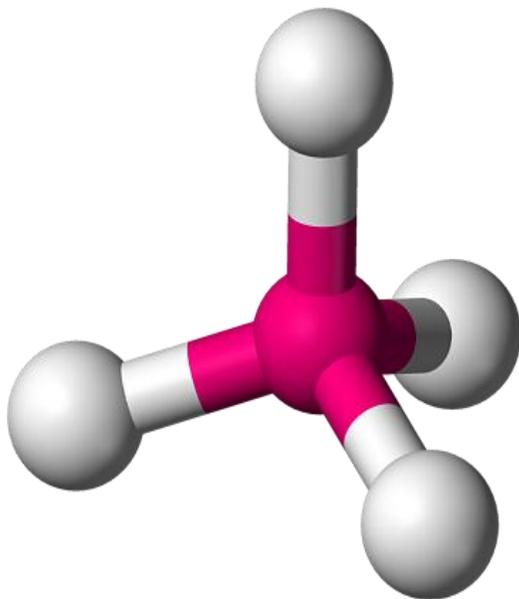


## Chemical Bonding and Molecular Structure

### Chemical bond:-

Chemical bond is the attractive force which holds various constituents together in a molecule.

There are three types of chemical bonds: Ionic Bond, Covalent Bond, Co-ordinate Bond.

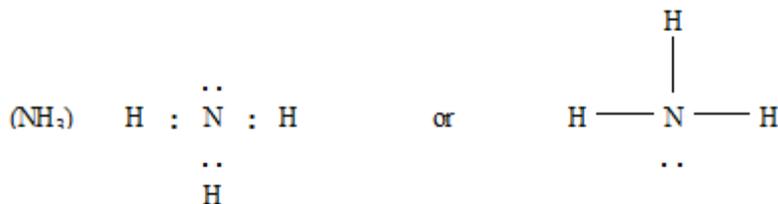


### Octet Rule:

Atoms form chemical bonds in order to complete their octet i.e. eight electrons in their valence shell.

### Lewis Structures:

- Pair of bonded electrons is by means of a 'dash' (-) usually called a 'bond'.
- Lone pairs or 'non-bonded' electrons are represented by 'dots'.
- Electrons present in the last shell of atoms are called valence electrons.



### Exceptions to the Octet Rule:

# Chemical Bonding and Molecular Structure

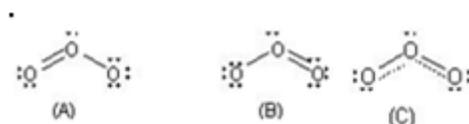
- Species with odd number of electrons: NO, NO<sub>2</sub>,
- Incomplete octet for the central atom: LiCl, BeH<sub>2</sub> and BCl<sub>3</sub>
- Expanded octet for the central atom: PF<sub>5</sub>, SF<sub>6</sub> and H<sub>2</sub>SO<sub>4</sub>

## Formal Charge:

- Formal charge is the difference between the number of valence electrons in an isolated atom and number of electrons assigned to that atoms in Lewis structure.
- Formal charge = [Total number of valence electrons in the free atom] - (Total number of lone pairs of electrons) - 1/2(Total number of shared electrons i.e. bonding electrons)]

## Resonance:

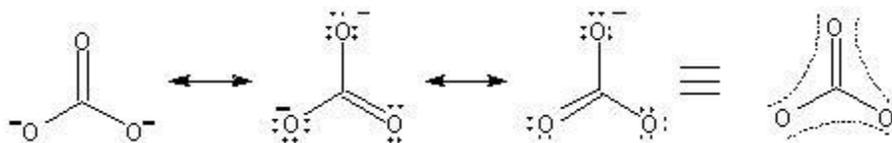
- For molecules and ions showing resonance it is not possible to draw a single Lewis structure.
- All the properties of such species can only be explained by two or more Lewis structures. Example: Resonance of O<sub>3</sub>



A and B are resonating or canonical structures and C is the resonance hybrid

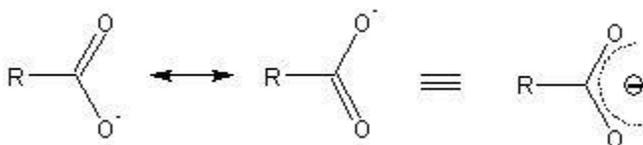
Some other examples

(i) CO<sub>3</sub><sup>2-</sup> ion



Example

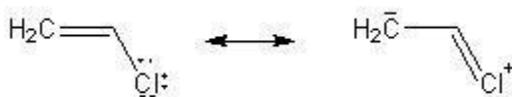
(ii) Carbon-oxygen bond lengths in carboxylate ion are equal due to resonance.



Benzene



(iv) Vinyl Chloride



## Ionic Bonding:

### Formation of Ionic Bond:

- Formation of ionic bond takes place between a metal and a non-metal by transfer of electron.
- Steps involved in formation of an ionic bond: :

Steps	Equation	Energy involved
Formation of gaseous cations	$A(g) + \text{I.E.} \rightarrow A^+(g) + e$	Ionization Energy
Formation of gaseous anions	$X(g) + e \rightarrow X^-(g) + \text{E.A.}$	Electron Affinity
Packing of ions of opposite charges to form ionic solids	$A^+(g) + X^-(g) \rightarrow AX(s) + \text{Energy}$	Lattice energy

### Conditions required of formation of ionic bonds:

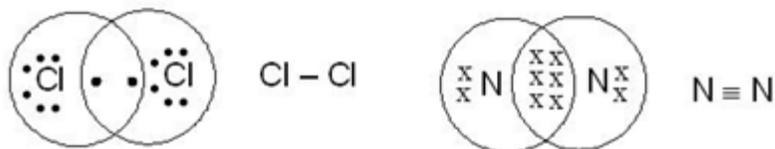
- Low I.E of cation.
- High E.A of anion.
- High lattice energy.

## Covalent Bonding:

- Covalent bond is formed between two non-metals by sharing of electrons.
- Electron pairs which participate in bonding are called bond pairs.

# Chemical Bonding and Molecular Structure

- Electron pairs which do not participate in bonding are called lone pairs.
- There could be single, double or triple covalent bonds between two elements depending on the number of electrons being shared.



## VSEPR (Valence Shell Electron Pair Repulsion) Theory:

- The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.
- Order of the repulsion: Lone pair ↔ Lone pair > Lone pair ↔ Bond pair > Bond pair ↔ Bond pair.
- Repulsion among the bond pairs is directly proportional to the bond order and electronegativity difference between the central atom and the other atoms.

### Determination of shape of molecules using VSEPR theory:

- Calculate X using following method.
  - $X = (\text{No. of valence electrons of central atom}) + (\text{No. of other atoms}) + (\text{Negative charge on the molecule}) - (\text{Positive charge on the molecule})$
  - Use the following chart to find the shape.

X	Shape	Examples
2	Linear	HgCl <sub>2</sub> /BeCl <sub>2</sub>
3	Triangular planar	BF <sub>3</sub>
3	Angular	SnCl <sub>2</sub> , NO <sub>2</sub>
4	Tetrahedral	CH <sub>4</sub> , BF <sub>4</sub> <sup>-</sup>
4	Trigonal Pyramidal	NH <sub>3</sub> , PCl <sub>3</sub>
4	Angular	H <sub>2</sub> O
5	Trigonal bipyramidal	PCl <sub>5</sub> , PF <sub>5</sub>
5	Irregular tetrahedral	SF <sub>4</sub> , IF <sub>4</sub> <sup>+</sup>
5	T-shaped	ClF <sub>3</sub> , BrF <sub>3</sub>
5	Linear	XeF <sub>2</sub> , I <sub>3</sub> <sup>-</sup>
6	Octahedral	SF <sub>6</sub> , PF <sub>6</sub> <sup>-</sup>
6	Square Pyramidal	IF <sub>5</sub>
6	Square planar	XeF <sub>4</sub> , ICl <sub>4</sub>

## Fajan's Rule:

It accounts for the covalent character in ionic compounds.

Covalency is favoured by

- Smaller cation .
- Larger anion and
- Large charge on either ion.

## Dipole Moment:

- Dipole moment of any bond is the product of the net positive or negative charge and distance between the two charged ends, i.e., the bond length. i.e. Dipole moment (m) = electronic charge (e) × Distance (d) Dipole moment is measured in debye unit (D);
- Dipole moment of a molecule is vector addition of all the individual bond moments.

## Percentage Ionic Character:

The percent ionic character =

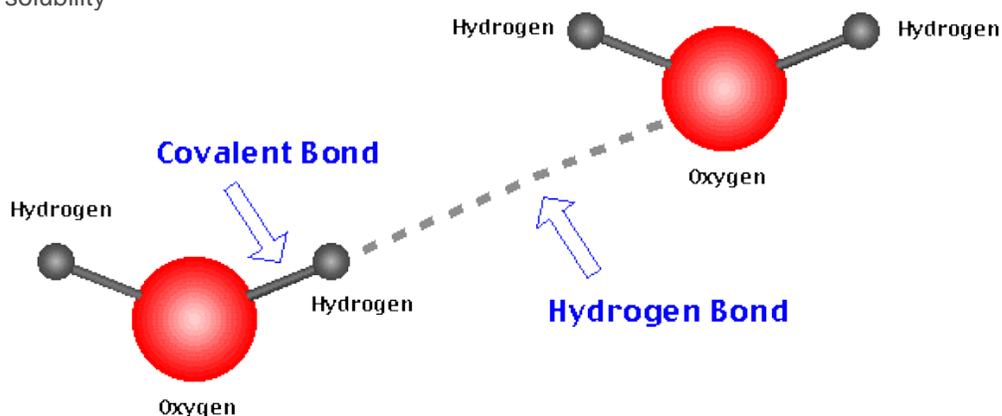
$$\frac{\text{Observed dipole moment}}{\text{Expected dipole moment}} \times 100$$

## Hydrogen Bonding:

- Hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule or a part of a molecule and an electronegative atom (such as F, O, N) of another molecule (Inter-molecular hydrogen bonding) or another part of the same molecule (intramolecular hydrogen bonding).
- Intermolecular hydrogen bonding increases boiling point of the compound and also its water solubility

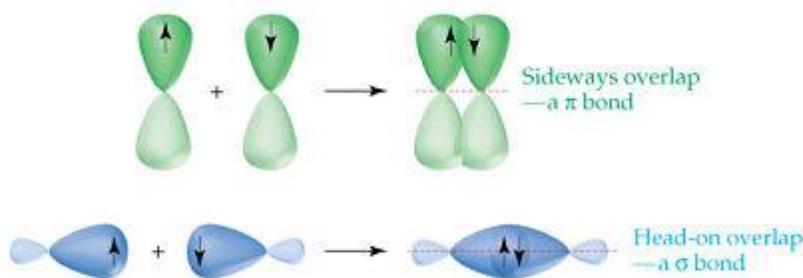
# Chemical Bonding and Molecular Structure

- Intramolecular hydrogen bonding decreases the boiling point of the compound and also its water solubility

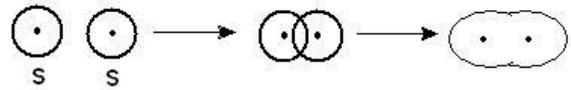
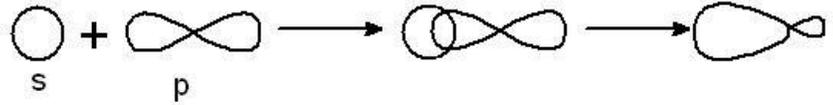
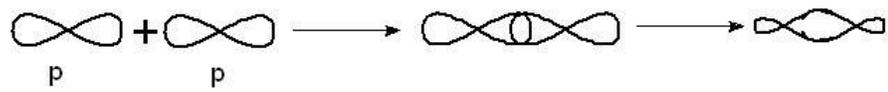


## Valence bond theory (VBT):

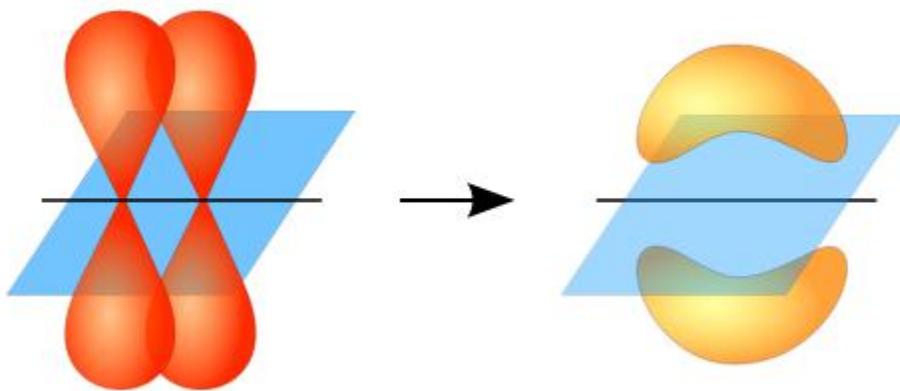
- A covalent bond is formed by overlapping of valence shell atomic orbital of the two atoms having unpaired electron.
- There is maximum electron density between the bonding atoms.
- Greater the overlapping of atomic orbital higher is the strength of chemical bond.
- The bond formed by lateral overlap of two atomic orbitals having maximum overlapping on both sides of the line connecting the centres of the atoms is called a  $\pi$ -bond. A  $\pi$ -bond possess a plane of symmetry, often referred to as the nodal plane.



**$\sigma$ -Bond** : When covalent bond is formed by overlapping of atomic orbitals along the same axis it is called s - bond. Such type of bond is symmetrical about the line joining the two nuclei e.g.

(a) s-s overlapping	
(b) s-p overlapping	
(c) p-p overlapping	

**$\pi$  - Bond:** This type of bond is formed by the sidewise or lateral overlapping of two half filled atomic orbitals.



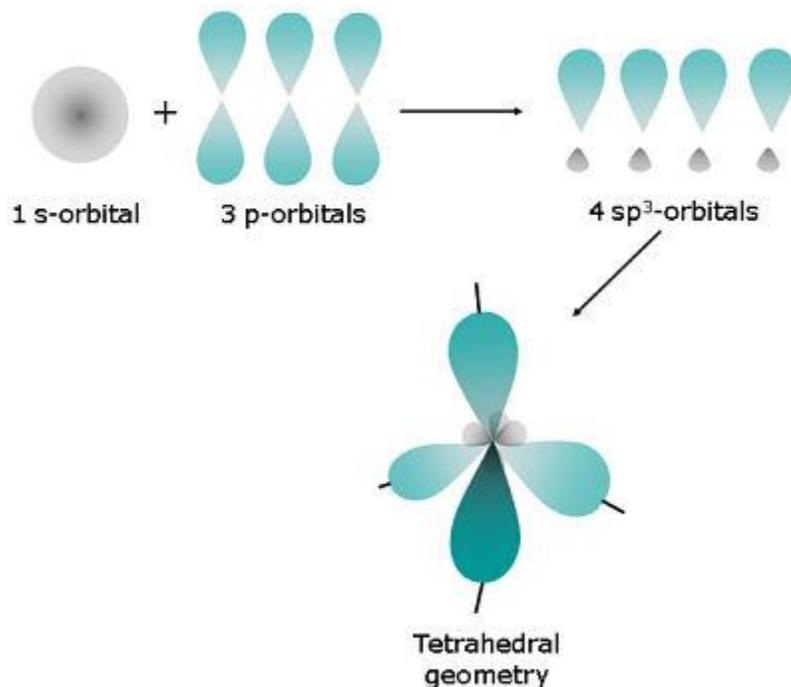
[The strength of a bond depends upon the extent of overlapping of half-filled atomic orbitals. The extent of overlapping is between two atoms is always greater when there is end to end overlapping of orbitals than, when there is sidewise overlapping of orbitals. Hence s-bond is always stronger than p-bond.]

The average distance between the nuclei of the two bonded atoms in a molecule is called bond length and the energy required to break one mole of bonds of particular type in gaseous state is called Bond energy or Bond strength. The same amount of energy is released in formation of one mol of particular bond.

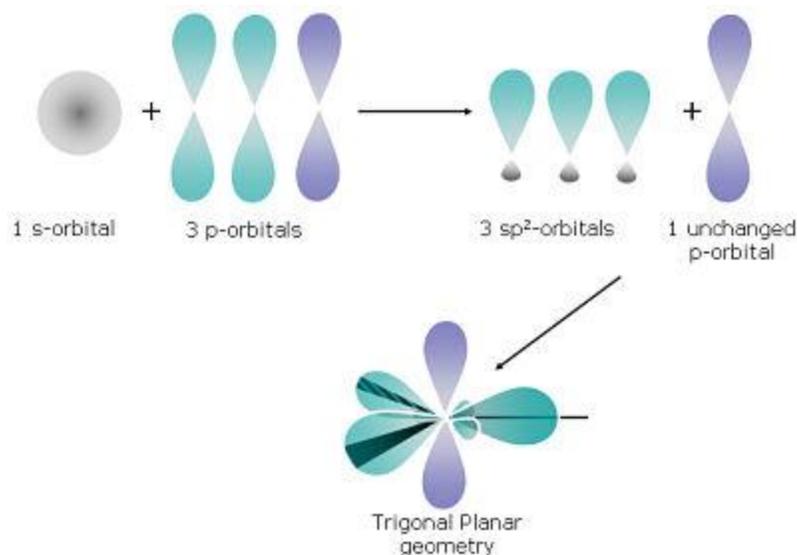
## Hybridization:

- The mixing of dissimilar orbital of similar energies to form new set of hybrid orbital.
- Number of hybrid orbital formed is equal to the no. of orbital taking part in hybridization.
- Depending upon the different combination of s and p orbitals, these types of hybridization are known.

**sp<sup>3</sup> hybridization:** In this case, one s and three p orbitals hybridise to form four sp<sup>3</sup> hybrid orbitals. These four sp<sup>3</sup> hybrid orbitals are oriented in a tetrahedral arrangement.

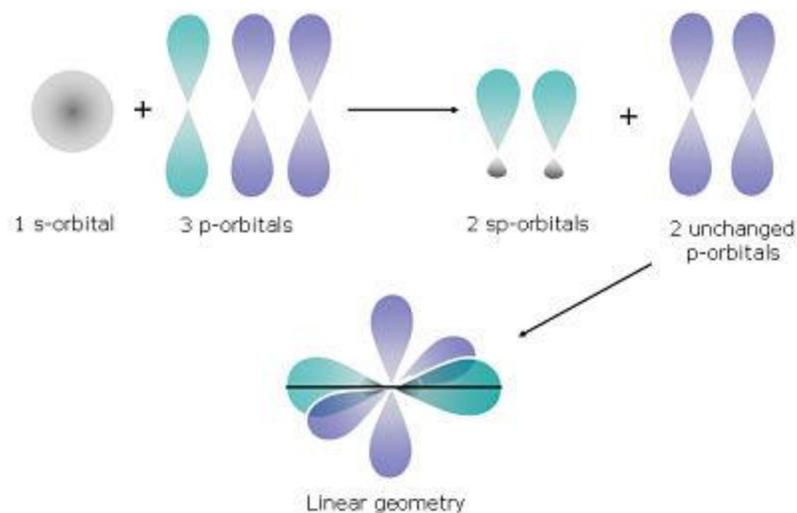


**sp<sup>2</sup> hybridization:** In this case one s and two p orbitals mix together to form three sp<sup>2</sup> hybrid orbitals and are oriented in a trigonal planar geometry.



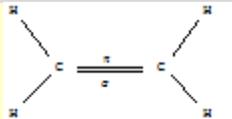
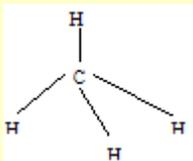
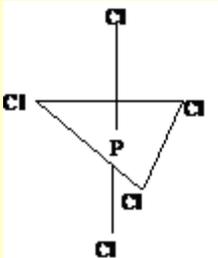
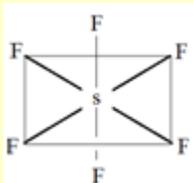
The remaining p orbital if required form side ways overlapping with the other unhybridized p orbital of other C atom and leads to formation of  $p_2C = CH_2$  bond as in H

**sp hybridization:** In this case, one s and one p orbital mix together to form two sp hybrid orbitals and are oriented in a linear shape .



The remaining two unhybridised p orbitals overlap with another unhybridised p orbital leading to the formation of triple bond as in  $HC \equiv CH$ .

Hybridization	Total Number of orbitals taking part	Shape	Examples
sp	2 (one s and one p)	Linear	$H-C \begin{matrix} \pi \\ \pi \\ \sigma \end{matrix} C-H$
$sp^2$	3 (one s and two p)	Trigonal planar	

			
$sp^3$	4 (one s and three p)	Tetrahedral	
$sp^3d$	5 (one s, three p and one d)	Trigonal bipyramidal	
$sp^3d^2$	6 (one s, three p and two d)	Octahedral	

## Bond Characteristics:

### Bond Length:

- The distance between the nuclei of two atoms bonded together is called bond length.
- It is expressed in angstrom ( $\text{\AA}$ ) units or picometer (pm).
- Bond length in ionic compound =  $r_c^+ + r_a^-$
- Bond length in covalent compound (AB) =  $r_A + r_B$

### Important features of bond length

1. The bond length of the homonuclear diatomic molecules are twice the covalent radii.
2. The lengths of double bonds are less than the lengths of single bonds between the same two atoms, and triple bonds are even shorter than double bonds. Single bond > Double bond > Triple bond (decreasing bond length)
3. Bond length decreases with increase in s-character since s-orbital is smaller than a p-orbital.  
 $sp^3C - H = 1.112\text{\AA}$ ;       $sp^2C - H = 1.103\text{\AA}$ ;       $spC - H = 1.08\text{\AA}$ ;

# Chemical Bonding and Molecular Structure



(25% s-character as in alkanes) (33.3% s-character as in alkenes) (50% s-character as in alkynes)

4. Bond length of polar bond is smaller than the theoretical non-polar bond length.

## Application of MOT to Homonuclear Diatomic Molecules

Species	Total number of electrons	Electronic configuration	Bond order	Magnetic Behaviour
$H_2^+$	1	$s\ 1s^1$	$(1-0)/2 = 1/2$	Paramagnetic
$H_2$	2	$s\ 1s^2$	$(2-0)/2 = 1$	Diamagnetic
$He_2^+$	3	$s1s^2, s^* 1s^1$	$(2-1)/2 = 1/2$	Paramagnetic
$He_2$	4	$s1s^2, s^* 1s^2$	$(2-2)/2 = 0$	Molecule does not exist
$O_2$	16	$s1s^2, s^* 1s^2, s2s^2, s^*2s^2, s2p_x^2, p2p_y^2, p2p_z^2, p^*2p_y^1, p2p_z^1$	$(10-6)/2 = 2$	Paramagnetic

## Application of MOT to Heteronuclear Diatomic Molecules

Molecules/Ions	Total No. of electrons	Magnetic behaviour
CO	14	Diamagnetic
NO	15	Paramagnetic
$NO^+$	14	Diamagnetic
$NO^-$	16	Diamagnetic
CN	13	Paramagnetic
$CN^-$	14	Diamagnetic