CHAPTER - 04
CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemical bond

It is the force of attraction between the constituent particles like ions, atoms, metal ions and molecules, in order to get the stability.
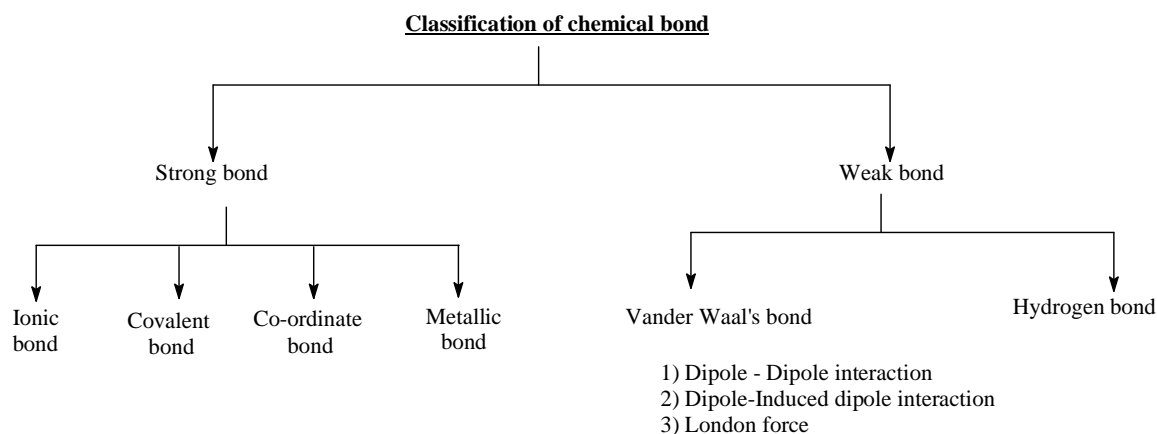
- Chemical bonding process accompanied by decrease in energy.

- Decrease in energy α strength of the bond.

Causes of chemical combination

I.   Tendency to acquire minimum energy.

1.   When two atoms approaches to each other. There is attractive forces between nucleus and electron and vice versa.

2.   Also repulsive forces present between nucleus and electrons of two atoms.

3.   Attractive forces are dominant than repulsive force, therefore total energy of the system decreases.

4.   Stability $\alpha \dfrac{1}{\text{energy}} \alpha$ attractive force $\alpha \dfrac{1}{\text{repulsive force}}$

5.   Bond formation is exothermic.

II.   Tendency to acquire stable configuration

<u>**Classification of chemical bond**</u>

Strong bond   Weak bond

Ionic bond   Covalent bond   Co-ordinate bond   Metallic bond   Vander Waal's bond   Hydrogen bond

1) Dipole - Dipole interaction
2) Dipole-Induced dipole interaction
3) London force

In order to explain the chemical bond as well as molecular structure the following theories are used.

1.   Lewis Langmuir - theory

2.   Octet theory

3.   Valence bond theory (VBT)

4.   VSEPR theory

5.   Molecular orbital theory (MOT)

Lewis and Kossel approach (1916)

Lewis approach to chemical bond

Lewis pictured the atom in terms of a positively charged 'Kernel' (The nucleus with the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. ie eight electrons occupy the corners of the cube, which surrounded the Kernel.
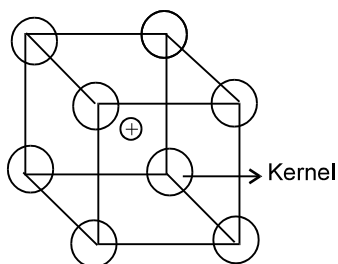
For eg: Sodium 2, 8, 1
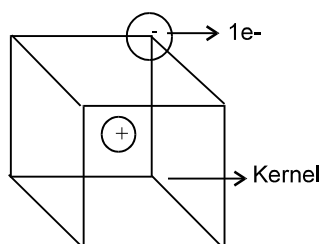
Inert gas

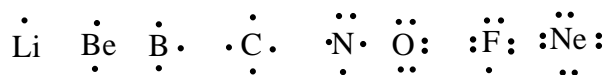Ne : $2,$ $\boxed{8}$

Ar : 2, 8, $\boxed{8}$

∴ This octet electrons, represent a particularly stable electronic arrangement.

∴ Lewis postulated an atom achieve the stable octet when they are linked by chemical bonds.

Lewis symbols

In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons.
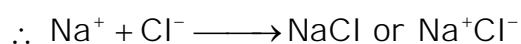
$$\overset{\bullet}{Li} \quad \overset{\bullet}{Be}\overset{}{} \quad \overset{\bullet}{\underset{\bullet}{B}}\bullet \quad \bullet\overset{\bullet}{\underset{\bullet}{C}}\bullet \quad \bullet\overset{\bullet\bullet}{\underset{\bullet}{N}}\bullet \quad \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \quad :\overset{\bullet\bullet}{\underset{\bullet}{F}}: \quad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{Ne}}:$$
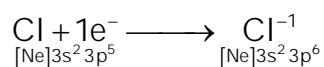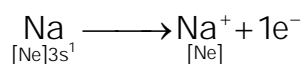
Significance of Lewis symbol

1. The symbol helps to calculate common group valence of the element.

    Group valency = Number of valence electrons (V) or (8 – V)

Kossel's approach to chemical bond

1. Highly electronegative atoms like halogens and highly electropositive atom like alkalimetals are separated by noble gases.

2. Formation of negative and positive ions are associated with gain of electron or lose of electron.

3. Negative and positive ions thus formed attain the stable noble gas electronic configuration.

4. Negative and positive ions are stabilized by electrostatic force of attraction.

$$\underset{[Ne]3s^1}{Na} \longrightarrow \underset{[Ne]}{Na^+} + 1e^-$$

$$\underset{[Ne]3s^2 3p^5}{Cl + 1e^-} \longrightarrow \underset{[Ne]3s^2 3p^6}{Cl^{-1}}$$

$$\therefore \ Na^+ + Cl^- \longrightarrow NaCl \ or \ Na^+Cl^-$$

The bond formed, as a result of the electrostatic force of attraction between the positive and negative ions was termed as **ionic bond.**

Octet rule

Kossel and Lewis (1916) developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding.

Octet rule. In order to get stability, an atom, gain, lose energy or take part in sharing of electron pair. Therefore their outermost shell contain 8 electrons.

Covalent bond

Langmuir (1919) refined the Lewis cubic arrangement of the octet and by introducing the term **covalent bond.**

Lewis-Langmuir theory

- The sharing of pair of electrons form a covalent bond.

- Two pairs of electrons are take part in the sharing between two atoms, double bonds are formed.

- Three pairs of electrons are take part in the sharing between two atom, triple bonds are formed.

- More than one electron pairs shared between the two atoms, multiple bonds are formed.
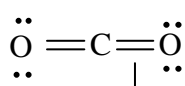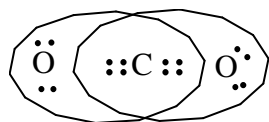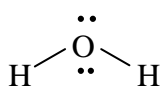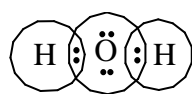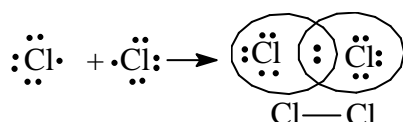
- The electron pair which take part in bond formation is known as bond pair of electrons.

- The electron pair which does not take part in bond formation is known as non-bonding pair or lone pair.

   In covalent bond Lewis representation of the compound is very important

    Lewis representation of compounds or simple molecules (Lewis structures)

   **Steps for writting the Lewis dot structures**

1. Find the total number of valence electrons of central atom and surrounding atom

2. For anions : Each negative charge would mean addition of one electron.

    For cation : Each positive charge would mean substraction of one electron.

3. Least electronegative atom occupies the central position in the molecule/ion

4. After accounting for the shared pairs of electrons for single bonds. The remaining electron pair are either utilised for multiple bonding or remain as the lone pairs.

5. The basic requirement being that each bonded atom gets an octet of electrons.

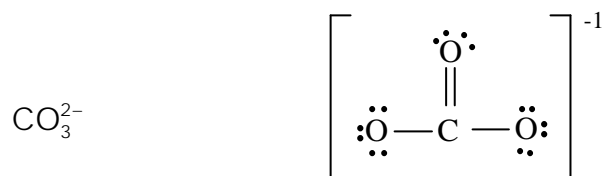   Total no.of valence electrons = 12
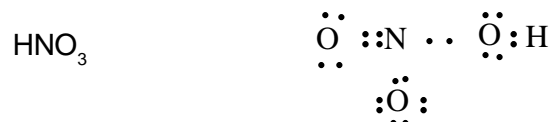
    Total no.of pairs = 12/2 = 6

    Eg : O_2

Eg : O_3
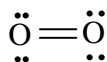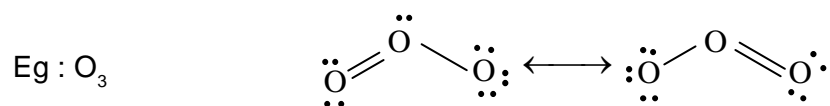
Total valence electron = 18 e⁻

Total pairs = 18/2 = 9

CO_3^{2-}

Total valence electron = 24

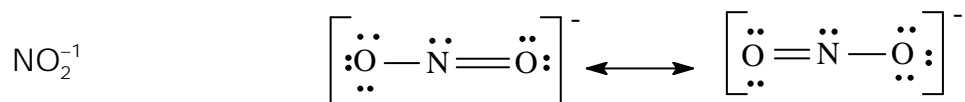Total no.of pairs = 24/2 = 12

HNO_3

Total valence electron = 24

Total no.of pairs = 24/2 = 12

CO

:C≡O

Total valence electron = 10/2 = 5
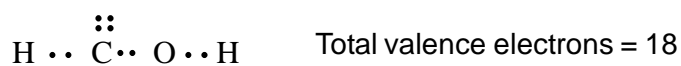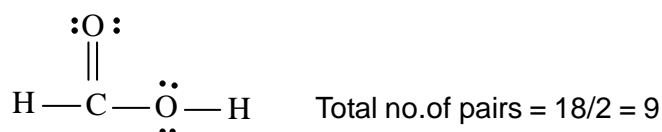
Total no.of pairs = 5

NO_2^{-1}

Total valence electrons = 18

Total no.of pairs = 18/2 = 9

NCERT (Exercise)

H – COOH (formic acid)

H ·· C·· O··H   Total valence electrons = 18

H — C — O — H   Total no.of pairs = 18/2 = 9

5

Formal charge

In a Lewis dot structure of poly atomic ions or compounds their actual charge is not a formal charge. That charge is the sum of all individual atoms charge. Those individual atoms charge is known as formal charge.
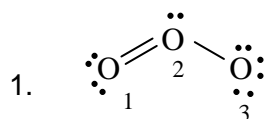
Formal charge = $(V - \ell - \frac{1}{2} b)$

Where V, ℓ and b are valence, lone pair and bond pair electrons respectively.

Importance of formal charges

Formal charges help in the selection of the lowest energy structure from the number of possible Lewis structure.

Lowest energy structure is the one with a factor based on a pure covalent bond between the two atoms.

Formal charge on O atoms in ozone.

1.

$$V - \ell - \frac{1}{2}b$$
$$O^1 = 6 - 4 - \frac{1}{2} \times 4 = 0$$
$$O^2 = 6 - 2 - \frac{1}{2} \times 6 = +1$$
$$O^3 = 6 - 6 - \frac{1}{2} \times 2 = -1$$

∴ Formal charges of O in O ion 0, +1, −1 or −1, +1, 0

2. N_3^{-1} **azide ion**

$$V - \ell - \frac{1}{2}(b)$$
$$N^1 = 5 - 4 - \frac{1}{2} \times 4 = -1$$
$$N^2 = 5 - 0 - \frac{1}{2} \times 8 = +1$$
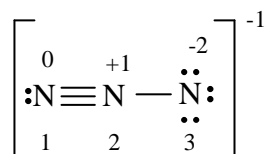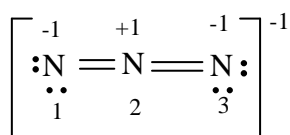$$N^3 = 5 - 4 - \frac{1}{2} \times 4 = -1$$

$$V - \ell - \frac{1}{2}(b)$$
$$N^1 = 5 - 2 - \frac{1}{2} \times 6 = 0$$
$$N^2 = 5 - 0 - \frac{1}{2} \times 8 = +1$$
$$N^3 = 5 - 6 - \frac{1}{2} \times 2 = -2$$

Octet theory (Lewis and Kossel)

In order to get the stability of atom, it acquire 8 electrons in the outer most shell either by lose of electron ,gain of electron or take part in the sharing of a pair of electron.

Limitations

1. H_2, He their stability could not clearly explained. It could clearly explained by duplet theory.

2. In complete octect molecules/electron deficient molecule /hypovalent compounds. Like LiCl, $BeCl_2$, BCl_3 , $AlCl_3$ etc.

3. Expanded octet molecules, hypervalent compounds/super octet compounds.

    PCl_5, SF_6, IF_7, H_2SO_4, SO_3

4. Odd electron molecules

    A compound contain central atom having unpaired electron or odd electron.

   For eg: NO, NO_2,

    $7e^-$
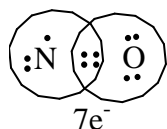
5. Xe and Kr are noble gases their outermost shell contain 8 electrons. But they form stable compounds like XeF_2, XeF_4, XeF_6, $XeOF_2$, KrF_2. Their formation and stability could not clearly explained.

6. Inability to explain the energy exchanges during the formation of stable molecule.

7. Inability to explain shape of molecules.

Ionic bond / electrovalent bond

It is the electrostatic force of attraction between the ions ie cations and anions, in order to get the stability.

Requirements for the formation of ionic bond

1. Ease of formation of cation and anion from the respective atom.

    Arrangement of positive and negative ions in respective atom.

2. Ionisation energy $(\Delta_i H)$ required to eject loosely bound outermost electron from neutral gaseous atom in ground state.

    $$Na \rightarrow Na^+ + 1e^- \longrightarrow \Delta_i H = 495.8 kJ \ mol^{-1} ....(1)$$
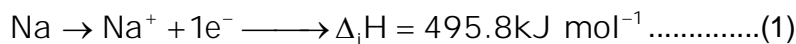
3. Electron gain enthalpy ($\Delta_{eg} H$) the energy released when one electron is accepted by a neutral gaseous atom in ground state.

    $$Cl + 1e^- \rightarrow Cl^- \rightarrow \Delta_{eg} H = -348.7 \ kJ \ mol^{-1} ....(2)$$

    (1) + (2)

    $$Na + Cl \rightarrow NaCl_{(s)} = +147.1 kJ \ mol^{-1}$$
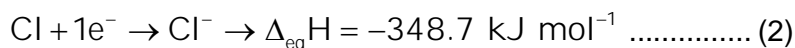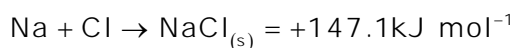
But actually formation NaCl is exothermic and $\Delta_f H^0_{NaCl}$ is –412 kJ/mol. Therefore some other factors are involved for the formation of ionic bond of NaCl.

In order to explain this, Born Haber cycle is used.

Born Haber Cycle

$$\Delta_f H^0_{NaCl} = \Delta_{sub}H_{Na} + \Delta_i H_{Na} + \frac{1}{2}D + \Delta_{eg}H + \Delta_{lattice}H^0$$
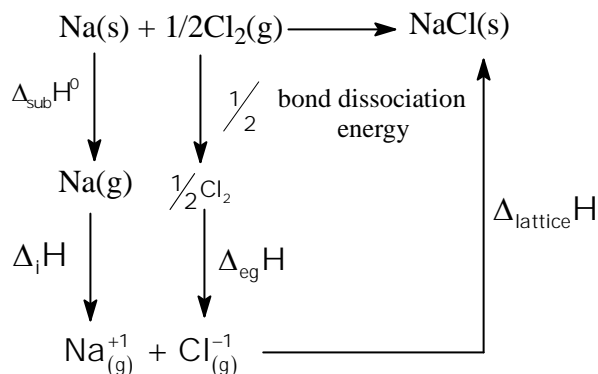
$$= 107.8 \ kJ/mol + 495.4 \ kJ/mol + \frac{1}{2}(242.6kJ) + -348.8 - 412.3kJ/mol = -788 \ kJ/mol$$

4. $\Delta_{sub}H^0 \rightarrow$ Energy required to sublime 1 mole of solid substance into gaseous substance at its sublime temperature.

5.   Dissociation energy - The energy required to dissociate one mole gaseous molecule into atoms

4.   Lattice energy/Lattice enthalpy : Energy release when one mole of solid ionic crystal is formed from the gaseous ions or energy absorbed to dissociate when one mole of solid ionic crystal into gaseous ions.

According to Coulombs law

Electrostatic/coloumbic force of attraction $f \ \alpha \ \dfrac{q_1 q_2}{r^2}$

$$f \times r \ \alpha \dfrac{q_1 q_2}{r^2} \times r$$

Lattice energy $U \ \alpha \ \dfrac{q_1 q_2}{r}$; $U = A\dfrac{q_1 q_2}{r}$

when $q_1 \ q_2$ are the quantity of charges on the cation and anion r is the distance between cation and anion. A is the madelung constant. This constant depend on the nature of the salt.

For Example :

Madelung constant for NaCl = 1.754

Madelung constant for CsCl = 1.76

Born Haber cycle is used to calculate Lattice enthalpy of ionic compounds as well as thermodynamic stability.

i) L.E. α $q_1 q_2$

ii) L.E. α $\dfrac{1}{r}$

	F^-	Cl^-	Br^-	I^-
Li^+	1036	853	807	757
Na^+	923	787	747	704
K^+	821	715	682	649
Rb^+	785	689	660	630
Cs^+	740	659	631	604

	OH^-	O^{2-}
Na^+	900	2481
Mg^{2+}	3006	3791
Al^{3+}	5627	15,916

Hydration enthalpy

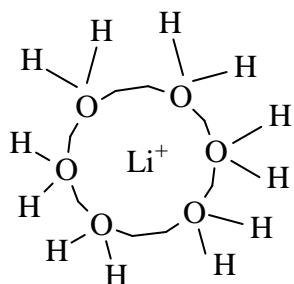The energy released, when 1 mole of gaseous ions get attach with water molecules. Smaller the size of ions higher will be the hydration energy.

For eg: In aqueous solution, order of h ydration energy

$$\underset{3.4\,A^0}{Li^+} > \underset{2.76\,A^0}{Na^+} > \underset{2.32\,A^0}{K^+} > \underset{2.28\,A^0}{Rb^+} > \underset{2.26\,A^0}{Cs^+}$$
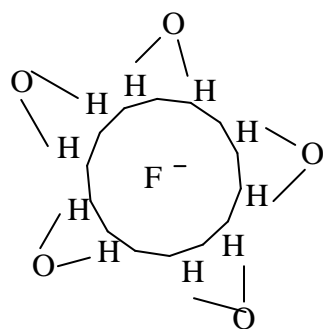
$\therefore$ The size of ions in aqueous solution.

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

Similarly in aqueous solution $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (Order of hydration and size)

Similarly anion like halides in aqueous solution

$F^- > Cl^- > Br^- > I^-$ (order of hydration)

$F^- > Cl^- > Br^- > I^-$ (size of ions)

Note: Hydration energy/enthalpy of ions increases solubility of that ion increases.

Solubility of ionic compounds in polar solvents mainly depend on hydration energy and lattice energy.

$\Delta_{hyd}H^0 > \Delta_{lattice}H^0$ solubility of salt increases

Note:

Solubility of ionic compounds in water depend upon the difference in the size of cation and anion.

$$\boxed{\text{solubility } \alpha \text{ difference in the size of cation and anion}}$$

Li^+ ClO_4^- NO_3^- I^{-1} Br^- Cl^-

Na^+

K^+ From top to bottom solubility decreases

Rb^+

Cs^+

Be^{+2} SO_4^{2-} CO_3^{2-} NO_3^-

Mg^{+2}

Ca^{+2} From top to bottom solubility decreases

Sr^{+2}

Ba^{+2}

F^- OH^- ⟶ Small size Be^{+2} OH^- F^-

Li^{+1} 1000 Mg^{+2}

Na^{+1} 900   From top to bottom Ca^{+2} From to to bottom
                            solubility increases   solubility increases
K^{+1} 600 Sr^{+2}

Rb^{+1} 500 Ba^{+2}

Cs^{+1} 400

This is because

Lattice energy steeply decreases than hydration energy (experimental data)

Thermal stability

Ionic compounds can with stand at high temperature without undergoing decomposition

I.   In monoatomic anion contain compounds

Lattice energy $\propto$ Thermal stability

Li^{+1} N^{-3} O^{-2} X^{-1}

Na^{+1}

K^{+1} From top to bottom L.E. decreases
thermal stability also decreases

Rb^{+1}

Cs^{+1}

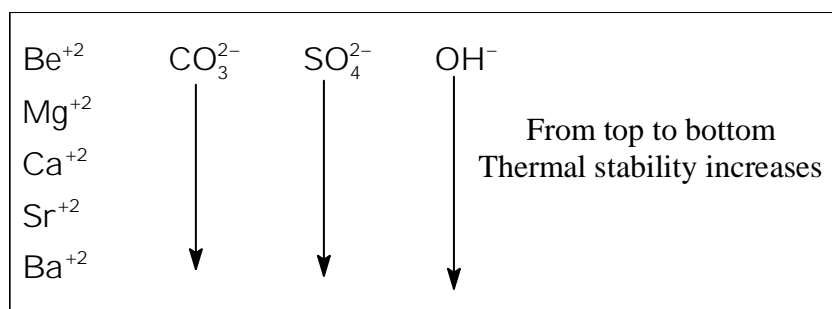**II.   In poly atomic anion contain compound**

Thermal stability depend on packing of the ions in lattice

or

High polarising power of cation $\alpha \dfrac{1}{\text{Thermal stability}}$

Li^{+} ClO$_3^{-}$ NO$_3^{-}$ CO$_3^{2-}$ OH^{-}

Na^{+}

K^{+1} From top to bottom
Thermal stability increases

Rb^{+1}

Cs^{+1}

Be^{+2} CO_3^{2-} SO_4^{2-} OH^-

Mg^{+2}

Ca^{+2} From top to bottom

Sr^{+2} Thermal stability increases

Ba^{+2}

CHARACTERISTIC FEACTURES OF IONIC BOND

1. Physical state. Ionic bonded compounds are hard and brittle.

2. They show isomorphism

   $FeSO_4.7H_2O \,|\, MgSO_4.7H_2O$

3. High density

4. High M.P. NaCl (801°C) KCl (776°C)

5. Ionic bond is non-directional bond: (Ions will attract oppositively charged ions in all directions)

6. They are thermally stable one

7. Ionic bonded compounds are more soluble in polar solvents like water(dielectric constant 80)

8. Ionic bonded compounds show high electrical conduction in molten state or aqueous state.

Covalent character in charged species

Covalent character of ionic bonded species depends on:-

1. Polarising power of cation

   The power of cation to cause distortion in the electron cloud of the negative ion is referred to as its polarising power.
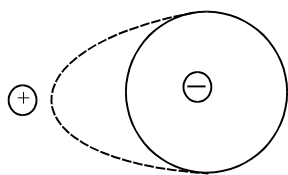
2. Polarisibility of anion

   The ability of anion to undergo distortion in the electron cloud of the negative ion is referred to as its polarisibility of anions.

The extent of covalent character based on Fajan's rule

Rule - I : Smaller the size of cation, Larger will be its polarising power.

Polarising power $\alpha \dfrac{\text{Charge of cation}}{\text{Radius of cation}}$

LiCl > KCl (Covalent character order)

$BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

Rule-II : Larger the charge on the cation , higher will be the polarising power.

$Na^+ < Mg^{2+} < Al^{3+} < Si^{+4}$

Rule-III : Larger the size of anion

LiCl < LiI (Covalent character)

$CaF_2 < CaCl_2 < CaBr_2 < CaI_2$ (Covalent character)

Pseudo inert gas configuration compounds have high polarising power and their compounds are more covalent.

Na^+Cl^- < $\overset{+1}{C}u\overset{-1}{Cl}$ Covalent   character

$1s^2 2s^2 2p^6$ $[Ne]$ $3s^2 3p^6 3d^{10}$
       $[Ne]$ Inert gas Pseudo inert gas configuration
     Inert gas

Eg: of pseudo inert gas configuration cations:

$Zn^{2+} > Cd^{2+} < Hg^{+2}$

$Cu^{+1} > Ag^+ < Au^{+1}$

$ZnCl_2 > CdCl_2 < HgCl_2$ covalent character order.

Effect of increased polarisation

1. Covalent character increases

2. Polarising power of cation increases, covalent character increases M.P. decreases.

    Order of M.P.

    NaX > KX > RbX > CsX > LiX   (X = Cl, Br)

    $NaF > KF > LiF > RbF > CsF$
    $KI > NaI > RbI > CsI > LiI$
    $NaF > NaCl > NaBr > NaI$ (ionic bond only)
        $\left(\text{In ionic bond LE } \alpha \text{ M.P}\right)$

    $BaX_2 > SrX_2 > CaX_2 > MgX_2 > BeX_2$

3.   Order of solubility in aqueous solutions

AgCl   AgBr   AgI
Partially so lub le   in so lub le in H_2O

$$\overset{+2}{Fe}(OH)_2 > \overset{+3}{Fe}(OH)_3$$
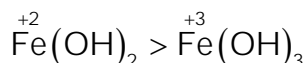
4.   Intensification of colour

Polarised anion has distorted electron, which absorb energy from light, its complementary colour is releasing.

AgCl(white)   AgI (yellow)

$HgCl_2$ (colourless) HgI_2 (red)

$SnCl_4$ (colourless) (SnI_4) (red)

$PbCl_2$ (colourless) PbI_2 (bright yellow)
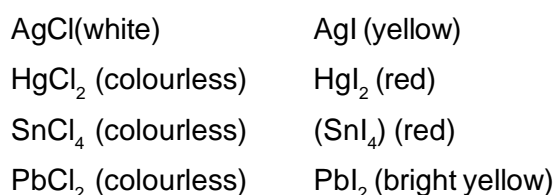
COVALENT BOND

A covalent bond is formed by the mutual sharing of a pair of electron.

Characteristic features of covalent bond, covalent bonded compounds

1.   Physical state : Generally exists as gases and liquids. S_8, P_4, I_2 exists as soft solids.

2.   M.P. : Covalent compounds have relatively low melting and boiling points except diamond.

SiC (Carborandum) and SiO_2 (Silica)

3.   Solubility in Non-polar solvents like benzene, ether, CCl_4 etc

4.   Electrical conductivity : Generally bad conductors of electricity except graphite.

5.   Covalent bonded compounds show isomerism

6.   Directional characteristics : Covalent bond is directional and give geometry of compounds.

1.   Valence bond theory (VBT)

Postulates :

1.   A covalent bond is formed by the overlapping of atomic orbitals

2.   Overlapping atomic orbitals should contain unpaired electron and opposite spin

3.   Extent of overlapping leads the stable bond is due to the repulsion between the nucleus in minimum.

4.   Excessive overlapping leads the unstable bond is due to the repulsion between the nucleus is maximum.

5.   One atomic orbital is take part in overlapping, single bond is formed, more than one atomic orbital take part in the overlapping multiple bonds are formed.

This could clearly explained with the formation of hydrogen molecules.

When two hydrogen atoms H_A and H_B approach each other, the following interactions occur

1. Attractive forces between e_A and nucleus of B

Attractive forces between e_B and nuleus of A

2. Repulsive forces between nucleus of A and nucleus of B e_A and e_B

During the formation of covalent bond, attractive forces are dominent than repulsive force.
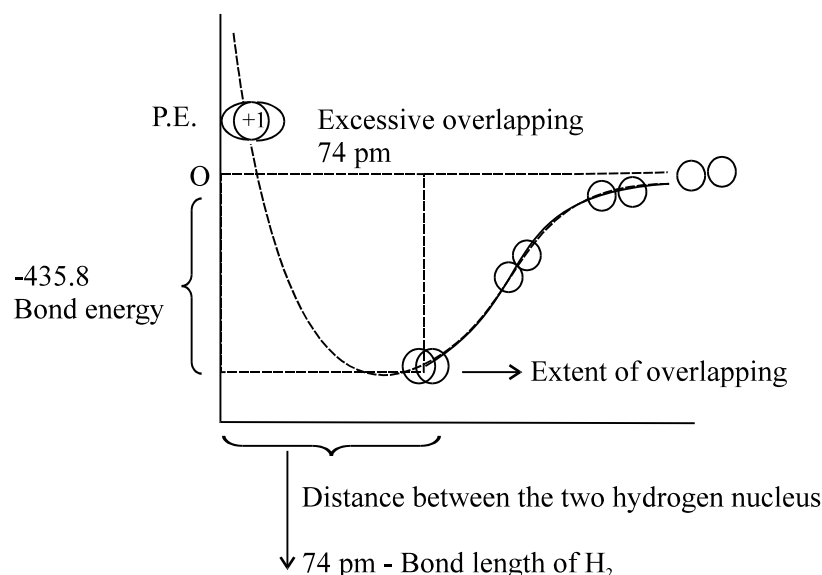
Orbital overlap concept of covalent bond formation

In covalent bonding, there is a change in electron densities in the combining atoms. Accumulation of electron densities between the two nuclei results in bond formation. When two atoms approach, there is overlapping of electron waves.

The main ideas of orbital overlap concept of covalent bond formation are

i. Covalent bonds are formed by overlapping of half filled atomic orbitals present in the valence shell of the atoms taking part in bonding.

ii. The orbitals undergoing overlapping must have electrons with opposite spins

iii. The strength of a covalent bond depends upon the extend of overlapping.

Overlapping of atomic orbitals

When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangement of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like CH_4, NH_3 and H_2O, the VB theory has to account for their characteristic shapes as well. We know that the shapes of CH_4, NH_3 and H_2O molecules are tetrahedral, pyramidal and bent respectivley.
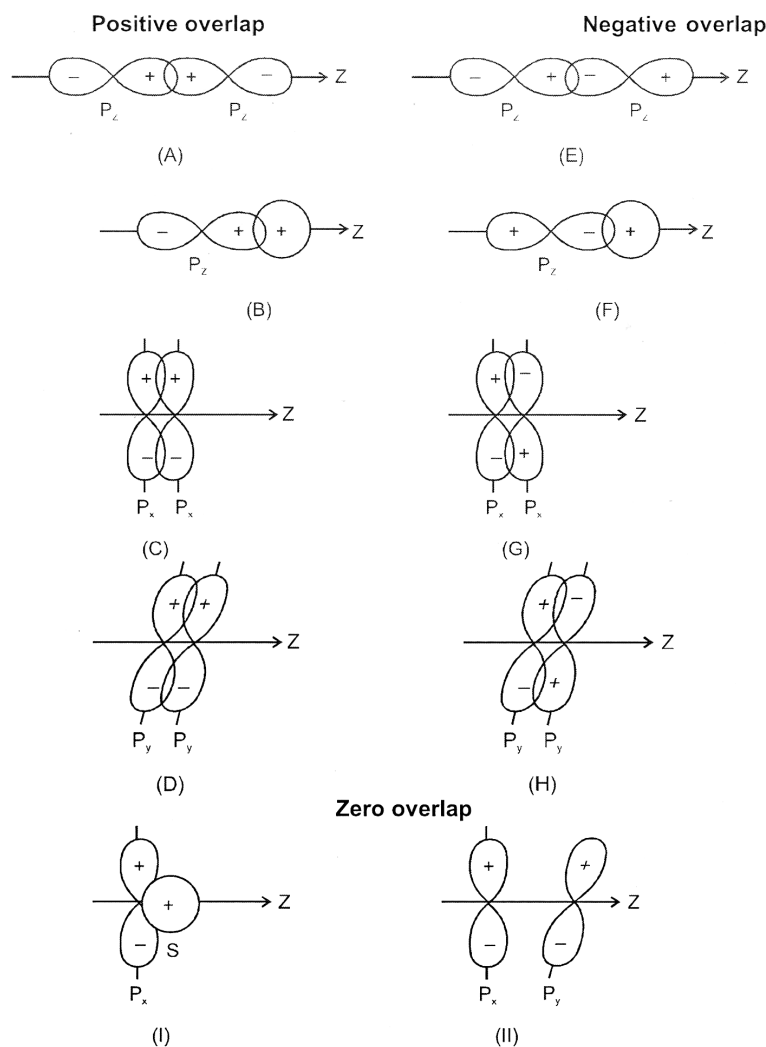
Positive overlap   Negative overlap

(A)   (E)

(B)   (F)

(C)   (G)

(D)   (H)

Zero overlap

(I)   (II)

Figure : Positive , negative and zero overlaps of s and p atomic orbitals

TYPES OF COVALENT BONDS

Sigma (σ) and pi (π) bonds

a.   **Sigma (σ) bond :** The bond formed by the axial (or head-on) overlap of atomic orbitals along the internuclear axis is known as **(σ)** bond. Sigma bond may be formed by any one of the following types of overlapping.

i.   **Overlapping of s-s orbitals :** Hydrogen molecule (H_2) formation is an example of 1s-1s overlap between two hydrogen atoms, resulting in the formation of a covalent bond.

17

ii.   Overlapping of s-p orbitals

The half filled s orbital of one of the two elements overlaps with the half-filled p-orbital of the other element resulting in the formation of a chemical bond. Examples of this type of s–p overlap are the formation of compounds HF, H_2O, NH_3, HCl etc. The general representation of an s–p orbital overlap can be made as shown.
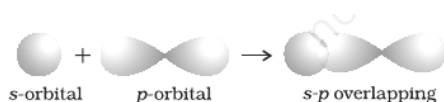
iii.   Overlapping of p–p orbitals

The half filled p orbital of one of the two elements overlaps with the half filled p orbital of the other element resulting in the formation of a chemical bond. Examples of this type are the formation of compounds like F_2, Cl_2 etc.
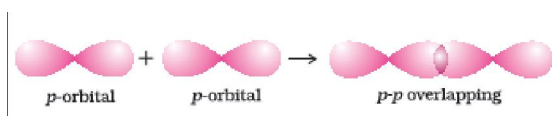
b.   Pi (π) bond: Covalent bond formed by the lateral or sidewise overlap of half-filled atomic orbitals is known as pi (π) bond. The atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.

18
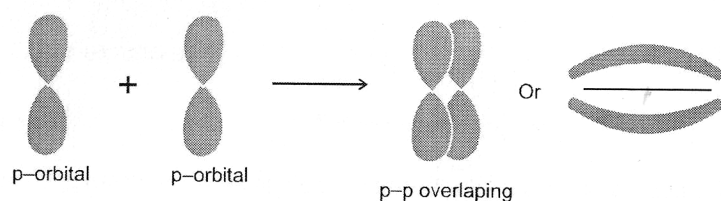
Differences between sigma and pi bonds

σ bond	π bond
It is formed by axial overlap of s-s or s-p or p-p orbitals of two atoms	It is formed by lateral overlap of p-p orbitals
Extent of overlappiing is quite large and hence σ bond is a strong bond	Overlapping is to a small extent and hence π bond is a weak bond
There can only be one σ bond between two atoms	There can be one or two π bonds between two atoms
Electron cloud is cylindrically symmetrical about the line joining the two nuclei	Electron cloud of π bond unsymmetrical about the internuclear axis.
σ bond may involve the overlapping of hybrid orbitals. They determine the shape of the molecule	π bond usually involves the overlapping of pure orbitals. They do not determine the shape of molecules.

HYBRIDISATION

It is defined as the intermixing of atomic orbitals of slightly different energy and shape so as to redistribute their energies, resulting in the formation of new set of orbitals of identical shape and similar energy. This explains why atoms like Be, B, C show a valency of 2, 3 and 4 respectively. The energy required for excitation is compensated by energy released during bond formation.

Characteristics of hybridisation

1. The number of hybridised orbitals formed is equal to the number of orbitals that get hybridised.

2. The hybridised orbitals are always equivalent in energy and shape.

3. The hybrid orbitals are more effective in forming stable bonds than unhybridised atomic orbitals.

4. The hybrid orbitals are directed in space in some preferred directions so as to have minimum repulsion between electron pairs. Therefore, the type of hybridisation indicates the geometry of the molecule.

Conditions for hybridisation

1. The orbitals present in the valence shell of an atom only undergo hybridisation

2. Only those orbitals which have approximately the same energy can undergo hybridisation

3. Promotion of electron in an atom is not necessary before hybridisation

4. Even, filled orbirtals of the valence shell may take part in hybridisation in certain cases.

Types of hybridisation

1. **sp hybridisation** : This involves one s and one p orbital of the valence shell of an atom resulting in the formation of two new equivalent hybridised orbitals. The sp hybrid orbitals have 50% s and 50% p character. The sp hybrid orbitals are linear and lie in the same line at an angle of 180° from each other.

    Structure of BeCl$_2$: In BeCl$_2$, Cl–Be–Cl, the central Be atom uses both its valence electrons in forming 2σ bonds with the two chlorine atoms.
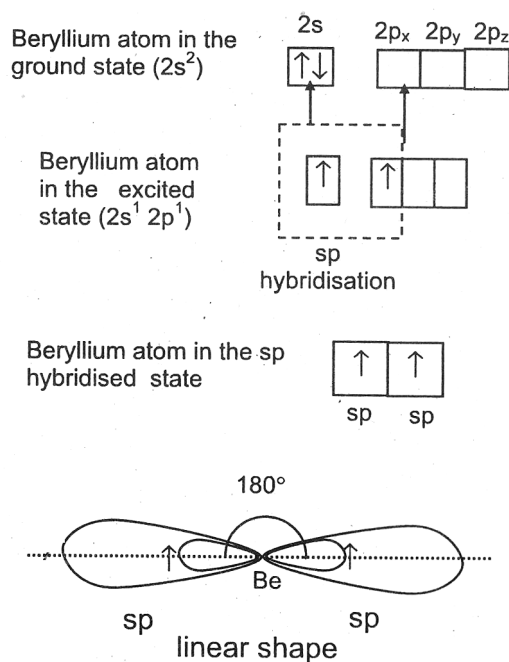
Each of these orbitals overlaps axially with half filled 3p orbitals of chlorine to form two Be–Cl bonds. Few other compounds which exhibit sp hybridization are BeF$_2$, CO$_2$, CH$_3$CN, HCN etc.

2. **sp^2 hybridisation :** This involves the mixing up of one s and two p orbitals of the valence shell of an atom to form three new equivalent orbitals. The three new equivalent sp^2 orbitals are formed with 33% s character and 67% p character. The three equivalent orbitals have a symmetrical distribution and are directed towards the corners of a trigonal planar structure at an angle of 120° from one another.

    Strucutre of BCl$_3$: In BCl$_3$, the ground state electronic configuraiton of the central boron atom is 1s^2 2s^2 2p^1. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital, as a result boron has three unpaired electrons. These three orbitals hybridise to form three sp^2 hybrid orbitals. The hybrid orbitals formed are oriented in a trigonal planar arrangement and overlap with the 2p orbitals of chlorine to form three B–Cl bonds.
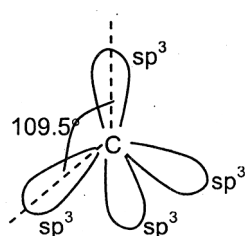
B (ground state)

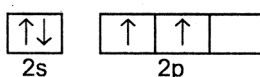**B (excited state)**

sp² hybridisation

120°
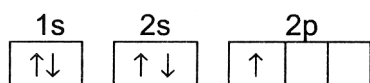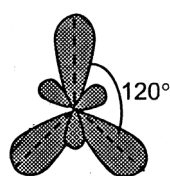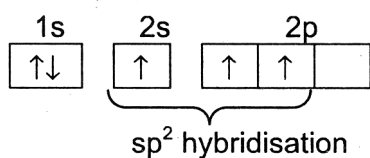
trigonal planar

3. **sp³ hybridisation** : This involves the mixing up of one s and three p orbitals of the valence shell of an atom to form four new equivalent orbitals. Each sp³ hybrid orbital has 25% s-character and 75% p-character. The four sp³ hybrid orbitals are directed towards the four corners of a tetrahedron to minimise repulsion. The angle between the sp³ hybrid orbitals is 109°28′ or approximately 109.5°.
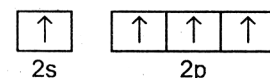

four equivalent sp³
hybridised orbitals

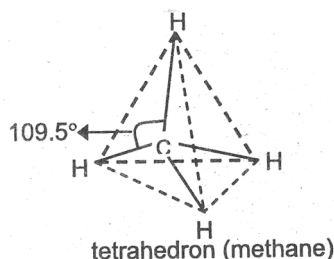**Structure of methane (CH₄)**

Carbon atom in the ground state

Carbon atom in the excited state

Carbon atom after sp³ hybridisation

tetrahedron (methane)

In methane, the four sp³ hybridised orbitals of carbon are directed towards the four corners of a regular tetrahedron with the carbon atom located at the centre and four hydrogen atoms at the corners.

Each of the four sp³ hybrid orbitals on carbon is singly filled. In the formation of methane, each of these hybrid orbitals overlap with the half filled 1s orbital of hydrogen. This results in four C–H bonds and these single bonds are known as sigma (σ) bonds. The axes of the sp³ orbitals are directed towards the four corners of a regular tetrahedron, with the carbon at the centr ewith H–C–H bond angle 109°28$'$

Energy is required for the promotion of a 2s electron to 2p orbital and for the hybridisation of the orbitals to give equivalent orbitals, but this is compensated by the release of energy in the formation of covalent bonds involving the sp³ hybrid orbitals.
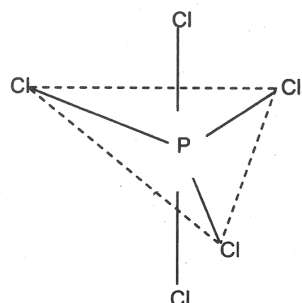
4.   **sp³d hybridisation** : When one s orbital, three p orbitals and one d orbital are involved in the hybridisaiton, it is called sp³d hybridisation. For example, phosphorus in PCl_5 is sp³d hybridised.

Structure of PCl$_5$: The structure of PCl_5 shows that the central atom P uses all its five electrons from its valence shell (3s² 3p³) in forming the 5σ bonds with five chlorine atoms.

P atom in the ground state :

P atom in the excited state:

sp³d hybridisation
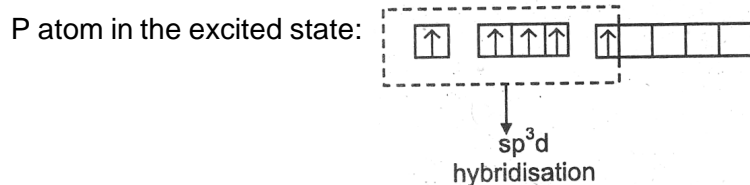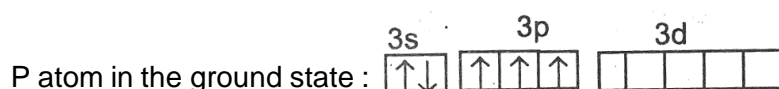
The result is that there are five non-equivalent sp³d hybrid orbitals with 2 axial orientations and 3 equatorial (lateral) orientations. sp³d hybrid orbitals are singly occupied with electrons. They form five σ bonds with five p orbitals of five chlorine atoms.

PCl_5 has a trigonal bipyramidal shape. Of the five bonds, three equatorial bonds are equal in length and two axial bonds are longer than the equatorial bonds. This is because axial bond pairs suffer more repulsive interaction from the equatorial bond pairs. Axial bonds are less stronger than equatorial bonds.

5. **sp^3d^2 hybridisation**: It involves the mixing up of one s orbital three p orbitals and two d orbitals to give six hybridised orbitals. Sulphur hexafluoride (SF_6) is an example of a molecule where sulphur shows sp^3d^2 hybridisation.

    Structure of SF_6 : In SF_6, all the six valence electrons of sulphur are used up. There are six sp^3d^2 equivalent orbitals formed after hybridisation with no lone pair of electrons. Each of the six hybridised sp^3d^2 orbitals are singly filled before bonding.

    Each one of these sp^3d^2 hybridised orbitals overlaps with p orbitals of six fluorine atoms to form SF_6. The molecule has an octahedral shape.

octahedral shape
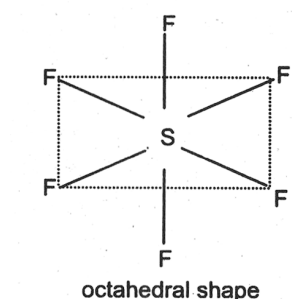
As the s-character in a hybrid orbital increases its electronegativity increases, since the s-electrons are more close to the nucleus.

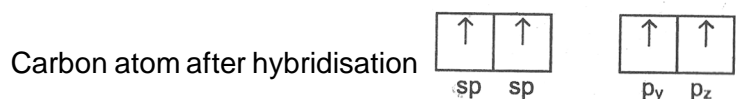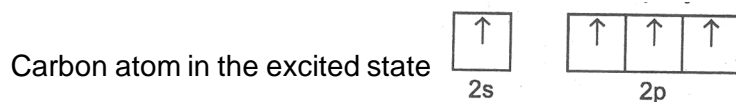| Hybridisation	sp^3	sp^2	sp
% s-character	25%	33.3%	50%
Electronegativity order	$sp^3 < sp^2 < sp$		

Hybridisation in organic compounds

Number of hybridised orbitals = Number of sigma bonds + number of lone pair on the central atom

If the hybridised orbitals number equal to 2, 3, 4 are sp, sp^2, sp^3 respectively.

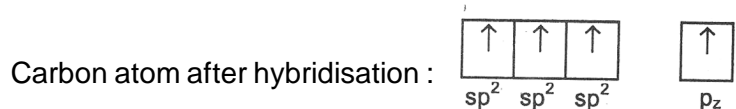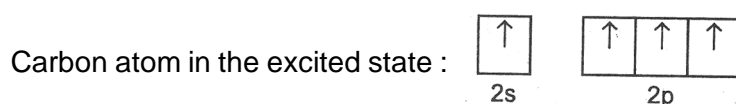### Structure of acetylene (H–C $\equiv$ C–H)

Both the carbons in acetylene are sp hybridised.

Carbon atom in the excited state

$$\boxed{\uparrow} \quad \boxed{\uparrow \mid \uparrow \mid \uparrow}$$
$$2s \qquad\qquad 2p$$

Carbon atom after hybridisation

$$\boxed{\uparrow \mid \uparrow} \qquad \boxed{\uparrow \mid \uparrow}$$
$$\text{sp} \quad \text{sp} \qquad p_y \quad p_z$$

One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other to form C–C sigma bond. The other sp hybrid orbital of each carbon overlaps axially with 1s orbitals of hydrogen atoms to form C–H sigma bonds. Each of the two unhybrisides orbitals ($2p_y$ and $2p_z$) of one carbon atom overlaps sidewise with similar orbitals of the other carbon atom to form two π bonds. Acetylene molecule is linear with bond angle of 180°.
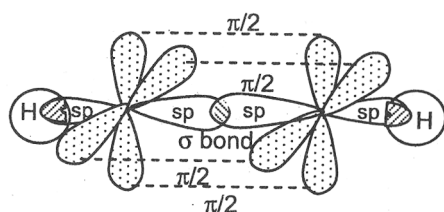
Structure of ethyelen (CH$_2$ = CH$_2$) : Both the carbons in ethylene are sp^2 hybridised.

Carbon atom in the excited state :

$$\boxed{\uparrow} \quad \boxed{\uparrow \mid \uparrow \mid \uparrow}$$
$$2s \qquad\qquad 2p$$

Carbon atom after hybridisation :

$$\boxed{\uparrow \mid \uparrow \mid \uparrow} \qquad \boxed{\uparrow}$$
$$sp^2 \;\; sp^2 \;\; sp^2 \qquad\quad p_z$$

The three sp² hybrid orbitals of carbon are oriented in a plane and are inclined at an angle of 120°. One sp² hybrid orbital of one carbon atom overlaps axially with sp² hybrid orbitals of the other carbon to form C–C sigma bond. The remaining two sp² hybrid orbitals of each carbon atom overlap axially with one s orbital of each carbon atom overlap axially with one s orbital of hydrogen to form C–H sigma bonds. The unhybridised two p orbitals ($2p_z$) of each carbon atom is oriented at right angles to the sp² hybridised orbitals. These unhybridised $2p_z$ orbitals of the two carbon atoms overlap sidewise to form a π bond. The π bond consist of two equal electron clouds distributed above and below the plane of other atom.
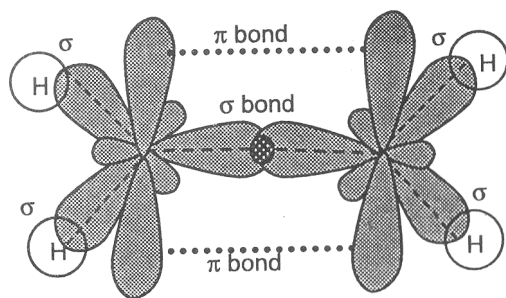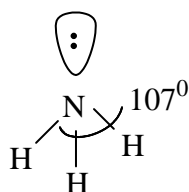

HYBRIDISED ORBITALS CONTAIN LONE PAIRS

When lone pairs come on the hybridised orbitals, the geometry distorted.

I.   In NH_3

$N_{(g)}$ $1s^2$ $2s^2$ $2p^3$:

$N_{(g)}$

sp³ hybridised orbitals with one lone pair
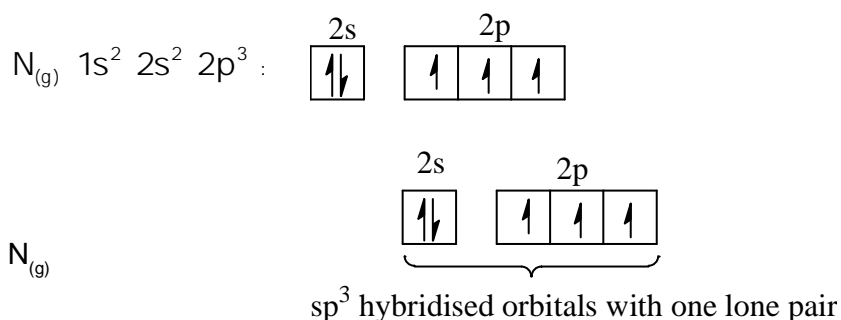
If one lone pair comes on the hybridised orbital geometry distorted and pyramid shape is formed. Bond angle decrease from 109°28′ to 107°. This is due to lone pair - bond pair repulsion is greater than bond pair - bond pair repulsion.
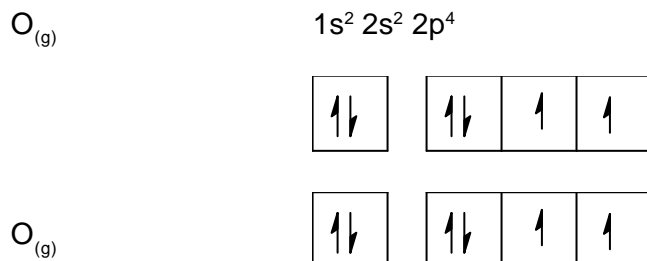

Pyramid shape

Hydrides of nitrogen family except NH_3 (PH_3, AsH_3, SbH_3) will not take part in hybridisation. Only pure P orbitals are used and their bond angles are near to 90°.
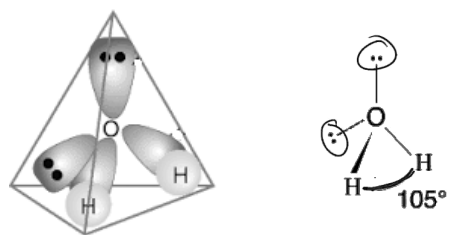
$\underset{93°.36^{/}}{PH_3}$ $\underset{91°.48^{/}}{AsH_3}$ $\underset{91°.18}{SbH_3}$
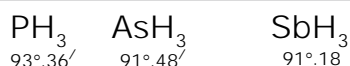
This is based on Drago's rule.

In H_2O

$O_{(g)}$ $1s^2\ 2s^2\ 2p^4$

$O_{(g)}$

sp^3 hybridised orbitals contain two lone pair. The geometry distorted and bent shape is formed. The bond angle reduced from 109° 28$^{/}$ to 104.5° this is because lone pair - lone pair repulsion is greater than lone pair - bond pair repulsion than bond pair - bond pair repulsion.

Hydrides of oxygen family except H_2O (H_2S, H_2Se, H_2Te) will not take part the hybridised orbitals. Only pure P orbitals are take part their bond angles are near to 90°.

H_2S H_2Se H_2Te
92°   91°   90°.30$^{/}$
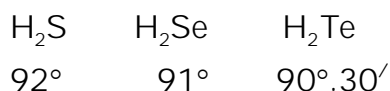
This is based on Drago's rule.

Predicting the hybridised orbitals of the central atom of the compound.

$$H = S + \frac{1}{2}\left[V - E + A - C\right]$$

where S is the number of surrounding atom, V is the valence electrons of the central atom, E is the valency of surrounding atom A and C are number of Anion charge and cation charge.

H geometry	Bond angle	Lone pair with shape of compound	orbital
2 sp linear	1.80°		
3 sp² trigonal planar	120°	1-bent shape	
4 sp³ tetrahedron	109°28ʹ	1-pyramid shape, 2-bent shape	
5 sp³d trigonal bipyramid	90° and 120°	1-See saw shape 2-T-shape 3-Linear	d_{z^2}
6 sp³d² octahedron	90°	1-square pyramid 2- square planar	$d_{x^2-y^2}$, d_{z^2}
7 sp³d³ pentagonal bipyramid	90°, 72°	1-distorted octahedron	$d_{x^2-y^2}$, dz^2, d_{xy}

In complexes compounds

$dsp^2 \rightarrow$ square planar $d_{x^2-y^2}$, P_x, P_y

$d^2sp^3 \rightarrow$ octahedron $d_{x^2-y^2,\ d_{z^2}}$

Overlapping strength of hybridised orbitals : $sp - sp < sp^2 - sp^2 < sp^3 - sp^3$

$p\pi - d\pi$ **overlapping**

SO₂

$S_{(g)} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^0$

π bond with p orbital of O atom $(p\pi - d\pi)$

π bond with p orbital of O atom $(p\pi - p\pi)$
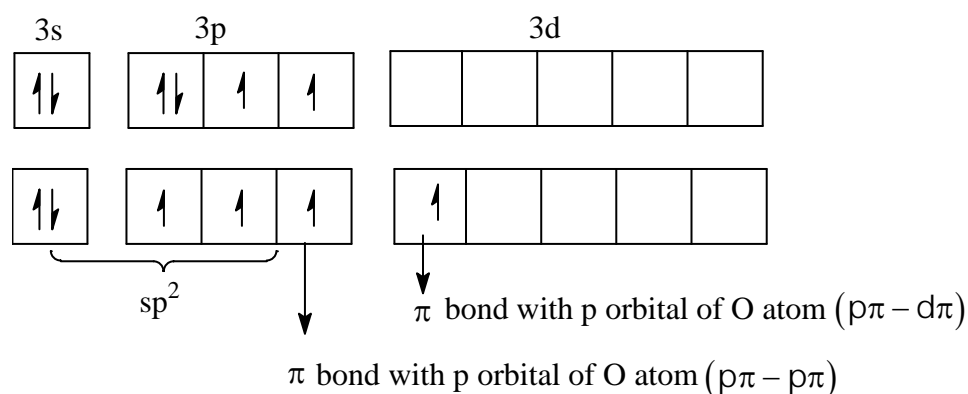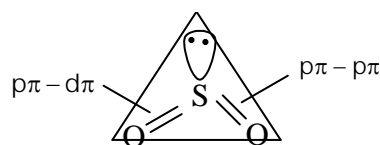
Bent's rule

i.   A lone pair of electrons prefers to occupy that hybrid orbital which has greater percentage of s-character (near to the nucleus)

ii. A more electron negative atom/group refers to occupy the hybridised orbitals having smaller percentage of s character (away from the nucleus) in Trigonal bipyramid geometry

1.   Axial bond length is greater than equitorial

2.   There are two different bond angles are present ie 90 and 120°.

3.   Lone pair occupy only in equitorial position

4.   Highly electronegative atom occupy in axial position first.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY :

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulaes of VSEPR theory are as follows:

i.   The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.

ii. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

iii. These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

iv. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

v.   A multiple bond is treated as it it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

vi. Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

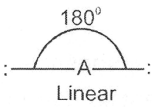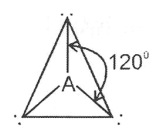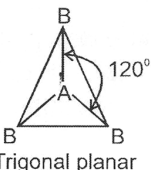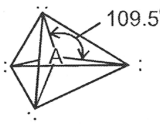**The repulsive interaction of electron pairs decreases in the order:**
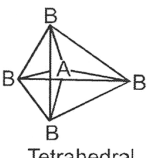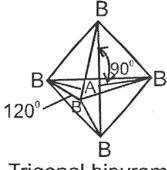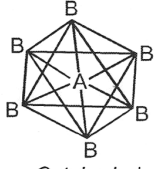
lone pair (ℓp) – lon pair (ℓp) > long pair (ℓp) – bond pair (bp) > bond pair (bp) > bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This resultant in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsion. These repulsion effects result in deviations from idealised shapes and alterations in bond

angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom / ion has one or more lone pairs.

Shape (molecular geometry) of some simple molecules/ions with central atom/ion having no lone pairs of electrons (E).

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	180^0 :—A—: Linear	B – A – B Linear	$BeCl_2$, $HgCl_2$
3	120^0 Trigonal planar	120^0 Trigonal planar	BF_3
4	109.5^0 Tetrahedral	Tetrahedral	CH_4, NH_4^+
5	90^0 120^0 Trigonal bipyramidal	90^0 120^0 Trigonal bipyramidal	PCl_5
6	90^0 90^0 Octahedral	Octahedral	SF_5

Shape (molecular geometry) of some simple molecules/ions with central atom/ions having one or more lone pairs of electrons (E).

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1		Bent	SO_2, O_3
AB_3E	3	1		Trigonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O
AB_4E	4	1		See saw	SF_4
AB_3E_2	3	2		T–shape	ClF_3
AB_5E	5	1		Square pyramidal	BrF_5
AB_4E_2	4	2		Square planar	XeF_4

Back bonding

It is a special kind of bonding observed when a lone pair of electron is donated from one of the atom into the vacant orbitals of other atom.

Due to back bonding there is a partial double bond character which increases the repulsion and hence bond angle increases.

sp^2

Partial π character
Repulsion increases
Bond angle increases
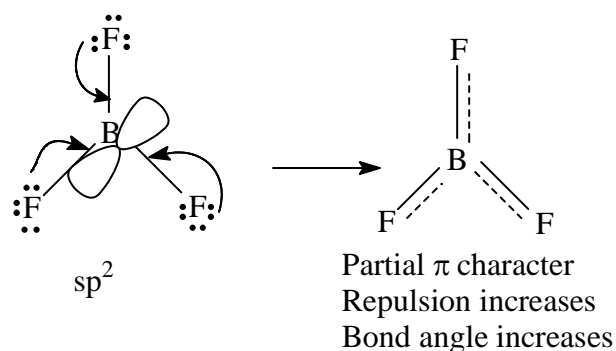
Back bonding order : BF_3 (due to matching size of B and F) > BCl_3 > BBr_3 > BI_3

Application

1. To predict Lewis acid nature - As Back bonding increases Lewis acid nature decreases

2. To predict bond angle - As Back bonding increases bond angle increases

3. To predict the structure of some compounds - As Back bonding increases the lone pair undergo delocalisation there by distorted geometry converted to ideal geometry.

Co-ordination bond or Dative bond (Perkins)

It is the sharing of pair of electron between the two atoms, the shared pair of electron come from one of the atom. ∴ This bond requires.

1. Electron rich species (Lewis base)

2. Electron deficient species (Lewis acid)
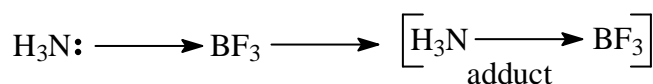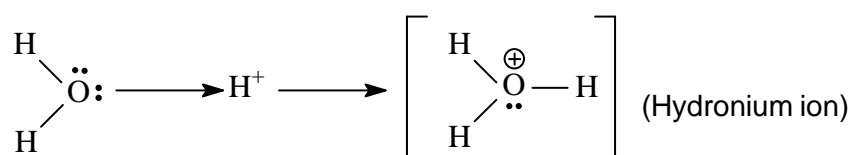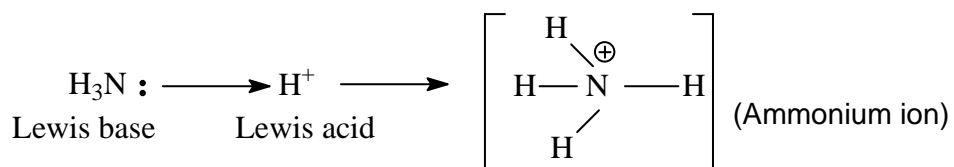
Polarity developed on a covalent bond, Non polar covalent bond

This is due to electronegativity difference between two bonded atoms.

Non polar covalent bond

A covalent bond formed by the overlapping of same atoms or having same electronegativity.

H $\circ\circ$ H   O $\underset{\circ\circ}{=}$ O
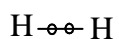
Polar covalent bond

A covalent bond formed by the overlapping of different atoms having different electronegativities.

$\overset{\delta^+}{H}$ —$\circ\circ$ $\overset{\delta^-}{Cl}$
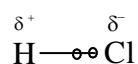
Dipole moment (μ) (Debye)

It is the movement of electron pair towards more electronegative atom in a covalent bond. It is a vector quantity ie dipole moment has direction and magnitude. The magnitude can be determined by the relation.
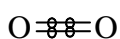
$$\boxed{\mu = e \times d}$$

where e is the electronic charge and d is the distance between the two atoms.

Value of e = $1.602 \times 10^{-19} C(SI) = 4.8 \times 10^{-10} esu(CGS)$

Unit of dipole moment is debye (D), esu cm and Cm

1D = 3.33564 $\times 10^{-30}$ cm

1D = $1 \times 10^{-18} esu$ cm

Application of dipole moment

1.   Prediction of percentage of ionic character

1. Electronegativity difference between the $= 1.7 \longrightarrow$ Both ionic and covalent
    bonded atoms

Ionic character ↑

(50%)

(50%)

Covalent character ↑
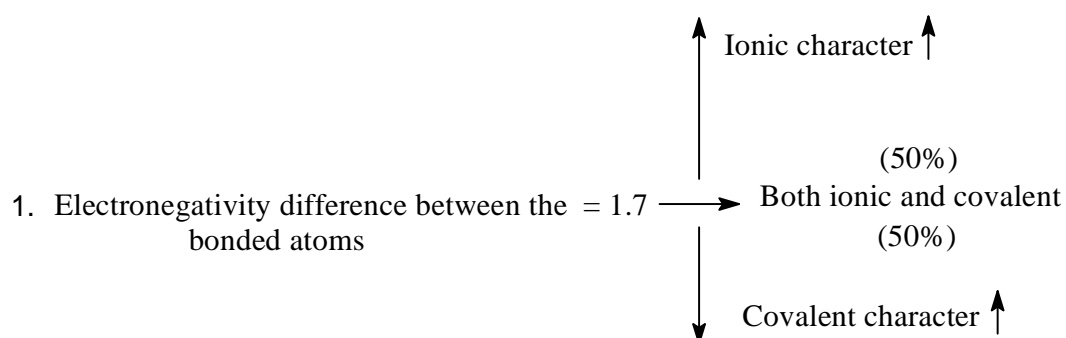
2. Hanney Smith relation

% of ionic character = $16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$

3. Percentage of ionic character = $\dfrac{\mu_{obs}}{\mu_{theoretical}\,(e \times d)} \times 100$

2.   **Prediction of geometry**

1. Co-linear molecule :   F —— Be —— F $\mu = 0$
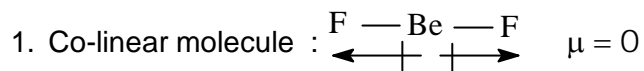
2. Co-planar molecule

$\mu = 0$
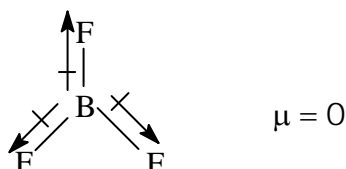
3. Regular geometry $\mu = 0$

A compound contain similar surrounding atoms and has no lone pair. If lone pair comes, symmetrical lone pair contain compound also regular geometry one.

PCl$_5$, SF$_6$
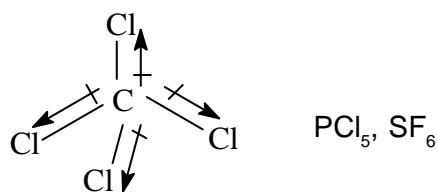
3.   **To find the resultant dipole moment**

If a compound contain similar surrounding atoms, the resultant dipole moment.

$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1 , \mu_2\, \cos\theta}$; where $\mu_1 = \mu_2$

$\therefore \mu_{resultant} = 2\mu_1 \cos \dfrac{\theta}{2}$

4.   **To predict the ortho, para, meta compounds.**

μ_1 > μ_2 > μ_3 $(\mu_3 = 0)$
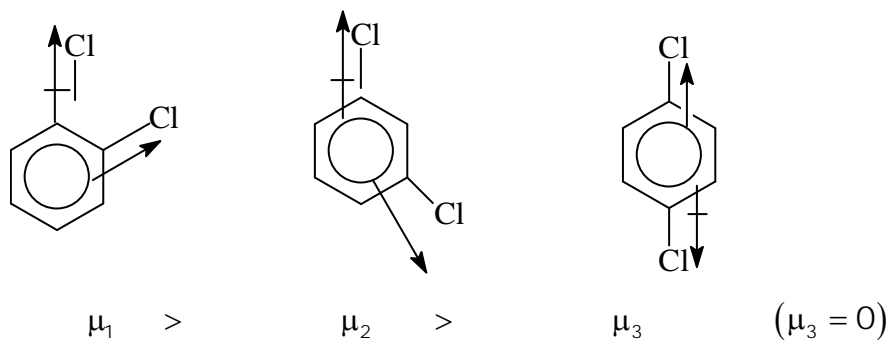
5.   To predict cis and trans isomers
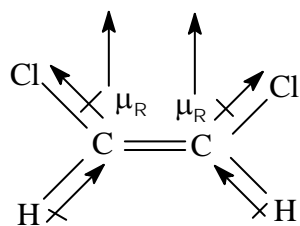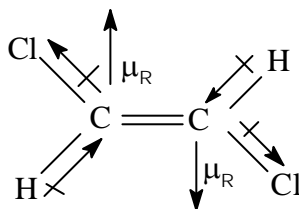
$$\mu_R \neq 0 \qquad\qquad\qquad \mu_R = 0$$

6.   Order of dipole moment

1. $HF > HCl > HBr > HI$

2. $NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

3. $H_3C - Cl > CH_2 - Cl_2 > CH - Cl_3 > CCl_4$

Exceptional

$H_3C - Cl > H_3C - F > H_3C - Br > H_3C - I$. This is due to in addition to electronegativity carbon-chlorine bond length also considering

Resonance

A compound, its all the properties could not clearly explained with a single structure it could clearly explained with more than one structures are known as resonating structures or canonical structures.

Resonating structures $\cong$ Resonance hybrid

Resonance hybrid
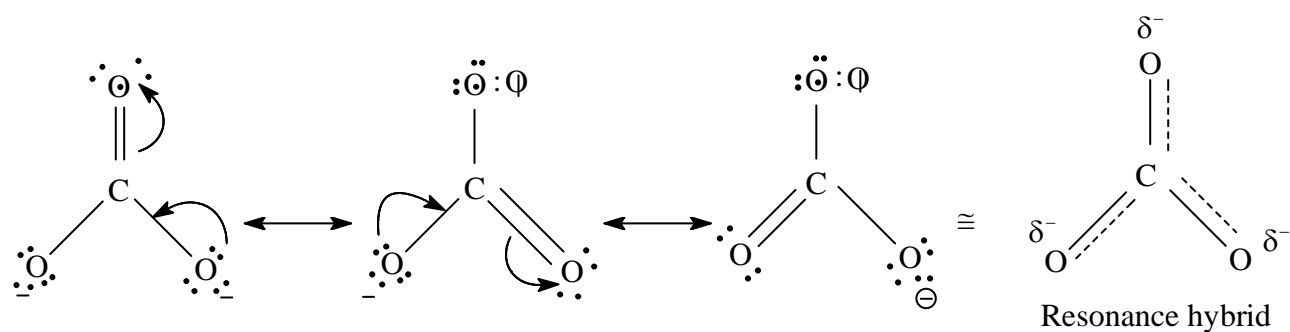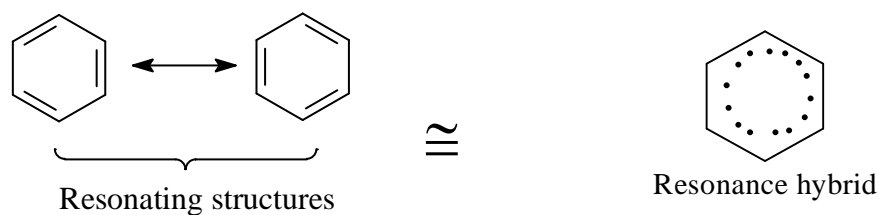
Conditions and characteristics features of resonance

1. In resonating structures, in identical point contain identical atoms.

2. There is an interchange of lone pair and π bond or π bonds

3. Resonating structures have high energy, least stable and cannot be isolated.

4. Resonance hybrid is the altogether of canonical forms and has least energy and most stable.

5. There is no exact double bond and single bond their average bond length is present

6. Resonance energy is the energy difference between the resonance hybrid and most stable canonical forms.

$$R.E. = E_{Resonance\ hybrid} - E_{stable\ canonical\ forms}$$

OR

$$R.E. = E_{observed/experimental} - E_{stable\ canonical\ form}$$

7. Resonance energy increases, stability of compound increases .

Bond parameters

Bond Length : It is the distance between the nuclei of covalent bonded atoms.

Factors influencing the bond length.

1. Size of bonded atom : Size of bonded atom increases bond length increases.

$$H-F < H-Cl < H-Br < H-I$$
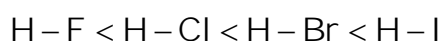
2. Electronegativity of bonded atom

    Electronegativity of bonded atom increases bond length decreases

$$H-F < H-Cl < H-Br < H-I$$
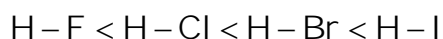
Bond Type	Covalent Bond Length (pm)
O–H	96
C–H	107
N–O	136
C–O	143
C–N	143
C–C	154
C=O	121
N=O	122
C=C	133
C=N	138
C≡N	116
C≡C	120

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N ≡ N)	109
O_2 (O = O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

3. Multiple bonds

   Multiple bonds increases bond length decreases.

   $$H_3C - CH_3 > H_2C = CH_2 > HC \equiv CH \ (C - C \ bond \ length)$$

4. Hybridisation

   % s charactor increases electronegativity of bonded atom increases, bond length decreases.

   $$\underset{\%s \ character \ 25\%}{H_3C - CH_3} > \underset{33.3\%}{CH_2 = CH_2} > \underset{50\%}{HC \equiv C - H}$$
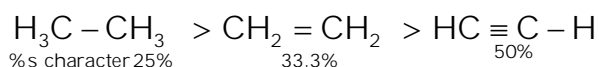
5. Back bonding

   Back bonding increases, bond length decreases.
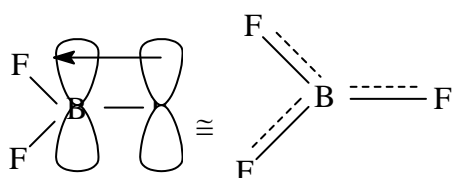
6. Resonance

Among resonating structures, there is no exact double bond and single bond their average bond length will be present.
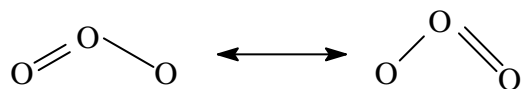
Arrange in the increasing order of bond length.
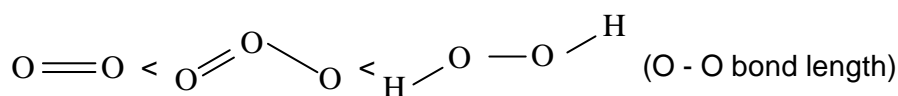
Bond angle :

Angle created between the two adjacent covalent bonds.

FACTORS INFLUENCING THE BOND ANGLE

1.　Hybridisation

$$\underset{(180^0)}{sp} \quad \underset{(120^0)}{sp^2} \quad \underset{(109^028')}{sp^3} \quad \underset{(120^0 \, \& \, 90^0)}{sp^3d} \quad \underset{(90^0)}{sp^3d^2}$$
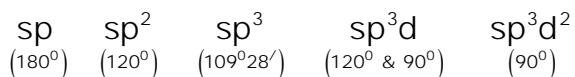
2.　Number lone pairs on the central atom

Number of lone pairs on the central atom increases, bond length decreases is due to the repulsion between $\ell p - \ell p > bp - \ell p$ and $bp - bp$

$$\underset{\ell p=0}{CH_4} > \underset{\ell p=1}{NH_3} > \underset{\ell p=2}{H_2O}$$
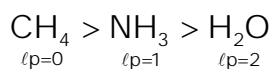
3.　Single electron on the central atom

Single electron on the central atom and bond pair repulsion is lower than bond pair - bond pair repulsion.

$NO_2 \quad H = {}^5\!/_2 = 2.5$. It is round to 3

$\quad\quad n\ell p = 0.5 \quad\quad \therefore H \Rightarrow 3 \; sp^2$
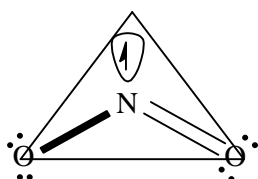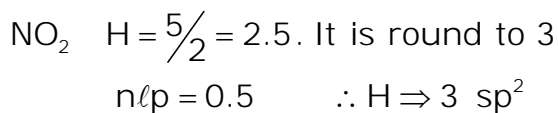
Bond angle > 120°

Bond angle = 132°

4.　Electronegativity of central atom

In three dimensional compounds, central atom having high electronegativity than surrounding atom, the bond angle will be maximum.
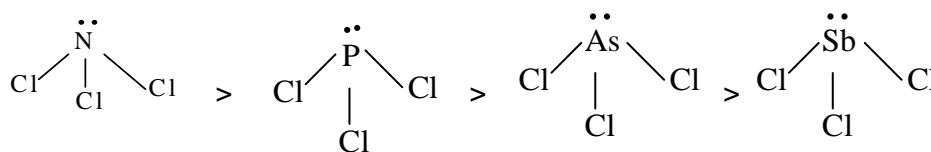
Electronegativity order = N > P > As > Sb. If all the above conditions are same,

5.　Bulky group on the central atom increases, bond angle increases.
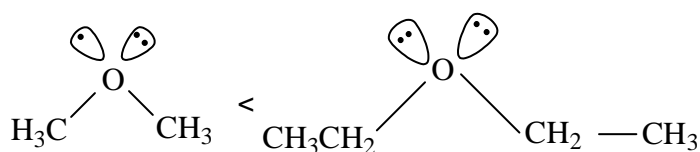
Bond order

Number of bonds between the two atoms.

Cl – Cl   B.O. = 1

O = O   B.O. = 2

N $\equiv$ N   B.O. = 3

Bond order α Bond energy /bond strength/bond dissociation energy.

Bond order α $\dfrac{1}{\text{Bond length}}$

Bond order = O, –ve the molecule will not exist.

In diatomic molecules

Total electrons	8	9	10	11	12	13	14	15	16	17	18	19	20
B.O.	0	0.5	1	1.5	2	2.5	3	2.5	2	1.5	1	0.5	0

In resonating structures

$$\text{B.O} = \frac{\text{No. bonds between the two atoms in all resonating structures}}{\text{Total number of resonating structures}}$$

For example in Benzene :
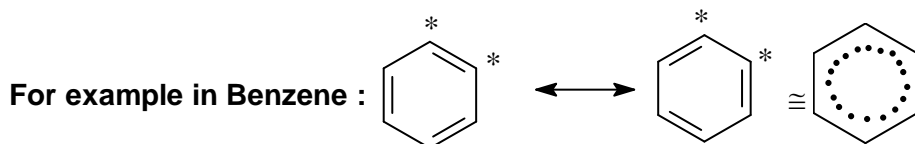
$$\text{B.O.} = \frac{2+1}{2} = 1.5$$

Bond dissociation energy

The energy required to dissociate one mole of a covalent bond in a compound.

Cl –Cl Bond dissociation energy = 242 kJ/mol

H–H Bond dissociation energy = 434 kJ/mol

Bond energy

The energy released, when one mole of covalent bond formed from the gaseous atoms.

Average bond enthalpy or mean bond enthalpy

In poly atomic similar surrounding atoms present in a compound, all the bonds are not same, their average bond length is taken.

For eg :

$$H_2O \longrightarrow H_{(g)} + OH_{(g)}; \; \Delta_a H_1 = 502 \text{ kJmol}^{-1}$$

$$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)}; \; \Delta_a H_2 = 427 \text{ kJ mol}^{-1}$$
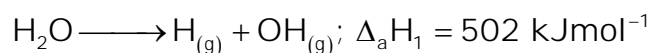
Bond length of O–H bond in water = $\dfrac{502 + 427}{2} = 464.5$ kJ

FACTORS INFLUENCING BOND DISSOCIATION ENERGY

1. **Size of bonded atom** : Size of bonded atom increases, bond dissociation energy decreases.

    Eg: HF > HCl > HBr > HI (Bond dissociation energy)

2. **Multiple bonds** : Multiple bonds between the two atoms increases ,bond dissociation energy decreases.

    Eg: $H_3C - CH_3 < H_2C = CH_2 < HC \equiv CH$ (C–C)

3. Lone pair on the bonded atom increases bond dissociation energy decreases.

$$H_3C\!-\!CH_3 \;>\; H_2\ddot{N}\!-\!\ddot{N}H_2 \;>\; \overset{H}{\underset{H}{\ddot{O}\!-\!\ddot{O}}} \;>\; :\ddot{F}\!-\!\ddot{F}:$$
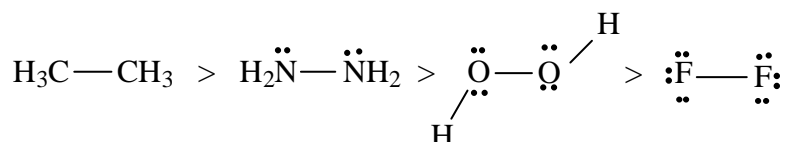
MOLECULAR ORBITAL THEORY

Molecular orbital (MO) theory was developed by F-Hund and R.S. Mulliken in 1932.The salient feature of this theory are

i. The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.

ii. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.

iii. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

iv. The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, tw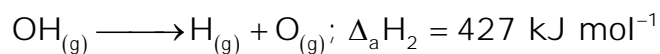o molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.

v. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

vi. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

vii. The molecular orbitals like atomic orbitals are filled in accordance with the aufbau prnciple obeying the Pauli's exclusion principle and the Hund's rule.

Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave functions $(\psi's)$ which represent the amplitude of the electron waves. These are obtained from the solution of Schrodinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrodinger wave equation. To overcome this problem, an approximate method known as **linear combination of atomic orbitals (LCAO)** has been adopted.

Let us apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions ψ_A and ψ_B. Mathematically , the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below:

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and $\sigma*$ are formed as:

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital $\sigma*$ formed by the subtraction of atomic orbital is called antibonding molecular orbital as depicted in figure.
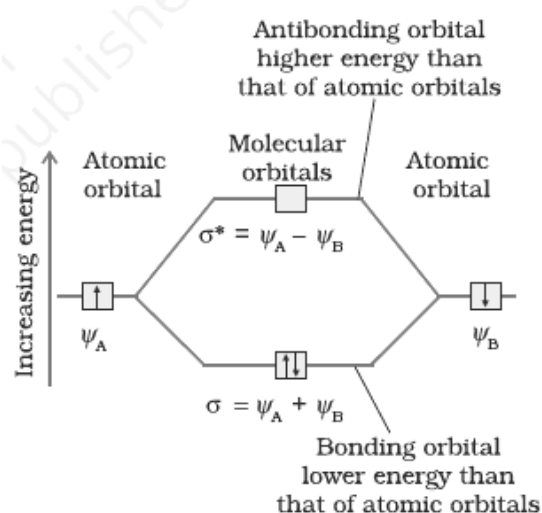
Formation of bonding (σ) and antibonding (σ^*) molecular orbitals by the linear combination of atomic orbitals ψ_A and ψ_B centered on two atoms A and B respectively.

Conditions for the combination of atomic orbitals

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. **The combining atomic orbitals must have the same or nearly the same energy.** This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different.

2. **The combining atomic orbitals must have the same symmetry about the molecular axis.** By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combie if they do not have the same symmetry. For example, $2p_z$ orbital of one atom can combine with $2p_z$ orbital of the other atom but not with the $2p_x$ or $2p_y$ orbitals because of their different symmetries.

3. **The combining atomic orbitals must overlap to the maximum extent.** Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

TYPES OF MOLECULAR ORBITALS

Molecular orbitals of diatomic molecules are designated as (σ) sigma, π (Pi), δ (delta) etc.

In this nomenclature, the sigma molecular orbitals are symmetrical around the bond-axis while pi molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ 1s and σ^* 1s. If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of $2p_z$ - orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$. Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and π^*.

A π bonding MO has larger electron density above and below the inter-nuclear axis. The π^* antibonding MO has a node between the nuclei.

Energy Level Diagram for Molecular Orbitals

We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as $\sigma 1s$ and $\sigma^* 1s$. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals:

Antibonding MOs $\sigma^* 2s$ $\sigma^* 2p_z$ $\pi^* 2p_x$ $\pi^* 2p_y$

Bonding MOs $\sigma 2s$ $\sigma 2p_z$ $\pi 2p_x$ $\pi 2p_y$
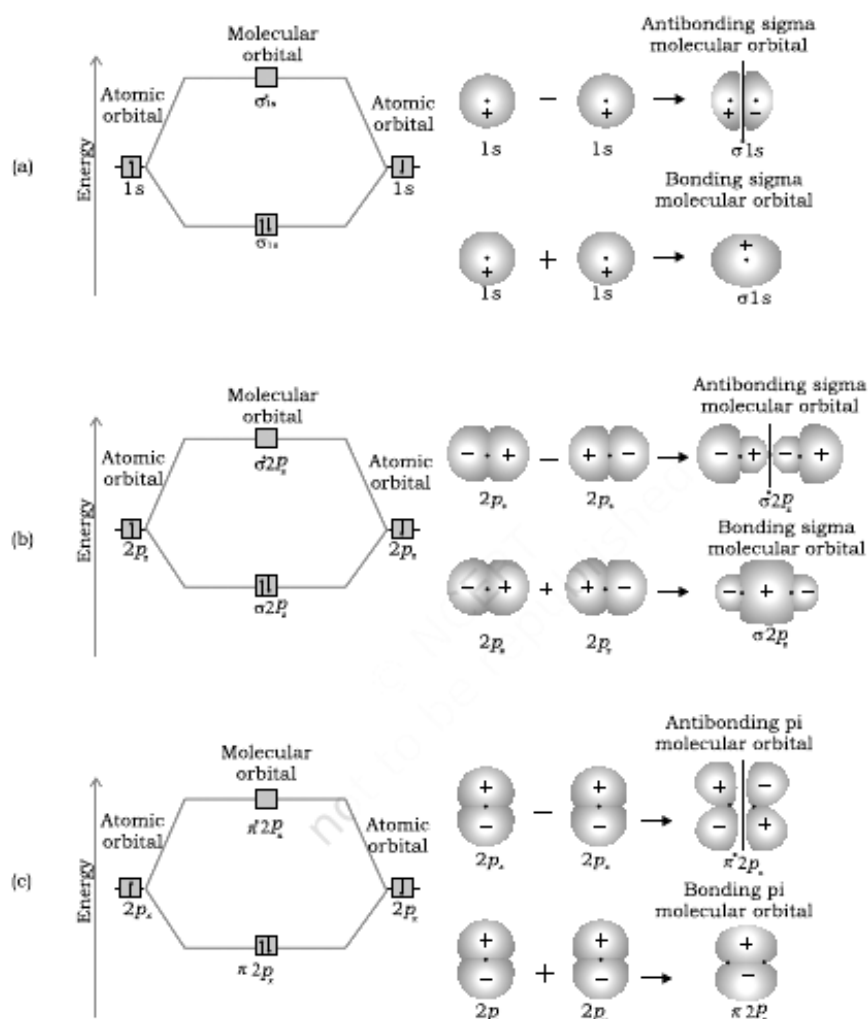
Number of nodal plane in MO's

$\sigma 1s, \sigma 2s, \sigma 2p_z = 0$

$\sigma^* 1s, \sigma^* 2s, \sigma^* 2p_z, \pi 2p_x$ and $\pi 2p_y = 1$

$\pi^* 2p_x$ and $\pi^* 2p_y = 2$ (perpendicular to each other)

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below.

$$\sigma ls < \sigma * ls < \sigma 2s < \sigma * 2s < \sigma 2p_z < (\pi\ 2p_x = \pi\ 2p_y)$$
$$< (\pi * 2p_x = \pi * 2p_y) < \sigma * 2p_z$$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, VC_2, N_2, etc, the increasing order of energies of various molecular orbitals is

$$\sigma ls < \sigma * ls < \sigma 2s < \sigma * 2s < (\pi\ 2p_x = \pi\ 2p_y)$$
$$< \sigma 2p_z < (\pi * 2p_x = \pi * 2p_y) < \sigma * 2p_z$$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.

Electronic configuration and Molecular Behaviour

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of Molecules : If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then (i) the molecule is stable if N_b is greater than N_a and (ii) the molecule is unstable if N_b is less than N_a. In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

Bond order :

Bond order is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals. i.e. Bond order (b.o.) = $\dfrac{1}{2}\left(N_b - N_a\right)$. The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows : A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e. $N_b < N_a$) or zero. (i.e. $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond

Integral bond order values of 1, 2 or 3 correspon to single, double or triple bonds respectively as studied in the classical concept.

Bond-length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature

If all the molecular orbitals in a molecule are doubley occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field). e.g. O_2 molecule.

**Bonding in some homonuclear diatomic molecules**

1. **Hydrogen molecule (H_2) :** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1 s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in $\sigma 1s$ molecular orbital. So electronic configuration of hydrogen molecule is

   $H_2 : (\sigma 1s)^2$. The bond order of H_2 molecule can be calculated as given below:

   Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{2 - 0}{2} = 1$

   This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJmol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

2. **Helium molecule (He_2) :** The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals leading to electronic configuration:
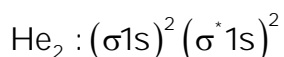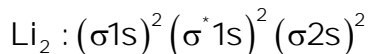
   $He_2 : (\sigma 1s)^2 (\sigma^* 1s)^2$

   Bond order of He_2 is 1/2 (2 - 2) = 0

   He_2 molecule is therefore unstable and does not exist. Similarly, it can be shown that Be_2 molecule $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ also does not exist.

3. **Lithium molecule (Li_2) :** The electronic configuration of lithium is $1s^2, 2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2 molecule, therefore, is

   $Li_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

   The above configuration is also written as $KK (\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2 (\sigma^* 1s)^2$. From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is ½(4 − 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

4. **Carbon molecule (C_2) :** The electronic configuration of carbon is $1s^2 2s^2 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

   $C_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ or $KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$
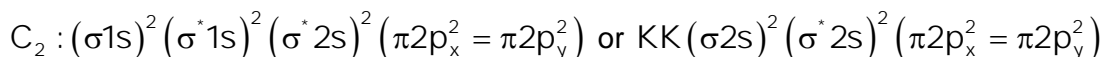
The bond order of C_2 is $\frac{1}{2}(8-4) = 2$ and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond. In a similar fashion the bonding in N_2 molecule can be discussed.

5.   **Oxygen molecuel (O_2)** : The electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^4$. Each oxygen atom has 8 electron. Hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

$$O_2 : \left(\sigma 1s\right)^2 \left(\sigma^* 1s\right)^2 \left(\sigma^* 2s\right)^2 \left(\sigma^* 2s\right)^2 \left(\sigma 2p_z\right)^2 \left(\pi 2p_x^2 \equiv \pi 2p_y^2\right)\left(\pi^* 2p_x^1 \equiv \pi^* 2p_y^1\right)$$

$$O_2 : \left[KK\left(\sigma 2s\right)^2 \left(\sigma^* 2s\right)^2 \left(\sigma 2p_z\right)^2 \left(\pi 2p^2 \equiv \pi 2p_y^2\right), \left(\pi^* 2p_x^1 \equiv \pi^* 2p_y^1\right)\right]$$

From the electronic configuration of O_2 molecle it is clear that ten electrons are present in bonding molecular orbitals and six electrons are present in antibonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a\right] = \frac{1}{2}\left(10 - 6\right) = 2$$

So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals, therefore, O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation. In this wa, the theory successfully explains the paramagnetic nature of oxygen.

Similarly, the electronic configurations of other homonuclear diatomic molecules of the second row of the periodic table can be written.

	With 2s-2p mixing			Without 2s-2p mixing			
	B_2	C_2	N_2	O_2	F_2	Ne_2	
σ^*_{2p}	☐	☐	☐	☐	☐	↑↓	σ^*_{2p}
π^*_{2p}	☐ ☐	☐ ☐	☐ ☐	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	π^*_{2p}
σ_{2p}	☐	☐	↑↓	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓	π_{2p}
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓	↑↓	σ_{2p}
σ^*_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	σ^*_{2s}
σ_{2s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	σ_{2s}

Bond energy / bond length values:
- B_2: 290 (159)
- C_2: 620 (131)
- N_2: 945 (110)
- O_2: 498 (121)
- F_2: 159 (143)

Bond order	1	2	3	2	1	0
Magnetic properties	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	–
Valence electron configuration	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\pi_{2p})^4(\sigma_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^2$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4$	$(\sigma_{2s})^2(\sigma^*_{2s})^2$ $(\sigma_{2p})^2(\pi_{2p})^4$ $(\pi^*_{2p})^4(\sigma^*_{2p})^2$

MO occupancy and molecular properties for B_2 through Ne_2.

In the figure are given the molecular orbital occupancy and molecular properties for B_2 through Ne_2. The sequence of MOs and their electron population are shown. The bond energy, bond length, bond order, magnetic properties and valence electron configuration appear below the orbital diagram.

Exception :

CO^+ has bond order of 3.5 because its Homo is σ^*2s

CO has bond order of 3 (iso electronic with N_2)

MOT for Heteroatomics

For isoelectronic species bond order must be same.

For Heteroatomics the orbitals of more electronegative element are less energetic but more stable than the orbitals of less electro negative element.

Note:

For molecules or ions involving resonance

Bond order = $\dfrac{\text{No.of bonds between any two atoms in all the resonting structres}}{\text{Total no.of resonating structures}}$

or Bond order = $\dfrac{\text{Total no.of bonds}}{\text{Total no.of resonating structures}}$
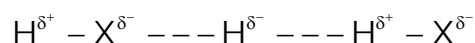
HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below:

$---H^{\delta^+}-F^{\delta^-}---H^{\delta^+}-H^{\delta^-}---H^{\delta^+}-F^{\delta^-}$. Here, hydrogen bond acts as a bridge between two atoms which holds one atom by covalent bond and the other by hydrogen bond. Hydrogen bond is represented by a dotted line (---) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

Cause of formation of Hydrogen bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge $\left(\delta^+\right)$ while 'X' attain fractional negative charge $\left(\delta^-\right)$.

This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as:

$H^{\delta^+}-X^{\delta^-}---H^{\delta^-}---H^{\delta^+}-X^{\delta^-}$

The magnitude of H-bonding depends on the physical state of the compound. It is maximum in the solid state and minimum in the gaseous state. Thus, the hydrogen bonds have strong influence on the structure and properties of the compounds.

Types of H-Bonds : There are two types of H-bonds

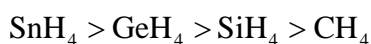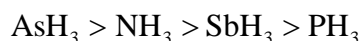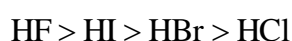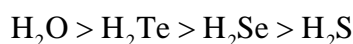i) Intermolecular hydrogen bond

ii) Intramolecular hydrogen bond

1. **Intermolecular hydrogen bond :** It is formed between two different molecules of the same or different compounds. For example, H– bond in case of HF molecule, alcohol or water molecules, etc.

2. **Intramolecular hydrogen bond** : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.
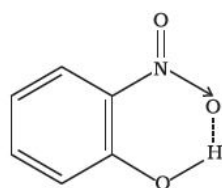
Intramolecular hydrogen bonding in o-nitrophenol molecule.

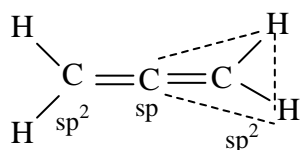**Inter molecular H bonded compounds have**

1. B.P., Viscosity, Surface tension, specific heat capacity are very high

2. Intermolecular hydrogen bonded compounds are less volatile than intramolecular H bonded compounds.

3. At room temperature, H_2O exists as liquid but H_2S exists as gas because in H_2O intermolecular H bond is present

4. Even though ethanol is a organic compoundwhich soluble in water is due to intermolecular H bonding

5. KHF_2 is known but $KHCl_2$ is not known because in KHF_2 intermolecular hydrogen bond is present

6. Order of B.P.

$$H_2O > H_2Te > H_2Se > H_2S$$

$$HF > HI > HBr > HCl$$

$$AsH_3 > NH_3 > SbH_3 > PH_3$$

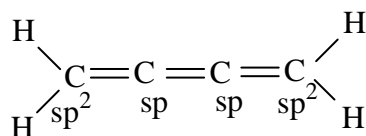$$SnH_4 > GeH_4 > SiH_4 > CH_4$$

ADDITIONAL INFORMATIONS

1. Hybridisation involving in other chapters.

Allene :

Central C atom used sp hybridised orbitals. Surrounding C atoms used sp^2 hybridised orbitals. End two hydrogen atoms are present in perpendicular plane.ie all the atoms are not in the same plane.
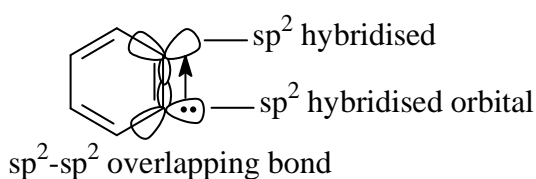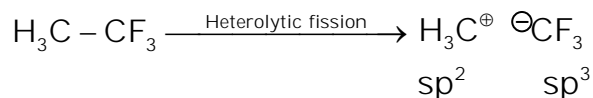
Cummelene

Central two carbon atoms are used sp hybridised orbital

End two carbon atoms are used sp^2 hybridised orbitals.
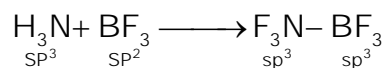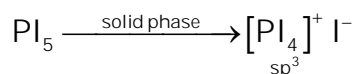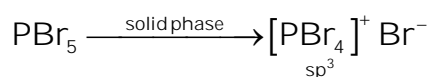
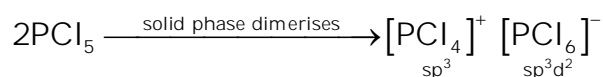All the atoms are in same plane.

Benzyne

sp^2-sp^2 overlapping bond

$$H_3C - CH_3 \xrightarrow{\text{Homolytic fission}} 2H_3C \cdot (sp^2)$$

$$H_3C - CF_3 \xrightarrow{\text{Heterolytic fission}} \underset{sp^2}{H_3C^{\oplus}} \; \underset{sp^3}{^{\ominus}CF_3}$$
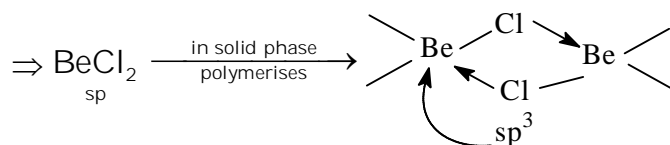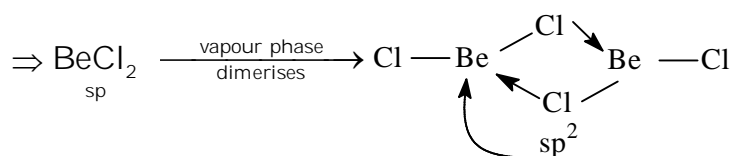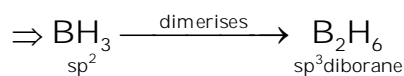
Exceptional

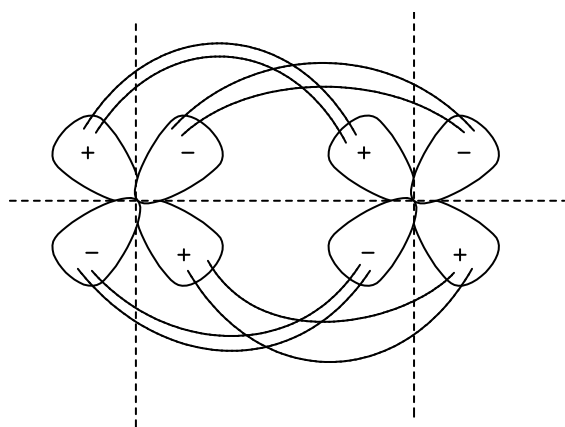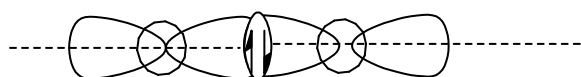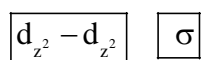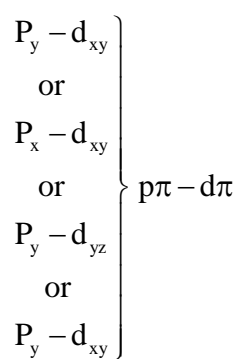• CF_3 trifluoromethyl radical. sp^3 hybridised orbitals used.

$\Rightarrow$ diamond $\rightarrow sp^3$

$\Rightarrow$ graphite and fullerene $\rightarrow sp^2$

$\Rightarrow \underset{sp^2}{BH_3} \xrightarrow{\text{dimerises}} \underset{sp^3 \text{diborane}}{B_2H_6}$

$\Rightarrow \underset{sp}{BeCl_2} \xrightarrow[\text{dimerises}]{\text{vapour phase}}$

Cl —— Be $\overset{Cl}{\underset{\underset{sp^2}{Cl}}{\Large\diagup\diagdown}}$ Be —— Cl

$\Rightarrow \underset{sp}{BeCl_2} \xrightarrow[\text{polymerises}]{\text{in solid phase}}$

Be $\overset{Cl}{\underset{\underset{sp^3}{Cl}}{\Large\diagup\diagdown}}$ Be

$PX_{5(g)} \longrightarrow sp^3d \qquad X = F, Cl, Br, I$

$2PCl_5 \xrightarrow{\text{solid phase dimerises}} \underset{sp^3}{[PCl_4]^+} \; \underset{sp^3d^2}{[PCl_6]^-}$

$PBr_5 \xrightarrow{\text{solid phase}} \underset{sp^3}{[PBr_4]^+} Br^-$

$PI_5 \xrightarrow{\text{solid phase}} \underset{sp^3}{[PI_4]^+} I^-$

$\underset{SP^3}{H_3N} + \underset{SP^2}{BF_3} \longrightarrow \underset{sp^3}{F_3N} - \underset{sp^3}{BF_3}$

$CuSO_4 \cdot 5H_2O$ contains

1. Ionic bonds
2. Covalent bonds
3. Co-ordinate bonds
4. Hydrogen bonds

$$\left.\begin{array}{c} P_y - d_{xy} \\ \text{or} \\ P_x - d_{xy} \\ \text{or} \\ P_y - d_{yz} \\ \text{or} \\ P_y - d_{xy} \end{array}\right\} p\pi - d\pi$$

$$\boxed{d_{z^2} - d_{z^2}} \quad \boxed{\sigma}$$
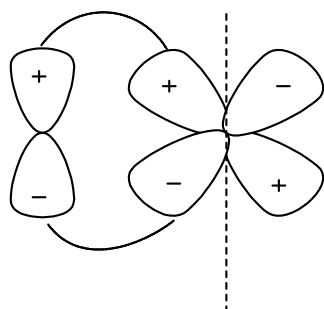
d_{xy} - d_{xy} δ bond

$d_{x^2-y^2} - d_{x^2-y^2}$ also form δ bond

Eg : $\left[Re_2 Cl_8 \right]^{2-}$. Di Rhenium Octa chloride ion. Contain quadraple bond.

$CuSO_4 . 5H_2O$