Chemical Bonding

Chemical Bond : The attractive force which holds various constituents such as atoms, ions etc., together in different chemical species is called a chemical bond.

To explain nature of chemical bond, different theories are given

(i) Octet rule

(ii) Valence bond theory

(iii) Valence shell electron pair repulsion theory

(iv) Molecular orbital theory.

Octet rule :

“Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

(i) It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.

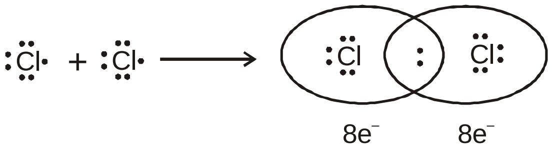
(ii) It means that these atoms must have a stable electronic configuration.

(iii) These elements (noble gases) have 8 electrons (ns^2 np^6) except helium which has 2 electrons ($1s^2$) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most shell configuration	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$

(iv) It is therefore concluded that ns^2 np^6 configuration in the outer energy level constitues a structure of maximum stability or minimum energy.

The **Octet rule** can be understood by considering the formation of the chlorine molecule, Cl_2. The Cl atom with electronic configuration, $[Ne]^{10}$ $3s^2$ $3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.



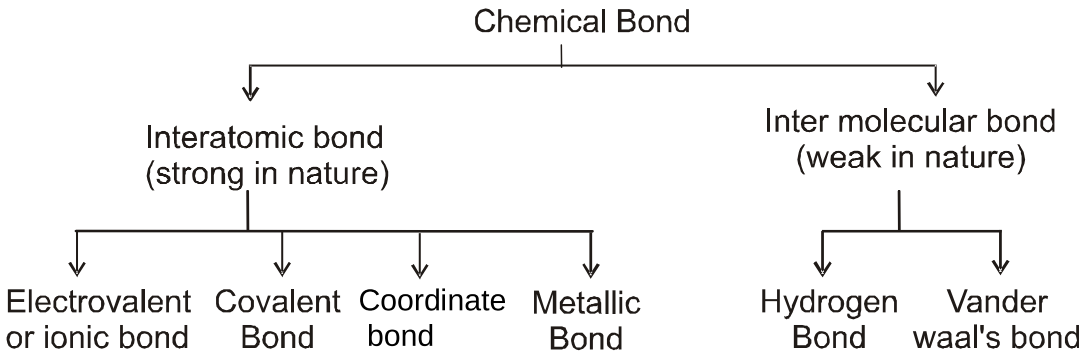
or Cl – Cl

Covalent bond between two Cl atoms

Figure

CLASSIFICATION OF CHEMICAL BONDS :

On the basis of electronic valency theory and structure, chemical bonds can be classified as follows.



Bond		**Bond Energy per mole**
Ionic, Covalent & Co–ordinate	————	200 kJ
Hydrogen bonding	————	10 – 40 kJ
Vander–waal’s	————	2 – 10 kJ

ELECTROVALENT OR IONIC BOND :

The chemical bond formed between two or more atoms as a result of complete transfer of one or more electrons from one atom to another is called ionic or electrovalent bond.

Electrovalent bond is not possible between similar atoms. This type of bonding requires two atoms of different nature. One atom should have the tendancy to loose electrons i.e. electropositive in nature and the other atom should have the tendency to accept electrons i.e. electronegative in nature.

Electropositive atom looses electrons (group IA to IIIA)

Electronegative atom gains electron (group IVA to VII A)

Example : IA and VII A group elements form strong ionic compound.

$$\underset{2,8,1}{Na} + \underset{2,8,7}{Cl} \longrightarrow \underset{\substack{2,8\\ \text{(Ne configuration)}}}{Na^{+}} + \underset{\substack{2,8,8\\ \text{(Ar configuration)}}}{Cl^{-}}$$

More the distance between two elements in the periodic table more will be the ionic character of the bond.

Total number of electrons lost or gained is called electrovalency.

Example :

(1) $Mg + O \longrightarrow MgO$

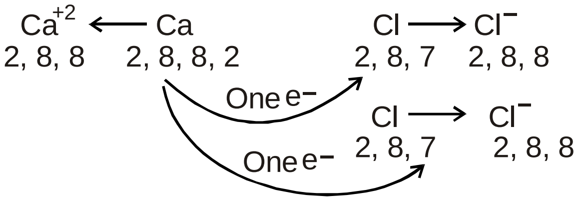
$$\underset{2,8}{Mg^{+2}} \longleftarrow \underset{2,8,2}{Mg} \qquad \underset{2,6}{O} \longrightarrow \underset{2,8}{O^{-2}}$$

$2e^{-}$

electrovalency of Mg = 2

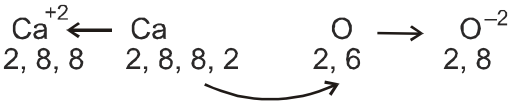
electrovalency of O = 2

(2) $Ca + 2Cl \longrightarrow CaCl_2$



electrovalency of Ca = 2
electrovalency of Cl = 1

(3) $Ca + O \longrightarrow CaO$



electrovalency of Ca = 2
electrovalency of O = 2

- Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond. Force of attraction is equal in all direction so ionic bond is non–directional.
- A definite three dimensional structure called crystal lattice is formed .
  Energy released during the formation of one mole crystal lattice is called lattice energy.

  e.g. $(6.023 \times 10^{23})Na^{+} + (6.023 \times 10^{23})\ Cl^{-} \longrightarrow (6.23 \times 10^{23})\ NaCl + 94.5$ K.cal (Lattice energy).
- Ionic compounds do not have a molecular formula, they only have empirical formula.

  e.g. NaCl is the empirical formula of sodium chloride.

Factors favouring formation of Ionic bonds :

Formation of ionic bond depends upon three factors :

(A) Ionisation energy (IE) :

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form positve ion or cation is called ionzation energy [energy is absorbed so it is an endothermic process]

$$M + I.E. \longrightarrow M^{+} + e^{-}$$

Less Ionisation energy ⇒ Greater tendency to form cation.

Example :

$$\left.\begin{array}{l} Na^{+} > Mg^{+2} > Al^{+3} \\ Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+} \end{array}\right\}\text{Cation formation tendency}$$

(B) Electron affinity :

Amount of energy released when an electron is added to an isotated gaseous atom to form negative ion or anion is called electron affinity [energy is released so it is an exothermic process]

$$X + e^{-} \longrightarrow X^{-} + EA$$

High electron affinity ⇒ Greater tendency to form anions

$$\left.\begin{array}{l} Cl^{-} > F^{-} > Br^{-} > I^{-} \\ F^{-} > O^{-2} > N^{-3} \end{array}\right\}\text{Anion formation tendency}$$

LATTICE ENTHALPY :

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol-1. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na^{+1} (g) and one mole of Cl^{-}(g) to an infinite distance.

This process involves both the attractive forces between Ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three- dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only.

Factors associated with the crystal geometry have to be included.

$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s)$ $\Delta H = \Delta H_{lattice} \Rightarrow$ –ve (always)

$Mg^{2+}(g) + 2Cl^{-}(g) \longrightarrow MgCl_2(s)$

Factors affecting L.E.

(i) Lattice energy (L.E.) $\alpha \frac{1}{r}$ $r = r_+ + r_-$

= interionic distance

(ii) L.E. $\alpha\ Z_+, Z_-$

$Z_+ \Rightarrow$ charge on cation in terms electronic charge

$Z_- \Rightarrow$ charge on anion in terms electronic charge

(iii) Charge density of cation ↑ L.E. ↑

(a) NaCl > KCl	(size)
(b) NaCl < MgO	(size, charge)
(c) $NaCl < MgCl_2$	(size, charge)

In size and charge, charge will dominate

$Na_2O > NaF$

$NaCl < Na_2S$

(d) Al_2O_3 Na_2O MgO

$Al_2O_3 > MgO > Na_2O$

Characteristics of ionic compounds :

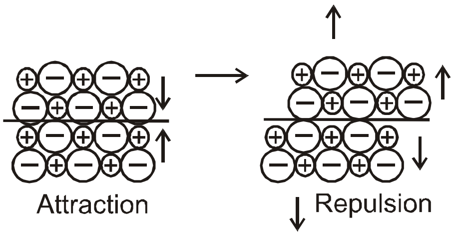
(i) Physical state

(a) Electrovalent compounds are generally crystalline, hard & brittle in nature.

(b) These compounds are generally made from ions which are arranged in a regular way as a lattice structure.

(c) Thus electrovalent compounds exist as three dimensional solid aggregates.

(d) Normally each ion is surrounded by a number of oppositively charged ions and this number is called co-ordination number



{Same charged ions comes near. So they repell each other}

(ii) Boiling point and melting point :

High boiling point and melting points are due to strong electrostatic force of attraction.

(iii) Electrical conductivity :

It depends on ionic mobility. In solid state there are no free ions so they are bad conductors of electricity In fused state or aqueous solution free ions are present so they are good conductors of electricity (Conductivity order) Solid state < Fused state < Aqueous solution

(iv) Ionic reactions :

✶ Ionic compounds show ionic reactions & covalent compounds show molecular reactions. Ionic reactions are fast reactions.

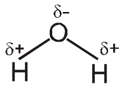
Example : When NaCl is added to $AgNO_3$ solution, white ppt of AgCl is formed at once.

$$Ag^+NO_3^- + Na^+Cl \rightleftharpoons Na^+NO_3^- + AgCl\downarrow$$

white ppt.

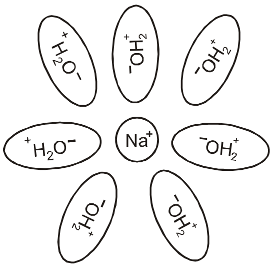
(v) Solubility – *Ionic compounds are soluble in polar solvent like H_2O, HF etc.*

To explain solubility of ionic compound consider an example of NaCl in water.

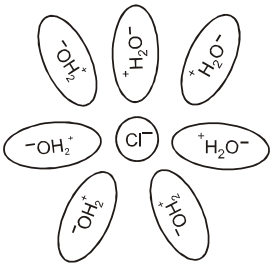
H_2O is polar solvent it can represent as 

✶ The Na^+ ions gets associated with partially negatively charged 'O' of water

✶ And Cl^- ions gets associated with partially positively charged 'H' of water.



Oxygen atom of H_2O gives its electron to $\overset{\oplus}{Na}$



H atom of H_2O gain electron from $Cl^{\ominus}$

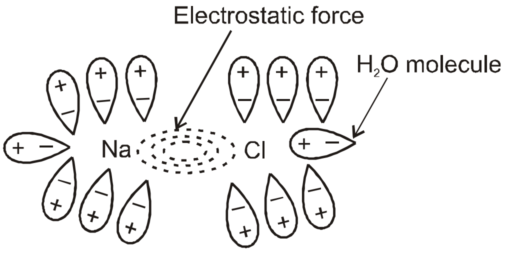
Thus charge on Na^+ and Cl^- decreases and electrostatic force also decreases which leads to free ion.

✶ Here, attraction force between H_2O and Na^+ or Cl^- (Hydration energy) > Electrostatic force between ions in lattice. (Lattice energy)

✶ Energy released due to interaction between polar solvent molecule and ions of solute is called solva tion energy. If water used as solvent it is called hydration energy.

✶ Condition of the solubility of ionic compound in water is (Hydration energy > Lattice energy)

Solvation or Hydration :



Whenever any compound generally ionic or polar covalent is dissolved in an polar solvent or in water then., different ions of the compound will get separated and will get surrounded by polar solvent molecules. This process is known as solvation or hydration. Energy released in this process is known as solvation energy or hydration energy

The ionic compound will be soluble only if solvation energy (H.E.) is more than the lattice energy

Applications of Hydration energy :

(a) Size of the hydrated ions: Greater the hydration of the ion greater will be its hydrated radii
$Li^+(aq) > Na^+(aq)$

(b) Mobility of the ion: more is the hydration smaller will be the mobility of the ions $\propto \frac{1}{\text{Hydrated radii}}$
$Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$.

(c) Electrical conductance : is related to mobility so follows the same order

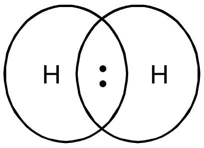
COVALENT BOND :

✶ A chemical bond formed by sharing of electrons between two elements is called as covalent bond.

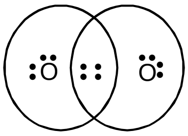
A—A *(Single bond)* : When 2 electrons are shared between the two combining elements.

A=A *(Double bond)* : When 4 electrons are shared between the two combining elements.

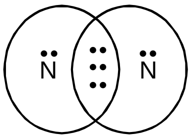
A≡A *(Triple bond)* : When 6 electrons are shared between the two combining elements.



H_2 molecule
H—H



O_2
O = O



N_2
N ≡ N

Covalency :

(i) It is defined as the number of electrons contributed by an atom of the element for sharing with other atom so as to achieve noble gas configuration.

(ii) It can also be defined as the number of covalent bonds formed by the atom of the element with other atoms.

(iii) The usual covalency of an element except hydrogen is equal to 8 minus the number of group to which the element belongs.

Lewis structure and covalent bond :

(i) Structures in which valency electrons are represented by dots are called Lewis structures.

(ii) All atoms in the formulae will have eight electrons in it's valence shell.H atom is an exception for it can form large number of bonds with the atom present at the center of any crystal structure. Other atoms surround it to complete their octet.

(iii) Lewis dot formulae shows only the number of valency electrons, the number and kinds of bonds, but does not depict the three dimensional shapes of molecules and polyatomic ions.

(iv) Lewis formulae are based on the fact that the representative elements achieve a noble gas configuration in most of their compounds i.e. 8 electrons in their outermost shell (except for H_2, Li^+ and Be^{2+} ions which have only 2 electrons)

Lewis Dot Structures :

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different.

To write the Lewis dot structure following steps are to be followed :

(i) The total number of electrons are obtained by adding the valence electrons of combining atoms.

(ii) For Anions, we need to add one electron for each negative chanrge.

(iii) For cations, we need to subtract one electron for each positive charge.

(iv) After then the central atom is decided.

To decide, Central atom, following steps are followed :

(i) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.

(ii) Generally the atom which is/are less in number acts as central atom.

(iii) Generally central atom is the atom which can form maximum number of bonds(which is generally equal to the number of electrons present in the valence shell of the atom).

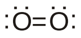
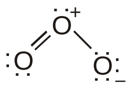
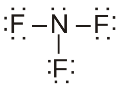
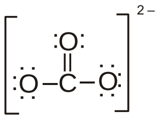
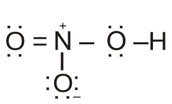
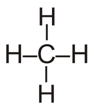
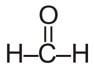
(iv) Atom of highest atomic number or largest atom generally acts as central atom.

Hence fluorine and hydrogen can never act as central atoms.

After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in the following Table

Table-1

Molecule/ion	H_2	O_2	O_3	NF_3	CO_3^{2-}	HNO_3	CH_4	HCHO
Lewis Representation	H – H							

Each H-atom attains the configuration of helium (a duplet of electrons)

Characteristics of covalent compounds :

(i) Physical state :

(a) Under normal temperature and pressure, they exist as gases or liquids of low boiling points.

(b) This is due to the fact that very weak forces of attraction (Vander waal's forces) exist between the molecules due to which molecules are far from each other.

(c) If their molecular masses are high they exist as soft solids ex. Sulphur, phosphorus and iodine

(ii) Crystal structures :

Various types of structures that are present in a covalent compound are as follows.

(a) Covalent solid – In this type of structure every atom is bonded to four other atoms by single covalent bonds resulting in the formation of a giant structure e.g. SiC, AIN and diamond these crystals are very hard and possess high melting point.

Diamond is sp^3 hybridized carbon atom and it forms a tetrahedral structure.

Graphite is sp^2 hybridized carbon atomsand it forms hexagonal layers which can slide over each other due to weak Vander waal's forces of attraction.Distance between C–C atom is 1.42 Å distance between layers is 3.6 Å. **Graphite is more stable than diamond due to high value of change in enthalpy.**

(b) Molecular solids : They are formed when one atom combines with another by a covalent bond and then the molecule combines with another similar molecule with the help of Vander waal's force of attraction or hydrogen bond

Example : CH_4(Solid), dry ice, ice

(iii) Melting and boiling points :

(a) With the exception of a few which have giant three dimensional structures such as diamond, carborundum (SiC), Silica (SiO_2), Boron steel (B_4C), others have relatively low melting and boiling points.

(b) This is due to the presence of weak attractive forces between the molecules.

(iv) Electrical conductivity :

(a) In general covalent substances are bad conductors of electricity. Since they do not contain charged particles or free electrons.

(b) Substances which have polar character like HCl in a solution, can conduct electricity.

(c) Graphite can conduct electricity since electrons can pass from one layer to other.

(d) Some show conductivity due to self ionisation. example Liq NH_3

$$NH_3 + NH_3 \longrightarrow NH_4^+ + NH_2^- \text{ (Amide ion)}$$

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

(v) Chemical reactions :

Covalent substances give molecular reactions. Reaction rate is usually low because it involves two steps (i) breaking of covalent bonds of the reactants (ii) establishing new bonds. While in ionic reactions there is only regrouping of ions.

(vi) Solubility :

(a) Non polar compounds are soluble in non polar solvents. Non polar solvents are CCl_4, Benzene, CS_2 etc.

(b) Polar compounds are soluble in polar solvents (i.e. ΔEN 0.9 to 1.8). Polar solvents are H_2O, $CHCl_3$, Alcohol etc.

(vii) Isomerism :

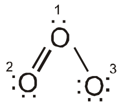
Covalent bonds are rigid and directional. On account of this there is a possibility of different arrangement of atoms in space. Covalent compounds can thus shows isomerism (structural and spatial)

Formal Charge :

The formal charge of an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the lewis structure.

$$\boxed{\begin{array}{l}\text{Formal charge (F.C.)}\\ \text{On an atom in a Lewis}\\ \text{structure}\end{array}} = \boxed{\left[\begin{array}{l}\text{Total number of valence}\\ \text{electron in the free atom}\end{array}\right] - \left[\begin{array}{l}\text{Total number of non bonding}\\ \text{(lone pair) electrons}\end{array}\right] - (\tfrac{1}{2})\left[\begin{array}{l}\text{Total number of}\\ \text{bonding (shared)}\\ \text{electrons}\end{array}\right]}$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3, may be drawn as :



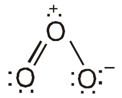
The atoms have been numbered as 1. 2 and 3. The formal charge on :

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows :



It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. **Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

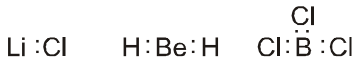
Note : The formal charge Is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

Limitations of the Octet Rule :

The octet rule, though useful, is not universal. It is quite useful for understanding .the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

1. The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom Is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3. BeF_2 , BF_3 , $AlCl_3$



$$\mathrm{Li:Cl} \qquad \mathrm{H:Be:H} \qquad \mathrm{Cl:\overset{Cl}{\ddot{B}}:Cl}$$

2. Odd-electron molecules

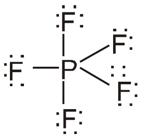
In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide. NO_2, the octet rule is not satisfied for all the atoms.

e.g. NO, ClO_2 , ClO_3

3. The expanded octet, Super octet or Hypervalent molecules

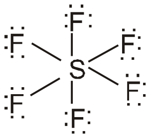
Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, PCl_5, HNO_3, SO_3, SO_2, H_2SO_4 and a number of coordination compounds.



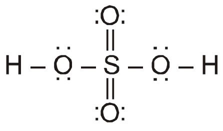
PF_5

10 electrons around the P atom



SF_6

12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

- Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.

4. Other drawbacks of the octet theory

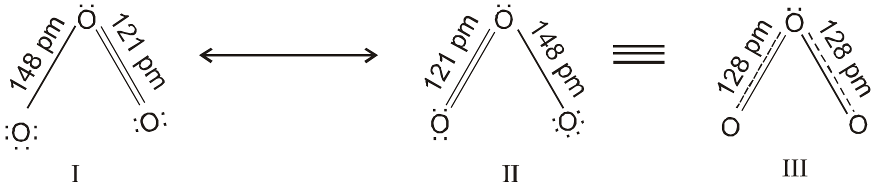
(i) It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , $XeOF_2$ etc.,

(ii) This theory does not account for the shape of molecules.

(iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule

Resonance :

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below :



Resonance in the O_3 molecule

Structures I and II represent the two canonical forms.

The structure III is the resonance hybrid

In both structures we have a O – O single bond and a O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively.

Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond.

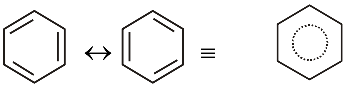
Obviously, this cannot be represented by either of the two Lewis structures shown above.

According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3, more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

Definition : Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound

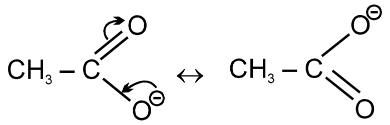
Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



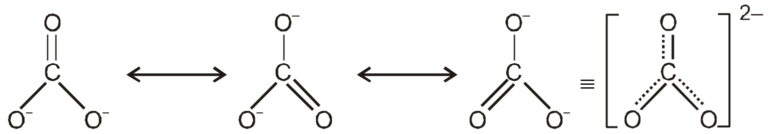
Resonance hybrid

Example :

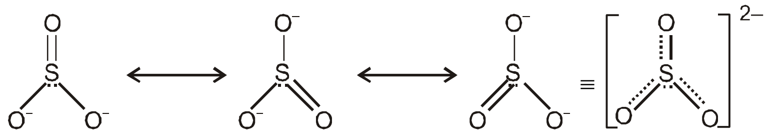
(i)



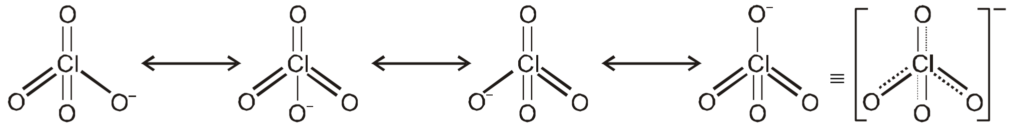
(ii)



(iii)



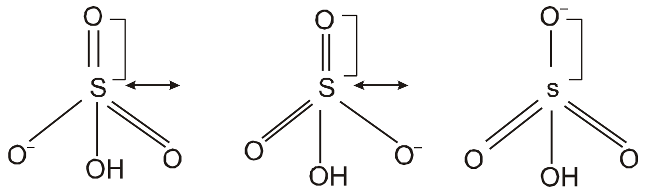
(iv)



- Resonance energy = Actual bond energy – Energy of most stable resonating structure.
- Stability of molecule α resonance energy.
- More is the number of covalent bonds in molecule more will be its resonance energy.
- Resonance energy α number of resonating structures.

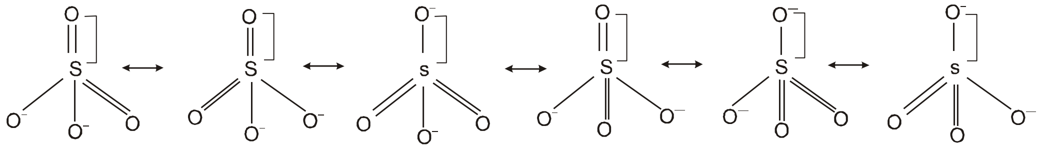
Bond order in oxoanions and corresponding acids :

Let's starts with example of HSO_4^-



- Bond order = $\dfrac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \dfrac{2+2+1}{3}$ = 5/3

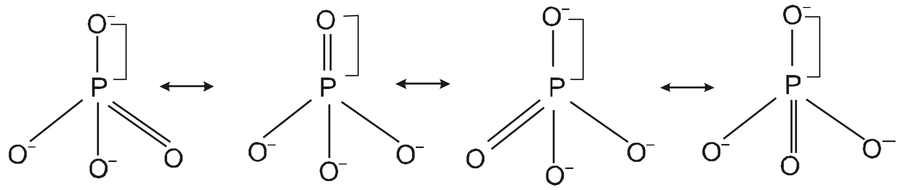
Consider another example of SO_4^{--} :



- Bond order = $\dfrac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}}$

$$= \frac{2+2+1+2+1+1}{6} = 1.5$$

Consider another example of PO_4^{---} :



- Bond order = $\dfrac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}}$

$$= \frac{1+2+1+1}{4} = 5/4$$

MODERN CONCEPT OF COVALENT BOND (VBT) :

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H_2 (435.8 kJ mol$^-$, 74 pm) and F_2 (150.6 kJ mol$^-$, 42 pm); although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two Important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between :
(i) nucleus of one atom and its own electron that is $N_A – e_A$ and $N_B – e_B$.
(ii) nucleus of one atom and electron of other atom i.e., $N_A – e_B$. $N_B – e_A$.

Similarly repulsive forces arise between :
(i) electrons of two atoms like $e_A – e_B$, (ii) nuclei of two atoms $N_A – N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig.).

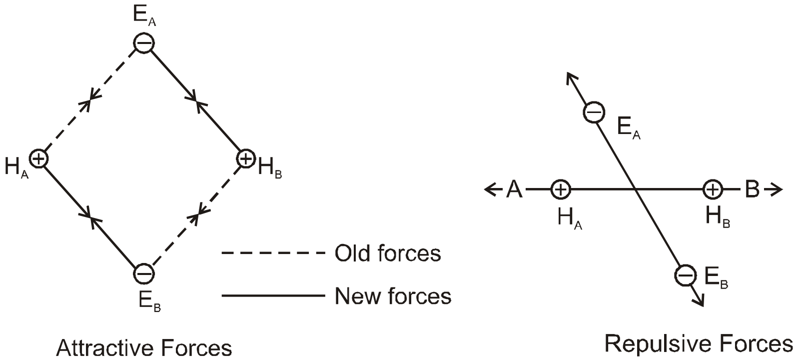


Fig- Forces of attraction and repulsion during the formation of H_2 molecule.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. Conversely. 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

$$H_2(g) + 435.8 \text{ kJ mol}^- \rightarrow H(g) + H(g)$$

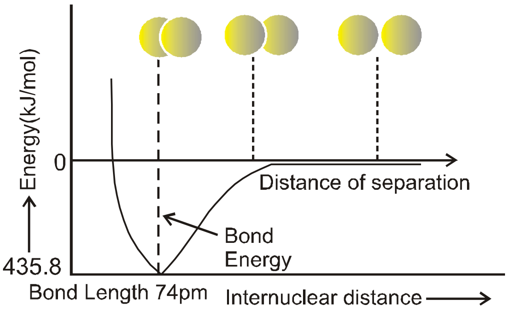


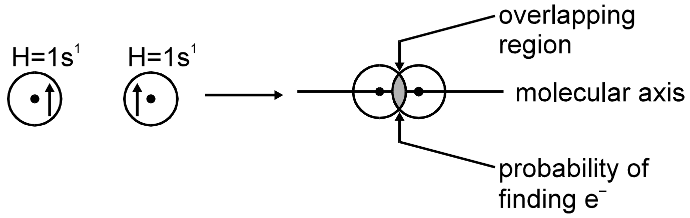
Fig. The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.

Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbltals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present In the valence shell having opposite spins.

Main points of valency bond theory :

(i) A covalent bond is formed by partial overlapping of two atomic orbitals



(ii) More is the extent of overlapping between the two atomic orbital, stronger will be bond.

[Principal Quantum no. same, n = 2]

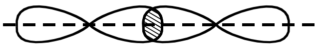
∵ s orbital are spherical in nature so they are least diffused hence it will provide less area for overlapping.

(iii) Orbitals which are undergoing overlapping must be such that

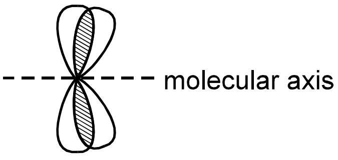
(a) Each orbital should have one electron with opposite spin (for formation of covalent bond)

(b) One orbital have pair of electron and the other orbital have no electron (for formation of co-ordinate bond)

(iv) If the overlapping is along the molecular axis then bond will be sigma (σ) & in the perpendicular direction, it will be pi(π) bond.



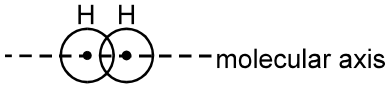
σ - bond



π - bond

☞ **Examples of overlapping of pure atomic orbitals.**

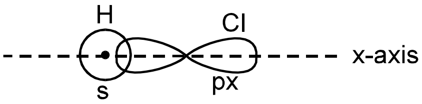
(i) H_2 (s–s) $H = \underset{1s}{\boxed{\uparrow}}$ $H = \underset{1s}{\boxed{\uparrow}}$



H_2 molecule

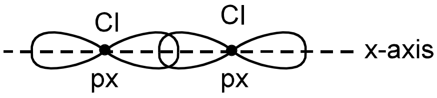
(ii) HCl gas molecule (s-p)

$H = \underset{1s}{\boxed{\uparrow}}$ | $_{17}Cl = 1s^2\ 2s^2p^6\ ,\ 3s^2p^5$ $\underset{3s}{\boxed{\uparrow\downarrow}}$ $\underset{3p}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}$



HCl molecule

(iii) F_2, Cl_2, Br_2, I_2 (p-p)



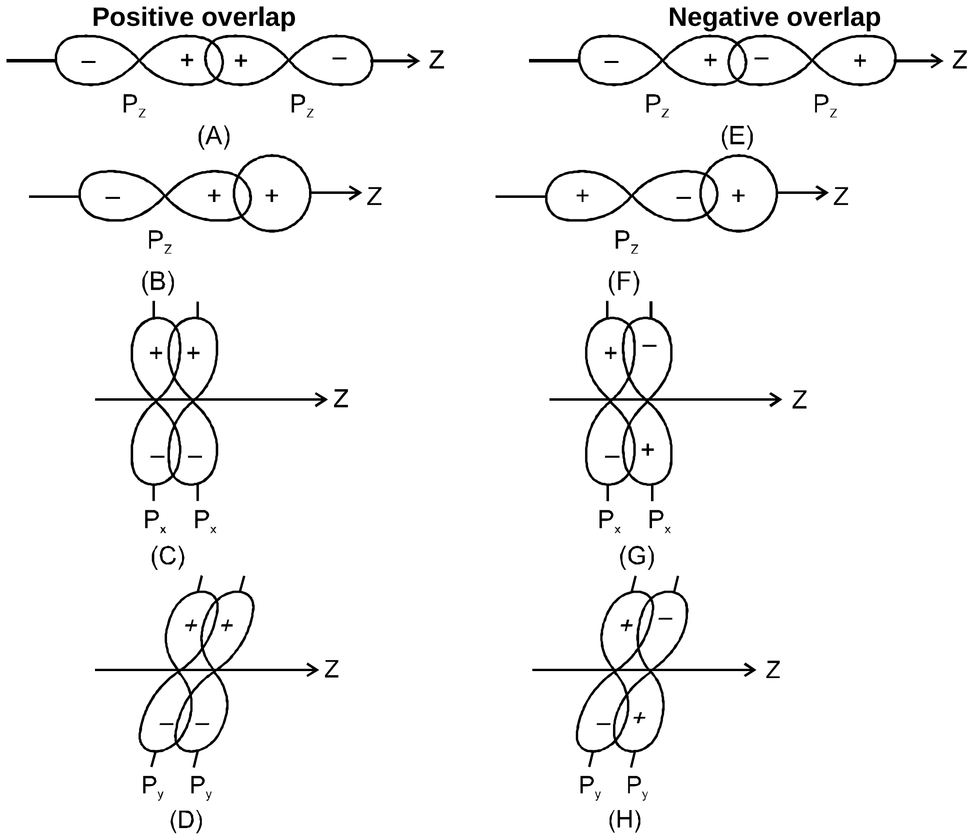
Cl_2 molecule

F_2	Cl_2	Br_2	I_2	
2p-2p	3p-3p	4p-4p	5p-5p	(Type of overlapped orbitals)

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 arrangements 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.



Zero overlap

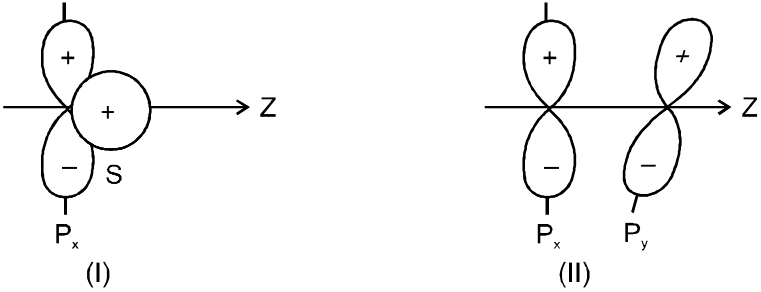


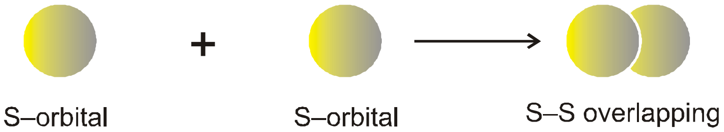
Figure : Positive, negative and zero overlaps of s and p atomic orbitals

Types of Overlapping and Nature of Covalent Bonds :

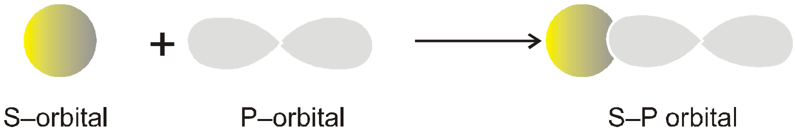
The covalent bond may be classified into two types depending upon the types of overlapping :
(i) Sigma (σ) bond, and (ii) pi (π) bond

(i) SIgma (σ) bond : This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the intemuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

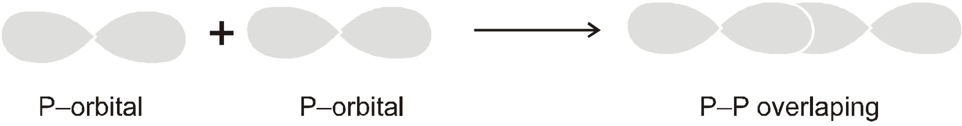
● s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the intemuclear axis as shown below :



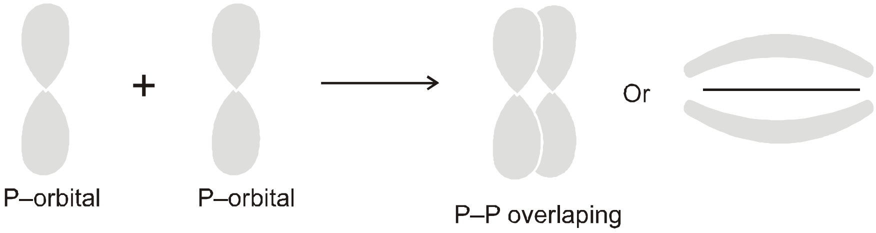
● s-p overlapping: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



● p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(iii) pi(π) bond : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the intemuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



Strength of Sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlaping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond . between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Diffenence in σ and π bonds :

Sigma (σ) bond	Pi (π) bond
1. It results from the end to end overlapping of two s orbitals or two p–orbitals or one s and one p–orbital.	It result from the sidewise (lateral) overlapping of two p orbitals.
2. Its bonded orbital consists of a single electron cloud symmetrical about internuclear Axis	Its bonded orbital consists of two electron clouds one above and the other below the plane of symimetry
3. Strong	Weak
4. Bond energy 80 Kcals	65 Kcals
5. More stable	Less Stable
6. Less reactive	More reactive
7. Can independently axis	Always exists alongwith a σ bond
8. Hybridization depends upon σ bond	doesn't depend on σ bond
9. The groups or atoms can undergo bond rotation about single sigma (σ) bonds	Due to resistance to rotation around the π bond the groups attached to it are not free to rotate.
10. The σ electrons are referred as localised	in π bond the electrons are held less firmly bond thus can be easily dissociated or polarised by an external charge and hence the π e^- are referred as mobile electrons.
11. Shape of the molecule is determined by the σ bonds present in the molecule	π bonding does not affect the shape of the molecule

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 postulates 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.

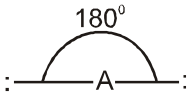
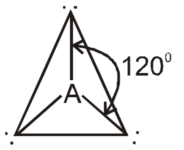
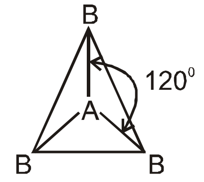
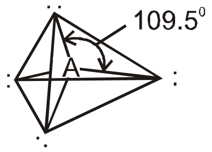
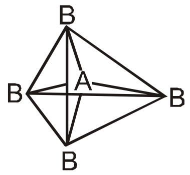
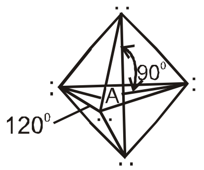
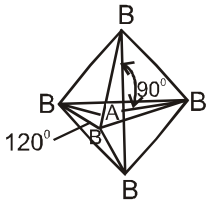
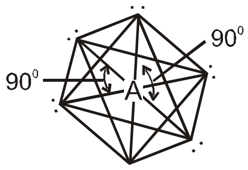
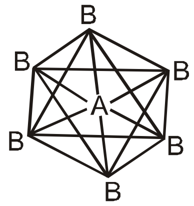
(v) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

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

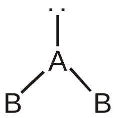
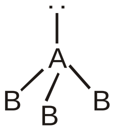
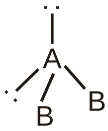
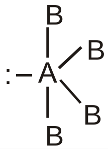
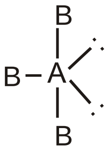
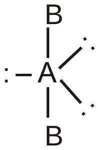
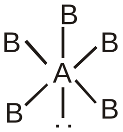
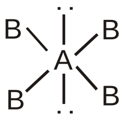
The repulsive interaction of electron pairs decreases in the order :

lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) -bond pair (bp)

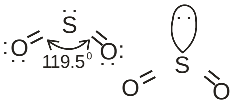
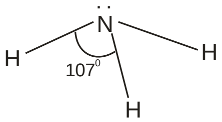
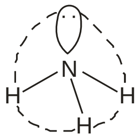
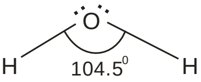
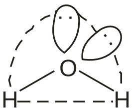
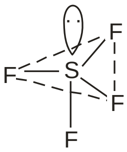
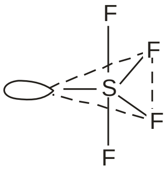
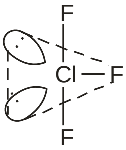
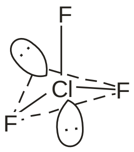
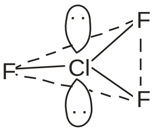
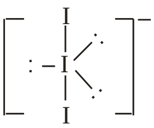
Shape (molecular geometry) of Some Simple Molecules / ions with central atom / ion having no Lone Pairs of Electrons (E).

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Example
2	 Linear	B – A – B Linear	$BeCl_2$,$HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4 , NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 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_2E_3	2	3		Linear	I_3^-,ICl_2^-,XeF_2
AB_5E	5	1		Square pyramidal	BrF_5
AB_4E_2	4	2		Square planar	XeF_4

Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No.of bonding pairs	No.of lone pairs		Shape	Reason for the shape acquired
AB_2E	4	1		Bent	It is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5^0 from 120^0.
AB_3E	3	1	 	Trigonal pyramidal	It is found to be trigonal pyramidal due to the repulsion between lp-bp (which is more than bp–bp repulsion) the angle between bond pairs is reduced to 107^0 to 109.5^0.
AB_2E_2	2	2	 	Bent	The shape is distored tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion. Thus , the angle is reduced to 104.5^0 from 109.5^0 .
AB_4E	4	1	(i)  (ii)  (More stable)	See-saw	In (i) the lp is present at axial position so there are three lp-bp repulsion at 90^0 . In (ii) the lp is an equatorial position, and there are two lp-bp repulsions. Hence , arrangement (ii) is more stable. The shape shown in (ii) is called as a distorted tetrahedron, a folded square or a see-saw.
AB_3E_2	3	2	(i)  (ii)  (iii) 	T–shape	In (i) the lone pairs are at equatorial position (120º) so there are less lp–bp repulsions as compared to others in which the lp are at axial positions.So structure (i) is most stable. (T – shaped).
AB_2E_3	2	3		Linear	I_3^-, ICl_2^-, XeF_2

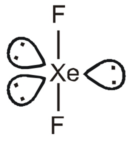
- The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small.

Solved Examples

Ex.2 Use the VSEPR model to predict the geometry of the following :
(a) XeF_2 (b) ClO_3^-

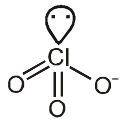
Sol. Species Structure

(a) XeF_2



lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.

(b) ClO_3^-



To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Hybridisation :

– Hypothetical concept Introduced by pauling and slater.

– Atomic orbitals combine to form new set of equivalent orbitals know as hybrid orbitals.

– This phenomenon is known hybridization.

– Process of Intermixing of the atomic orbitals of equal or slightly different energies in the formation of new set of orbitals of equivalent energies and shape is known as hybridization.

Salient features of hybridisation : The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic 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 the pure atomic orbitals.

4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is the orbital that undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) belonging to valency shell when hybridize to form four hybrid orbitals , one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

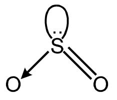
Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

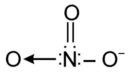
Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.

Note : This rule is not applicable to molecules/ions which have odd e$^-$ (ClO_2, NO, NO_2), free radicals and compounds like B_2H_6 which involve 3 centre 2e$^-$ bond (banana bond).

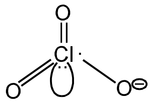
For example : O = C = O S.No. = 2 + 0 = 2



S.No. = 2 + 1 = 3



S.No. = 3 + 0 = 3



S.No. = 3 + 1 = 4

Table-4

Steric number	Types of Hybridisation	Geometry	Involving orbitals
2	sp	Linear	ns, np_x/ p_z / p_y
3	sp^2	Trigonal planar	ns, np_x, p_z / p_y ,p_z/p_x, p_y
4	sp^3	Tetrahedral	ns, np_x, p_z , p_y
5	sp^3 d	Trigonal bipyramidal	ns, np_x, p_z , p_y d_{z^2}
6	sp^3 d^2	Octahedral	ns, np_x, p_z , p_y d_{z^2} $d_{x^2-y^2}$
7	sp^3 d^3	Pentagonal bipyramidal	ns, np_x, p_z , p_y d_{z^2} $d_{x^2-y^2}$ d_{xy}

sp hybridisation :

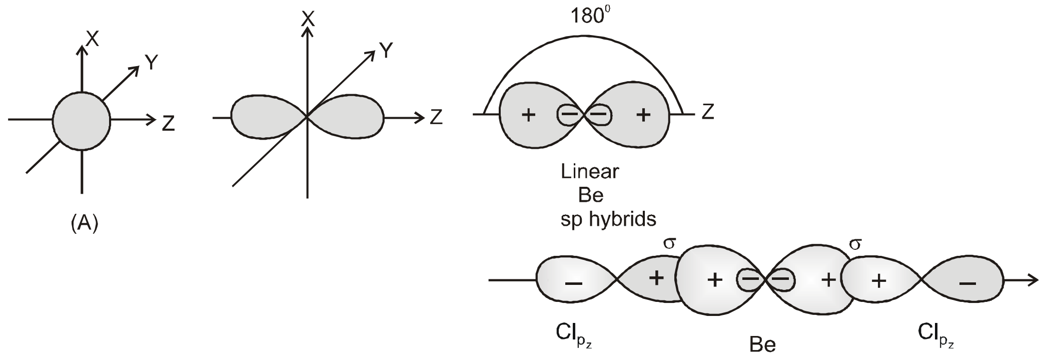
❍ This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.

❍ Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

❍ The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of a molecule having sp hybridisation

$BeCl_2$: The ground state electronic configuration of Be is $1s^2$ $2s^2$. In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its divalency. One 2s and one 2p-orbitals get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds.



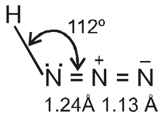
(A)

(B) $BeCl_2$

Figure : (A) Formation of sp hybrids from s and p orbitals ; (B) Formation of the linear $BeCl_2$ molecule.

Examples of sp hybridisation.

Species	**Important characteristic**
$H - C \equiv N$	Linear, highly posionous, weak acid
$H - C \equiv C - H$	Linear, π bond planes are perpendicular
$O = C = O$	Linear, both π bond are perpendicular to each other
$H_2C = C = CH_2$	Non planar both hydrogen are perpendicular to each other
N_3^- (azide ion)	Iso electronic with CO_2 and linear in shape. Both N–N bonds are similar
$\overset{-}{N} = \overset{+}{N} = \overset{-}{N}$	
$HgCl_2$	
NO_2^+ (nitronium ion),	
N_2O	
Azide ion	



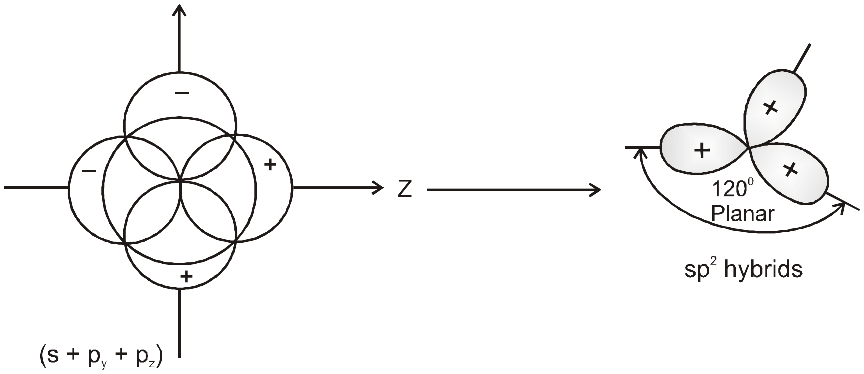
sp^2 hybridisation :

(i) Mixing of one s and two p orbitals to form 3 equivalent sp^2 hybridized orbitals.

For example, in BCl_3 molecule , the ground state electronic configuration of 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 (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented In a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B–Cl bonds.

Therefore, in BCl_3, the geometry is trigonal planar with CI-B-Cl bond angle of 120°.



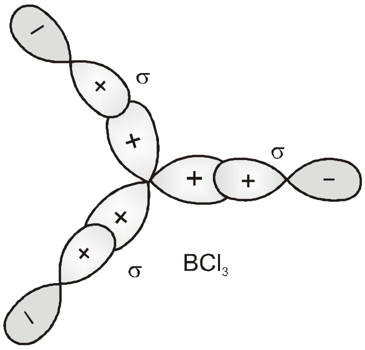


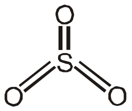
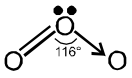
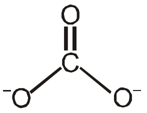
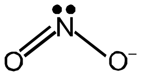
Figure : Formation of sp^2 hybrids and the BCl_3 molecule

Steric No. = 3 Geometry = Trigonal planar Ideal bond angle = 120°

Table-5

Type	**AB_3**	**AB_2L**
Shape	Trigonal	V-shape (bent)
Example	C_6H_6, CO_3^{2-}, HCO_3^- H_2CO_3, graphite, BF_3 $B(OH)_3$, SO_3, NO_3^- C_{60} (Fullerene)	NOCl, O_3, NO_2 NO_2^-

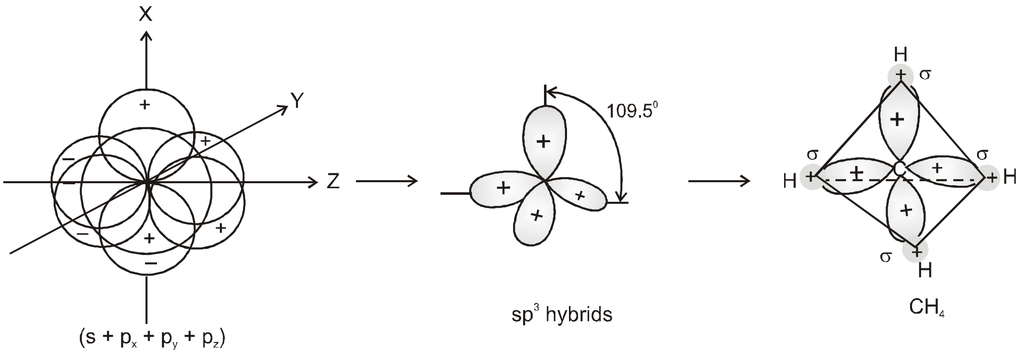
Where A = central atom, B = side atom, L = lone pair of e^-

Molecule	**Structure**	**Statements**
SO_3		All three S–O bonds are equivalent. out of 3p bond one pπ-pπ other to are pπ-dπ.
O_3		V shaped molecule. Both O–O bond length are equal.
CO_3^{--}		All three C–O bonds are equivalent. Bond lengths are shorter than single bond length but longer than double bond length.
NO_2^-		Bond order of N–O bond is 1.5, planar molecule.

sp^3 hybridisation :

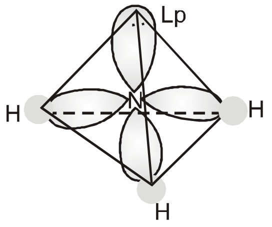
- ❍ mixing of one s and three p orbitals to form 4 equivalent sp^3 hybridized orbitals.
- ❍ 4 sp^3 orbitals are directed towards four corner of tetrahedron.
- ❍ This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp^3 hybrid orbital of equivalent energies and shape.

- There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron.
- The angle between sp^3 hybrid orbital is 109.5° as shown in figure.



Figure

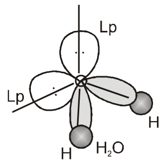
Ammonia



Ammonia NH_3

Three hybrid orbitals overlap with H atoms. One hybrid orbital contains lone pair.Geometry gets distorted and bond angle is reduced to 107° from 109.5°

Water



Two hybrid orbitals overlap with H atoms. Rest two hybrid orbital contains lone pair. Molecule acquires a V-shape or angular geometry and bond angle is reduced to 104.5° from 109.5°

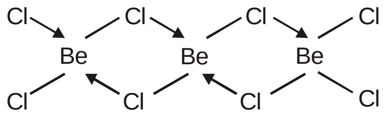
Steric No. = 4 Geometry = tetrahedral Ideal bond angle = 109° 28′

Table-6

Type	AB_4	AB_3L	AB_2L_2	ABL_3
Shape	tetrahedral	pyramidal	V-shape or bent	Linear
Example	CH_4	XeO_3	OBr_2	^-OCl

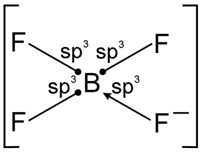
Some other Examples of sp^3 hybridisation

(a) $\boxed{\text{Be}}$ ❍ $BeCl_2$ (s) ,



Beryllium chloride in vapour phase contains $BeCl_2$ and $Be(Cl_2)_2$. In solid state it is in polymeric form.

(b) $\boxed{\text{B}}$ ❍ BF_4^- ;

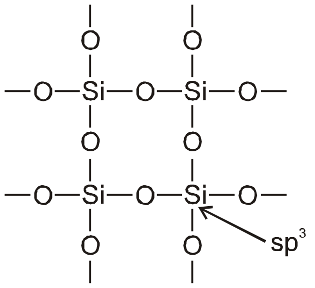


BF_4^- ions have a very low tendency to form complexes in aqueous solutions.

(c) $\boxed{\text{C}}$ ❍ Diamond, CCl_4 , $:CH_3^{\ominus}$, all alkane ;

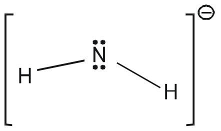
(d) Si ❍ $SiCl_4$, Silicates etc.

Structure of SiO_2



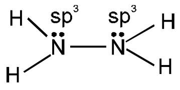
SiO_2 is a covalent network solid like diamond

(e) N ❍ NH_2^- (amide ion)

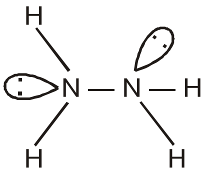


V-shape

❍ $NH_2–NH_2$ (hydrazine)

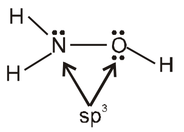


Each N atom is tetrahedrally surrounded by one N, two H and a lone pair.



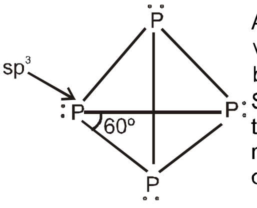
Structure is similar to that of ethane. The two halves of the molecules are rotated 95° about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.

❍ NH_2OH (hydroxylamine)



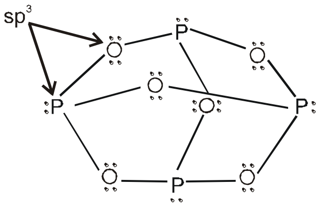
lp-lp repulsion increases the N–O bond length.

(f) P ❍ P_4 (White phosphorus)



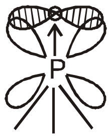
All phosphorus atoms occupy all four vertexes of tetrahedron. There are six P–P bonds and ∠P–P–P is 60°. Since bond angle is 60° (against normal tetrahedral bond angle, 109.5°) so, P_4 molecule is a strained molecule. So it is chemically very reactive.

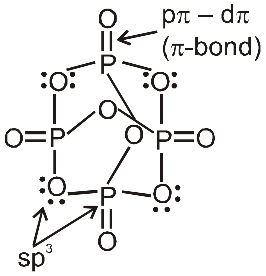
❍ P_4O_6



P–O bond length shows that the bridging bonds on the edges are 1.65 Å and are normal single bonds. There is no. P–P bonds.

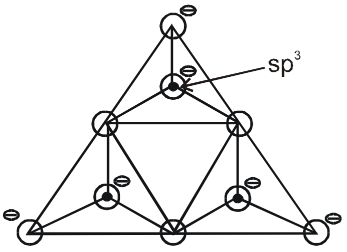
- P_4O_{10}





The P – O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P = O bonds on the corners are 1.43 Å and this P = O is formed by pp – dp back bonding. A full p-orbital on the oxygen atom overlaps sideway with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P – P bonds.

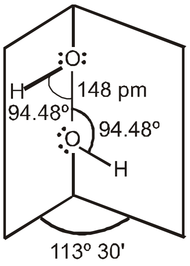
- Structures of cyclic silicates : $[Si_3O_9]^{6-}$



= Silicon ; O = Oxygen

Oxygen atom bonded with two Si atoms can not have negative charge. There is no oxygen–oxygen bond. All silicates contain only Si–O bond and there is no Si – Si Bond.

- H_2O_2



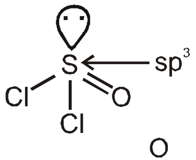
$H_2O_2(g)$

O – O bond length (148 pm) is larger than the expected due to the repulsions between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book 113°30').

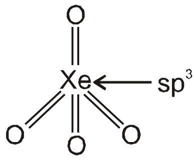
The H_2O_2 is the smallest molecule known to show restricted rotation, in this case about the O – O bond, and this is presumably due to repulsion between the OH groups. A similar structure is retained in the liquid and solid, but bond lengths and angles are slightly changed because of hydrogen bonding.

- $SOCl_2$ (Thionyl chloride)



Trigonal pyramidal

- XeO_4



tetrahedral

- **sp^3d hybridisation :**

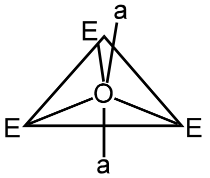
Steric number = 5 Geometry = trigonal bipyramidal

Table-7

Type	AB_5	AB_4L	AB_3L_2	AB_2L_3
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	PCl_5, PBr_5, PF_5 etc.	SF_4 , XeO_2F_2	ClF_3, $[XeF_3]^+$	XeF_2 , I_3^- , $[ICl_2]^-$

Important points regarding sp^3d -

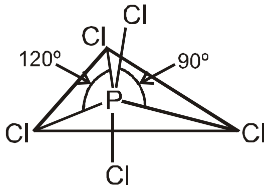
(i) According to VSEPR theory lone pair will occupy equatorial positions but not axial.



(ii) More electronegative atoms will prefer to occupy axial positions.

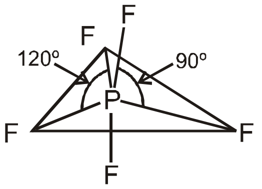
(iii) Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.

$\boxed{AB_5}$ PCl_5 (g)



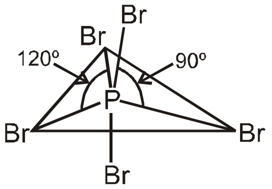
It is covalent in the gas but in solid state exists as ionic solid consisting of $[PCl_4]^+$ (tetrahedral) and $[PCl_6]^-$ (octahedral). All P–Cl bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.

PF_5 (g)



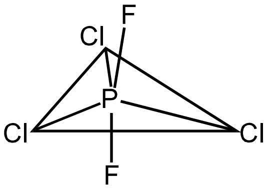
PF_5(g) is trigonal bipyramidal and the electron diffraction shows that some bond angles are 90° and others are 120°, and the axial P–F bond lengths are 1.58 Å while the equatorial P–F lengths are 1.53 Å. But NMR studies suggest that all five atoms are equivalent because of pseudo rotation. PF_5 remains covalent and is trigonal bipyramidal in the solid state.

PBr_5 (g)



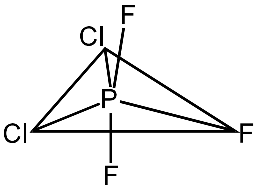
PBr_5 exist as $(PBr_4)^+Br^-$ in solid state.

PCl_3F_2



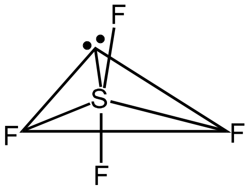
PCl_3F_2 is non polar molecule as all three Cl atoms are at equatorial position and both F atoms in axial position.

PCl_2F_3



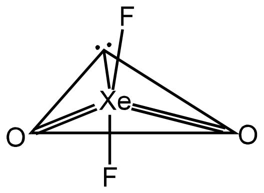
PCl_2 F_3 is polar molecule as both Cl atoms and one F atom are at equatorial position and both F atoms in axial position.

$\boxed{AB_4L}$ SF_4



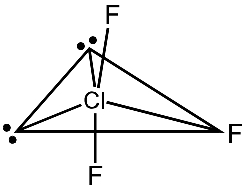
SF_4 molecule have See-saw shape/structure.

XeO_2F_2



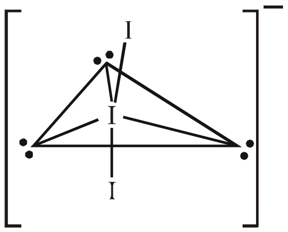
Both F atoms will be at equatorial position.

$\boxed{AB_3L_2}$ ClF_3



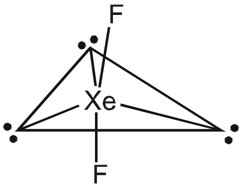
shape/structure of ClF_3 is T-shape

I_3^-



I_3^- has linear shape as both I atoms are at axial position.

XeF_2



XeF_2 has linear shape as both F atoms are at axial position.

sp^3d^2 hybridization :

Steric number = 6 Geometry = octahedral

Table-8

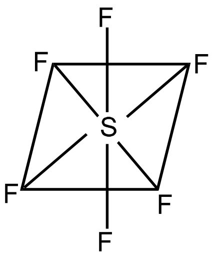
Type	AB_6	AB_5L	AB_4L_2
Shape	Octahedral	Square Pyramidal	Square Planar
Example	SF_6, PF_6^-, $[SiF_6]^{2-}$, $[AlF_6]^{3-}$, $[XeO_6]^{4-}$	BrF_5 , IF_5 $XeOF_4$	ICl_4^- XeF_4

Important : Since, octahedral is a symmetrical figure hence

(a) positions of a lone pair can be any where

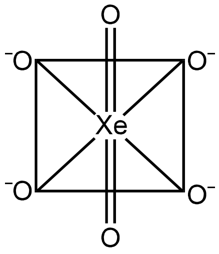
(b) but if there are two lone pairs (max.) then these must be in the trans position.

$\boxed{AB_6}$ **SF_6**



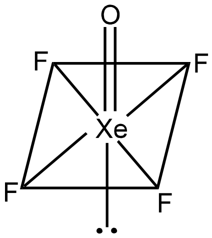
Bond angle = 90°
Due to over-crowding and maximum valency of S, SF_6 is much less active (almost inert) than SF_4 .

$[XeO_6]^{4-}$



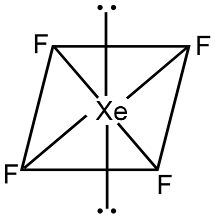
$[XeO_6]^{4-}$ is perxenate ion & H_4XeO_6 is called perxenic acid. But $H_2[XeO_4]$ is called xenic acid.

$\boxed{AB_5L}$ **$XeOF_4$**



Molecule has square pyramidal geometry.

$\boxed{AB_4L_2}$ **XeF_4**



Molecule has square plannar geometry.

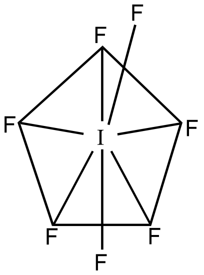
$sp^3\ d^3$ Hybridization :

Steric number = 7 Geometry = Pentagonal bi-pyramidal

Table-9

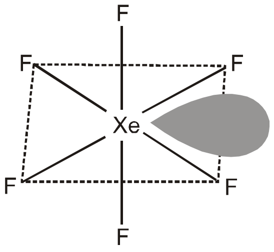
Type	AB_7	AB_6L	AB_5L_2
Shape	Pentagonal bi-pyramidal	Distorted octahedral	Pentagonal planar
Example	IF_7	XeF_6	$XeF_5^{\odot}$

$\boxed{AB_7}$ **IF_7**



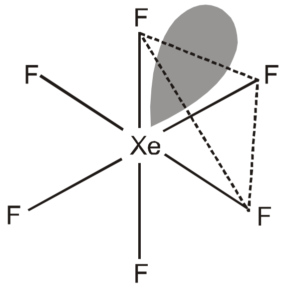
Bond angle = 72° & 90°

$\boxed{AB_6L}$ **XeF_6 (g)**

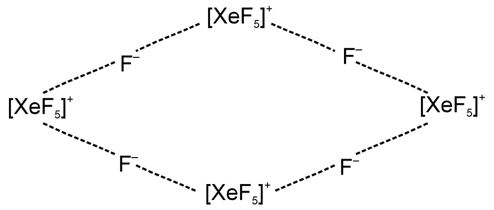


Distorted octahedron with a nonbonding electron pair either at the centre of a face or the midpoint of an edge.

or

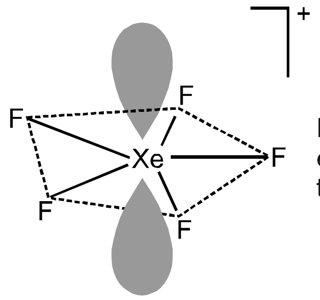


❍ $XeF_6(s)$



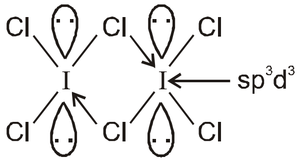
$XeF_6(s)$ is found to be ionic solid consisting of $[XeF_5]^+$ and F^- ions It is found that F^- is forming a bridge between two XeF_5^+ ions.

❍ $[XeF_5]^-$



Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.

❍ I_2Cl_6



ICl_3 does not exist, but the dimer I_2Cl_6 is bright yellow solid. Its structure is planar. The terminal I–Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridging I–Cl bonds appreciably longer (2.68 Å and 2.72Å) suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl_2 to I.

Note : The liquid has an appreciable electrical conductance due to self ionization.

$I_2Cl_6 \rightleftharpoons [ICl_2]^+$ (bent) + $[ICl_4]^-$ (square planar)

BOND LENGTH AND BOND ANGLE COMPARISION

Bond Length

(i) Size of atom (see along the group) $\propto$ bond length

$HF < HCl < HBr < HI$

$F-F < Cl-Cl < Br-Br < I-I$

$CH_4 < SiH_4 < GeH_4 < SnH_4$

(ii) Multiplicity of bond (nearly same period element)

single bond > double bond > triple bond

$C—C > C{=}C > C{\equiv}C$

$F—F > O{=}O > N{\equiv}N$

(iii) Electronegativity difference (See along the period)

$H—C > H—N > H—O > H—F$

HOW TO COMPARE BOND ANGLES

Bond angle depends on the following factor

I. Hybridisaition
II. No. of lone pair
III. Size or electronegativity of central atom
IV. Size or electronegativity of terminal atom

1. **Hybridisaition :**

$sp > sp^2 > sp^3 > sp^3d^2$

180° 120° 109°28' 90°

2. **Number of lone pair :** If hybridisation of the central atom is same but number of lone pair is different then more is the number of lone pair less is the bond angle.

e.g.	CH_4	NH_3	H_2O
hybridisaition	sp^3	sp^3	sp^3
lone pair	ℓ.P. = 0	ℓ.P. = 1	ℓ.P. = 2
B.A.	109°28'	107°	104.5°

3. **Size or electronegativity of central atom :** When hybridisation is same and no. of lone pair is same but central atom is different then see the electronegativity of central atom. More is the electronegativity more is the bond angle.

e.g.	NH_3	PH_3	AsH_3	SbH_3
hybridisaition	sp^3	no	no	no
lone pair	ℓ.P. = 1	ℓ.P. = 1	ℓ.P. = 1	ℓ.P. = 1
B.A.	107°	93°	92°	91°

4. Size or electronegativity of terminal atom :

Hybridisation same, lone pair same, central atom same but terminal atom is different then greater is the size of the terminal atom greater will be the bond angle. Only in case of flourine the electronegativity factor is considered, due to greater electronegativity of the flourine atom the bond angle for it comes out to be smallest(due to smaller bond bond pair repulsions)

e.g.	PF_3	PCl_3	PBr_3	PI_3
hybridisaition	sp^3	sp^3	sp^3	sp^3
lone pair	ℓ.P. = 1	ℓ.P. = 1	ℓ.P. = 1	ℓ.P. = 1
B.A.	98°	100°	101°	102°

Reasion : As the E.N. of x ↑, b.p.–b.p. repulsion will less but l.p. compression will work as usual

Drago rule :

Element of 3rd period (p-Block) and lower than 3rd period does not allow hybridisation in molecule when they form compound with less electronegative elements such as hydrogen

eg : PH_3, SiH_4, AsH_3, H_2S not have hybridisation

Bent rule :

According to Bent's rule, more electronegative atoms prefer hybrid orbitals having less S character and more electropositive atoms prefer hybrid orbitals having more S character.

eg : In CH_2F_2, F–C–F bond angle less than 109.5° indicating less than 25% S character.
H–C–H bond angle more than 109.5° indicating more than 25% S character.

Solved Examples

Ex.3 Which is linear PH_4^+ , H_3S^+ or NO_2^+ ?

(A) Phosphonium ion (PH_4^+) (B) Sulphonium (H_3S^+)
(C) Nitronium ion (NO_2^+) . (D) None of these

Sol. Phosphonium ion (PH_4^+) is tetrahedral, sulphonium (H_3S^+) is pyramidal, but nitronium ion (NO_2^+) is linear ; $O = \overset{\oplus}{N} = O$ (sp hybridisation). **Ans. (C)**

Ex.4 The triodide ion (I_3^-) in which the I atoms are arranged in a straight line is stable, but the corresponding F_3^- ion does not exist.

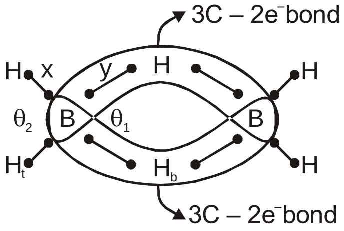
Sol. F_3^- and I_3^- are of same group. Iodine can expand its octet but F cannot and thus, in I_3^- octet rule is not violated, but in F_3^- octet rule is violated.

Electron deficient bonding:

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bonds(two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds(3c-2e) present in diborane B_2H_6, $Al_2(CH_3)_6$, $BeH_2(s)$, bridging metal carbonyls.

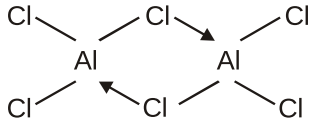
B_2H_6 (diborane) ⇒ It is having (3centre – 2electron) bond / (banana bond) / (electron deficient bond)

B_2H_6



B_2H_6 have 4 2c-2e bonds and 2 3c-2e bonds. Bridging bonds have bigger bond length than terminal bonds. Angle between terminal bonds is more than angle between bridging bonds if all 4 terminal bonds are in one plane then bridging bonds are in perpendicular plane.

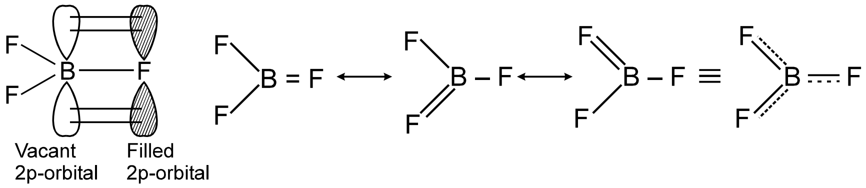
Al_2Cl_6



Only covalent bond, no electron deficient bond is present.

Back Bonding :

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.



- ❍ Decrease in B – F bond length is due to delocalised pπ–pπ bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :

$BF_3 > BCl_3 > BBr_3$

There is pπ-pπ back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

- ❍ The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order :

Si > P > S > Cl

- The extent of pπ-pπ overlapping $\propto \frac{1}{\text{Lewis acid character}}$

MOLECULAR ORBITAL THEORY (MOT) :

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

(i) Just as elctrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.

(ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

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

(iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.

(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 nuclues in an atom is given by an atomic orbital , the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.

(vii) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

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

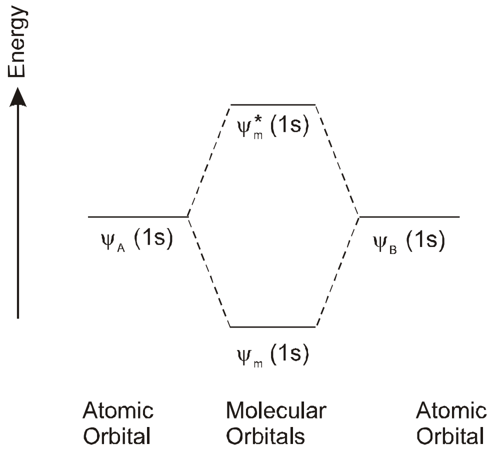


Figure 1. The formation of molecular orbitals for H_2.(a) ψ_A and ψ_B for individuals (b) $\psi_A + \psi_B = \psi_m$ (c) Probability function for the bonding orbital, $(\psi_m)^2$. (d) $\psi_A - \psi_B = \psi^*_m$. (e) Probability function for the antibonding orbital, $(\psi_m)^2$.

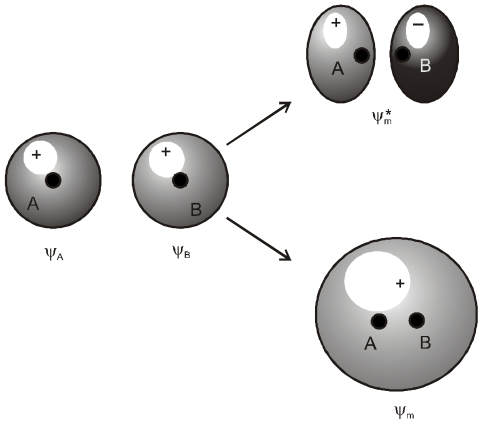


Figure 2. Another representation of the formation of molecular orbitals for H_2. The σ and σ* orbitals

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. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.

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 combine 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(pie), δ(delta) etc.

In this nomenclature, the **sigma (σ) moleuclar orbitals are symmetrical around the bond-axis while pi (π) 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 orbital's are of the σ type and are designated as σ 1s and σ*1s [Fig.(a)]. If internuclear axis is taken to be in the 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 $\sigma^* 2p_z$. [Fig. (b)] Molecular orbitals obtained from $2p_x$ and $2p_y$ orbitals are not symmetrical around the bond axis because of the presence of positive lobes plane. Such molecular orbitals, are labelled as π and π* [Fig. (c)]. A π bonding MO has large electron density above and below the inter nuclear axis. The π* antibonding MO has a node between the nuclei.

δ-type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

Difference between π molecular orbitals and the σ orbitals.

(1) For π overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.

(2) For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.

(3) The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the inter nuclear line a change in the sign of lobe occurs. The π bonding orbitals are therefore ungerade, where as all σ bonding MO's are gerade. Conversely the antibonding π MO's are gerade while all σ antibonding MO's are ungerade.

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

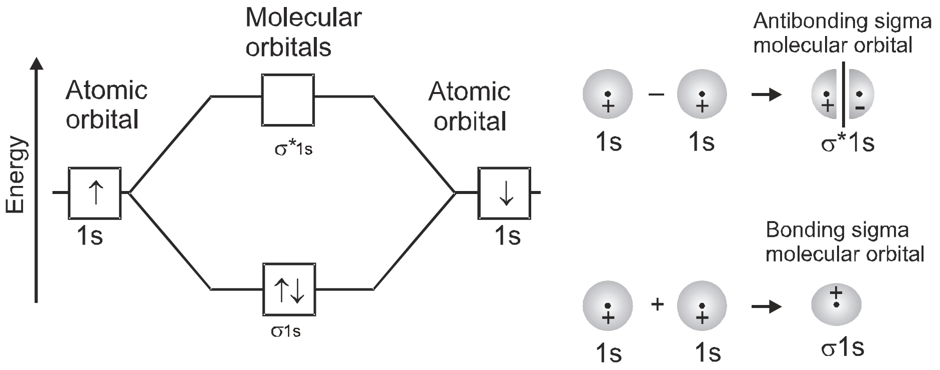
The energy levels of molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^*2p_x = \pi^*2p_z) < \sigma^*2p_z$.

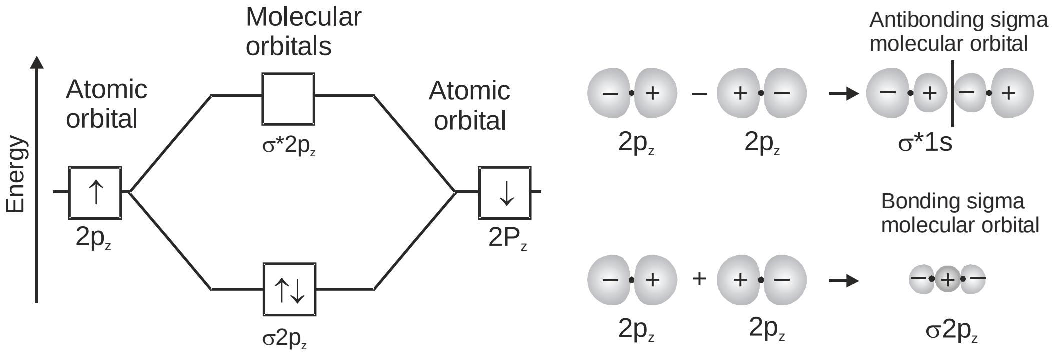
The increasing order of energies of various molecular orbitals for Be_2, B_2, C_2, N_2 etc., is :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^*2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$

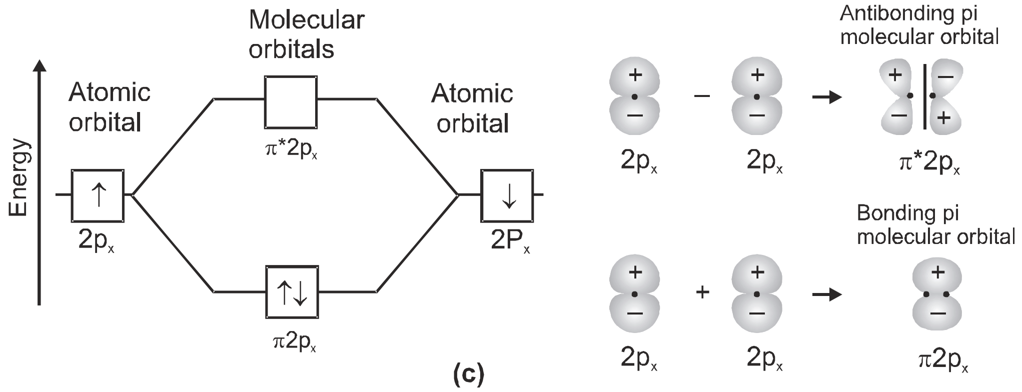
The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**



(a)



(b)



(c)

Fig. Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.

Electronic configuration and molecular behaviour :

Bond order

Bond order (b.o.) 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.) = ½ ($N_b - N_a$)

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 correspond to single, double or triple bonds respectively.

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.

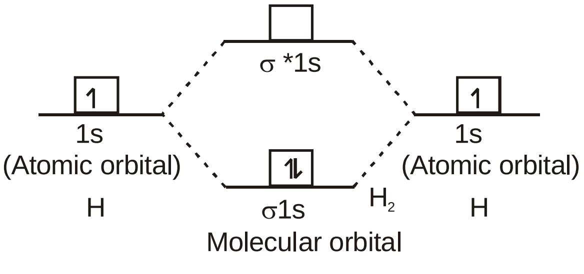
Magnetic nature

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule. 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

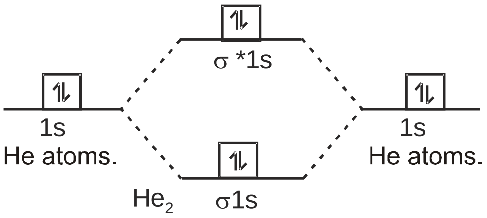
1. **Hydrogen molecule (H_2) :** $H_2 : (\sigma 1s)^2$

   Bond order $= \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$, it is diamagnetic.



2. **Helium molecule (He_2) :** $He_2 : (\sigma 1s)^2 \ (\sigma^* 1s)^2$

   Bond order of He_2 is ½(2 – 2) = 0, bond order of zero - in other words, no bond



3. **Lithium molecule (Li_2) :** $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$

Its bond order, therefore, is 1/2(4 – 2) = 1. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic.

4. **Beryllium (Be_2) :** $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$

Be_2 has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He_2, Be_2 is not a stable chemical species.

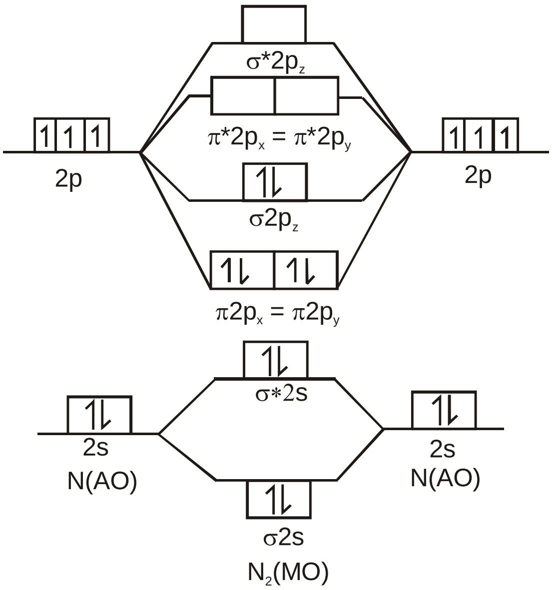
5. **Boron (B_2) :** $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p^1_x = \pi 2p^1_y)$ $(\sigma p_z)^0$ The bond order of B_2 is 1/2(6 – 4) = 1. B_2 is paramagnetic. B_2 is found only in the gas phase; solid boron is found in several very hard forms with complex bonding, primarily involving B_{12} icosahedra.

B_2 is also a good example of the energy level shift caused by the mixing of s and p orbitals.

6. **Carbon molecule (C_2) :** $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$ or KK $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$

The bond order of C_2 is 1/2 (8–4) = 2 and C_2 should be diamagnetic.

7. **Nitrogen molecule (N_2) :** $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$ $(\sigma 2p_z)^2$

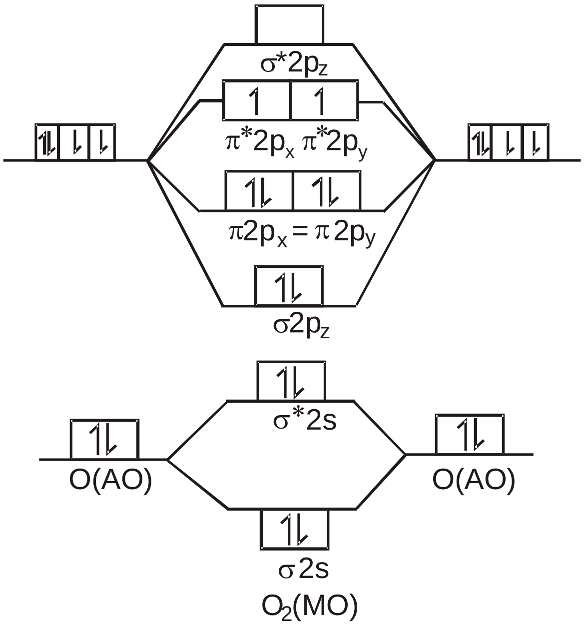


M.O. Energy level diagram for N_2 molecule

N_2 has a triple bond according to both the Lewis and the molecular orbital models.

The bond order of N_2 is 1/2(10 – 4) = 3. It contains one sigma and two π bonds.

8. **Oxygen molecule (O_2) :** O_2 : $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$ $(\pi^*2p_x^1 = \pi^*2p^1_y)$



M.O. Energy level diagram for O_2molecule

O_2 is paramagnetic. The bond order of O_2 is $\frac{1}{2}\left[N_b - N_a\right] = \frac{1}{2}[10-6] = 2$. So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in π^*2p_x and π^*2p_y molecular orbitals, therefore, **O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation.** Several ionic forms of diatomic oxygen are known, including O_2^+, and O_2^{2-}. The internuclear O – O distance can be conveniently correlated with the bond order predicated by the molecular orbital model, as shown in the following table.

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
O_2^+ (dioxygenyl)	2.5	112.3	1
O_2 (dioxygen)	2.0	120.07	2
O_2^- (superoxide)	1.5	128	1
O_2^{2-} (peroxide)	1.0	149	0

Note : Oxygen-oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unsually long bond distance.

9. Fluorine molecule (F_2) : $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$ $(\pi^*2p_x^2 = \pi^*2p^2_y)$

The molecular orbital picture of F_2 shows a diamagnetic molecule having a single fluorine-fluorine bond, in agreement with experimental data on this very reactive molecule.

10. Neon molecule (Ne_2) : $(\sigma 1s)^2$ $(\sigma^*1s)^2$ $(\sigma 2s)^2$ $(\sigma^*2s)^2$ $(\sigma 2p_z)^2$ $(\pi 2p^2_x = \pi 2p^2_y)$ $(\pi^*2p_x^2 = \pi^*2p^2_y)$ $(\sigma^*2p_z)^2$

All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The Ne_2 molecule is a transient species, if it exists at all.

Note : **HOMO :** Highest Occupied Molecular Orbital.

LUMO : Lowest Unoccupied Molecular Orbital

Solved Examples

Ex.5 Though O_2 molecule is paramagnetic yet it is a colourless gas. Why ?

Sol. It is because the energy gap between HOMO and LUMO levels in O_2 molecule is so large that radiations of visible light cannot excite a e^- from HOMO to LUMO. In fact O_2 gas shows absorption in UV zone. So it is colourless.

Ex.6 Correct order of bond energy is:

(A) $N_2 > N_2^+ > N_2^- > N_2^{2-}$ (B) $N_2^+ > N_2^- > N_2^{2-} > N_2$ (C) $N_2 > N_2^- = N_2^+ > N_2^{2-}$ (D) $N_2^- > N_2 = N_2^+ > N_2^{2-}$

Sol. **(A)** Bond order is directly proportional to the bond energy.

Bond order of $N_2 = 3$, N_2^+ , $N_2^- = 2.5$ $N_2^{2-} = 2$

But N_2^- has more electrons in antibonding MO's and thus N_2^+ is more stable than N_2^-. So correct order of bond energy will be $N_2 > N_2^+ > N_2^- > N_2^{2-}$

Ex.7 Which of the following species have a bond order of 3 ?

(A) CO (B) CN^- (C) NO^+ (D) O_2^+

Sol. **(A,B,C)** Species CO, CN^-, NO^+ are isoelectronic with 14 electrons to N_2 which has bond order of 3 (i.e. $\frac{10-4}{3} = 3$), so their bond order will be equal to three.

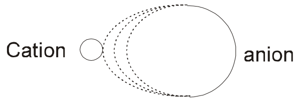
Ex.8 Which of the following are diamagnetic ?

(A) C_2 (B) O_2^{2-} (C) Li_2 (D) N_2^+

Sol. **(A,B,C)** Species C_2, O_2^{2-}, Li_2 have all the electrons paired but N_2^+ has one unpaired electron in bonding molecular orbital so it is paramagnetic.

COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE) :

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a near by anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

(i) **Size of cation :** **Size of cation α 1/polarisation.**

e.g. $BeCl_2$ $MgCl_2$ $CaCl_2$ $SrCl_2$ $BaCl_2$

$\longrightarrow$

Size of cation increases Polarisation decreases Covalent character decreases

(ii) **Size of anion :** **Size of anion α polarisation**

e.g., LiF LiCl LiBr LiI

$\longrightarrow$

(iii) **Charge on cation : Charge on cation α polarisation.**

e.g., NaCl MgCl$_2$ AlCl$_3$
Na^+ Mg^{2+} Al^{3+}

$\longrightarrow$

(iv) **Charge on anion : Charge on anion α polarisation.**

e.g., AlF$_3$ Al$_2$O$_3$ AlN
F^- , O^{2-} , N^{3-}

$\longrightarrow$

(v) **Pseudo inert gas configuration of cation :** Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.

Cu^+ = [Ne] $3s^2\ p^6\ d^{10}$	$Na^+ = 1s^2\ 2s^2\ p^6$
$18e^-$	$8e^-$
Pseudo inert gas configuration	Inert gas configuration
(poor shielding of d-electrons)	(more shielding of s and p electrons)

Application & Exceptions of Fajan's Rules :

(i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.

(ii) $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus charge is more. Therefore, $Fe(OH)_3$ is more covalent than $Fe(OH)_2$.

(iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example :

AgCl is white AgBr, AgI, Ag_2CO_3 are yellow. Similarly, $SnCl_2$ is white but SnI_2 is black. $PbCl_2$ is white but PbI_2 is yellow.

The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

(iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]

$BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

————————>————————————>–

Ionic charater increases, melting point increases ; since size of cation increases & size of anions is constant.

CaF_2, $CaCl_2$, $CaBr_2$, CaI_2

————————>————————————>–

Covalent character increase, melting point decrease ; since size of cations constant & size of anions is increases.

Ex. AgCl is colourless whereas AgI is yellow, because of :

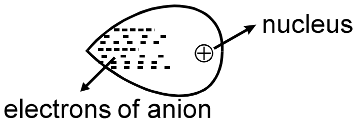
(A) Ag^+ have 18 electron shell to screen the nuclear charge.

(B) Ag^+ shows pseudo inert gas configuration.

(C) distortion of I^- is more pronounced than Cl^- ion.

(D) existence of d – d transition.

Sol. (C) the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



POLARITY OF BONDS :

In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, for example in H_2, O_2, Cl_2, N_2 or F_2 the shared pair of electrons is equally attracted by the atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

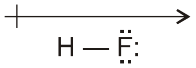
As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (D). The conversion factors are

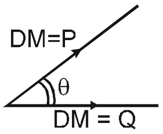
- 1 D = 3.33564×10^{-30} Cm, where C is coulomb and m is meter.
- 1 Debye = 1×10^{-18} e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as



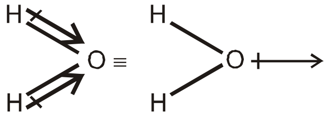
The shift in electron density is represented by crossed arrow ($+\!\!\!\longrightarrow$) above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$, where R is resultant dipole moment.

For example of H_2O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} Cm (1D = 3.33564×10^{-30} Cm) is the resultant of the dipole moments of two O—H bonds.



Net Dipole moment, $\mu = 1.85\text{ D} = 1.85 \times 3.33564 \times 10^{-30}\text{ Cm} = 6.17 \times 10^{-30}$ Cm.

(A) Diatomic molecules :

(i) Dipole moment is a vector quantity i.e., it has magnitude as well as direction. It is often represented by an arrow with its tail at the positive centre and head pointing towards the negative end

$(+ \rightarrow -)$

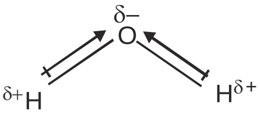
(ii) As a polar diatomic molecule posses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond e.g. in case of HCl, the molecular dipole moment is equal to the dipole moment of H–Cl bond i.e. 1.03 D. Thus.

$\overset{+\delta}{H} \Longrightarrow \overset{-\delta}{Cl}$ $\mu = 1.03$ D

(B) Polyatomic molecules :

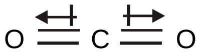
(i) As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bonds.

(ii) For example dipole moment of H_2O is 1.84 D which is equal to the resultant dipole moment of two O–H bonds.

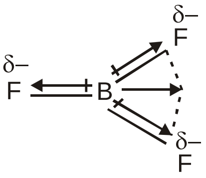


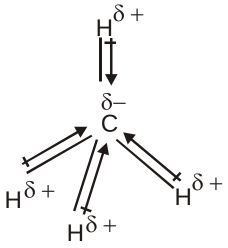
$\mu = 1.84$D

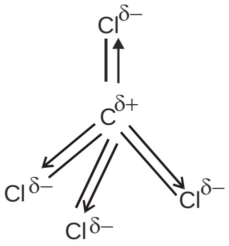
(iii) Think about CO_2 molecule though C = O bond is polar due to electronegativity difference but the resultant dipole moment of molecule is zero as the individual dipole moments are of equal moment and opposite sign. This shows that CO_2 is a linear molecule.



(iv) Again in case of symmetrical molecules such as BF_3, CH_4 and CCl_4 the molecular dipole moment is found to be zero. This is due to the fact that individual dipole moments cancels out on account of symmetry of the molecule.





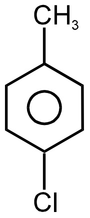


- **Following compounds have zero dipole moment :**
  BF_3, CO_2, SO_3, CF_4, PF_5(g), SF_6, XeF_2, CS_2, CCl_4, PCl_5(g), XeF_4

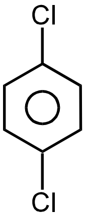
- **Some important orders**

HF	>	HCl	>	HBr	>	HI
1.92 D		1.08		0.78		0.38
CH_3Cl	>	CH_2Cl_2	>	$CHCl_3$	>	CCl_4
1.86		1.6		1.0		0

- Usually for disubstituted Benzene order is o > m > p
  But it all depends on the substituents



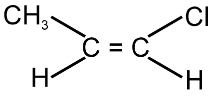
D.M ≠ 0

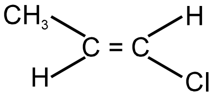


D.M = 0

Note : For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.

For example :

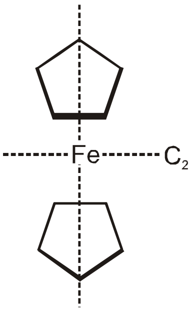




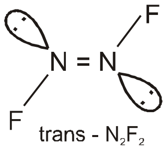
cis - form (low dipole moment) trans - form (high dipole moment)

- The presence of a centre of symmetry, i, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule.

  Thus $[CoF_6]^{3-}$, trans – N_2F_2 and the staggered conformer of ferrocene do not have dipole moments.



staggered-ferrocene ($\mu = 0$)



trans - N_2F_2

Some important points about dipole moment :

- A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B–F bonds are polar in BF_3 but BF_3 has $\mu = 0$ due to its symmetrical geometry.
- If molecule have $\mu = 0$, then it should be linear or having symmetrical geometry.
  e.g. linear – CO_2, CS_2, $BeCl_2$ (g) ; symmetrical geometry – BF_3 , CH_4 , PCl_5 , SF_6 , IF_7 , XeF_4.
- If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.
  $SnCl_2$, $PbCl_2$, SO_2 , angular molecular geometry.
  NH_3, H_2O, NF_3, SF_4, H_2S, unsymmetrical molecular geometry.
- % Ionic character = $\frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100 = \frac{\mu_{\text{(Observed)}}}{\mu_{\text{(100\% Ionic compound)}}} \times 100$

Solved Examples

Ex.9 What should be the percentage ionic character in CsF when electronegativity difference is 3.3

(1) 90.9% (2) 0.09% (3) 93.3% (4) 95.7%

Ans. (1)

Ex.10 What is the increasing order of ionic character in H_2Se, H_2S, H_2O

(1) $H_2Se < H_2S < H_2O$ (2) $H_2Se > H_2S > H_2O$ (3) $H_2Se < H_2S > H_2O$ (4) None of these

Ans. (1)

Ex.11 Which of the following molecules should not have $\mu = 0$:–

(1) H_2 (2) CO_2 (3) Cl_2 (4) SO_2

Ans. (4)

Ex.12 Which of the following compounds should have higher dipole moment than the remaining three :–

(1) HF (2) H_2O (3) NH_3 (4) NF_3

Ans. (2)

HYDROGEN BOND :

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied 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 called as hydrogen bond and is weaker than covalent bond. For

example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below : $---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}$
Here, hydrogen bond acts as a bridge between 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.

❍ Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pairs tend to line up and hold the molecules together. Other atoms with high electronegativity, such as Cl ; can also form hydrogen bonds in strongly polar molecules such as chloroform, $CHCl_3$.

Conditions required for H-bond :

(i) Molecule should have more electronegative atom (F, O, N) linked to H-atom.
(ii) Size of electronegative atom should be smaller.
(iii) A lone pair should be present on electronegative atom.

Strength of H-bond :

The strength of H-bond is usually very low (5 - 10 kJ/mol) but in some cases this value may be as high as 50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also form stronger bonds. The strength of the H-bond can be compared by the relative bond energies and the geometry of the various compounds as given below.

$F^- + HF \longrightarrow [FHF]^-$; $\Delta H = -161 \pm 8$ kJ mol^{-1}

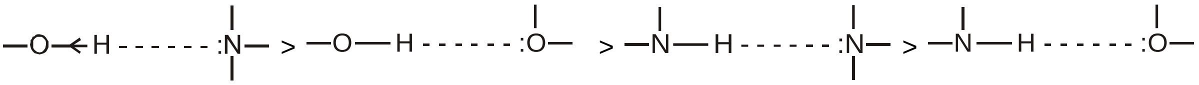
$(CH_3)_2CO + HF \longrightarrow (CH_3)_2CO \ldots\ldots HF$; $\Delta H = -46$ kJ mol^{-1}

$H_2O + HOH \longrightarrow H_2O \ldots\ldots HOH$ (ice) ; $\Delta H = -25$ kJ mol^{-1}

$HCN + HCN \longrightarrow HCN \ldots\ldots HCN$; $\Delta H = -12$ kJ mol^{-1}

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

❍ Order of H-bond strength



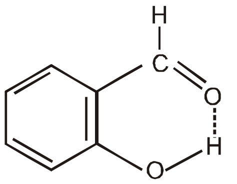
$$-O-H\text{------}:\overset{|}{\underset{|}{N}}- \;>\; -O-H\text{------}:\overset{|}{O}- \;>\; -\overset{|}{N}-H\text{------}:\overset{|}{\underset{|}{N}}- \;>\; -\overset{|}{N}-H\text{------}:\overset{|}{O}-$$

Types of Hydrogen Bonds :

(A) Intramolecular H-Bonding :

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.

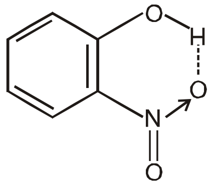
(a)



o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

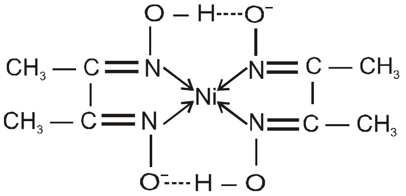
(b)



o-nitro phenol

It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.

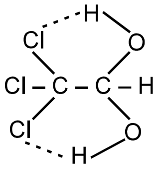
(c)



Nickel dimethyl glyoximate (a chelate)

Extra stability of the complex is because of intramolecular hydrogen bonding in addition to the chelating effect.

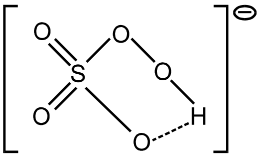
(d)



Chloral hydrate

Chloral hydrate is stable only on account of intramolecular hydrogen bonding.

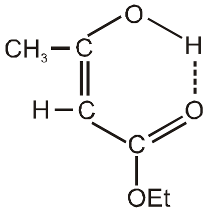
(e)



Persulphate ion (HSO_5^-)

K_1 of peroxomono sulphuric acid (i.e., caros acid) is greater than K_2. After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult.

(f)



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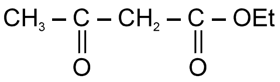


$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OEt$

Aceto acetic ester (enolic form)

The intramolecular hydrogen bonding attributes the stability of enolic form of aceto acetic ester.

Necessary conditions for the formation of intramolecular hydrogen-bonding :

(a) the ring formed as a result of hydrogen bonding should be planar.

(b) a 5- or 6- membered ring should be formed.

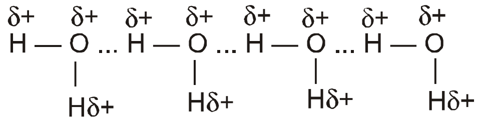
(c) interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

(B) Intermolecular H-Bonding :

Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

(a) **In water molecules**

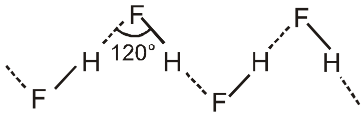
Due to polar nature of H_2O there is association of water molecules giving a liquid state of abnormally high boiling point.



$$\overset{\delta+}{H}-\underset{\underset{H\delta+}{|}}{\overset{\delta+}{O}}\cdots\overset{\delta+}{H}-\underset{\underset{H\delta+}{|}}{\overset{\delta+}{O}}\cdots\overset{\delta+}{H}-\underset{\underset{H\delta+}{|}}{\overset{\delta+}{O}}\cdots\overset{\delta+}{H}-\underset{\underset{H\delta+}{|}}{\overset{\delta+}{O}}$$

- When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence, volume increases and hence density decreases. Thus, water has maximum density at 4°C.

(b) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(HF)_n$ in both the solid and also in the liquid.

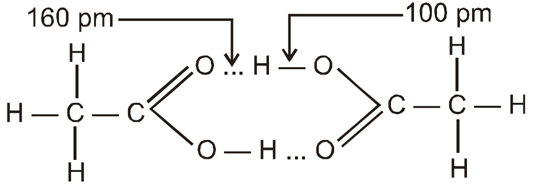


Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF.

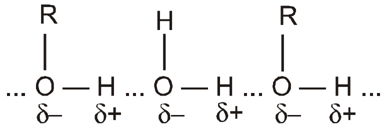
Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $M[HF_2]$; in KHF_2, for example, an X-ray diffraction study together with a neutrons diffraction study shows that there is a liner symmetrical anion having an over all, F–H–F distance of 2.26 Å, which may be compared with the H–F bond length of 0.92Å in hydrogen fluoride monomer.

(c) There is also similar H-bonding in alcohol (R—OH) ammonia (NH_3) and phenol (C_6H_5OH) molecules.

(d) Carboxylic acid dimerises in gaseous state due to H-bonding



(e) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and R—OH molecules).

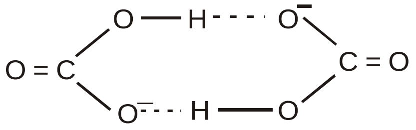


$$\cdots\underset{\delta-}{\overset{\overset{R}{|}}{O}}-\underset{\delta+}{H}\cdots\underset{\delta-}{\overset{\overset{H}{|}}{O}}-\underset{\delta+}{H}\cdots\underset{\delta-}{\overset{\overset{R}{|}}{O}}-\underset{\delta+}{H}\cdots$$

However isomeric ether is less soluble in water due to less polar nature of ether.

$$CH_3-CH_2-\underbrace{\overset{\delta-}{O}-\overset{\delta+}{H}}_{\text{polar}}\qquad CH_3-\underbrace{\overset{\delta-}{O}-\overset{\delta+}{CH_3}}_{\text{less polar}}$$

(f) HCO_3^- ions exist as dimer in $KHCO_3$

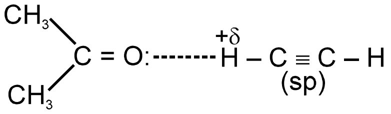


In $Na^+HCO_3^-$, the HCO_3^- ions are linked in to an infinite chain through intermolecular H-bonding.

Solved Examples

Ex.13 C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.

Sol.



In hybridisation as %S character increase, electronegativity increase hence C_2H_2 forms H–bonds with O–atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O.

Ex.14 Why $SnCl_2.2H_2O$ readily loses one molecule of water at 80ºC ?

Sol. One water molecule is coordinated to lone pair of electrons on $SnCl_2$ and the other is hydrogen bonded to coordinated water molecules .

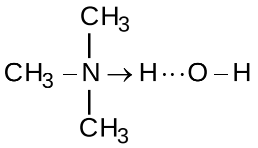
Ex.15 Why crystalline sodium peroxide is highly hygroscopic in nature.

Sol. Na_2O_2 forms stable hydrates on account of H-bonding.

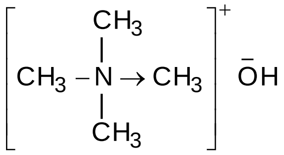
$$---O_2^{2-}---(H_2O)_8---O_2^{2-}---(H_2O)_8---$$

Ex.16 Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.

Sol.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{N}}}}\rightarrow H\cdots O-H$$



$$\left[CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{N}}}}\rightarrow CH_3\right]^+\overset{-}{O}H$$

In the trimethyl compound the O–H group is hydrogen bonded to Me_3NH group and this makes it more difficult for the OH group to ionize and hence it is a weak base.
In the tetramethyl compound, hydrogen bonding can not occur, so the OH^- group ionizes easily and thus it is a much stronger base.

Intermolecular forces (Van der Waal's Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

(a) Dipole-dipole attraction :
(b) Ion-induced dipole attraction :
(c) Dipole-induced dipole attraction :
(d) Instantaneous dipole- Instantaneous induced dipole attraction : (Dispersion force or London forces)

strength of van der Waal's forces a > b > c > d

(a) Dipole-dipole attraction :

This is electrostatic attractions between the oppositively charged ends of permanent dipoles. Exists between polar molecules and due to this force gas can be liquified.

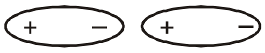
H^{δ^+}——Cl^{δ^-} H^{δ^+}——Cl^-

(b) Ion-induced dipole attraction :

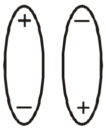
Exists between ion and non-polar molecules (e.g., an atom of a noble gas such as Xenon).

(c) Dipole-induced dipole attraction :

Exists between polar and non-polar molecules.



Head to tail arrangement of dipoles



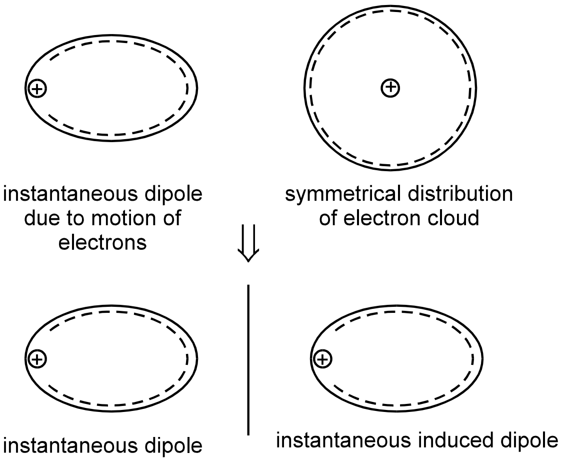
Antiparallel arrangement of dipoles

$\overset{\delta^+}{H}—\overset{\delta^-}{Cl}$ (polar) $\overset{\delta\delta\delta^+}{Cl}—\overset{\delta\delta\delta^-}{Cl}$ (non-polar)

(d) Instantaneous dipole- Instantaneous induced dipole attraction :

Exists among the non-polar molecules like H_2, O_2, Cl_2 etc. in solid or liquid states. Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary inbalances in electron distribution.

London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly, with the molecular volume and the number of polarizable electrons.



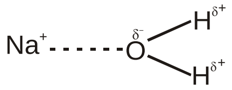
e.g., $\overset{\delta\delta\delta\delta^-}{Cl}—\overset{\delta\delta\delta\delta^+}{Cl}\ \ \overset{\delta\delta\delta\delta^-}{Cl}—\overset{\delta\delta\delta\delta^+}{Cl}$

Special Point : attractive forces between an ion and a dipole are known as ion-dipole forces and these are not vander waal forces.

- Ion- dipole forces are stronger then all vander waal forces because the charge of any ion is much greater than the charge of a dipole.
- Ion dipole bonding is also stronger then hydrogen bonding.

Ion-dipole attraction :

Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion -dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as $Na(OH_2)_x^+$ and $F(H_2O)_y^-$ (for solution of NaF in H_2O) are found. Hence this force is responsible for hydration.



Note : Fluoro carbon have usually low boiling points because tightly held electrons in the fluorine atoms have a small polarizability.

❍ Strength of vander waal force ∝ molecular mass.

❍ van der Waal's force ∝ boiling point.

Intermolecular forces

There are certain forces that condense matter. These forces can be both bonding forces and non-bonding forces which are called intramolecular forces and intermolecular forces respectively.

(i) Intramolecular forces : (Bonds that exist within molecules) :

Example : Ionic bond, Covalent bond

(ii) Intermolecular forces (forces that exist between molecules) : Intermolecular forces are the physical forces or just the interactions which act between the neighbouring bonded molecules. The intermolecular forces are weaker than the intramolecular forces.

van der Waals (1837 – 1923), a Dutch scientist explained that the attractive forces present between the molecules lead to the deviation of real gases from the ideal gas behaviour which we will study later in this chapter. So, to honor the scientist, intermolecular forces are also known as vander Waals forces. These forces of attraction exist between polar as well as non-polar molecules. These are the electrostatic forces of attraction that exist between an area of negative charge on one molecule and an area of positive charge on a second molecule. There are three types of van der Waals forces or interactions.

(i) Dispersion forces or london forces
(ii) Dipole-Dipole forces
(iii) Dipole-Induced Dipole forces

Fourth type is a particularly strong type of dipole-dipole interactions called hydrogen bonding.

(i) Dispersion forces or london forces : (Associated with NON POLAR structures) These forces are present in non-polar molecules like H_2, O_2 and N_2 and also in nonpolar monoatomic molecules such as noble gases like He, Ne, Ar etc., which exist with intermolecular forces and no bonding at all.

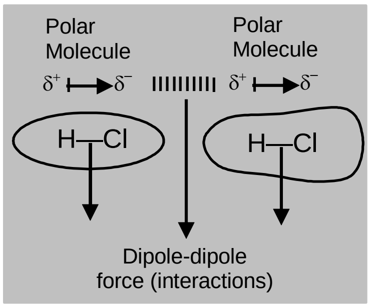
London forces are attractive in nature and the interaction energy is inversely proportional to the sixth power of the distance between the two interacting particles.

Interaction energy $\propto \frac{1}{r^6}$ where r is the intermuclear distance between two interacting particles.

Larger the polariesability, stronger are the london forces.

(ii) Dipole-Dipole Forces : (Associated with POLAR structures) : Polar molecules have a partially positive side and a partially negative side or a dipole. dipole-dipole forces operate between the molecules which are through neutral but possess permanent dipole. The separation of partial charges depends upon the electronegativity of the bonded atoms in a molecule. The partial charges are indicated by the Greek letter delta (δ) In these type of forces the partial positive end of the one molecules is attracted towards the negative end of the other molecule.

Example : Dipole-dipole forces are present between the two HCl molecules. Chlorine being more electronegative pulls the shared pair of electrons towards itself. So, it has a partial negative charge (δ^-) on it and hydrogen atom has a partial positive charge (δ^+).



The interaction energy is dependent upon the distance between the polar molecules.

(a) Stationary polar molecules : Dipole-dipole interaction energy is inversely proportional to the third power of the distance between stationary polar molecules (in solids)

Interaction energy $\propto \frac{1}{r^3}$

(b) Rotating polar molecules : Dipole-dipole interaction energy is inversely proportional to the sixth power of the distance between the rotating polar molecules (like water)

Interaction energy $\propto \frac{1}{r^6}$

Dipole-dipole forces are stronger than the london forces because permanent dipoles are involved but weaker than the ion-ion interaction because partial charges present in the polar molecules are always less than the unit electronic charge (1.6×10^{-19}) present on the ions.

(iii) Dipole-Induced Dipole Forces : (Between a polar and a non-polar molecule) This type of forces operate between a polar molecule which has a permanent dipole and a non-polar molecule whose electron density is symmetrical. A polar molecule may sometimes polarise a non-polar molecule.

Solved Examples

Ex.17 Give the order of boiling point of following

Cl_2, HCl

Sol. $Cl_2 - Cl_2$ < HCl – HCl (boiling point)

dispersion force dipole-dipole attraction

As dipole-dipole attraction is stronger than dispersion force.

Ex.18 Arrange the inert gases, according to their increasing order of boiling points

Sol. He < Ne < Ar < Kr < Xe (boiling point)

Because strength of van der Waal's force increases down the group with increase in molecular mass.

METALLIC BOND :

Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electrons interactions among 8 to 12 nearest neighbours (which is also called coordination number). Bonding in metals is called metallic bonding. It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.

Two models are considered to explain metallic bonding:

(A) Band model (B) Electron-sea model

(A) Band Model

The interaction of two atomic orbitals, say the 3s-orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital. If N atomic orbitals interact, N molecular orbitals are formed. Atoms interact more strongly with nearby atoms than with those farther away . The energy that separates bonding and antibonding molecular orbitals decreases as the interaction (overlap) between the atomic orbitals decreases. When we consider all the possible interactions among one mole of Na atoms, there is formation of series of very closely spaced molecular orbitals ($3\sigma s$ and $3\sigma^* s$). This consists of a nearly continuous band of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole (6.02×10^{23}) of valence electrons thus, 6.02×10^{23} orbitals in the band are half-filled.

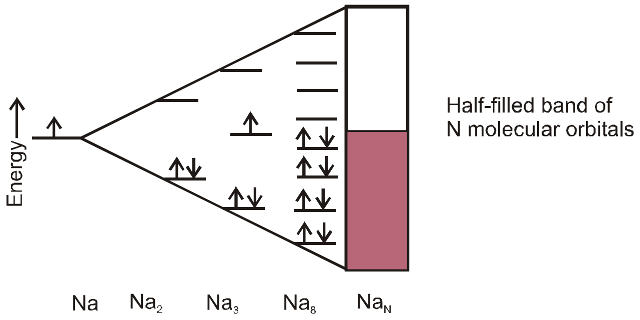


Fig. The band of orbitals resulting from interaction of the 3s - orbitals in a crystal of sodium

The empty 3 p atomic orbitals of Na atoms also interact to form a wide band of 3 × 6.07 × 10^{23} orbitals. The 3s and 3p atomic orbitals are quite close in energy , so that these bands of molecular orbitals overlap. The two overlapping bands contain 4 × 6.02 ×10^{23} orbitals. Because each orbital can hold two electrons, the resulting combination of bands is only one-eighth full.

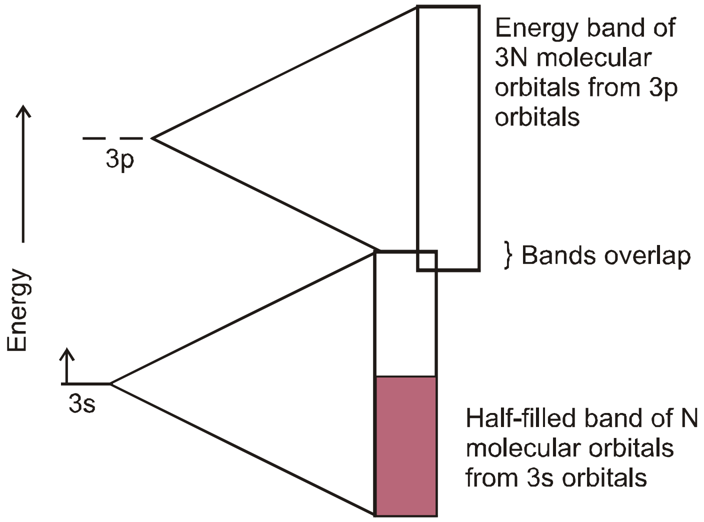


Fig. Overlapping of a half–filled “3s” band with an empty “3p” band of Na_N crystal

According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band within which (or into which) electrons must move to allow electrical conduction is called a conduction band. The electrical conductivity of a metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

Crystalline non-metals, such as diamond and phosphorus, are insulators, they do not conduct electricity. It is due to the fact that their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty bond (conduction band) by an energy difference called the band gap. In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band.

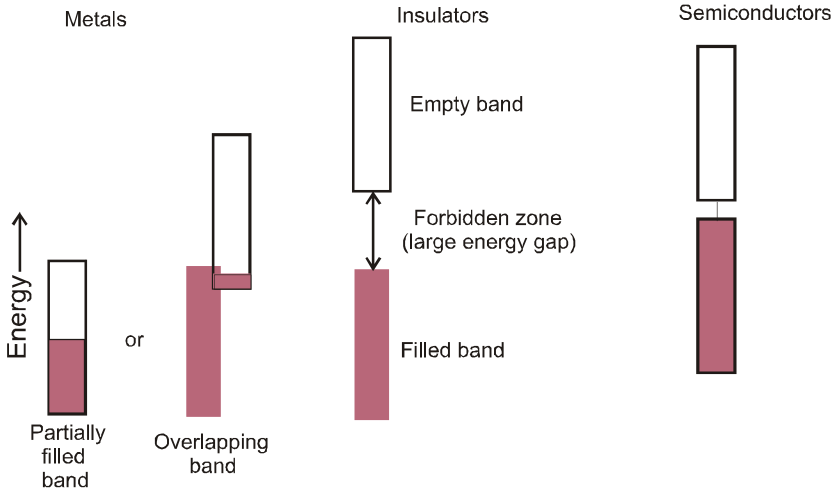


Fig. Distinction among metals, insulators and semiconductors. In each case an unshaded area represents a conduction band.

Elements that are semiconductors have filled bands that are only slightly below, but do not overlap with empty bands. They do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band.

(B) Electron-Sea Model

Metals have ability to conduct electricity, ability to conduct heat, ease of deformation [that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility)] and lustrous appearance.

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a "sea of electrons". In lithium the ions would be Li^+ and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

In thermal conductivity no electrons leave or enter the metal but those in the region being heated gain kinetic energy and transfer this to other electrons.

According to the electron-sea model, the case of deformation of metals can be thought of in this way : If one layer of metal ions is forced across another, perhaps by hammering, the internal structure remains unchanged as the sea of electrons rapidly adjusts to the new situation.

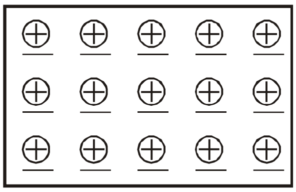
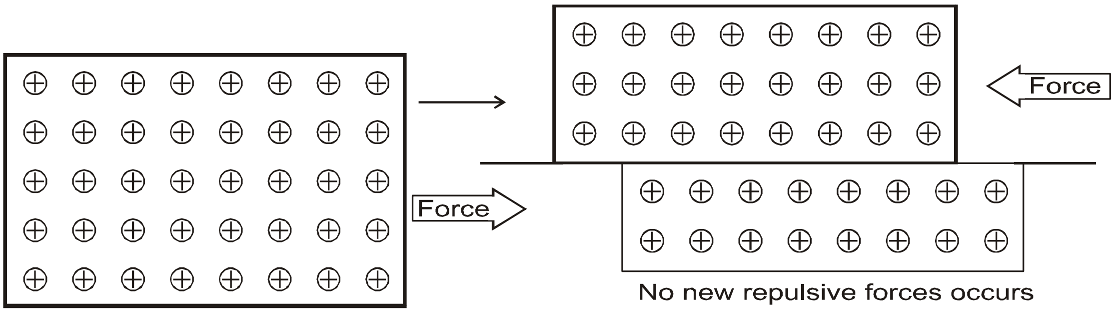


Fig. Metallic Bonding
in Electron-Sea Model



No new repulsive forces occurs and sheets and wires remain intact.

Fig. Effect of Distortion (by hammering) on Metal Sheet (assuming Electron Sea Model)

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :

(a) SiSi bond in $Cl_3SiSiCl_3$ (b) SiCl bond in $Cl_3SiSiCl_3$

(c) CaF bond in CaF_2 (d) NH bond in NH_3

Sol. (a) Covalent, due to identical electronegativity.

(b) Covalent, due to less electronegativity difference.

(c) Ionic, due to more electronegativity difference.

(d) Covalent, due to nearly similar electronegativity.

2. (a) Which one has highest and lowest melting point and why?

NaCl KCl RbCl CsCl

(b) Why melting points of cesium halide (CsX) decrease in the order given below ?

CsF > CsCl > CsBr > CsI.

Sol. (a) NaCl will have highest lattice energy on account of the smaller Na^+ while CsCl has lowest lattice energy on account of the larger Cs^+. Hence NaCl has highest melting point and CsCl has lowest melting point .

(b) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.

3. Which of the compounds $MgCO_3$ and $ZnCO_3$ is thermally more stable ? Explain.

Sol. Mg^{+2} has less polarising power due to inert gas configuration while Zn^{+2} has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn^{2+} with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the CO_3^{2-} ion and as such the metal carbonate ($ZnCO_3$) gets readily decomposed into CO_2 and the oxide of the metal, ZnO. Thus $ZnCO_3$ is less stable than $MgCO_3$.

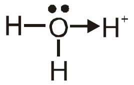
4. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?

Sol. It exists as HCl (bond formed by equal sharing of electrons) but in aqueous solution ionises as H^+ (or H_3O^+) and Cl^- due to polarity of HCl.

5. Which type of hybridisation is found in H_3O^+ ?

Sol. According to steric no. rule

Steric number = Number of bond pair(s) + number of lone pair(s) at central atom



So, steric number = 3 + 1 = 4.

Thus the hybridisation of oxygen in H_3O^+ is sp^3.

6. Which of the following will be strongest Lewis base ?

(A) CH_3CN (B) CH_3NH_2 (C) N_2 (D) None of these

Sol. **(B)** In CH_3 NH_2, hybridisation of N is sp^3 while in CH_3 CN hybridisation of N is sp. N_2 is also sp hybridised.

We know that in hybridisation, as s-character increases the electronegativity of atom also increases. Due to this tendency the release of lone pair of electrons becomes some what difficult. In methyl amine the nitrogen is in sp^3 hybridisation and therefore the donation of the lone pair of electron will be quite easier; so it is strongest Lewis base.

7. Which is **incorrect** statement ?

(A) In $CF_2 = C = CF_2$ molecule all the four fluorine atoms are not in the same plane.

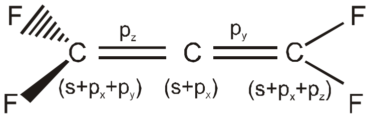
(B) Ka_2 of fumaric acid is more than Ka_2 of maleic acid due to intra molecular hydrogen bonding in maleic acid.

(C) The O – O bond length in $O_2[AsF_4]$ is longer than KO_2.

(D) The bond angle order in halogen – S – halogen is $OSF_2 < OSCl_2 < OSBr_2$

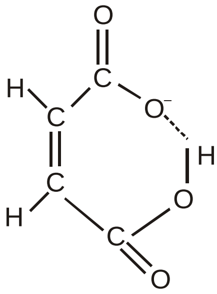
Ans. (C)

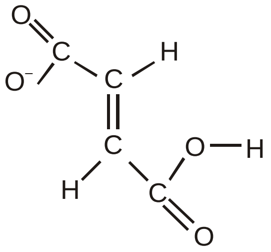
Sol. (A)



As both carbon atoms are in different planes, all the four fluorine atoms are not in the same plane.

(B) maleic acid fumaric acid





Due to intramolecular hydrogen bonding the maleate ion gets stabilized and thus removal of second hydrogen becomes quite difficult.

(C) $O_2[AsF_4] = O_2^+$ B.O = 2.5

$KO_2 = O_2^-$ B.O = 1.5

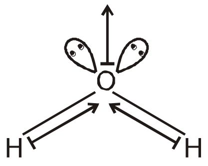
Bond order $\propto \frac{1}{\text{bond length}}$; so O_2^+ has smaller bond length than O_2^-

(D) Greater the size of the halogen atoms greater will be the steric repulsions and thus larger will be the bond angles.

8. Why BeF_2 has zero dipole moment whereas H_2O has some dipole moment ?

Sol. BeF_2 has linear molecule and H_2O has bent molecule.

$\mu = 0$



$\mu \neq 0$

9. Why crystals of hydrated calcium sulphate are soft and easily cleaved where as anhydrous calcium sulphate are very hard and very difficult to cleave ?

Sol. With in the Ca^{2+} / SO_4^{2-} layer the ions are held together by strong electrovalent bonds but these separated Ca^{2+} / SO_4^{2-} layers are linked by relative weak H–bond. The weak H-bonds link SO_4^{2-} ion in the intermediate region.

10. Super oxides are coloured and paramagnetic why ?

Sol. Super oxides contain one unpaired electron in anti bonding molecular orbital and are coloured due to transition of HOMO orbital electron within visible region.

11. Of the species O_2^+, O_2^-, O_2 and O_2^{2-} which would have the maximum bond strength ?

Sol. O_2^+ has higher bond order i.e. 2.5 than O_2(2) and O_2^- (1.5) and bond strength is directly proportional to bond order.

12. A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is equal to 1.0Å then the fraction of an electronic charge on each atom is :

(A) 25% (B) 37% (C) 52% (D) 42%

Ans. (A)

Sol. Assuming complete charge transfer then dipole moment = (4.8×10^{-10} esu) (10^{-8} cm) = 4.8 D

so % ionic character = $\frac{1.2}{4.8} \times 100\ \% = 25\%$

13. The dipole moment of KCl is 3.336×10^{-29} Coulomb meter. The interionic distance in KCl is 2.6Å. Find the % ionic character in KCl.

Sol. The theoretical dipole moment in KCl = e × d = $1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ C meter

% ionic character = $\frac{\text{experimental dipole moment}}{\text{theoretical dipole moment}} \times 100 = (3.336 \times 10^{-29}/4.1652 \times 10^{-29}) \times 100$

14. The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67×10^{-8} cm. Calculate the percentage ionic character in KCl molecule.

Sol. Dipole moment of compound would have been completely ionic

= (4.8×10^{-10} esu) (2.67×10^{-8} cm) = 12.8 D

so % ionic character = $\frac{10.0}{12.8} \times 100\% = 78.125\ \% \simeq 78\%$ **Ans.**

15. CO forms weak bonds to Lewis acid such as BF_3. In contrast CO forms strong bonds to transition metals. Why explain ?

Sol. $CO \xrightarrow{\sigma} BF_3$

Transition metal $\underset{\sigma}{\overset{\pi}{\rightleftarrows}}$ CO

This is called synergic interaction and because of it the bond between CO and transition metal is stronger.

16. $SnCl_4$ has melting point - 15°C where as $SnCl_2$ has melting point 535°C. Why?

Sol. According to Fajan's rule, as charge on cation increases its polarising power increases resulting in to the greater polarisation of anion. Thus covalent character increases and melting point decreases.

17. Inorganic benzene is more reactive than organic benzene. Why?

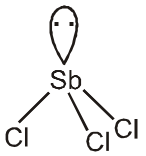
Sol. Inorganic benzene ($N_3B_3H_6$) contains polar covalent B – N bonds while benzene (C_6H_6) contains non-polar covalent C–C bonds.

18. Which compound has the smallest bond angle in each series ?

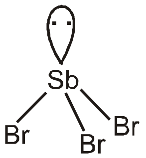
(a) $SbCl_3$ $SbBr_3$ SbI_3

(b) PI_3 AsI_3 SbI_3

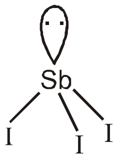
Sol. **(a)**



97.1°



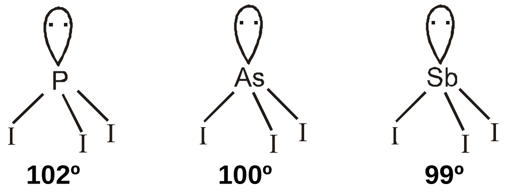
98.2°



99°

Cl, the most electronegative of the halogens in this series, pulls shared electrons the most strongly away from Sb, reducing electron density near Sb. The consequence is that the lone pair exerts the strongest influence on shape in $SbCl_3$.

(b)



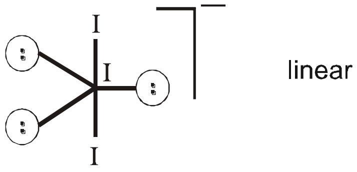
Phosphorus is the most electronegative of the central atoms. Consequently, it exerts the strongest pull on shared electrons, concentrating these electrons near P and increasing bonding pair-bonding pair repulsions–hence, the largest angle in PI_3. Sb, the least electronegative central atoms, has the opposite effect : Shared electrons are attracted away from Sb, reducing repulsions between the Sb–I bonds. The consequence is that the effect of the lone pair is greatest in SbI_3, which has the smallest angle.

Atomic size arguments can also be used for these species. Larger outer atoms result in larger angles ; larger central atoms result in smallest angles.

19. Why NO_2^+ and I_3^- are linear species ?

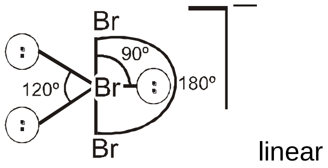
Sol. In NO_2^+ the N has sp hybridisation ; so it is linear $O = \overset{+}{N} = O$

In I_3^- there are 5 electron pairs around central iodine atom (3 lone pairs and 2 bond pairs). The hybridisation of iodine is thus sp^3d. To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.



20. Draw an electron dot structure for Br_3^-. Deduce an approximate value of the bond angle.

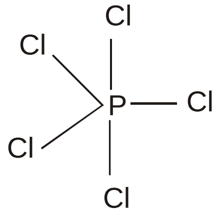
Sol. In Br_3^- there are 5 electron pairs around central bromine atom (3 lone pairs and 2 bond pairs). The hybridisation of bromine is thus sp^3d. To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.



21. PCl_5 has the shape of a trigonal bipyramidal where as IF_5 has the shape of square pyramidal. Explain.

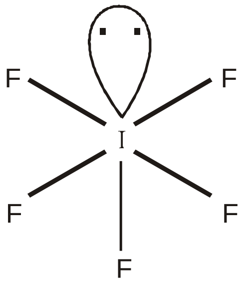
Sol. In PCl_5 there are 5 electron pairs around central phosphorus atom and all are bond

pairs. The hybridisation of phosphorus is thus sp^3d. To have minimum repulsions between bp-bp it acquires trigonal bipyramidal shape as shown below.



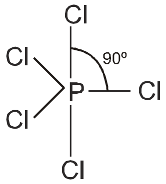
In IF_5 there are 6 electron pairs around central iodine atom. The hybridisation of iodine is thus sp^3d.

6 electron pairs contain 5 bond pairs and one lone pair so it will be square pyramidal to have minimum repulsions between lp-bp and bp-bp.



22. Why axial bonds of PCl_5 are longer than equatorial bonds ?

Sol. This is due to greater repulsion on the axial bond pairs by the equatorial bond pairs of electrons.



23. (b) NCl_5 is not possible but PCl_5 is possible. Why ?

(c) F_3^- does not exist but I_3^- , Br_3^- exist. Why ?

(d) SCl_6 does not exist but SF_6 exists. Why ?

Sol. (b) This is because of the absence of d-orbitals in nitrogen for sp^3d^2 hybridisation.

(c) Because of the absence of d-orbitals in fluorine it can not expand its covalency.

(d) Bigger size of chlorine can not be accommodated around sulphur atom because of steric crowding.