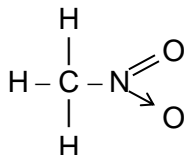
### (ii) Hydronium ion, $\text{H}_3\text{O}^+$



### (iii) Aluminium chloride, $\text{Al}_2\text{Cl}_6$



### (iv) Nitromethane, $\text{CH}_3\text{NO}_2$



## 1.9 CHARACTERISTICS OF COORDINATE COVALENT COMPOUNDS

As is to be expected the properties of coordinate covalent compounds are mostly similar to the properties of covalent compounds.

- (i) The nuclei in coordinate covalent compounds (such as in  $\text{NH}_4^+$ ) are held firmly by shared electrons and so do not form ions in water.
- (ii) Their covalent nature makes them sparingly soluble in water and more soluble in organic solvents.
- (iii) The coordinate bond is also rigid and directional, just like covalent bonds.

## 2. MOLECULAR GEOMETRY AND VSEPR THEORY

Molecular geometry is the three-dimensional arrangement of atoms in a molecule. A molecule's geometry affects its physical and chemical properties such as melting point, boiling point and the types of reactions it undergoes. In general, bond length and bond angles are determined by experiments. However, there is a simple procedure to predict the overall geometry of a molecule or ion with considerable accuracy, if we know the number of electrons surrounding a central atom in its Lewis structure. The basis of this approach is the assumption that electron pairs in the valence shell (outermost electron-occupied shell of an atom) of an atom repel one another. In a polyatomic species, the repulsion between electrons in different bonding pairs causes them to remain as far as possible. Thus, the geometry assumed by the species ultimately minimizes the repulsion. This approach is called valence-shell electron-pair repulsion (VSEPR) theory because it accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs.

Molecules in this theory are divided into two categories, depending on whether the central atom has lone pair of electrons or not.

### 2.1 Molecules in which the central atom has no lone pairs.

For simplicity, we will consider molecules that contain only two types of atoms, A and B, of which A is the central atom. These molecules have the general formula  $AB_x$ , where  $x$  is an integer 2, 3 .....(if  $x = 1$ , the molecule will be diatomic, which is linear by definition).

#### (a) Molecules having general formula $AB_2$

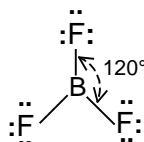
$BeCl_2$  is representing the general formula  $AB_2$ . The Lewis structure of beryllium chloride in the gaseous state is

$$\begin{array}{c} :\ddot{Cl}-Be-\ddot{Cl}: \\ \quad \quad \quad \nwarrow \quad \nearrow \\ \quad \quad \quad 180^\circ \end{array}$$

Since the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus,  $ClBeCl$  bond angle is predicted to be  $180^\circ$  and the molecule is *linear*.

#### (b) Molecules having general formula $AB_3$

The general formula  $AB_3$  is represented by the molecule  $BF_3$ .  $BF_3$  has three bonding pairs, which points to the corners of an equilateral triangle with boron at the center of the triangle.



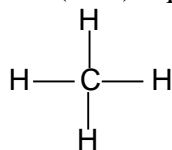
This geometry of  $BF_3$  is referred as *trigonal planar* with  $FBF$  bond angle to be  $120^\circ$ . In this structure, all four atoms lie in the same plane,



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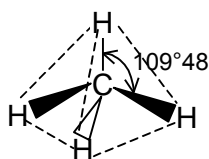
### (c) Molecules having general formula $AB_4$

Methane ( $CH_4$ ) represents the best example of this class of molecules. The Lewis structure of  $CH_4$  is



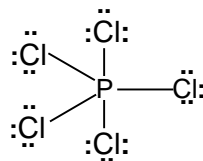
The four bonding pairs in  $CH_4$  can be arranged to form a tetrahedron, so as to minimize the repulsion between them. A tetrahedron has four faces, all of which are equilateral triangles.

In a **tetrahedral** molecule, the central atom (carbon) is located at the center of the tetrahedron and the other four atoms (H) are at the corners. The HCH bond angles are all  $109^\circ 48'$ .



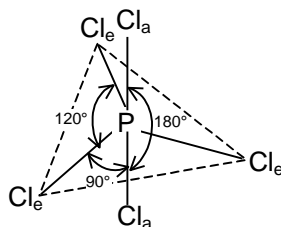
### (d) Molecules with general formula $AB_5$

The general formula  $AB_5$  is represented by the molecule  $PCl_5$ . The Lewis structure of  $PCl_5$  (in gas phase) is



The only way to minimize the repulsive forces among the five bonding pairs is to arrange the P–Cl bonds in the form of a **trigonal bipyramid**. Joining two tetrahedrons along a common triangular base can generate a trigonal bipyramid.

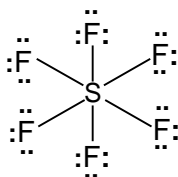
The central atom (P) is at the center of the common triangular with the surrounding atoms positioned at the five corners of the trigonal bipyramid. The atoms that are above and below the triangular plane are said to occupy axial positions and those, which are in the triangular plane, are said to occupy equatorial positions. The angle between any two equatorial bonds is  $120^\circ$ , that between an axial bond and an equatorial bond is  $90^\circ$  and that between two axial bonds is  $180^\circ$ .



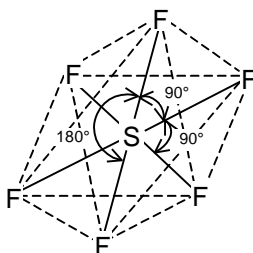
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### (e) Molecules having general formula $AB_6$

The molecule  $SF_6$  exhibits the general formula  $AB_6$ . The Lewis structure of  $SF_6$  is



The most stable arrangement of the six S–F bonding pairs is in the shape of an **octahedron**. An octahedron has eight faces and can be generated by joining two square pyramids on a common base. The central atom (S) is at the center of the square base and the surrounding atoms (F) are at the six corners. All bond angles are  $90^\circ$  except the one made by the bonds between the central atom and the pairs of atoms that are diametrically opposite each other, which is  $180^\circ$ . Since, all the bonds are equivalent in an octahedral molecule, the terms axial and equatorial are not used here.



## 2.2 MOLECULES IN WHICH CENTRAL ATOM HAS LONE PAIRS

In such molecules, there are three types of repulsive interactions—between bonding pairs, between lone pairs and between a bonding pair and a lone pair. In general, according to VSEPR theory, the repulsive forces decrease in the following order: lone pair–lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion.

Bond pair electrons are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less “spatial distribution” than lone pairs i.e., they take up less space than lone pair electrons, which are associated with only one nuclei (or one atom). Because lone–pair electrons in a molecule occupy more space, they experience greater repulsion from neighbouring lone pairs and bonding pairs.

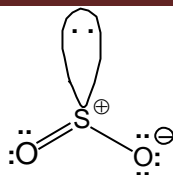
To keep track of total number of bonding pairs and lone pairs, we designate molecules with lone pairs as  $AB_xE_y$ , where A is the central atom, B is the surrounding atoms and E is a lone pair on A. Both  $x$  and  $y$  are integers,  $x = 2, 3, \dots$  and  $y = 1, 2, \dots$ . Thus,  $x$  and  $y$  denote the number of surrounding atoms and number of lone pairs on the central atom, respectively.

### (a) Molecules with general formula $AB_2E$

Example of this type is  $SO_2$ . The Lewis structure of  $SO_2$  is  $\ddot{O}=\overset{+}{S}=\ddot{O}^-$

VSEPR theory treats double bond and triple bonds as though they were single bonds. Thus,  $SO_2$  molecule can be viewed as having three electron pairs on the central atoms, of which, two are bonding pairs and one is a lone pair. The overall arrangement of three electron pairs is trigonal planar. But since one of the electron pair is a lone pair, the  $SO_2$  molecule looks like

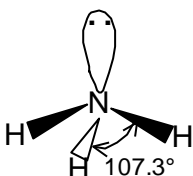
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This shape is referred to as ***bent or angular***. The shape is determined only by the bonding pairs and not by lone pairs. Since lone pair repels the bonding pairs more strongly, the SO bonds are pushed together slightly and the OSO angle is less than  $120^\circ$ .

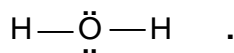
### (b) Molecules having general formula $AB_3E$

The general formula  $AB_3E$  is exhibited by the molecule  $NH_3$ . Ammonia has overall four electron pairs, of which three are bonding pairs and one is lone pair. The overall arrangement of four electron pairs is tetrahedral but since one of the electron pairs is a lone pair, so the shape of  $NH_3$  is ***trigonal pyramidal***. Because the lone pair repels the bonding pairs more strongly, the three N–H bonds are pushed closer together. Thus the HNH bond angle is smaller than the ideal tetrahedral angle of  $109^\circ 48'$ .

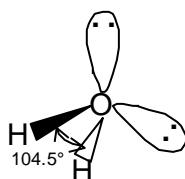


### (c) Molecules with general formula $AB_2E_2$

Example of such a molecule is  $H_2O$ . A water molecule has 2 bonding pairs and two lone pairs

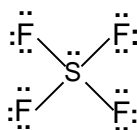


The overall arrangement of the four electron pairs in water is tetrahedral. However, unlike  $NH_3$ ,  $H_2O$  has 2 lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each other and  $H_2O$  shows even greater deviation from tetrahedral angle than in  $NH_3$ . The shape of  $H_2O$  is referred to as ***bent or angular*** with HOH bond angle of  $104.5^\circ$ .



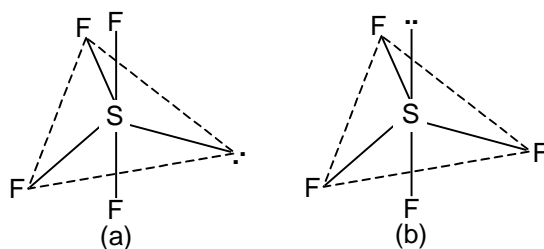
### (d) Molecules having general formula $AB_4E$

Example to this class of molecule is  $SF_4$ . The Lewis structure of  $SF_4$  is



The S atom in  $SF_4$  has 5 electron pairs, which can be arranged as trigonal bipyramidal. In  $SF_4$ , since one of the electron pair is a lone pair, so the molecule can have any one of the following geometries:

## CHEMICAL BONDING and MOLECULAR STRUCTURE

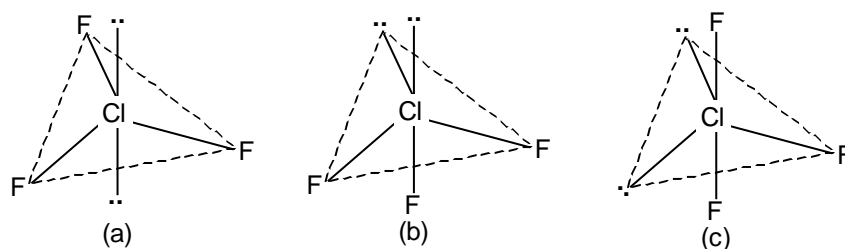


In (a), the lone pair occupies an equatorial position and in (b), it occupies an axial position. Repulsion between the electron pairs in bonds only  $90^\circ$  apart are greater than repulsion between electron pairs in bonds  $120^\circ$  apart. Each axial bond has three electron pairs  $90^\circ$  away while each equatorial bond has only two electron pairs  $90^\circ$  away. Thus axial bonds (electron pairs) experience greater repulsion than the equatorial bonds. Thus, atoms at the equatorial positions are closer to the central atom than atoms at the axial positions i.e. equatorial bond lengths are smaller than axial bond lengths. Thus, when the central atom also has lone pairs along with the bonding pairs, it will occupy a position where the repulsions are less, so lone pairs in trigonal bipyramidal are more comfortable at equatorial positions. Thus, (a) is the appropriate structure of  $\text{SF}_4$ . It is referred as **see-saw shaped or irregular tetrahedron**.

### (e) Molecules with general formula $\text{AB}_3\text{E}_2$

Example of this type is  $\text{ClF}_3$ . The Lewis structure of  $\text{ClF}_3$  is

The Cl atom in  $\text{ClF}_3$  has 5 electron pairs, of which 2 are lone pairs and 3 are bonding pairs. The molecule can have any of the following three geometries:



In structure (a), there are 6 lone pair–bond pair repulsions at  $90^\circ$  and one lone pair–lone pair repulsion at  $180^\circ$ . In structure (b), 1 lone pair – lone pair repulsion is at  $90^\circ$  and there are 3 lone pair–bond pair repulsions at  $90^\circ$ , 2 at  $120^\circ$  and 1 at  $180^\circ$ . While in structure (c), there are 4 lone pair–bond pair repulsions at  $90^\circ$ , 2 at  $120^\circ$  and one lone pair–lone pair repulsion at  $120^\circ$ . The structure (b) is out rightly ruled out since the lone pair–lone pair repulsion is of highest magnitude. Among structures (a) and (c), each structure has 4 lone pair–bond pair repulsions at  $90^\circ$ . Apart from these repulsions, (a) has 1 lone pair–lone pair repulsion at  $180^\circ$  and 2 lone pair–bond pair repulsions at  $90^\circ$  while (c) has 1 lone pair–lone pair repulsion at  $120^\circ$  & 2 lone pair–bond pair repulsions also at  $120^\circ$ . So, the structure (c) has overall lesser repulsions than (a). Thus, (c) is the appropriate structure of  $\text{ClF}_3$ . It is called **T-shaped** structure.

## CHEMICAL BONDING and MOLECULAR STRUCTURE

### 2.3 PREDICTING GEOMETRY OF SPECIES USING VSEPR THEORY

With the help of VSEPR theory, we can predict the geometry of various species in a systematic way. The scheme makes use of the following steps:

- (i) Identify the central atom and count the number of valence electrons on the central atom.
- (ii) Add to this, the number of other atoms (which form single bonds only). Here, oxygen atoms are not added as they form two bonds.
- (iii) If the species is an anion, add negative charges and if it is a cation, subtract positive charges.
- (iv) This gives us a number, which we refer as N.
- (v) Divide N by 2 and we get the sum of bonding and non-bonding electron pairs.  

$$\frac{N}{2} = \text{Number of other atoms} + \text{number of lone pairs.}$$
- (vi) Compare the result  $\left(\frac{N}{2} \text{ value}\right)$  with the value given in table, corresponding to the given number of lone pairs.

N/2 value	Geometry	Lone pairs	Shape of the species	Example
2	Linear	0	Linear	HgCl <sub>2</sub> , BeCl <sub>2</sub>
3	Trigonal planar	0	Trigonal planar	BF <sub>3</sub> , AlCl <sub>3</sub> , BH <sub>3</sub> , NO <sub>3</sub> <sup>-</sup> , SO <sub>3</sub>
		1	Angular or bent	SnCl <sub>2</sub> , SO <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>
4	Tetrahedral	0	Tetrahedral	CCl <sub>4</sub> , BeF <sub>4</sub> <sup>2-</sup> , BF <sub>4</sub> <sup>-</sup> , PCl <sub>4</sub> <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup>
		1	Trigonal pyramidal	NH <sub>3</sub> , PCl <sub>3</sub> , PF <sub>3</sub> , ClO <sub>3</sub> <sup>-</sup>
		2	Angular or bent	H <sub>2</sub> O, H <sub>2</sub> S, OF <sub>2</sub> , ClO <sub>2</sub> <sup>-</sup>
		3	Linear	ClO <sup>-</sup>
5	Trigonal bipyramidal	0	Trigonal bipyramidal	PCl <sub>5</sub> , PF <sub>5</sub>
		1	See-saw or irregular tetrahedron	SF <sub>4</sub> , IF <sub>4</sub> <sup>+</sup>
		2	T-shaped	ClF <sub>3</sub> , BrF <sub>3</sub>
		3	Linear	I <sub>3</sub> <sup>-</sup> , Br <sub>3</sub> <sup>-</sup> , XeF <sub>2</sub>
6	Octahedral	0	Octahedral or square bipyramidal	SF <sub>6</sub> , PCl <sub>6</sub> <sup>-</sup>
		1	Square pyramidal	BrF <sub>5</sub> , IF <sub>5</sub>
		2	Square planar	ICl <sub>4</sub> <sup>-</sup> , XeF <sub>4</sub> <sup>-</sup> , IF <sub>4</sub>
7	Pentagonal bipyramidal	0	Pentagonal bipyramidal	IF <sub>7</sub>
		1	Capped octahedron.	XeF <sub>6</sub>

## CHEMICAL BONDING and MOLECULAR STRUCTURE

Let us see the usefulness of the VSEPR theory to predict the geometry of few molecules/ ions.

### (i) $\text{BeCl}_2$ molecule:

The central atom is Be and it has two other Cl atoms.

$$\therefore \frac{N}{2} = \frac{2+2}{2} = 2$$



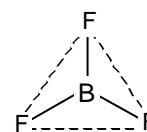
Since, the number of other atoms is 2, so the number of lone pairs is zero. Thus, shape of  $\text{BeCl}_2$  is **linear**.

### (ii) $\text{BF}_3$ molecule:

In  $\text{BF}_3$ , central atom is boron and it has three other atoms.

$$\therefore \frac{N}{2} = \frac{3+3}{2} = 3$$

Since, the number of other atoms is three, so the number of lone pairs is zero. Therefore, shape is **triangular planar**.

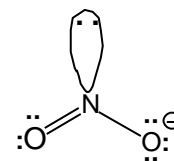


### (iii) $\text{NO}_2^-$ ion:

The central atom in  $\text{NO}_2^-$  is N and it has two other atoms.

$$\therefore \frac{N}{2} = \frac{5+1}{2} = 3$$

Since, the number of other atoms is 2, so the number of lone pairs would be 1. Thus, shape of  $\text{NO}_2^-$  ion is **angular or bent**.

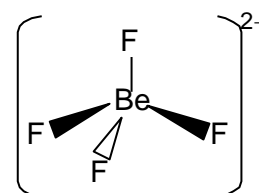


### (iv) $[\text{BeF}_4]^{2-}$ ion:

In  $\text{BeF}_4^{2-}$ , the central atom is Be and it has four other F atoms.

$$\therefore \frac{N}{2} = \frac{2+4+2}{2} = 4$$

The number of lone pairs is zero, as the number of other atoms is 4. Therefore, shape of  $\text{BeF}_4^{2-}$  is **tetrahedral**.

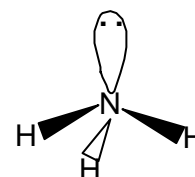


### (v) $\text{NH}_3$ molecule:

In  $\text{NH}_3$ , the central atom is N and it has 3 other H atoms.

$$\therefore \frac{N}{2} = \frac{5+3}{4} = 4$$

Since, the number of other atoms is 3, so the number of lone pairs would be 1. Therefore, shape of  $\text{NH}_3$  molecule is **trigonal pyramidal**.



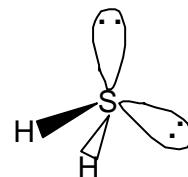
## CHEMICAL BONDING and MOLECULAR STRUCTURE

### (v) $\text{H}_2\text{S}$ molecule:

The central atom is S and there are 2 other H atoms in  $\text{H}_2\text{S}$  molecule.

$$\therefore \frac{N}{2} = \frac{6+2}{2} = 4$$

Since, the number of other atoms is 2, so the number of lone pairs would be 2. Thus, the shape of  $\text{H}_2\text{S}$  is **angular or bent**.

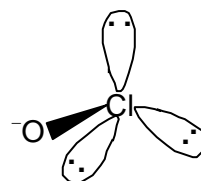


### (vi) $\text{ClO}^-$ ion:

The central atom is Cl and it has one other atom.

$$\therefore \frac{N}{2} = \frac{7+1}{2} = 4$$

The number of lone pairs would be 3 as the other atom is only one. Thus, the shape of  $\text{ClO}^-$  is **linear**.

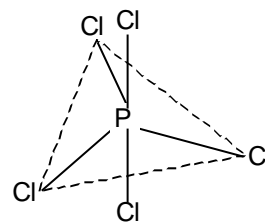


### (viii) $\text{PCl}_5$ molecule:

The central atom in  $\text{PCl}_5$  is P and it has 5 other Cl atoms.

$$\therefore \frac{N}{2} = \frac{5+5}{2} = 5$$

The number of lone pairs would be zero, as the number of other atoms is 5. Thus, the shape of  $\text{PCl}_5$  is **trigonal bipyramidal**.

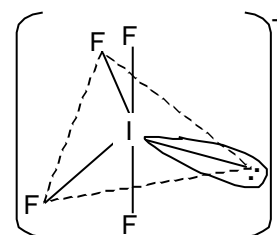


### (ix) $[\text{IF}_4]^+$ ion:

The central atom in  $\text{IF}_4^-$  ion is I and it has 4 other F atoms.

$$\therefore \frac{N}{2} = \frac{7+4-1}{2} = 5$$

Since, the number of other atoms is 4, so the number of lone pairs would be 1. Thus, the shape of  $\text{IF}_4^+$  ion is **see-saw shaped or distorted tetrahedral**.

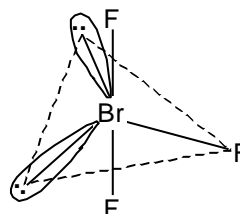


### (x) $\text{BrF}_3$ molecule:

In  $\text{BrF}_3$  molecule, the central atom is Br and it has 3 other F atoms.

$$\therefore \frac{N}{2} = \frac{7+3}{2} = 5$$

Since, the number of other atoms is 3, so the number of lone pairs is 2. Therefore, the shape of  $\text{BrF}_3$  is **T-shaped**.



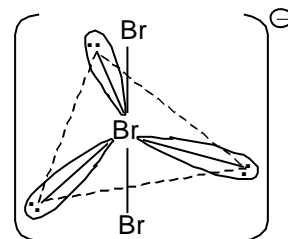
## CHEMICAL BONDING and MOLECULAR STRUCTURE

### (xi) $[\text{Br}_3]^-$ ion:

The central atom is a Br atom and it has 2 other Br atoms as surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+2+1}{2} = 5$$

Since, the number of other atoms is 2, so the number of lone pairs is 3. Thus, the shape of  $\text{BrO}_3^-$  ion is **linear**.

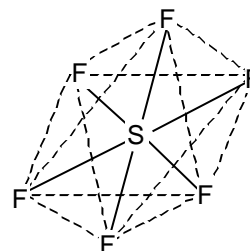


### (xii) $\text{SF}_6$ molecule:

The central atom in  $\text{SF}_6$  is S and it has 6 other F atoms as surrounding atoms.

$$\therefore \frac{N}{2} = \frac{6+6}{2} = 6$$

Since, the number of other atoms is 6, so the number of lone pairs is zero. Thus, the shape of  $\text{SF}_6$  molecule is **octahedron or square bipyramidal**.

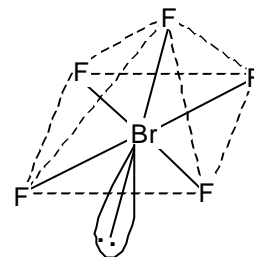


### (xiii) $\text{BrF}_5$ molecule:

In  $\text{BrF}_5$ , the central atom is Br and 5 F atoms are the surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+5}{2} = 6$$

Since, the number of other atoms is 5, so the number of lone pairs would be 1. Therefore, the shape of  $\text{BrF}_5$  is **square pyramidal**.

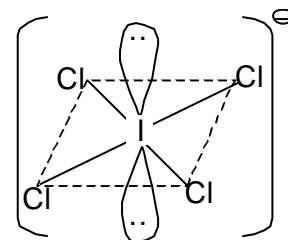


### (xiv) $[\text{ICl}_4]^-$ ion:

In  $\text{ICl}_4^-$  ion, the central atom is I and 4 Cl atoms are the surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+4+1}{2} = 6$$

The number of lone pairs would be 2 as the number of other atoms is 4. So, the shape of  $\text{ICl}_4^-$  ion is **square planar**.

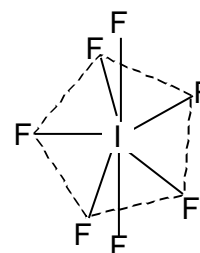


### (xv) $\text{IF}_7$ molecule:

In  $\text{IF}_7$  molecule, the central atom is I and 6 F atoms are the surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+7}{2} = 7$$

Since, the number of other atoms is 7, so the number of lone pairs would be zero. Thus, the shape of  $\text{IF}_7$  molecule is **pentagonal bipyramidal**.





### 3. POLARIZATION of COVALENT BONDS

The shared pair of electrons may be shared equally between two atoms; then the covalent bond is said to be non-polar. Equal sharing occurs between identical atoms, as in  $\text{H} - \text{H}$  or  $\text{Cl} - \text{Cl}$  (i.e., in homonuclear molecules) or between identical atoms with identical neighbours as in  $\text{H}_3\text{C}-\text{CH}_3$ . When the two bonded atoms are dissimilar (i.e., in heteronuclear molecules) the sharing is unequal. For example a chlorine atom has a greater electron attracting power than a hydrogen atom; so in  $\text{H} - \text{Cl}$ , the shared pair of electrons are drawn more towards chlorine and away from hydrogen. The result is separation of charges within the molecule, the chlorine end acquiring a slight negative charge and the hydrogen end a slight but equal positive charge:  $\overset{\delta+}{\text{H}} - \overset{\delta-}{\text{Cl}}$ . Such covalent bonds are said to be polar (i.e., bonds formed by sharing a pair of electrons between two atoms but displaced towards the nucleus of more electronegative atom).

***The net tendency of a bonded atom in a covalent molecule to attract the shared pair of electrons towards itself is known as electronegativity.*** (This word does not mean the actual content of the electric charge, but just the tendency to acquire it in a molecule). Thus F is highly electronegative, but  $\text{F}^-$ , which has already an extra electron, is not.

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca			As	Se	Br
0.8	1.0			2.0	2.4	2.8
Rb	Sr			Sb	Te	I
0.8	1.0			1.9	2.1	2.5

**Electronegativities of elements (Pauling Scale)**

To assess the tendency of an atom of a given element to attract electrons towards itself in a covalent bond, relative electronegativity values are used. Above Table gives the relative electronegativity values of atoms calculated by Pauling (adopting arbitrarily the value of 4 units for the electronegativity of fluorine).

- ☛ (i) Electronegativity values increase across a period and decrease down a group.
- (ii) Smaller atoms have greater electronegativity than larger ones and so they attract electrons more towards them than larger ones. Alkali metals have low electronegativities and halogens high electronegativities.
- (iii) Atoms with nearly filled shells of electrons (e.g., halogens) have greater electronegativity than those with sparsely occupied shells.

## CHEMICAL BONDING and MOLECULAR STRUCTURE

(iv) Elements with low electronegativity values such as Cs (0.8) and Rb (0.8) tend to form positive ions, i.e., these are metals. Elements with high electronegativity values such as F(4.0) and O(3.5) tend to form negative ions, i.e., these are non-metals.

(v) Electronegativity value may be used to make rough predictions of the type of bonding to be found in a compound. The larger the difference between electronegativity values of two combining atoms, the more polar the covalent bond. If the difference is greater than 2, the chance for ionic bonding (i.e., the chance of covalent bond assuming ionic character) will be greater. From this point of view ionic bond may be considered to be an extreme case of a polar bond (with total separation of charges).

If the difference between the electronegativities of the combining atoms is zero or small, the bond is essentially non-polar.

Let  $X_A$  and  $X_B$  represent the electronegativities of two atoms A and B. If  $X_B - X_A = 1.7$ , the covalent bond A – B is said to have 50% ionic character. On this basis, the % ionic character in some typical bonds is calculated. These calculations are very qualitative.

**% Ionic Character of Bonds**

C – H	N – H	O – H	F – H
4%	19%	39%	60%
C – F	C – Cl	C – Br	C – I
43%	11%	3%	0%

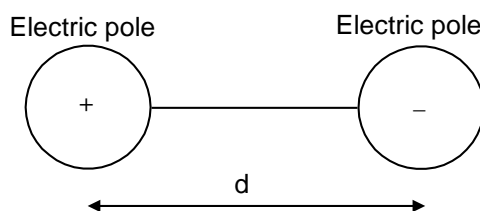
(vi) Pauling pointed out that for any pair of atoms AB, the electronegativity difference  $|X_A - X_B| = 0.208 \sqrt{\Delta}$  where  $\Delta = E_{AB} - \frac{1}{2} [E_{AA} + E_{BB}]$ , where  $E_{AB}$ ,  $E_{AA}$  and  $E_{BB}$  are the experimentally determined bond energies of AB, AA and BB respectively. ( $\Delta$  is in kcal/mol).  $\Delta$  was subsequently modified as  $\Delta = E_{AB} - \sqrt{E_{AA} E_{BB}}$ . Pauling adopted  $X_H$  for hydrogen = 2.1 (arbitrarily as reference).  $|X_A - X_B| = 0.1017 \sqrt{\Delta}$ , where  $\Delta$  is in kJ/mole.

The percent ionic character of a covalent bond may be calculated using Haney and Smyth equation:

$$\% \text{ ionic character} = 16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

### 3.1 DIPOLE MOMENT

A dipole consists of a positive and an equal negative charge separated by a distance within a molecule. The degree of polarity of a bond is given by the dipole moment ( $\mu$ ), which is the product of charge ( $e$ ) and the distance ( $d$ ) between them.  $\mu = d \times e$ . The dipole moments may be expected to have values around  $10^{-10} \times 10^{-8} = 10^{-18}$  esu-cm. It is however, general practice to express dipole moments in **Debye units** (D),  $1 \text{ D} = 10^{-18}$  esu-cm.



If the charge is in SI units (Coulombs) and  $d$  in metre,  $\mu$  will be coulomb-metre (C · m) units.  $1 \text{ D} = 3.336 \times 10^{-30} \text{ C} \cdot \text{m}$

## CHEMICAL BONDING and MOLECULAR STRUCTURE

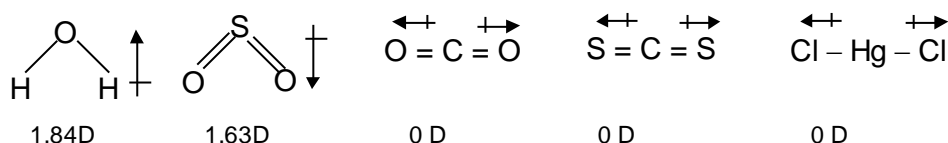
Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compounds containing such bonds will have dipole moments. The **polarity of the molecule as a whole is the vector sum of the individual bond dipole moments**. For example,  $\text{CO}_2$  has zero dipole moment, although the  $\text{C}=\text{O}$  bond is a polar bond. This shows that  $\text{CO}_2$  is a linear molecule,  $\text{O}=\text{C}=\text{O}$ , so that the dipole moments of the two  $\text{C}=\text{O}$  bonds cancel out. The  $\text{C} \rightarrow \text{Cl}$  bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4  $\text{C}-\text{Cl}$  bond moments is zero. On the contrary  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  have definite dipole moments.

### 3.2 APPLICATIONS OF DIPOLE MOMENT MEASUREMENTS

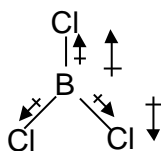
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shapes of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated fairly.

#### (A) Inorganic substances:

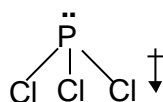
- (i) **Monatomic molecules** such as He, Ne, etc., have zero dipole moment because they are symmetrical.
- (ii) **Diatomic molecules** such as  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{N}_2$  have no dipole moment; so these molecules are symmetrical.
- (iii) **Triatomic molecules:** Some of these molecules possess zero dipole moment; so they have a symmetrical linear structure, e.g.,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{HgCl}_2$ . Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)



- (iv) **Tetratomic molecules:** Some molecules like  $\text{BCl}_3$  have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other examples are  $\text{BF}_3$ ,  $\text{BBr}_3$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ .

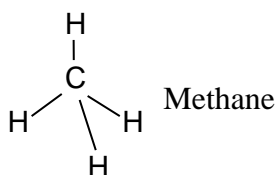


$\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{H}_3\text{O}^+$  have appreciable dipole moment. They possess trigonal pyramidal structures.



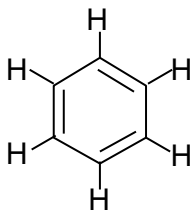
#### (B) Organic substances

- (i) **Methane and  $\text{CCl}_4$**  have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.



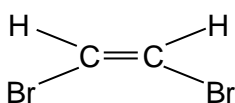
## CHEMICAL BONDING and MOLECULAR STRUCTURE

- (ii) **Benzene** has zero dipole moment. All the 6 C and 6 H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

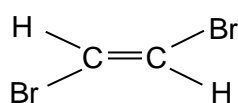


- (iii) **Measurement of dipole moments will enable** us to detect cis-and trans-isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans- isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.



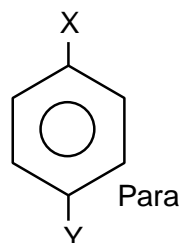
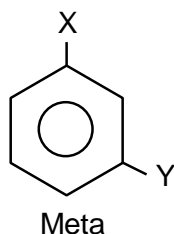
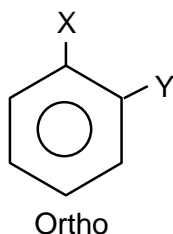
cis-dibromoethylene ( $\mu = 1.4 \text{ D}$ )



trans-dibromoethylene ( $\mu = 0$ )

- (iv) **Dipole moment in aromatic ring system**

The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers, o-nitrophenol, m-nitrophenol and p-nitrophenol. We have also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



In those cases where  $X = Y$ , the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other ( $\text{NO}_2$ ) is electron withdrawing while in aminophenols, both the groups (OH and  $\text{NH}_2$ ) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment. Then calculation of dipole moment follows as:

**Case (i):** When X and Y both are electron pushing or electron withdrawing.

Let the bond dipole of C-X bond is represented by  $\mu_1$  and that of C-Y bond by  $\mu_2$ . Now let us assume that the electron pushing groups have +ve bond moment and the electron withdrawing groups have -ve bond moment. The net dipole moment is the resultant of two bond dipoles at different orientations.

$$\mu_{\text{ortho}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cdot \frac{1}{2}}$$

$$\therefore \mu_0 = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$\mu_{\text{meta}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 120^\circ}$$

$$\therefore \mu_m = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$\mu_{\text{para}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2} = \mu_1 - \mu_2$$

From the above expressions of  $\mu_0$ ,  $\mu_m$  and  $\mu_p$ , it is clear that when both X and Y are of the same nature i.e., both are electron withdrawing or both are electron pushing the para product has the least dipole moment and ortho product has the highest dipole moment. When  $X = Y$ ,  $\mu_1 = \mu_2$ , thus  $\mu_p$  would be zero.

**Case (ii):** When X is electron pushing and Y is electron withdrawing or vice versa.

Let the bond moment of C–X dipole is  $\mu_1$  and that of C–Y dipole is  $\mu_2$ .

$$\mu_0 = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 60^\circ}$$

$$= \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$= \sqrt{(\mu_1 + \mu_2)^2 - 3\mu_1\mu_2}$$

$$\mu_{\text{meta}} = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 120^\circ}$$

$$= \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$= \sqrt{(\mu_1 + \mu_2)^2 - \mu_1\mu_2}$$

$$\mu_{\text{para}} = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 180^\circ}$$

$$= \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} = \mu_1 + \mu_2$$

Looking at the expressions of  $\mu_0$ ,  $\mu_m$  and  $\mu_p$ , it is clear that the para isomer has the highest dipole moment and ortho has the least.

### 3.3 DIPOLE MOMENT AND PERCENTAGE IONIC CHARACTER

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge =  $4.8 \times 10^{-10}$  e.s.u.

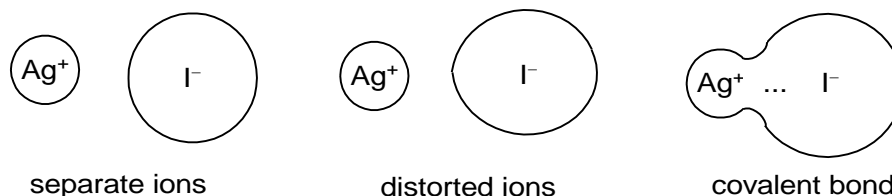
1 D =  $1 \times 10^{-18}$  e.s.u.–cm =  $3.336 \times 10^{-30}$  C·m

$$\therefore \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Theoretical dipole moment is confined to when we assume that the bond is 100 % ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

### 3.4 COVALENT CHARACTER IN IONIC BOND – FAJANS' RULE

Just as a covalent bond may have partial ionic character, an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



### 3.5 FACTORS INFLUENCING POLARIZATION (FAJAN'S RULES)

#### Polarizing Power of Cation:

The tendency of cation to polarize the valence electron cloud of anion is called polarizing power. Polarizing power of the cations varies as:

- (i) More the positive charge on cation more will be its ability to attract electron cloud of anion and more will be its polarizing power.  $\text{Na}^+ < \text{Mg}^{+2} < \text{Al}^{+3}$
- (ii) Smaller the size of cation more will be its +ve charge density and ability to attract electron cloud of anion and more will be its polarizing power.  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
- (iii) Cations with pseudo noble gas electronic configuration have exceptionally high polarizing power. A cation with 18 electrons in outermost shell such as  $\text{Ag}^+$  ( $[\text{Kr}] 4d^{10}$ ) polarizes anions more strongly than a cation with 8 electron arrangement as in  $\text{K}^+$ . The 'd' electrons in  $\text{Ag}^+$  do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in  $\text{K}^+$ . Thus AgI is more covalent than KI, although  $\text{Ag}^+$  and  $\text{K}^+$  ions are nearly of the same size. Cuprous and Mercurous salts are covalent.

#### Polarizability of Anions

The ability of anion to get its valence electron cloud polarized by the cation is called polarizability of anion. Polarizability of anions varies as:

- (i) More the negative charge on anion more will be its ability to get polarized and more will be polarizability.  $\text{F}^- < \text{O}^{2-} < \text{N}^{3-}$
- (ii) Larger the size of anion lesser will be hold of its nucleus on its own valence electron cloud and more will be its polarizability.  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

**Note:** Increase in polarizing power or the polarizability of anion will increase the extent of polarization and hence increase the covalent character. More the covalent character lesser will be thermal stability of the compound (lesser will be temperature required to decompose the compound).

## 4. Valence Bond Theory (Modern Approach of Covalent Bond)

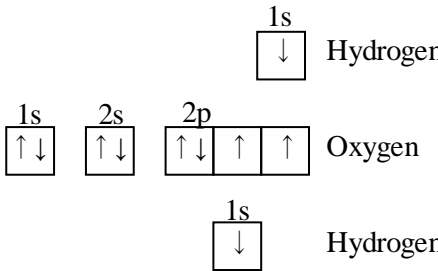

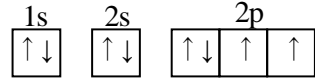
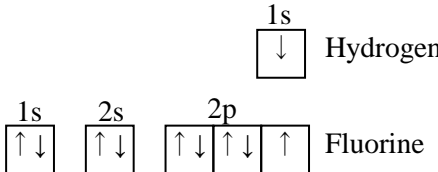

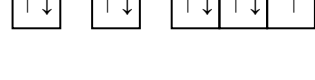
Heitler and London proposed that a covalent bond is formed by overlapping of atomic orbitals and this idea was later extended by Pauling and Slater. Valence bond theory is the most important theory for covalent bonding and is widely used to explain the chemistry of compounds in general. Important features of valence bond theory are:

- (i) Only valence orbitals of an atom participate in formation of covalent bond.
- (ii) A covalent bond is formed by overlapping of half-filled valence orbital of one atom by half-filled valence orbital of other atom.
- (iii) Two half-filled atomic orbitals can overlap with each other only if the electrons present in the orbitals have opposite spin.
- (iv) More the extent of overlapping, stronger will be the covalent bond and more will be the bond energy. It must be remembered that atoms approach each other in such a way to generate maximum extent of overlapping.
- (v) The number of covalent bonds formed by an element is equal to the number of half-filled orbitals present in the valence shell of an atom.
- (vi) During bond formation, atoms can undergo unpairing of electrons by excitation within valence shell.
- (vii) Since orbitals are directional (except s orbital), maximum overlapping of orbitals occur when other orbitals (atoms) approach from a particular direction i.e. covalent molecules have definite arrangement and orientation of atoms in space (shape of molecules).

Formation of water molecules is illustrated with the help of square box method where each square box represents one orbital and each arrow represents one electron. Arrows pointing upward and pointing downwards are used to represent opposite spin of electrons.

### Formation of Water:

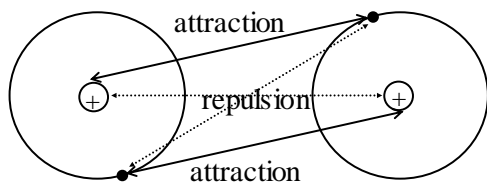
Electronic configuration of oxygen is  $1s^2 2s^2 2p^4$  which contains two half-filled orbitals hence oxygen can form two covalent bonds. Electronic configuration of hydrogen is  $1s^1$  which contains one half filled atomic orbital hence hydrogen can form one covalent bond. Therefore, each oxygen form two covalent bonds (one with each hydrogen atom) and they combine to form  $H_2O$  molecules.

In two covalent bonds (one with each hydrogen atom) and they combine to form $H_2O$ molecules.				
<b>Formation of <math>H_2O</math></b>		Element	Electronic configuration	Covalency
		Hydrogen		1
		Oxygen		2
		Hydrogen		
<b>Formation of HF</b>				
		Hydrogen		1
		Fluorine		1

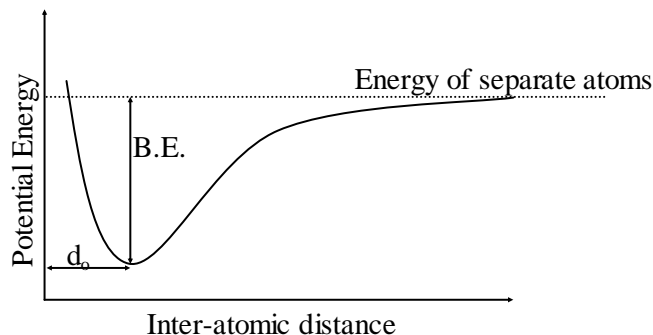
# CHEMICAL BONDING and MOLECULAR STRUCTURE

## 4.1 Concept of Minimum Energy

When atoms approach each other for overlapping of orbitals, new attractive and repulsive forces are generated. When attractive forces of attraction are stronger than repulsive forces, energy is decreased and results in the formation of a bond. The inter-atomic distance, when energy is minimum, is called bond length and the energy released during the process is called bond energy.



**Attractive and repulsive forces when hydrogen atoms approach each other**



The plot of potential energy versus interatomic distance indicates that potential energy decreases when atoms approach each other, attains a minimum value and again starts increasing if atoms are taken further closer. At a distance  $d_0$ , the potential energy is minimum and  $d_0$  is called bond length. The difference between the potential energy of separated atoms and the minimum potential energy corresponds to bond energy.

Valence bond theory further explained that unpairing of electrons may occur during bond formation if energy required during excitation is less than energy released during additional bond formation. This occurs when during unpairing excitation occurs within the valence shell.

(i) Beryllium:

Electronic configuration of Beryllium in ground state	<table><tr><td>1s</td><td>2s</td><td>2p</td></tr><tr><td><div>↑↓</div></td><td><div>↑↓</div></td><td><div></div><div></div><div></div></td></tr></table>	1s	2s	2p	<div>↑↓</div>	<div>↑↓</div>	<div></div> <div></div> <div></div>
1s	2s	2p					
<div>↑↓</div>	<div>↑↓</div>	<div></div> <div></div> <div></div>					
Electronic configuration of Beryllium in excited state:	<table><tr><td>1s</td><td>2s</td><td>2p</td></tr><tr><td><div>↑↓</div></td><td><div>↑</div></td><td><div>↑</div><div></div><div></div></td></tr></table>	1s	2s	2p	<div>↑↓</div>	<div>↑</div>	<div>↑</div> <div></div> <div></div>
1s	2s	2p					
<div>↑↓</div>	<div>↑</div>	<div>↑</div> <div></div> <div></div>					

Beryllium can form two bonds

(ii) Boron:

Electronic configuration of Boron in ground state:	<table><tr><td>1s</td><td>2s</td><td>2p</td></tr><tr><td><div>↑↓</div></td><td><div>↑↓</div></td><td><div>↑</div><div></div><div></div></td></tr></table>	1s	2s	2p	<div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div></div> <div></div>
1s	2s	2p					
<div>↑↓</div>	<div>↑↓</div>	<div>↑</div> <div></div> <div></div>					
Electronic configuration of Boron in excited state:	<table><tr><td>1s</td><td>2s</td><td>2p</td></tr><tr><td><div>↑↓</div></td><td><div>↑</div></td><td><div>↑</div><div>↑</div><div></div></td></tr></table>	1s	2s	2p	<div>↑↓</div>	<div>↑</div>	<div>↑</div> <div>↑</div> <div></div>
1s	2s	2p					
<div>↑↓</div>	<div>↑</div>	<div>↑</div> <div>↑</div> <div></div>					

Boron can form three bonds



## CHEMICAL BONDING and MOLECULAR STRUCTURE

(iii) Carbon:

Electronic configuration of Carbon in ground state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">1s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">2s ↑↓</div> <div style="display: inline-block; text-align: center;">2p ↑ ↑</div>
Electronic configuration of Carbon in excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">1s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">2s ↑</div> <div style="display: inline-block; text-align: center;">2p ↑ ↑ ↑</div>

Carbon can form four bonds

(iv) Nitrogen:

Electronic configuration of Nitrogen in ground state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">1s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">2s ↑↓</div> <div style="display: inline-block; text-align: center;">2p ↑ ↑ ↑</div>
Electronic configuration of Nitrogen in excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">1s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">2s ↑↓</div> <div style="display: inline-block; text-align: center;">2p ↑ ↑ ↑</div>

Nitrogen can form three bonds

Since no vacant orbital is present in the valence shell of nitrogen atom, excitation within valence shell is not possible. Hence nitrogen can form only three bonds and not five bonds.

(v) Phosphorus:

Electronic configuration of Phosphorus in ground state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑ ↑ ↑</div> <div style="display: inline-block; text-align: center;">3d □ □ □ □ □</div>
Electronic configuration of Phosphorus in excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑ ↑ ↑</div> <div style="display: inline-block; text-align: center;">3d ↑ □ □ □ □</div>

Since vacant d orbitals are present in the valence shell of phosphorus atom, excitation within valence shell is possible to make five half-filled orbitals, phosphorus can form three bonds as well as five bonds.

(vi) Chlorine:

Electronic configuration of Chlorine in ground state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑↓ ↑↓ ↑</div> <div style="display: inline-block; text-align: center;">3d □ □ □ □ □</div>
Electronic configuration of Chlorine in first excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑↓ ↑ ↑</div> <div style="display: inline-block; text-align: center;">3d ↑ □ □ □ □</div>
Electronic configuration of Chlorine in second excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑↓</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑ ↑ ↑</div> <div style="display: inline-block; text-align: center;">3d ↑ ↑ □ □ □</div>
Electronic configuration of Chlorine in third excited state:	<div style="display: inline-block; text-align: center; margin-right: 10px;">3s ↑</div> <div style="display: inline-block; text-align: center; margin-right: 10px;">3p ↑ ↑ ↑</div> <div style="display: inline-block; text-align: center;">3d ↑ ↑ ↑ □ □</div>

## CHEMICAL BONDING and MOLECULAR STRUCTURE

Since vacant d orbitals are present in the valence shell of chlorine atom, excitation within valence shell is possible to make 3, 5 and 7 half-filled orbitals. Chlorine, therefore, can show covalency of 1, 3, 5 and 7.

### 4.2 Inert pair Effect

As the size of atom increases, unpairing of s-electrons within the valence shell becomes less favourable because extra bonds formed by larger atoms are weak and lesser energy is released. Hence, tendency of s electron pair to participate in bonding goes on decreasing while going down in a group of periodic table i.e. s-electron pair starts becoming inert. This is called inert pair effect.

Indium (In), a member of boron group, shows valency of 1 and 3. Thallium (Tl), a member of boron group, shows valency of 1 and 3 and univalent thallium is more stable than trivalent thallium.

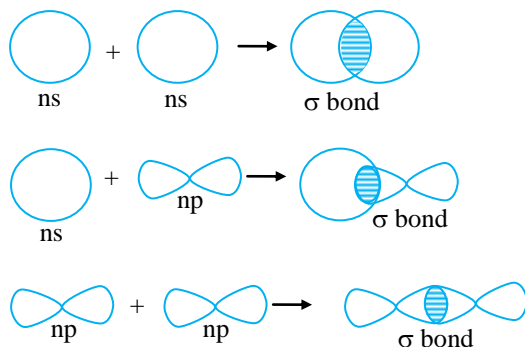
Similarly Tin (Sn) and Lead (Pb), members of carbon group show valency of 2 and 4 and divalent lead is more stable than tetravalent lead.

Similarly Antimony (Sb) and Bismuth (Bi), members of nitrogen group show valency of 3 and 5 and trivalent bismuth is more stable than pentavalent bismuth.

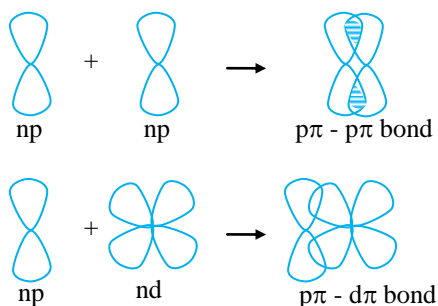
### 4.3 Modes of Orbital Overlapping and Types of Covalent Bond

On the basis of modes of overlapping, covalent bonds are classified in two categories: sigma ( $\sigma$ ) bonds and pi ( $\pi$ ) bonds.

**Sigma bonds:** When overlapping of atomic orbitals takes place at inter nuclear axis (head on overlapping), the covalent bond is called  $\sigma$  bond.  $\sigma$  bond is formed by s-s overlapping, s-p overlapping and p-p overlapping as shown below:



**Pi Bond:** When overlapping of atomic orbitals occur in sideways manner (not along inter nuclear axis), the covalent bond is called pi bond. Pi bond can be formed by p-p overlapping and p-d overlapping as shown below:



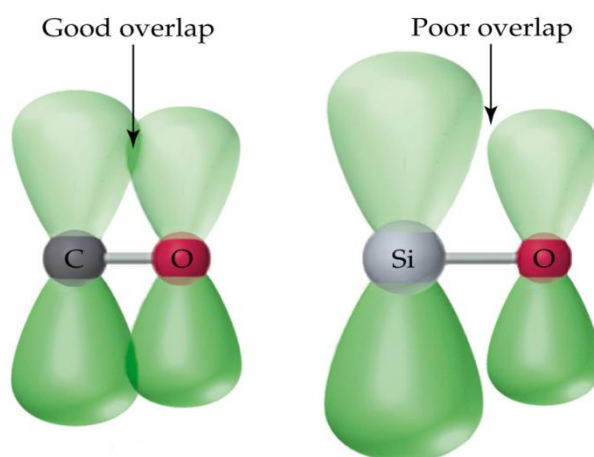
## CHEMICAL BONDING and MOLECULAR STRUCTURE

$\sigma$ bonds	$\pi$ bonds
$\sigma$ bonds are formed by head on overlapping of atomic orbitals	$\pi$ bond can be formed only if both the atoms also contains $\sigma$ bond.
$\sigma$ bonds are more stronger and more stable due to greater extent of overlapping	$\pi$ bonds are weaker and less stable due to lesser extent of overlapping
$\sigma$ bond can be formed independently. There can be only one $\sigma$ bond between two atoms.	$\pi$ bond cannot be formed independently. $\pi$ bond is formed only when the atoms have $\sigma$ bond between them.
$\sigma$ bonds can be rotated freely as free rotation does not affect overlapping	$\pi$ bonds cannot be rotated freely as free rotation will diminish the extent of overlapping
$\sigma$ bonds are formed by s-s overlapping, s-p overlapping and p-p overlapping. Hybrid orbitals also form $\sigma$ bonds.	$\pi$ bonds are formed by p-p overlapping and p-d overlapping

### Important point to remember about $\pi$ bonds:

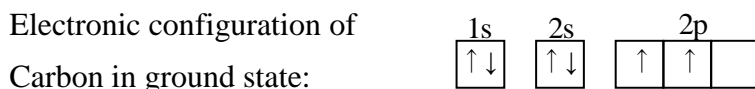
1. Larger the size of the atom, weaker is the  $\pi$  bond and lesser is the tendency of atom to form  $\pi$  bonds.
2.  $p\pi-p\pi$  bond of larger atoms ( $3^{\text{rd}}$  period elements) are less stable. However,  $p\pi-p\pi$  bond of larger atoms are stable because of effective overlapping.

$p\pi-p\pi$  bond is stronger than  $p\pi-d\pi$  bond. Moreover, tendency to form  $p\pi-p\pi$  bond decreases with increasing size of atom. Large atoms like Si have very little tendency to form  $p\pi-p\pi$  bond. Therefore, molecules like  $\text{CO}_2$  exist but molecules like  $\text{SiO}_2$  do not exist. A molecule having  $p\pi-p\pi$  bond between large atoms generally is unstable, even if it exists, it will have tendency to undergo polymerization like  $(\text{R}_2\text{SiO}, \text{SO}_2, \text{SO}_2, \text{P}_2\text{O}_3, \text{P}_2\text{O}_5)$ .



## 5. HYBRIDIZATION

Let us consider the structure and shape of  $\text{CH}_4$  molecules. Carbon atom has the electronic configuration  $1s^2 2s^2 2p_x^1 2p_y^1$ . It has two half-filled orbitals. It should be expected to show a covalency of 2 in ground state. In its millions of compounds carbon shows tetravalency. This can be explained on the basis of excitement of electrons within the valence shell.



Four half-filled atomic orbitals of excited carbon can overlap with half-filled atomic orbitals of four hydrogen atoms to generate  $\text{CH}_4$  molecules. Out of these four bonds, three are formed by  $2p$ - $1s$  overlapping and one bond is formed by  $2s$ - $1s$  overlapping, hence all the four bonds should not be identical.

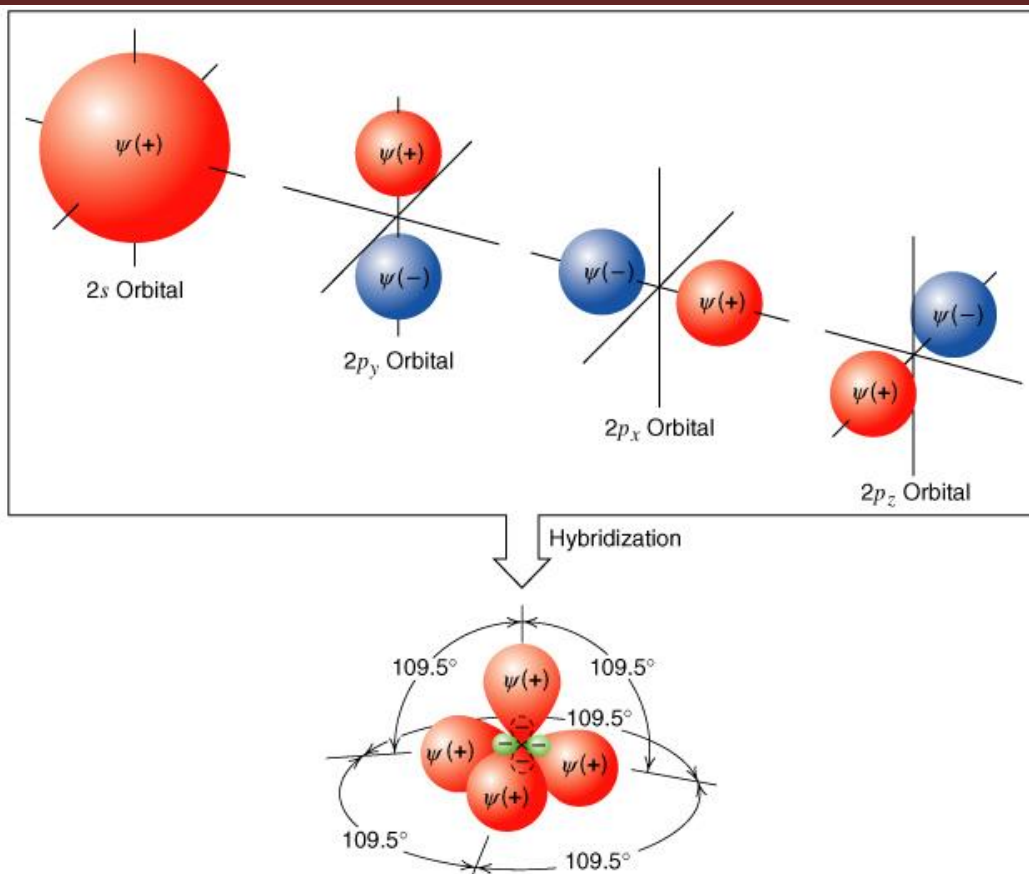
Experimental observations, however, indicate that all the four C – H bonds in methane are identical which could not be explained merely on the basis of valence bond theory. This identical nature of C – H bonds was later explained by Pauling by introducing a term '**Hybridization**'. He explained that four valence orbitals of carbon are somehow converted to identical orbitals during formation of the bonds.

### 5.1 RULES FOR HYBRIDISATION

- (i) Orbitals of comparable energy only can participate in hybridization.
- (ii) Number of orbitals participating in hybridization and number of hybrid orbitals formed is always same.
- (iii) Hybrid orbitals of an atom either form  $\sigma$  bond or contain unshared electron (usually lone pair). They cannot remain vacant.
- (iv) Hybrid orbitals of an atom are identical in shape, size, energy etc.
- (v) Hybrid orbitals repel in each other and tend to lie far apart in space resulting in specific geometries.
- (vi) Hybrid orbitals can overlap more effectively and generally form stronger bonds than pure orbitals.
- (vii) More the % s character in hybridization of an atom, stronger and shorter will be bond of that atom.

### 5.2 $sp^3$ HYBRIDISATION

Carbon atom (in excited state) has the electronic configuration  $1s^2 2s^2 2p_x^1 2p_y^1$ . It has four half-filled orbitals. These four orbitals (one s and three p-orbitals) get mixed up and form four new 'hybrid' orbitals, of equal energy. These hybrid orbitals are called  $sp^3$  hybrid orbitals, as they are formed by the mixing up (or blending) of one s and three p-orbitals.

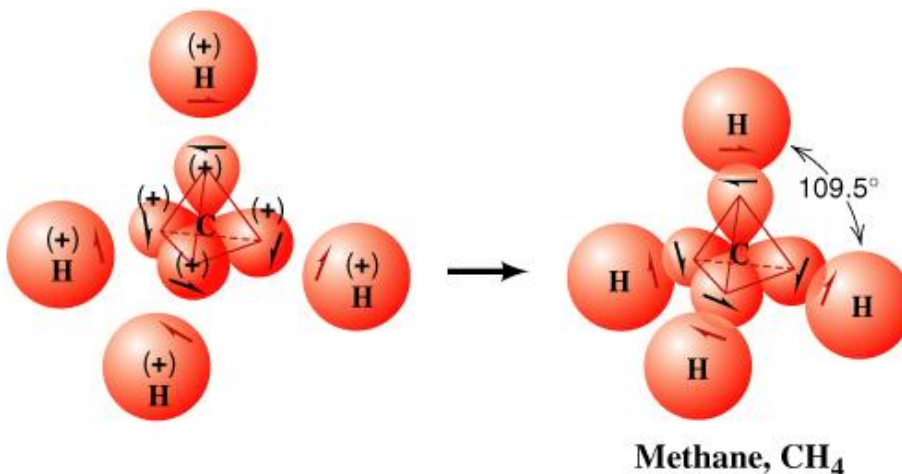


## $sp^3$ hybridisation of carbon atom

So hybridisation is nothing but *combination of a certain number of atomic orbitals of slightly different energies to form the same number of new (hybrid) orbitals of equal energy*.

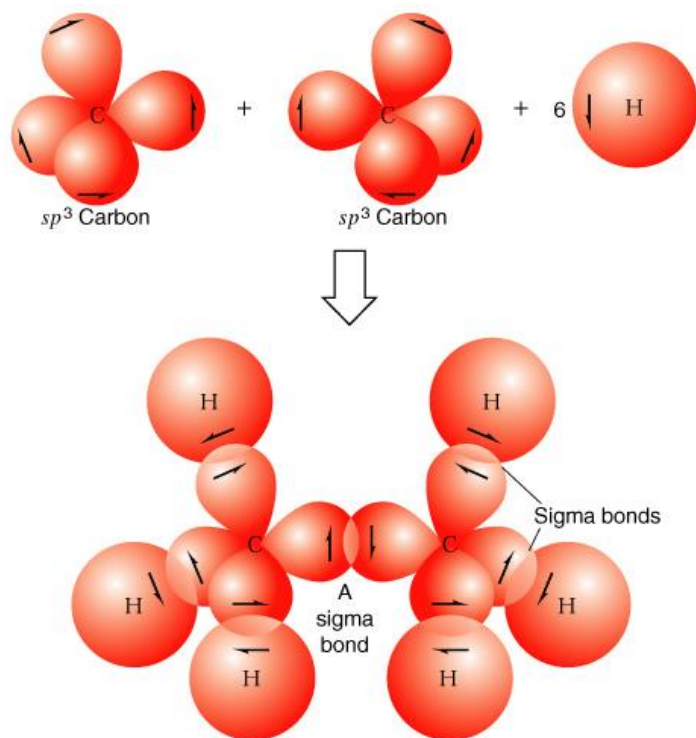
Each  $sp^3$  hybrid orbital is like a p-orbital, but with 2 lobes of unequal size (In figures, the small lobe is usually omitted to avoid confusing orbital overlapping).

Since the  $sp^3$  hybrid orbitals repel one another, they orient themselves with an angle of  $109^\circ 28'$  between them and point to the four corners of a regular tetrahedron. Each hybridised orbital overlaps the 1s-orbital of a hydrogen atom and forms a  $\sigma$  bond. Each  $sp^3$  hybrid orbital has one fourth s character and three-fourths p character. Note that a hybrid atomic orbital from s and p-orbitals can form only  $\sigma$  bonds. (4 C – H  $\sigma$  bonds).



## Formation of Ethane

In this case there is  $sp^3-sp^3$  overlap resulting in the formation of the C – C bond and  $sp^3-s$  overlap forming C – H bonds. (1 C – C  $\sigma$  bond and 6 C – H  $\sigma$  bonds.)



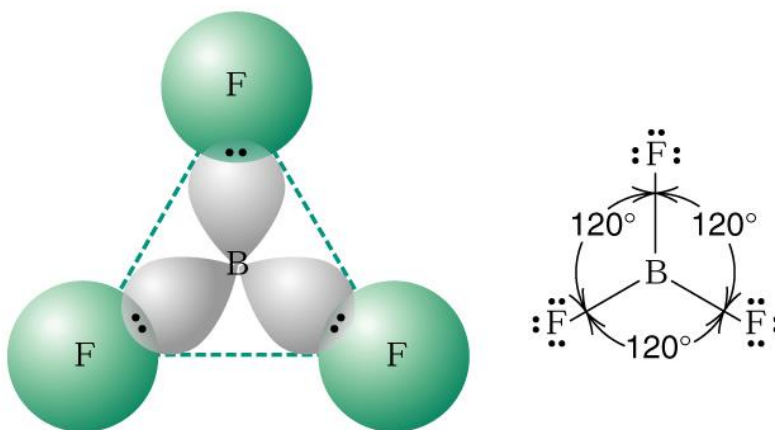
**Formation of Ethane**

## 5.3 $sp^2$ HYBRIDISATION

### Formation of boron trifluoride/trichloride, $BF_3/BCl_3$

Boron has the electronic configuration  $1s^2 2s^2 2p_x^1$ . One of the s electrons is promoted to a vacant  $p_y$ -orbital (excited state). Then **one s-orbital and two p-orbitals** hybridise to form three  $sp^2$  hybrid orbitals of equivalent energy. This kind of hybridisation is called  **$sp^2$  (trigonal) hybridisation**.

The three  $sp^2$  hybrid orbitals are **co-planar** and are at angles of  $120^\circ$  to each other. Each hybrid orbital overlaps with the vacant p-orbital of the chlorine atom and forms a  $\sigma$  bond. The other halides or Boron have similar structures. An  $sp^2$  hybrid orbital has one-third s character and two-thirds p character. (3  $\sigma$  bonds.)



**$sp^2$  hybridisation of Boron of  $BF_3$**



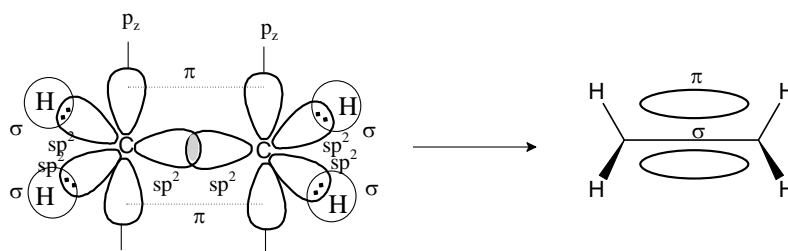
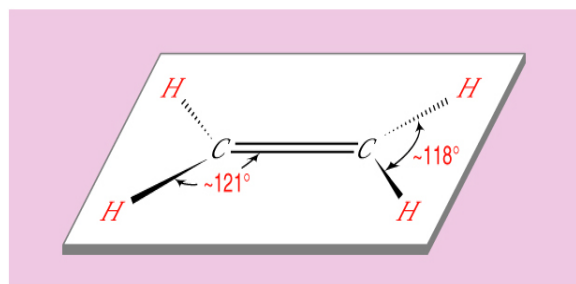
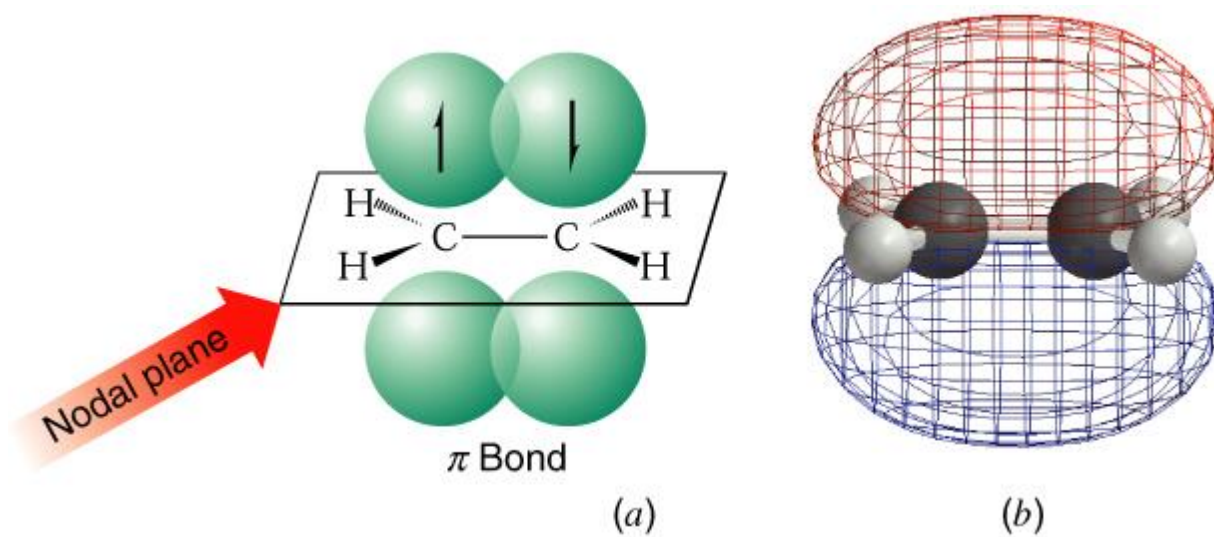
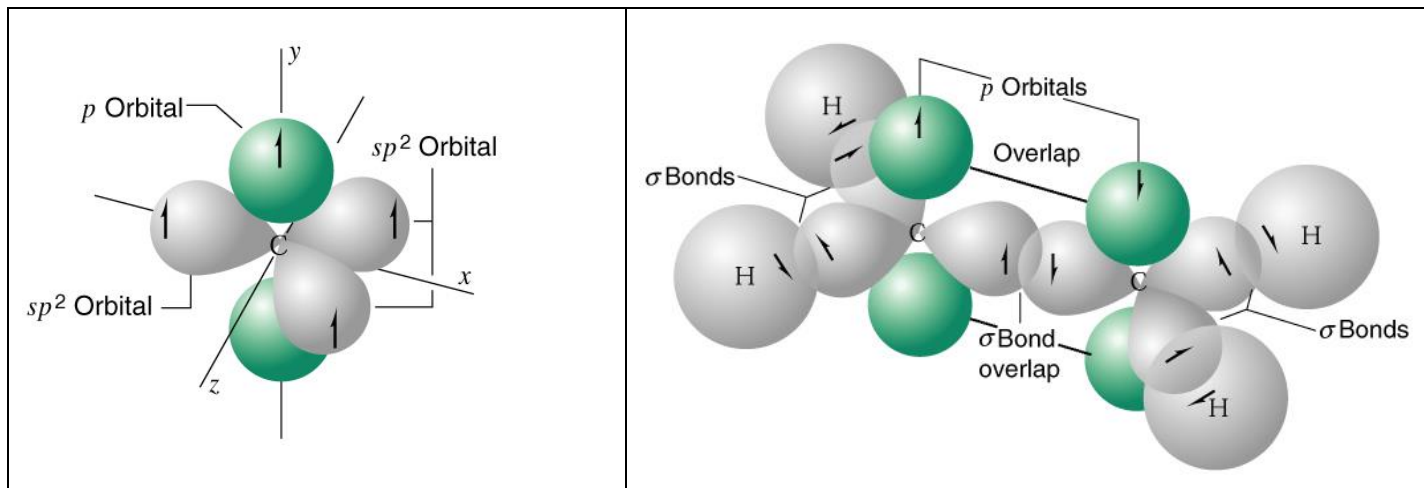
# CHEMICAL BONDING and MOLECULAR STRUCTURE

## Formation of Ethylene molecule

In the formation of ethylene, carbon atom undergoes  $sp^2$  hybridisation. Two of the  $sp^2$  orbitals of each atom form  $\sigma$  bonds with 1s-orbitals of hydrogen atoms by axial overlapping.

The  $sp^2$ - $sp^2$  overlap results in the formation of a C – C  $\sigma$  bond. The two carbon atoms and the four hydrogen atoms are all in the same plane and the bond angles are  $120^\circ$ .

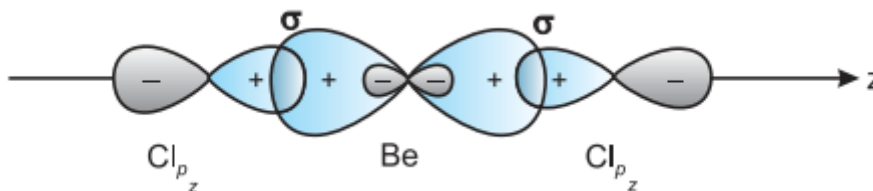
At right angles to this plane there remains the  $2p_z$  orbital of each carbon atom which overlap laterally to form a  $\pi$  bond between the two carbon atoms. The double bond between the two carbon atoms consists of a  $\sigma$  bond and a  $\pi$  bond. (4 C – H  $\sigma$  bonds, 1 C – C  $\sigma$  bond and 1  $\pi$  bond)



## 5.4 sp HYBRIDISATION

One s and one p-orbital combine to form two hybrid orbitals known as sp (or linear or diagonal) orbitals. They are of equal energy and are collinear. Each sp-orbital has one-half s character and one-half p character.

### (i) Formation of beryllium chloride

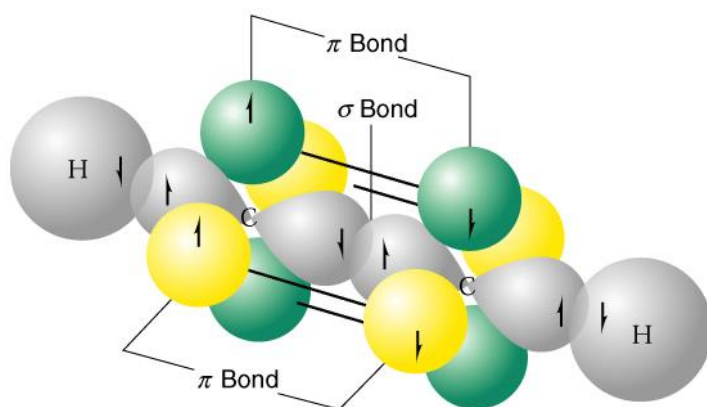


sp hybridization of Beryllium

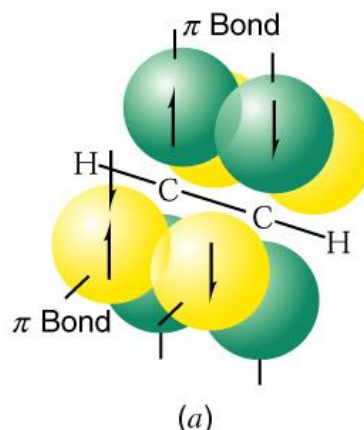
The sp hybrid orbitals of beryllium atom overlap with the vacant  $p_x$ -orbitals of two chlorine atoms and form two  $\sigma$  bonds. Since sp hybrid orbitals protrude along the axis farther than the corresponding s or p-orbitals they are able to overlap better and form stronger bonds than s or p-orbitals alone.

### (ii) Formation of acetylene

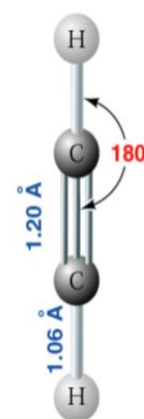
Hybridization of the one 2s and 2p carbon orbitals leads to the formation of two sp hybrid orbitals. sp-sp overlap between two carbon atoms form a  $\sigma$  bond between them. The other sp orbital on each carbon atom forms a  $\sigma$  bond with the 1s orbital of a hydrogen atom.



Orbital picture of Acetylene



Pi orbital picture in Acetylene



Acetylene

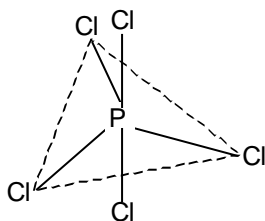
Each of the carbon atom has two remaining p-orbitals which are mutually at right angles to each other. They laterally overlap and form two  $\pi$  bonds, sometimes pictured as a cylindrical sheath about the line joining the nuclei. Each carbon forms four bonds 1 C – C  $\sigma$  bond, 1 C – H  $\sigma$  bond and 2  $\pi$  bonds (triple bond between 2 carbon atoms contains one C–C  $\sigma$  bond and 2  $\pi$  bonds; one single bond with hydrogen consists of C – H  $\sigma$  bond).

The carbon-carbon triple bond is made up of one strong  $\sigma$  bond and two weaker  $\pi$  bonds; it has a total strength of 198 kcal/mole. It is stronger than a carbon-carbon double bond (163 kcal) or C–C single bond in ethane (88 kcal) and therefore is shorter than either.



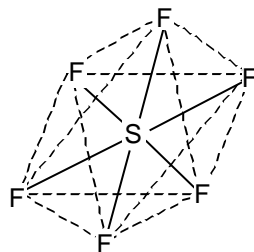
## 5.5 $sp^3d$ HYBRIDIZATION

In this type of hybridization, one 's', three 'p' and one 'd' orbitals of the same shell mix to give five  $sp^3d$  hybrid orbitals. These five  $sp^3d$  hybrid orbitals orient themselves towards the corners of a trigonal bipyramidal.



## 5.6 $sp^3d^2$ HYBRIDIZATION

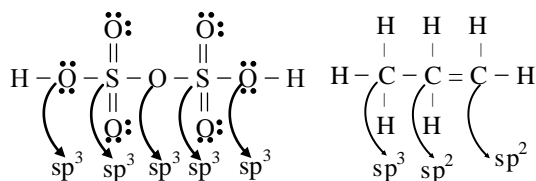
In this type of hybridization, one 's', three 'p' and two 'd' orbitals of the same/different shell mix to give six  $sp^3d^2$  hybrid orbitals. These six  $sp^3d^2$  hybrid orbitals orient themselves towards the corners of an octahedron. This type of hybridization is exhibited by  $SF_6$ ,  $SCl_6$  etc.



## 5.7 DETERMINING HYBRIDIZATION OF CENTRAL ATOM

- (i) Identify the central atom of the species (Usually less electronegative atom is central atom. However, H and F can never be central atom because they form only one bond.
- (ii) Write outermost electronic configuration of the central atom.
- (iii) Determine oxidation state of the central atom.
- (iv) Excite the electrons (if necessary) to the orbitals of higher energy in order to make the number of unpaired electrons equal to the oxidation state of the central atom.
- (v) Now start putting orbitals into hybridization pocket, beginning from 's' orbitals. The number of orbitals added to the pocket must have orbitals with unpaired electrons equal to number of other atoms bonded to central atom.
- (vi) All the orbitals added to the pocket (including s orbital, whether it has paired or unpaired electrons) are now summed. If there are one 's' and one 'p' orbital in the pocket, then the hybridization is  $sp$ . If there are one 's' and '2p' orbitals in the pocket, it is  $sp^2$  hybridization, and so on.
- (vii) Each unpaired electron left (outside the pocket) usually forms a pi-bond.
- (viii) Each orbital with paired electrons in the pocket will exist as lone pair on the central atom.

Alternatively, the number of hybrid orbitals of an atom in a species (one or more central atom) is equal to the sum of  $\sigma$  bonds of that atom, lone pairs on that atom and sometimes unpaired electron on that atom if any (unpaired electrons of carbon normally do not participate in hybridization).



## CHEMICAL BONDING and MOLECULAR STRUCTURE

### Alternative Method of determining the number of Hybrid orbitals:

The number of hybrid orbitals in a species can be determined by determining the total number of valence electrons (N) in that species as below:

$$N = \text{Valence electrons of all atoms} - \text{charge on that species.}$$

Total valence electrons are then divided by 8 and then the remainder by 2.

The number of hybrid orbitals is the sum of first quotient ( $Q_1$ ), second quotient ( $Q_2$ ) and second remainder  $R_2$ . However,  $Q_1 + Q_2 + R_2$  must not be 1 and each of these should not be a fractional quantity. Therefore, if  $n \leq 8$ , take  $Q_1 = 0$ .

$$\begin{array}{r} \overline{8 \overline{N}} \quad Q_1 \\ - 8Q_1 \\ \hline \overline{2 \overline{R_1}} \quad Q_2 \\ - 2Q_2 \\ \hline R_2 \end{array}$$

$$\begin{array}{r} \overline{8 \overline{8}} \quad 1 \\ - 8 \\ \hline \overline{2 \overline{0}} \quad 0 \\ - 0 \\ \hline 0 \end{array}$$

$$\begin{aligned} Q_1 + Q_2 + R_2 &= 1 + 0 + 0 \\ &= 1 \text{ (wrong)} \end{aligned}$$

$$\begin{array}{r} \overline{8 \overline{8}} \quad 0 \\ - 0 \\ \hline \overline{2 \overline{8}} \quad 4 \\ - 8 \\ \hline 0 \end{array}$$

$$\begin{aligned} Q_1 + Q_2 + R_2 &= 0 + 4 + 0 \\ &= 4 \end{aligned}$$

**The above method cannot be applied if the molecule or species has more than one central atom. In such cases, hybridization can be determined from structure only.**

## CHEMICAL BONDING and MOLECULAR STRUCTURE

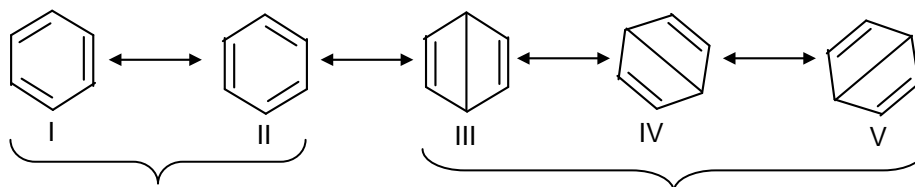
### 5.8 Examples to illustrate determination of hybridization

Species	Calculation	Types of hybridisation
BeF <sub>2</sub>	$N = 2 + 7 \times 2 = 16$ $Q_1 + Q_2 + R_2 = 2 + 0 + 0 = 2$	sp hybridisation
NO <sub>2</sub>	$N = 5 + 6 \times 2 = 17$ $Q_1 + Q_2 + R_2 = 2 + 0 + 1 = 3$	sp <sup>2</sup> hybridisation
ClO <sub>2</sub>	$N = 7 + 6 \times 2 = 19$ $Q_1 + Q_2 + R_2 = 2 + 1 + 1 = 4$	sp <sup>3</sup> hybridisation
ClO <sub>4</sub> <sup>-</sup>	$N = 7 + 6 \times 4 - (-1) = 32$ $Q_1 + Q_2 + R_2 = 4 + 0 + 0 = 4$	sp <sup>3</sup> hybridisation
NH <sub>4</sub> <sup>+</sup>	$N = 5 + 1 \times 4 - (1) = 8$ $Q_1 + Q_2 + R_2 = 0 + 4 + 0 = 4$	sp <sup>3</sup> hybridisation
XeOF <sub>2</sub>	$N = 8 + 6 \times 1 + 7 \times 2 = 28$ $Q_1 + Q_2 + R_2 = 3 + 2 + 0 = 5$	sp <sup>3</sup> d hybridisation
XeOF <sub>4</sub>	$N = 8 + 6 \times 1 + 7 \times 4 = 42$ $Q_1 + Q_2 + R_2 = 5 + 1 + 0 = 6$	sp <sup>3</sup> d <sup>2</sup> hybridisation
SF <sub>4</sub>	$N = 6 + 7 \times 4 = 34$ $Q_1 + Q_2 + R_2 = 4 + 1 + 0 = 5$	sp <sup>3</sup> d hybridisation
XeF <sub>6</sub>	$N = 8 + 7 \times 6 = 50$ $Q_1 + Q_2 + R_2 = 6 + 1 + 0 = 7$	sp <sup>3</sup> d <sup>3</sup> hybridisation
I <sub>3</sub> <sup>-</sup>	$N = 7 \times 3 - (-1) = 22$ $Q_1 + Q_2 + R_2 = 2 + 3 + 0 = 7$	sp <sup>3</sup> d hybridisation
XeO <sub>3</sub>	$N = 8 + 6 \times 3 = 26$ $Q_1 + Q_2 + R_2 = 3 + 1 + 0 = 4$	sp <sup>3</sup> hybridisation

## 6. RESONANCE

Sometimes a species (molecule or ion) can be assigned more than one Lewis structures but none of them can explain all the properties of that species and none of them is actually true representation of that species. However, the average of these structures can explain all the properties and is the true representation of that species. This phenomenon is called resonance, various possible Lewis structures are called canonical or contributing or resonating structures while their average is called resonance hybrid structure.

Benzene,  $C_6H_6$  is a resonance hybrid of the following structures (hexagonal, planar).

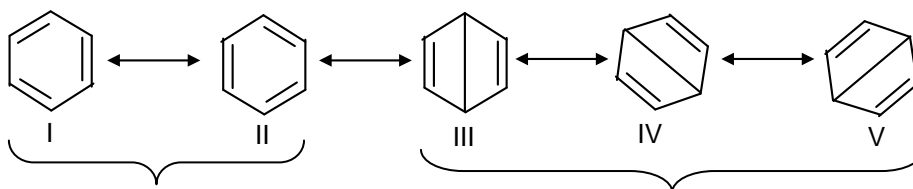


Kekule Structures

Dewar Structures

C–C bond length is  $1.54 \text{ \AA}$ ; C=C bond length is  $1.34 \text{ \AA}$ . In benzene, all the C–C bonds are identical in length,  $1.39 \text{ \AA}$ , i.e., intermediate between those of single and double bonds. Note that shortening of bond length and therefore increased stability is an indication of the existence of resonance. Resonance energy of benzene is  $152 \text{ kJ/mol}$ . Further,  $C_6H_6$  is quite stable and does not show the characteristic reactions of the C = C group, as shown by alkenes.

It is now obvious that none of these structures actually represents  $C_6H_6$ . To explain this difficulty the concept of resonance was introduced, according to which  $C_6H_6$  cannot be accurately depicted by any Lewis formula. The actual structure of  $C_6H_6$  is a resonance hybrid of the five structures:



These different structures are called the **canonical or contributing structures**. The actual structure of  $C_6H_6$  is different from the canonical structures and although it is closely related to them, the actual structure cannot be represented on paper using the accepted symbols. All the molecules of  $C_6H_6$  have the same structure. Usually, a double headed arrow  $\longleftrightarrow$  is used between the canonical structures.

### 6.1 CONDITIONS FOR RESONANCE

Resonance can occur when the canonical structures

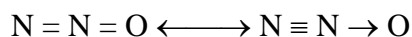
- (i) have the constituent atoms in the same relative positions;
- (ii) have nearly the same energy;
- (iii) have the same number of unpaired electrons (to allow for continuous change from one type of bond to another);
- (iv) differ in the distribution of electrons around the constituent atoms;
- (v) Molecules or ions are either planar or the structures are identical.

## 6.2 RESONANCE ENERGY

The resonance hybrid is a more stable structure than any of the contributing structures. This means that resonance hybrid has less energy than any of the contributing structures. *The difference in energy between the most stable of the contributing structures and the actual observed energy of the resonance hybrid is called resonance energy.*

## 6.3 OTHER EXAMPLES OF RESONANCE

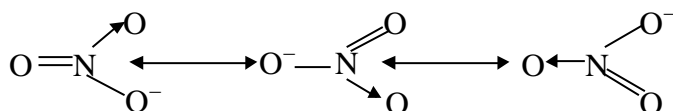
(i) Nitrous oxide (dinitrogen oxide),  $\text{N}_2\text{O}$



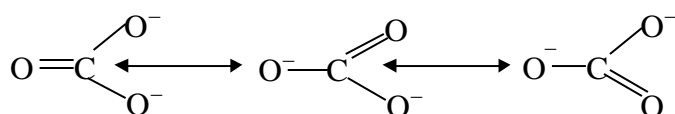
(ii) Nitric oxide,  $\text{NO}$



(iv) Nitrate ion,  $\text{NO}_3^-$  (planar, triangular)



(vii) Carbonate ion,  $\text{CO}_3^{2-}$  (planar, triangular)

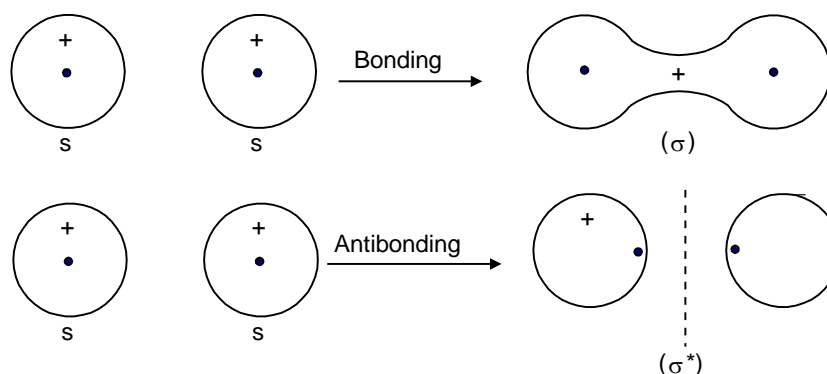


## 7. MOLECULAR ORBITAL THEORY

The Valance Bond Theory (V.B. Theory) with the concepts of hybridisation and resonance is used to explain the structure and properties of several molecules, but there are limitations. For example, the V.B. theory in its original form, is not able to explain the paramagnetic behaviour of  $O_2$  molecule. Hence, the Molecular Orbital Theory (or M.O. Theory) was proposed by Hund and Mulliken. The following are the essential features of the M.O. Theory.

1. In the M.O. model, all the electrons are taken together and considered as moving in the field of all the nuclei. (In the V.B. model, only the bonding electrons are considered and they are taken to move in the field of the nuclei involved in bonding.)
2. The atomic orbitals are combined to form, what are called molecular orbitals and electrons are fed into these orbitals. (In the V.B. model, electrons are fed into the atomic orbitals, which are then supposed to overlap.)
3. The number of combining atomic orbitals is equal to the number of molecular orbitals formed.
4. When two atomic orbitals combine, two M.O's are formed, of which one has a lower energy, while the other has a higher energy. The former is known as the bonding orbital and the latter antibonding. Mathematically, if  $\psi_1$  represents the wave function corresponding to orbital 1 and  $\psi_2$  for orbital 2, the total function is a linear combination of  $\psi_1$  and  $\psi_2$  i.e.,  $\psi = \psi_1 \pm \psi_2$  (omitting the constants). This is known as linear combination of atomic orbitals (L.C.A.O.). Of these,  $\psi_1 + \psi_2$  corresponds to the bonding M.O., while  $\psi_1 - \psi_2$  corresponds to antibonding M.O. i.e.,  $\psi_b = \psi_1 + \psi_2$  and  $\psi_a = \psi_1 - \psi_2$ . The electron density or probability of finding an electron is directly proportional to  $\psi^2$ .

For the bonding orbital,  $\psi_b^2 = (\psi_1 + \psi_2)^2 = \psi_1^2 + \psi_2^2 + 2\psi_1\psi_2$ , which is greater than  $\psi_1^2 + \psi_2^2$  i.e., the electron density between the two nuclei is concentrated when the bonding M.O. is formed, than when no such combination of orbitals is made.



For the antibonding orbital,  $\psi_a^2 = (\psi_1 - \psi_2)^2 = \psi_1^2 + \psi_2^2 - 2\psi_1\psi_2$ , which is less than  $\psi_1^2 + \psi_2^2$  i.e. the electron density between the nuclei is withdrawn in an antibonding M.O. In the bonding M.O., since the electron density between the two nuclei is large, it holds the two nuclei together; hence the name bonding orbital; in the antibonding M.O. the bonding of the nuclei is poor.

5. There are different notations for representing bonding and anti-bonding M.O's obtained from A.O's. We give a simple notation below.

Atomic orbitals that are mixed	ns and ns	$np_z$ and $np_z$	$np_x$ and $np_x$	$np_y$ and $np_y$
Bonding M.O.	$\sigma_{ns}$	$\sigma_{np_z}$	$\pi_{np_x}$	$\pi_{np_y}$

## CHEMICAL BONDING and MOLECULAR STRUCTURE

Antibonding M.O.	$\sigma^*ns$	$\sigma^*np_z$	$\pi^*np_x$	$\pi^*np_y$
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We have assumed the two  $p_z$  orbitals to overlap end to end, so that the M.O. formed is of the ' $\sigma$ ' type (similar to the ' $\sigma$ ' bond in V.B. theory); then the two  $p_x$  atomic orbitals, as also the two  $p_y$  orbitals will overlap laterally to give M.O's of the  $\pi$  type. Some authors follow the convention of choosing two  $p_x$  orbitals for end to end (i.e., axial) overlap, so that the M.O's formed are  $\sigma(p_x)$  and  $\sigma^*(p_x)$ .

6. When electrons are successively placed in the M.O's, Aufbau principle, Hund's rule and Pauli's principle are followed, as in the case of the atomic orbitals.

Aufbau Principle: M.O's are occupied in the order of increasing energy. The following is the general arrangement of M.O's in the order of increasing energy.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z) \dots \text{etc.}$$

The above is only a general order and slight variations often occur due to interaction between s and p orbitals. For example, sometimes,  $\pi(2p_x) = \pi(2p_y) < \sigma(2p_z)$  for molecules upto 14 electron.

7. Pauli's Exclusion Principle:

Each orbital can have maximum 2 electrons that too with opposite spin.

8. Hund's rule of maximum multiplicity:

The degenerate M.O's are occupied singly, before any pairing could occur. All unpaired electrons possess same spin.

9. Only atomic orbitals of equal or nearly equal energies combine to give the M.O's. In the case of homonuclear diatomic molecules, energies of corresponding A.O's of the two atoms are equal. So the above condition of combination of A.O's assumes special significance in the case of heteronuclear diatomic molecules and it has to be used with caution.
10. It has been already pointed out that electrons in the bonding M.O's tend to pull the nuclei together and that the electrons in the antibonding M.O's tend to separate them. Hence the combined influence of bonding and antibonding electrons may either stabilize or destabilize the molecule, depending on the relative number of these two types of electrons. The stabilizing power is expressed in terms of what is called the "bond order".

$$\text{Bond order} = \frac{1}{2} \left[ \left( \text{number of electrons in the bonding M.O.} \right) - \left( \text{number of electrons in the antibonding M.O.} \right) \right]$$

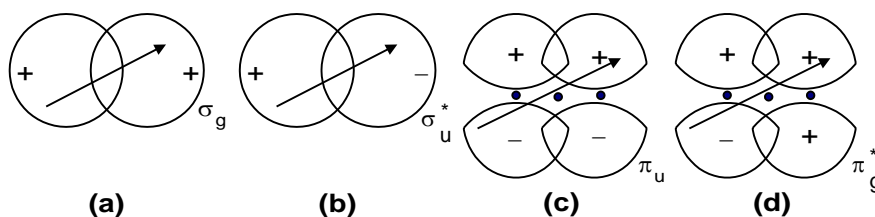
The greater the bond order, the greater the bond stability and the shorter the bond distance.

11. The M.O's are also named on symmetry grounds. For **homonuclear diatomic molecules**, the symbols 'g' ('gerade' meaning 'even') and 'u' ('ungerade' meaning 'uneven' or 'odd') are used. The symbol 'g' is used, if the orbital has a centre of symmetry. i.e., if along any straight line passing through the centre (This is called the centre of inversion), at equal distances from it, the electron densities are equal and the orbital signs are the same (i.e., the wave function has the same amplitude and sign at the two points which are opposite and equidistant from the centre). If the electron densities are equal, but the orbital signs are opposite at the two points mentioned above, the symbol 'u' is used.

In the ' $\sigma$ ' type of orbitals, the bonding orbitals are 'g' and the antibonding 'u'; in the ' $\pi$ ' type of orbitals, the bonding orbitals are 'u' and the antibonding 'g'. Figure (a) and (b) below correspond to

## CHEMICAL BONDING and MOLECULAR STRUCTURE

overlap of 's' orbitals to form 'σ' type of M.O's; Figure (c) and (d) correspond to the formation of 'π' type of M.O's from 'p'-orbitals.



The equivalence of the different notations used to represent the M.O's is shown for a few cases (the x, y, z subscripts in the case of p-orbitals are dropped).

$$\sigma(2s) \Rightarrow \sigma_g(2s)$$

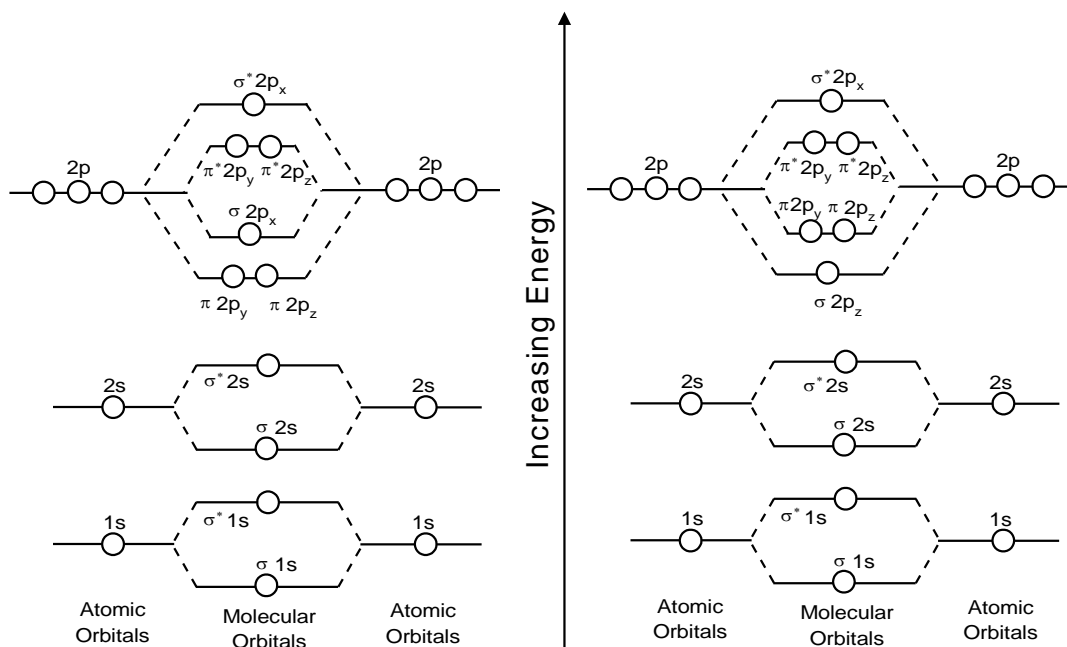
$$\sigma^*(2s) \Rightarrow \sigma_u^*(2s)$$

$$\sigma(2p) \Rightarrow \sigma_g(2p)$$

$$\sigma^*(2p) \Rightarrow \sigma_u^*(2p)$$

$$\pi(2p) \Rightarrow \pi_u(2p)$$

$$\pi^*(2p) \Rightarrow \pi_g^*(2p)$$



**For elements with  $Z < 7$**

**For elements with  $Z > 7$**

**Molecular orbital energy level diagram      Molecular orbital energy level diagram**

### 7.1 HOMONUCLEAR DIATOMIC MOLECULES

We shall now consider the electronic configuration of a few homonuclear diatomic molecules.

1.  $H_2$ : Electronic configuration of H atom:  $1s^1$ .

$\therefore$  in  $H_2$  molecule there are 2 electrons. M.O. configuration of  $H_2$  is  $\sigma 1s^2$ . There is no electron in antibonding M.O.  $\therefore$  Bond order (B.O.) =  $\frac{2-0}{2} = 1$

2.  $He_2$ : Electronic configuration of He atom:  $1s^2$

$\therefore$  in  $He_2$  molecule there are 4 electrons. The M.O. configuration for He is  $\sigma 1s^2, \sigma^* 1s^2$ .



$$\therefore \text{Bond order} = \frac{2-2}{2} = 0.$$

$\therefore$  He<sub>2</sub> molecule is not stable and does not exist.

In He<sub>2</sub><sup>+</sup>, the structure is  $\sigma 1s^2, \sigma^* 1s^1$ .

$$\therefore \text{B.O.} = \frac{2-1}{2} = \frac{1}{2}.$$

$\therefore$  He<sub>2</sub><sup>+</sup> is stable and can exist.

- 3.** Li<sub>2</sub>: (Li atom:  $1s^2 2s^1$ ). Total number of electrons in Li<sub>2</sub> = 6. Molecular orbital configuration of Li<sub>2</sub> is  $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^0$  or [KK]  $\sigma 2s^2, \sigma^* 2s^0$ .

where KK corresponds to filled  $\sigma(1s)$  and  $\sigma^*(1s)$  levels. The contribution of [KK] to bond order is zero. Therefore, we can ignore it and consider only the valence electrons.

$$\text{B.O.} = \frac{2-0}{2} = 1$$

$\therefore$  Li<sub>2</sub> is stable and it is found to exist to some extent in lithium vapour.

- 4.** Be<sub>2</sub>: (Be:  $1s^2 2s^2$ )

Molecular orbital structure of Be<sub>2</sub> is:

[KK]  $\sigma 2s^2, \sigma^* 2s^2$ . Ignoring [KK],

$$\text{B.O.} = \frac{2-2}{2} = 0. \therefore \text{Be}_2 \text{ is not stable.}$$

- 5.** B<sub>2</sub>: (B:  $1s^2 2s^2 2p^1$ )

M.O. structure of B<sub>2</sub> is

[KK]  $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^1, \pi 2p_z^1$ .

Note that though  $\pi(2p)$  orbital is usually more energetic than  $\sigma(2p)$ , there is an inversion of the order here due to mixing (hybridization) of  $\sigma(2s)$  and  $\sigma(2p)$  orbitals. Also note that the degenerate M.O's  $\pi(2p_y)$  and  $\pi(2p_z)$  have one electron in each according to Hund's principle.

$$\text{B.O.} = \frac{4-2}{2} = 1$$

$\therefore$  B<sub>2</sub> is stable.

Since there are two unpaired electrons in the molecule, B<sub>2</sub> is paramagnetic.

- 6.** C<sub>2</sub>: (C:  $1s^2 2s^2 2p^2$ ).

M.O. picture of C<sub>2</sub> is:

[KK]  $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi 2p_z^2$

Here again  $\pi(2p)$  orbital is less energetic than  $\sigma(2p)$ .

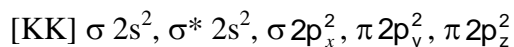
$$\text{B.O.} = \frac{6-2}{2} = 2 \text{ and the molecule is stable.}$$

## CHEMICAL BONDING and MOLECULAR STRUCTURE

Since there is no unpaired electron,  $C_2$  is diamagnetic. [If  $\pi(2p)$  orbital had been more energetic than  $\sigma(2p)$ ,  $C_2$  would have been paramagnetic, which is contrary to experimental observation.]

### 7. $N_2$ : (N: $1s^2 2s^2 2p^3$ ).

M.O. picture of  $N_2$  is:



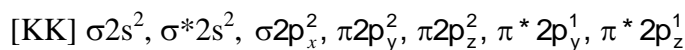
Ignoring the subscripts  $x$ ,  $y$  and  $z$  for the  $p$ -orbital and considering, only valence electrons, the representation is  $[KK] \{\sigma(2s)\}^2 \{\sigma^*(2s)\}^2 \{\pi(2p)\}^4 \{\sigma(2p)\}^2$ .

$$B.O. = \frac{8-2}{2} = 3$$

The molecule is diamagnetic. For  $N_2^+$ ,  $B.O. = \frac{7-2}{2} = 2.5$ .

### 8. $O_2$ : [O: $1s^2 2s^2 2p^4$ ]

M.O. structure of  $O_2$  is:



$$B.O. = \frac{8-4}{2} = 2$$

Due to the presence of unpaired electrons in the two antibonding orbitals (Hund's rule),  $O_2$  is paramagnetic. The M.O. theory here is superior to the V.B. theory, which does not explain the paramagnetic behaviour of  $O_2$ .

Let us now compare the bond strengths of  $O_2$ ,  $O_2^+$ ,  $O_2^-$ ,  $O_2^{2-}$ . For  $O_2$ ,  $B.O. = 2$ .

For  $O_2^+$ : one electron from the antibonding M.O. has been removed.

$$\therefore B.O. = \frac{8-3}{2} = 2.5$$

For  $O_2^-$ : one electron is added to the antibonding M.O.

$$\therefore B.O. = \frac{8-5}{2} = 1.5$$

$$\text{For } O_2^{2-}: B.O. = \frac{8-6}{2} = 1$$

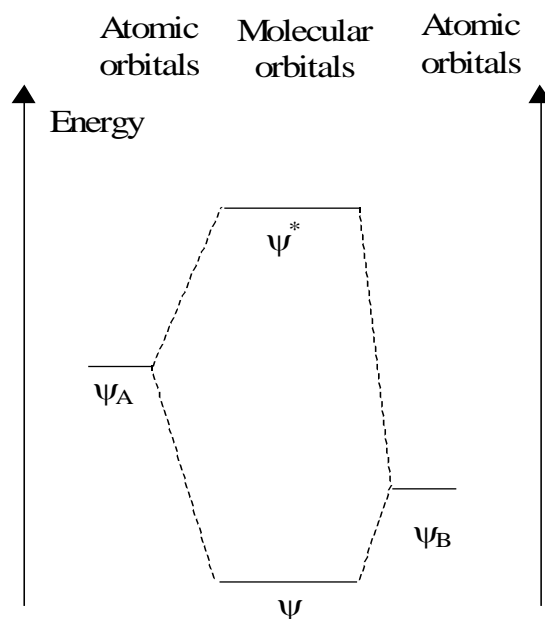
$\therefore$  the bond is strongest in  $O_2^+$  and the bond length the least.

## 7.2 HETERONUCLEAR DIATOMIC MOLECULES

The same principles apply when combining atomic orbitals from two different atoms as applied when the atoms were identical, that is:

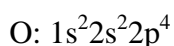
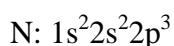
1. Only atomic orbitals of approximately the same energy can combine effectively.
2. They should have the maximum overlap.
3. They must have the same symmetry.

Since the two atoms are different, the energies of their atomic orbitals are slightly different. A diagram showing how they combine to form molecular orbitals are slightly different. A diagram showing how they combine to form molecular orbitals is given below:



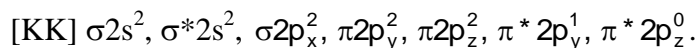
The problem is that in many cases the order of MO energy levels is not known with certainty. Thus we will consider first some examples where the two different atoms are close to each other in the periodic table and consequently it is reasonable to assume that the order of energy for the MO's is the same as for homo-nuclear molecules.

Eg. Nitric oxide (NO)



Simple combination of A.Os takes place, if they have nearly the same energy. This condition is approximately satisfied in the present case.

M.O. picture of NO is:



$$\text{B.O.} = \frac{8-3}{2} = 2.5$$

Due to the presence of an unpaired electron in an antibonding orbital, NO is paramagnetic.

Let us compare the B.Os in NO, NO<sup>+</sup>, NO<sup>2+</sup>, NO<sup>-</sup>.

For NO : B.O. = 2.5

For NO<sup>+</sup> : B.O. =  $\frac{8-2}{2} = 3$  (note that NO<sup>+</sup> is isoelectronic with N<sub>2</sub>)

## CHEMICAL BONDING and MOLECULAR STRUCTURE

$$\text{For NO}^{2+} : \text{B.O.} = \frac{7-2}{2} = 2.5$$

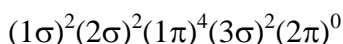
[NO<sup>2+</sup> is formed by removing 1e<sup>-</sup> from an antibonding orbital and 1e<sup>-</sup> from a bonding orbital of NO]

$$\text{For NO}^- : \text{B.O.} = \frac{8-4}{2} = 2 \text{ (Since B.O. is the greatest for NO}^+, \text{ the bond length is the least).}$$

Mostly, in a heteronuclear diatomic molecule, the energies of A.O's in one atom differ largely from the corresponding A.O's in the other atom. Hence the simple treatment of A.O. overlap discussed previously in the case of homonuclear diatomic molecules cannot be applied in the present case. A method based on hybridization of orbitals is employed, which we shall not discuss.

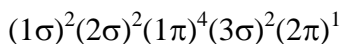
Let us take the case of **carbon monoxide** molecule. Let us apply the simple treatment of homonuclear diatomic molecules to the present case. The total number of **valence** electrons equals to 4 (from carbon) + 6 (from oxygen) will be distributed in the M.O's as: [KK]  $\sigma(2s)^2$ ,  $\sigma^*(2s)^2$ ,  $\sigma(2p)^2$ ,  $\pi(2p)^4$ , so that the bond order =  $\frac{8-2}{2} = 3$ . But this description does not explain all the properties of CO. For instance

on the basis of the simple treatment above, CO<sup>+</sup> must have a smaller bond order, equal to  $\frac{7-2}{2} = 2.5$ , since one electron has been removed from the bonding orbital  $\pi(2p)$  of CO. But the experimental observation is otherwise. The hybridization treatment however offers the explanation. Here again,  $\sigma$ ,  $\sigma^*$ ,  $\pi$  and  $\pi^*$  orbitals are formed, but through hybridisation (sp). The various orbitals (both bonding and antibonding) are numbered in a serial order and similarly the  $\pi$  orbitals. For the present case of CO, the M.O's in the ascending order of energy, formed from the 2s and 2p orbitals of C and O, are designated and the number of valence electrons in each M.O shown below.



According to one view,  $(1\sigma)^2$  and  $(3\sigma)^2$  electrons are **non-bonding**. The  $(2\sigma)^2$  electrons and the  $(1\pi)^4$  electrons are **bonding**, accounting for the triple bond in CO, one bond being of the ' $\sigma$ ' type and the other two of the ' $\pi$ ' type and the bond order = 3. The non-bonding  $(3\sigma)^2$  electrons are responsible for the donor character of CO, whereas the antibonding  $(2\pi)^0$  orbital, which is empty explains the acceptor property of CO in metal carbonyls (See "Importance of antibonding orbitals" by Orchin and Jaffe). According to another view, the orbital preceding the empty antibonding  $(2\pi)^0$  orbital must also have some antibonding character. In the formation of CO<sup>+</sup>, one electron is removed from this antibonding orbital, so that the bond order of CO<sup>+</sup> is expected to be greater than that of CO and this is experimentally observed (i.e., CO<sup>+</sup> is stable than CO).

In the case of the molecule NO, the difference in the electronegativities of N and O is not so much as that between C and O in CO. Hence the naive treatment of overlap of A.O's to give M.O's is able to explain the experimental observations for NO. (see an earlier paragraph). However, based on the hybridisation concept, as for CO, the M.O's for NO with the valence electrons in each M.O, are shown as:



Due to the presence of one electron in the  $(2\pi)$  antibonding orbital, the bond order of NO is  $\frac{1}{2}$  less than that of CO. So it is 2.5 (NO is paramagnetic). By removing the electron from the antibonding  $(2\pi)$  orbital, the species produced viz NO<sup>+</sup> (which is isoelectronic with N<sub>2</sub> and CO) gets a bond order of 3 and it is more stable than NO. By adding an electron to the  $(2\pi)$  orbital of NO, we get the species NO<sup>-</sup>, which has a bond order of 2 (less stable than NO).

## 8. Inter Molecular forces of attraction

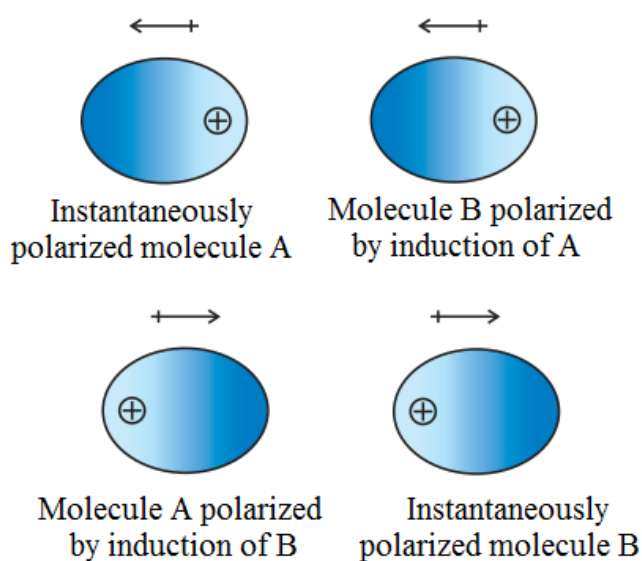
Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions (ionic bonds) and the forces that hold atoms of a molecule together (covalent bonds).

### 8.1 Van der Waals Forces

Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837-1923). Van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category. At this point, it is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces.

#### Dispersion Forces or London Forces

Atoms and nonpolar molecules are electrically symmetrical and have no net dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other. It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical i.e., the charge cloud is more on one side than the other. This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'. The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as London force. Another name for this force is dispersion force. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e.,  $1/r^6$  where  $r$  is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarizability of the particle.

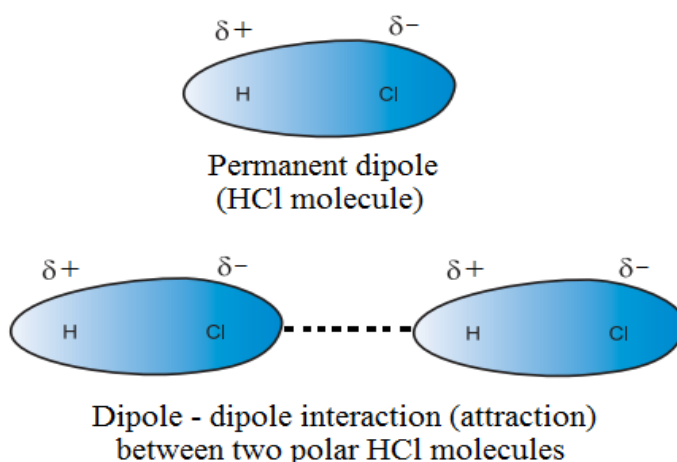


#### Dispersion forces or London forces between Non polar Molecules

## CHEMICAL BONDING and MOLECULAR STRUCTURE

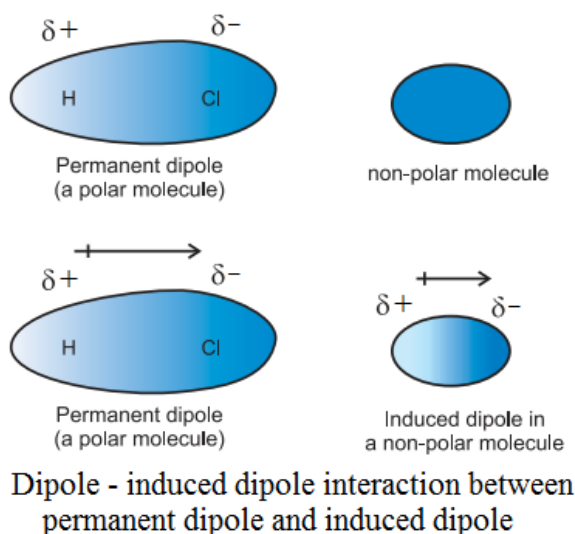
### Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter delta ( $\delta$ ). Partial charges are always less than the unit electronic charge ( $1.6 \times 10^{-19}$  C). The polar molecules interact with neighbouring molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to  $1/r^3$  and that between rotating polar molecules is proportional to  $1/r^6$ , where  $r$  is the distance between polar molecules. Besides dipole dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecules increases.



### Dipole–Induced Dipole Forces

This type of attractive forces operates between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to  $1/r^6$  where  $r$  is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarizability of the electrically neutral molecule. We have already learnt that molecules of larger size can be easily polarized. High polarizability increases the strength of attractive interactions. In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.



# CHEMICAL BONDING and MOLECULAR STRUCTURE

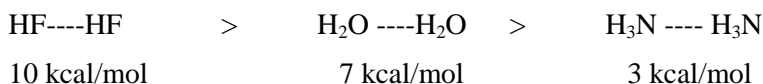
## 8.2 HYDROGEN BOND

A particularly strong type of dipole-dipole interaction is called hydrogen bonding. It is defined as the electrostatic attractive force between hydrogen atom attached to a highly electronegative and small atom (F / O / N only) and another highly electronegative atom (such as F, O, N and sometimes Cl). Hydrogen bond is merely a strong electrostatic force and not a normal chemical bond. It is denoted by dotted line (...)

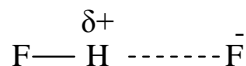


### Facts about Hydrogen-Bonding

- (a) Hydrogen bond is merely an electrostatic force rather than a chemical bond. Bond energy of Hydrogen bond is in the range of 3 to 10 k cal/mole. Which is about  $(1/10)^{\text{th}}$  the energy of a covalent bond (50 to 100 k cal/mole).
- (b) Hydrogen bond is much stronger attraction than weak Van der Waal's forces of attraction.
- (c) Hydrogen bond never involves more than two atoms.
- (d) With the increase of electronegativity and decrease in size of the atom to which hydrogen is covalently linked. The strength of the Hydrogen bond increases as



- (e) Strongest hydrogen bond is formed between  $\text{F}^-$  and HF



- (f) Hydrogen bonding is of two types (Intermolecular hydrogen bond & Intramolecular hydrogen bond).

### INTERMOLECULAR HYDROGEN BONDING

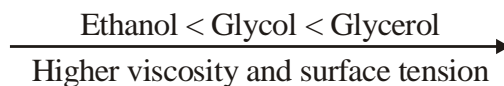
It is hydrogen bond between two molecules of same or different compound.

#### Condition of Inter Molecular Hydrogen Bond:

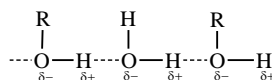
Condition of intermolecular hydrogen bond is the presence of at least 1 H covalently bonded to a highly electronegative and small neutral atom like F, O or N.

#### Effects of Intra Molecular Hydrogen Bond:

- (i) Inter molecular hydrogen bonds are strong intermolecular forces of attraction. Therefore, compounds capable of forming intermolecular hydrogen bond will have higher viscosity and surface tension, less volatility, low vapour pressure, high boiling points.

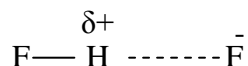


- (ii) Usually covalent compounds are insoluble in water. However, covalent compounds capable of forming intermolecular hydrogen bond with water are fairly soluble in water. Methanol, ethanol and dimethyl ethers are miscible with water. Compounds like glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) and sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) are highly soluble in water.



## CHEMICAL BONDING and MOLECULAR STRUCTURE

- (iii) Intra molecular hydrogen bond can explain the existence of compound like  $\text{KHF}_2$ .  $\text{KHF}_2$  exists as  $\text{K}^+$  ions and  $\text{HF}_2^-$  that is formed because of hydrogen bond.



### Examples of Intra Molecular Hydrogen Bond:

#### (i) Hydrogen fluoride:

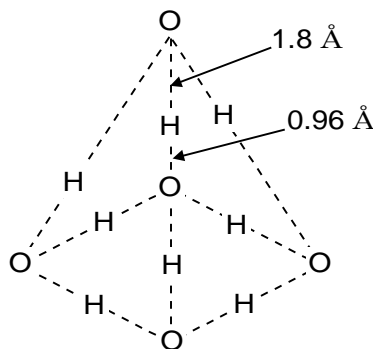
From molecular measurements, it is known that hydrogen fluoride is associated (i.e., many molecules are joined together).  $\text{HF}$  is a polar molecule, with the fluorine atom acquiring a slight negative charge and the hydrogen atom acquiring an equal positive charge. The electrostatic attraction between the oppositely charged ends results in hydrogen bonding as shown below.



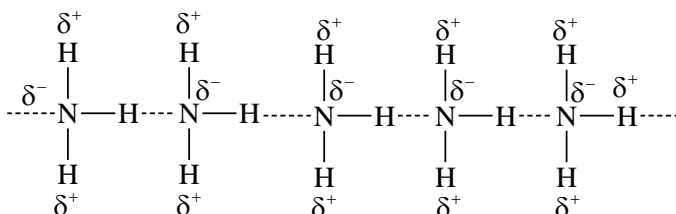
Many  $\text{H} - \text{F}$  units are held together, as  $(\text{HF})_n$ , by hydrogen bonding. The covalent  $\text{H} - \text{F}$  bond is much shorter than the  $\text{F} \dots \text{H}$  hydrogen bond; so a hydrogen bond is much weaker than a covalent bond. Fluorine, with the highest electronegativity forms the strongest hydrogen bond. The nature of the hydrogen bond is considerably electrostatic.

- (ii) **Water:** The high boiling point compared to that of hydrogen sulphide is due to molecular association through hydrogen bonding.

The crystal structure of ice shows a tetrahedral arrangement of water molecules. Each water molecule is surrounded tetrahedrally by 4 other water molecules. Hydrogen bonds link pairs of oxygen atoms together as shown in Figure given below. The arrangement of water molecules in ice is a very open structure and this explains the low density of ice. When ice melts, the structure breaks down and the molecules pack more closely together so that water has a higher density; this packing goes to a maximum upto a temperature of  $4^\circ\text{C}$ .



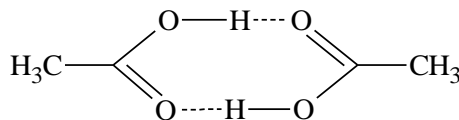
- (iii) **Ammonia** is also associated through hydrogen bonding; hence it has higher boiling point than  $\text{PH}_3$  or  $\text{AsH}_3$ .





## CHEMICAL BONDING and MOLECULAR STRUCTURE

- (iv) **Alcohols and phenols:** Lower alcohols and phenols are associated due to intermolecular hydrogen bonding. Methanol, ethanol and phenol have relatively much higher boiling points than methane or chloromethane, ethane or chloroethane, benzene or chlorobenzene respectively.
- (v) **Carboxylic acids:** In non-polar solvents, carboxylic acids exist as dimers. The dimer of acetic acid is represented as



In aqueous solution molecules of a carboxylic acid link up with water molecules through hydrogen bonding rather than forming dimers.

### INTRAMOLECULAR HYDROGEN BONDING

Sometimes hydrogen bonding may take place between 2 parts within a molecule; this is known as intramolecular (or internal) hydrogen bonding. It may lead to the linkage of two groups to form a ring; such an effect is known as chelation, in the case of complex compounds.

#### Conditions for Intra Molecular Hydrogen Bond:

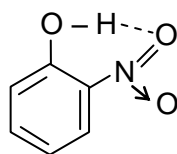
- Molecule must have at least 1 H covalently bonded to a highly electronegative but small atom like F, O or N.
- Molecule must have at least 1 another highly electronegative atom like F, O, N or Cl.
- Both the above parts must be close to each other.
- Intramolecular hydrogen bond does not result in the formation of 3 and 4 membered rings, although, larger rings can be formed.

#### Effects of Intra Molecular Hydrogen Bond:

- Intramolecular hydrogen bond decreases energy of the molecule and increases stability of molecule or ion.
- Intramolecular hydrogen bond increases attraction between two parts of a molecule and does not directly affect intermolecular forces of attractions.
- Intra molecular hydrogen bond originates at the expense of intermolecular hydrogen bond. While comparing isomers, we can say that isomer having intramolecular hydrogen bond will have lesser tendency to form intermolecular hydrogen bonds. Therefore, isomers capable of forming intramolecular hydrogen bond will have, more volatility (steam volatile), higher vapour pressure, lower boiling points and lesser solubility in water.

#### Examples of Intra Molecular Hydrogen Bond:

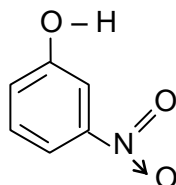
##### (i) Nitrophenols



o – nitrophenol

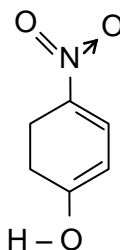
B.P.214°C

less soluble in water



m – nitrophenol

B.P.290 °C



p – nitrophenol

B.P.279 °C

comparatively more soluble

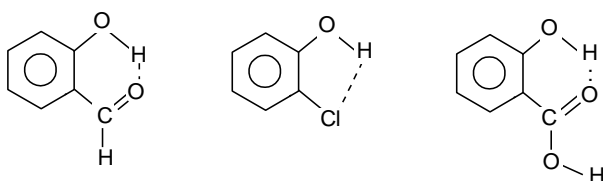
## CHEMICAL BONDING and MOLECULAR STRUCTURE

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Because of the proximity of  $-OH$  and  $-NO_2$  groups in o-nitrophenol there is intramolecular hydrogen bonding which prevents intermolecular hydrogen bonding between two or more molecules. Since molecular association cannot take place, the boiling point of o-nitrophenol is lower than that of the other two. Because of the distance between  $-OH$  and  $-NO_2$  groups in m- and p-nitrophenols there is no possibility of intramolecular hydrogen bonding. Intermolecular hydrogen bonding may take place to a certain extent which causes some degree of molecular association; this is responsible for the higher boiling points of the two nitrophenols.

Further the formation of intramolecular hydrogen bonding in o-nitrophenol prevents it from entering into intermolecular hydrogen bonding with water and this explains its reduced solubility.

- (ii) Other molecules in which intramolecular hydrogen bonding is present are o-hydroxybenzaldehyde, o-chlorophenol and o-hydroxybenzoic acid.

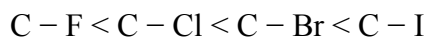


## 9. Important Characteristics of Bond Angle

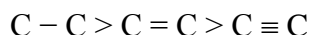
### 9.1 Bond Length

The average distance between centers of two bonded atoms is called bond length. Bond length depends upon:

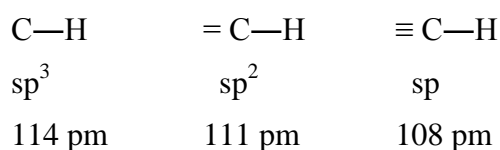
- (i) Size of Atom: Larger the size of atom more will be the bond length.



- (ii) Multiplicity of Bond (Bond Order): Bond length decreases with increasing multiplicity of bond (Bond Order).



- (iii) Type of Hybridisation: Size of s orbital is smallest. Hence more the percentage of s character, smaller will be the bond. C – H bond length is given as:



Bond lengths of few common bonds are given below:

$\text{H}_3\text{C} - \text{CH}_3$	$\text{H}_2\text{C} = \text{CH}_2$	$\text{HC} \equiv \text{CH}$	$\text{C} - \text{H}$	$= \text{C} - \text{H}$	$\equiv \text{C} - \text{H}$
154 pm	134 pm	120 pm	114 pm	111 pm	108 pm

### 9.2 Bond Energy

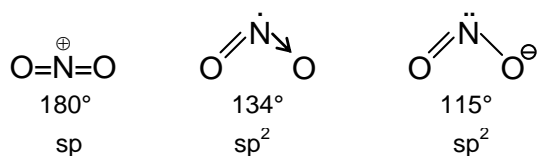
The energy required to break one mole bonds of a particular type to produce isolated gaseous atoms is called bond dissociation energy. Stronger the bond, greater will be the bond dissociation energy. Since a particular type of bond present in different molecules (O – H bond in  $\text{H}_2\text{O}$ , ROH etc) or even in same molecules (four C – H bonds in  $\text{CH}_4$ ) do not possess same bond dissociation energy, therefore an average value called bond energy is used. Bond energy of a particular bond depends on:

- (i) Size of atoms: Larger the size of atoms, more is bond length and lesser is bond strength & bond energy.  
 (ii) Multiplicity of bond: Higher the multiplicity of bond, shorter and stronger will be the bond and higher will be the bond energy.  
 (iii) Type of Hybridisation: Size of s orbital is smallest. Hence more the percentage of s character, stronger will be the bond.

### 9.3 Bond Angle

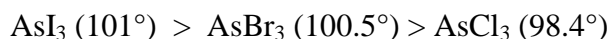
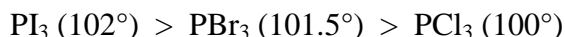
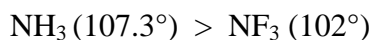
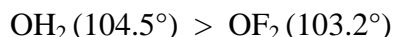
The angle between the atoms bonded to a common atom is called bond angle. Since covalent bonds are directional in nature, covalent molecules have specific angles between bonded atoms. Bond angle depends on the type of hybridization, on the presence of lone pairs in the molecule and on steric hindrance (repulsion) of two non-bonded atoms or group.

1. Lone pair causes greater repulsions than a lone electron. For example,

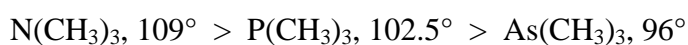
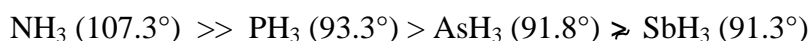
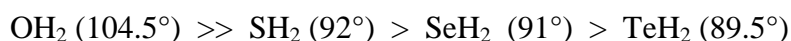


## CHEMICAL BONDING and MOLECULAR STRUCTURE

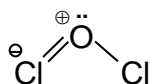
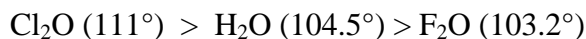
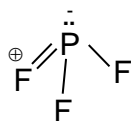
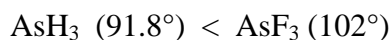
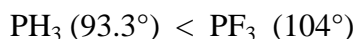
2. More the electronegativity of surrounding atom more is distance of bond pairs from central atom as well as from each other. Therefore, repulsion and the angle between bonds decrease with increasing electronegativity of surrounding atom. For example,



3. More the electronegativity of central atom lesser is distance of bond pairs from central atom as well as from each other. Therefore, repulsion and the angle between bonds increase with increasing electronegativity of central atom. For example,



4. When an atom with a filled valence shell & one or more lone pairs is bonded to an atom with an incomplete valence shell, or a valence shell that can become incomplete by electron shifts, there is a tendency for the lone pairs to be partially transferred from the filled to the unfilled shell.



5. Repulsion by a lone pair or by a double & triple bond is more than repulsion by a single bond.

Using above facts one can rationalize the bond angle trends which are given below:

Molecule	Angles		
	XCX	XCO	XCC
F <sub>2</sub> CO	108°	126°	—
Cl <sub>2</sub> CO	111°	124°	—
(NH <sub>2</sub> ) <sub>2</sub> CO	118°	121°	—
F <sub>2</sub> SO	93°	107°	—
H <sub>2</sub> C=CF <sub>2</sub>	110°	—	125°
OPF <sub>3</sub>	103°	—	—
OPCl <sub>3</sub>	104°	—	—
H <sub>2</sub> C=CCl <sub>2</sub>	114°	—	123°

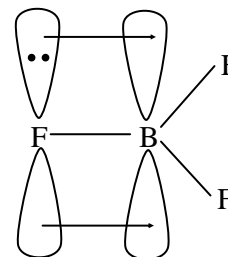
### 9.4 GENERAL CHARACTERISTICS OF COVALENT COMPOUNDS

- (i) In a purely covalent compound the electrons in the bond are shared equally between the atoms linked by the bond; the resultant particles formed are not electrically charged. So, separate molecules of the covalent compounds exist. Covalent compounds may therefore be expected to be gases or low boiling liquids or soft, low melting solids at ordinary temperature. In the solid state they may be amorphous or present as molecular crystals, the molecules being held together by what are called weak van der Waals' forces of attraction.
- (ii) Since the molecules are held together by weak van der Waals' forces, covalent compounds (except those consisting of giant molecules) have low melting and boiling points; very little thermal energy is needed to overcome these weak intermolecular forces.
- (iii) They are non-electrolytes, i.e., they do not contain ions. Even in giant molecules such as diamond there are no free electrons. So they are very poor conductors of electricity.
- (iv) They are generally soluble in organic (non-polar) solvents such as benzene or carbon tetrachloride but are insoluble in water or other ionizing solvents. (The solubility of covalent compounds is very much dependent on the size of the molecules; giant molecules are practically insoluble in nearly all solvents.)
- (v) Reactions between covalent compounds are slow and often incomplete and reversible. This is so because the reaction involves breaking and making of bonds i.e., energy considerations are involved for reactants, activated complexes and products.
- (vi) A covalent bond is a space-directed bond and it may exhibit isomerism.

## 10. Special Bonding Situation

### 10.1 BACK BONDING

When a highly electronegative atom is covalently bonded to an electron deficient atom, electron deficiency is further expected to increase. However, if the highly electronegative atom contains a lone pair in an orbital and electron deficient atom also contains an empty p orbital, they can overlap with each other to form a coordinate bond or dative bond. This type of bonding is called back bonding or back donation.



This back donation compensates the electron deficiency of boron atom and decreases the Lewis acidic strength. This type of back bonding is more effective in small atoms.

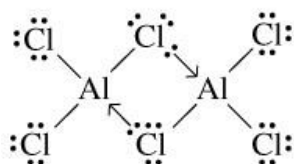


Order of Acidic strength

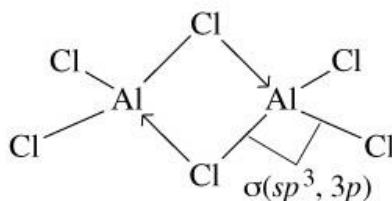
$p\pi - d\pi$  bonding in  $\text{SO}_4^{2-}$  can also be explained in the same manner.

### 10.2 Dimerization through $\sigma$ coordination bonds

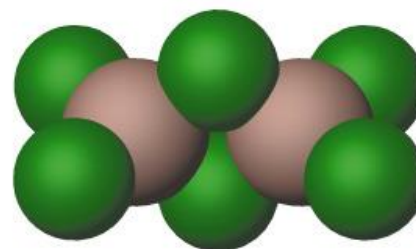
When a larger atom is covalently bonded to form an electron deficient central atom, lone pair of orbitals of surrounding atom cannot effectively overlap with each other to form a coordinate  $\pi$  bond or dative  $\pi$  bond. In such conditions, lone pair of surrounding atom will prefer to form coordinate  $\sigma$  bond or dative  $\sigma$  bond.



Lewis structure



Bonding scheme

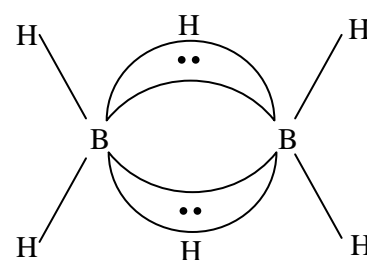
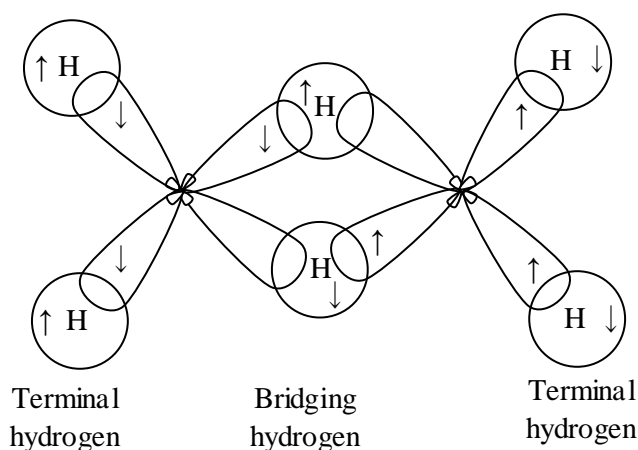
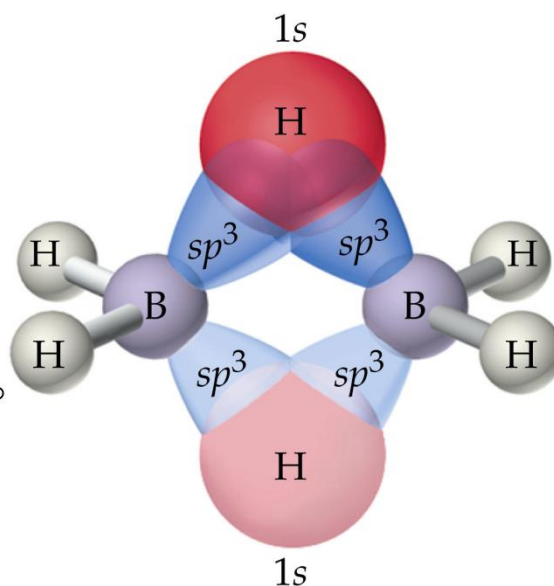
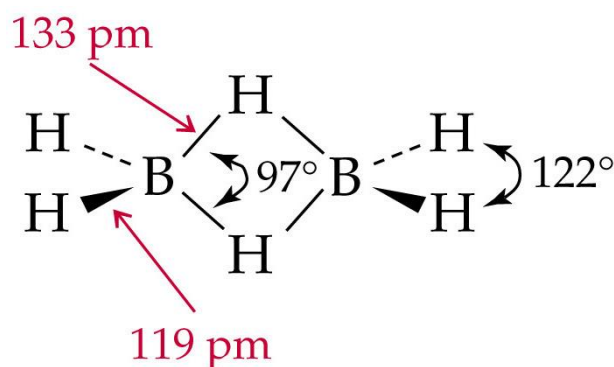


Space-filling model

### 10.3 BANANA BONDING (two electron-three center bond)

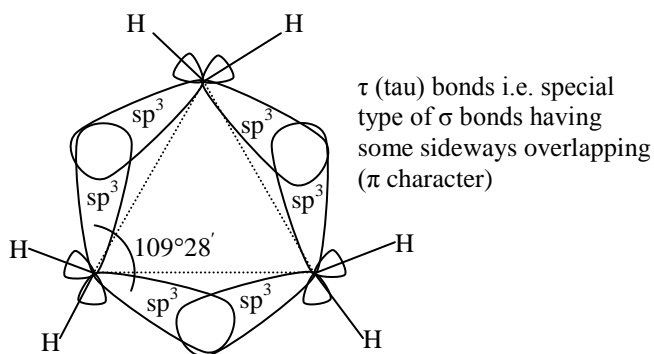
Dilthey explained the structure of  $\text{B}_2\text{H}_6$  (Dimer of  $\text{BH}_3$ ) by introducing the concept of two electron-three center bond. The experiments revealed that  $\text{B}_2\text{H}_6$  contains two different types of hydrogen atom (Terminal and bridging). According to him, each boron atom in  $\text{B}_2\text{H}_6$  is  $sp^3$  hybrid (three  $sp^3$  hybrid orbitals are half filled and one is empty). Two hybrid orbitals of each boron atom overlap with one s orbital of hydrogen atom resulting in the formation of four sigma bonds.

One of the remaining orbital of each boron (one half filled orbital of one boron atom and empty orbital of other boron atom) overlaps simultaneously with half-filled orbitals of hydrogen atom. This bond is called two electron three center bond or banana bond due to its banana like shape.



## 10.4 STRAIN IN A CYCLIC COMPOUND

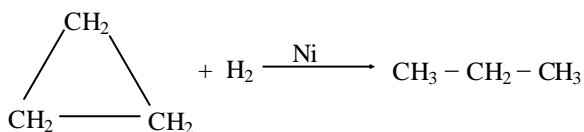
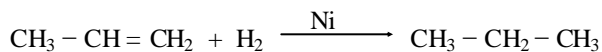
If the angles between the atoms and angle between the orbitals are not same, the overlapping of orbitals cannot occur along the internuclear axis but occur in a slightly sideways manner as shown below:



Since the overlapping of hybrid orbitals is sideways, the extent of overlapping is lesser than inter nuclear head on overlapping and the bonds are weaker than the normal bond. Strength of such bonds lies between those of  $\sigma$  bonds and  $\pi$  bonds. Such molecules are said to be destabilized due to this bond strain. Bond strain does not mean that the angle between the orbitals is decreased by force; rather bond strain means that bond angle is less than the angle between orbitals and the resultant  $\sigma$  bonds are slightly weaker due to lesser extent of overlapping.

## CHEMICAL BONDING and MOLECULAR STRUCTURE

More the deviation of bond angles from the orbitals angles, lesser is the strength of resultant bond and more is the strain in the bonds.

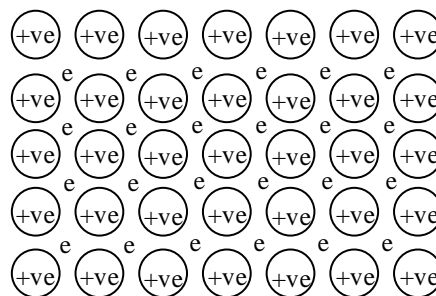


Cyclopropane, for example, can undergo hydrogenation like propene, although at a slightly higher temperature i.e. with a slight more difficulty.

### 10.5 Metallic Bond:

#### (a) Electron Sea Model or Electron Gas Model

The constituent particles of metallic solids are held together by strong forces called metallic bond. Lorentz proposed that metals lose their valence electrons due to small ionization energy and form positively charged species called metal kernels. In crystal lattice metal kernels occupy the lattice positions, whereas, the electrons occupy the vacant space (voids) between the metal kernels. The strong electrostatic force of attraction between the electrons and the metal kernels hold them together in the crystal lattice. Since the electrons are free and can move in the entire lattice, this model of metallic bond is called electron gas model or electron sea model. This model can explain the properties of metals.



Electron Sea Model

The forces of attraction between metals are due to valence electrons (free electrons), hence, more the valence electrons in metal stronger will be the metallic bond.

#### Properties of Metals:

The characteristics of metallic bonds explain a number of the unique properties of metals as shown below:

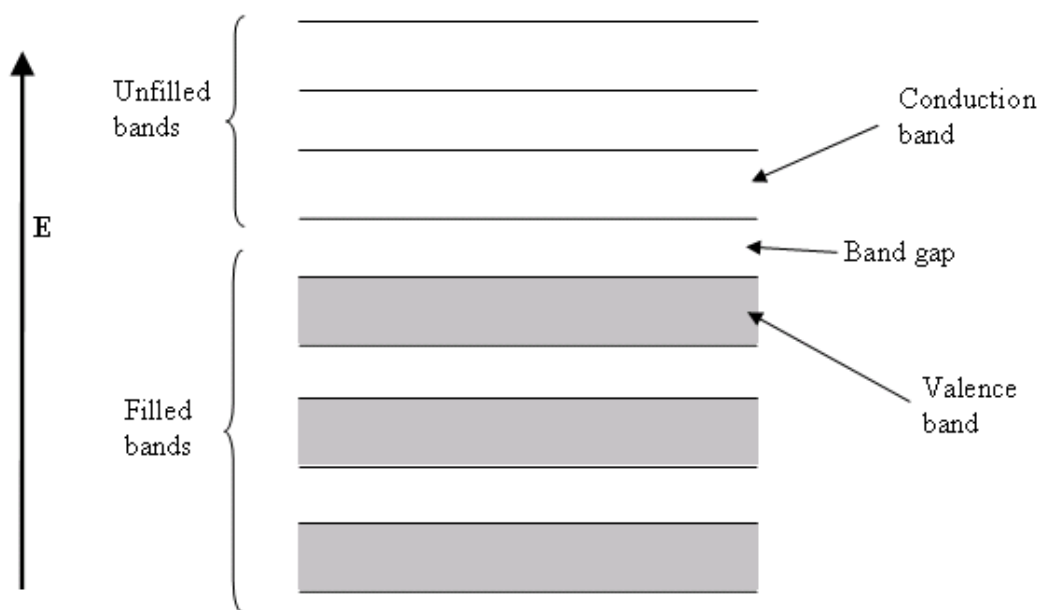
- Metals are good conductors of electricity because the electrons in the electron sea are free to flow and carry electric current.
- Metals are ductile (able to be drawn out into thin wires) and malleable (they can be hammered or pressed permanently out of shape without breaking or cracking) because local bonds can be easily broken and reformed.
- Metals are shiny. Light cannot penetrate their surface; the photons simply reflect off the metal surface. However, there is an upper limit to the frequency of light at which the photons are reflected.
- Metallic bonds can occur between different elements, forming an alloy. Aluminium foil and copper wire are examples of metallic bonding in action.
- Metallic bonds are mediated by strong attractive forces. This property contributes to the low volatility, high melting and boiling points, and high density of most metals. The group-12 metals (zinc, cadmium, and mercury) are exceptions to this rule.



## CHEMICAL BONDING and MOLECULAR STRUCTURE

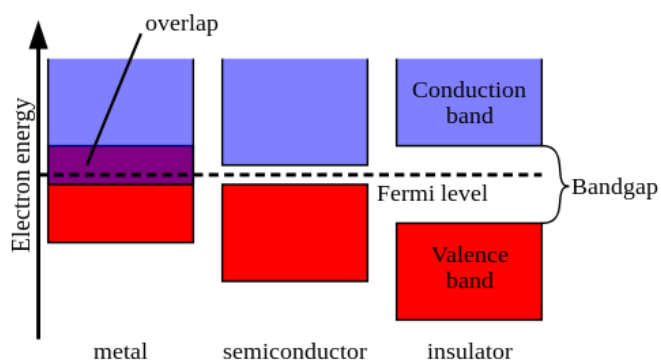
### (b) Band Theory

Electrons in free atoms have discrete energy values. In contrast, the energy states available to the free electrons in a metal sample form a continuum of "energy bands." In the atomic lattice of a substance, there is a set of filled atomic energy "bands" with a full complement of electrons, and a set of higher energy unfilled "bands" which have no electrons. The highest energy band containing valence electrons is available for chemical reactions. The conduction band is the band above the valence band. Electrons in the conduction band are free to move about in the lattice and can conduct current. In order for a substance to conduct electricity, its valence electrons must cross the band gap, which is the energy gap between the valence band and conduction band.



Band Structure

The gap between the valence and conduction bands determines whether a substance will conduct electricity easily or not. If the gap between the valence and conduction bands is large, then the substance does not conduct electricity easily (it is an insulator). On the other hand, these bands overlap in metallic samples, which make these samples excellent conductors of electricity. In the case of semiconductors, the gap is small enough for electrons to jump to the conduction band due to thermal or some other excitation.



Energy Bands in Solids

The overlap or size of the gap between the valence and conduction bands determines the electrical conductivity of a substance. Because the band gap is so small for semiconductors, doping with small amounts of impurities can dramatically increase the conductivity of the material. Doping, therefore, allows scientists to exploit the properties of sets of elements referred to as "dopants" in order to modulate the conductivity of a semiconductor.