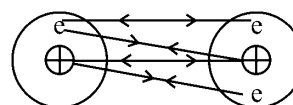
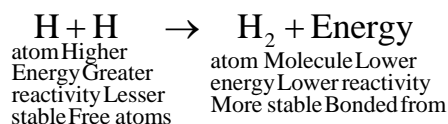


CHEMICAL BONDING

Introduction:

Atom is the smallest particle of an element which generally cannot exist in Free State. They have a tendency to combine with one another or with atoms of other elements and exist in **bonded state** (molecular form). The bonded form (molecular form) of atoms is more stable than free atoms.

When atoms of different or same element approach each other and form molecule, there is an overall *decrease in the energy* of the system. For example:



- Bond is formed when attractive force between two atoms is more than repulsive force.
- Bond formation process is exothermic.
- When two atoms A and B approach each other, they will form a bond only when there is an overall decrease in the energy of the system.
- Atoms of zero group elements do not have combining capacity under ordinary conditions.

Electronic theory of valency:

This theory was proposed by **Kossel and Lewis**. The following are the important points of the theory —

1. Electrons of outermost shell of atoms of an element take part in bond formation, i.e. when two atoms combine to form a bond; there is redistribution in the number of electrons in the outermost shell of both the atoms.
 - In transitional elements, electrons of (n-1) d sub-shell also participate in chemical bonding.
2. Atoms of inert gas elements do not possess combining capacity because in their atoms outermost shell is saturated with electrons, i.e., they have stable octet of electrons in outermost shell (except helium which has a stable duplet of electrons).
 - When K-shell is the outermost shell of an atom, only two electrons are needed for stability.
 - The electronic configuration, $ns^2 np^6$ is associated with minimum energy and hence maximum stability.
3. The atoms which do not have stable electronic configuration in their outermost shell have a tendency to acquire their nearest inert gas like configuration. It is known as the **octet rule**. The rule is stated as, “It is tendency of every atom to complete its octet (or duplet) i.e. to acquire eight electrons in the outermost shell (or two electrons if only one shell is present) so that stability may be attained.”
 - This tendency of the atom to complete its octet (or duplet) is responsible for its chemical reactivity.

- An atom can acquire stability by loss, gain or sharing of electrons with other atoms.
- The number of electrons lost, gained or shared by one atom of an element is known as its valency.

Chemical bond: Combination between atoms leads to the formation of a chemical bond. A bond may be defined as the force holding the atoms together, i.e., the attraction between the atoms within a molecule.

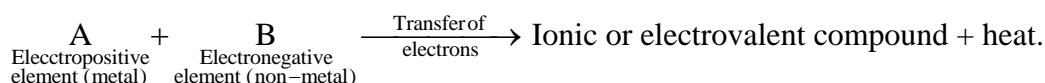
Types of Chemical bonds: Depending upon the nature of atoms which combine to give molecules, the following types of bonds are formed:

- Electrovalent or Ionic Bond.**
- Covalent Bond.**
- Co-ordinate or Dative Bond.**

Apart from these, some other types of bonds such as **metallic bond** and **hydrogen bond** etc. are also formed.

1. ELECTROVALENT or IONIC BOND:

This bond results due to the complete transference of one or more electrons from the outermost shell of one atom to the outermost shell of other atom. The necessary condition for the formation of this bond is that one of the atoms (element) should have tendency to lose electrons i.e., it should be electropositive (metal) and the other electronegative (non-metal). Thus, electrovalent bond is formed between **metal** and a **non-metal**.



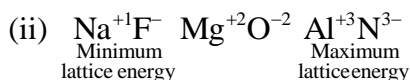
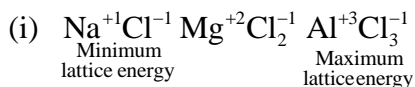
The atom which loses electrons (*i.e.* electropositive element) converts into a *cation* (positive ion), while the other atom which accepts the electrons (electro-negative element) forms an *anion* (negative ion). Thus, electrically charged species (ions) are formed which are held together by strong electrostatic forces of attraction. Since, the attractive forces exist between the ions, so this bond is called **ionic bond**. Similarly, the name *electrovalent bond* can be explained as the forces are experienced between electrically charged species (oppositely charged ions). For example, let us consider the formation of NaCl by the reaction between Na and Cl₂.

- The formation of ionic bond is favoured by:**
 - Low ionization potential of metal (electropositive element).**
 - Greater value of electron affinity of non metal (electronegative element).**
 - Higher value of lattice energy of the resulting ionic compound.**

Lattice energy: Lattice energy of an ionic solid may be defined as, “the amount of energy released when required number of gaseous positive (cations) and negative ions (anion) are condensed into one gram mole of an ionic solid”. Higher the lattice energy of the ionic solid, greater will be the case of its formation and higher will be its stability.

Variation of lattice energy: Lattice energy of an ionic solid is a measure of the electrostatic force of attraction between oppositely charged ions. It depends upon the following factors:

(1) **Magnitude of charge on cations and anions:** Lattice energy increases with increasing charge on cation, anion or both because forces of attraction increase between the ions, For example,



(2) **Size of cation:** For a common anion, the lattice energy decreases with increase in cation size. For example, among LiCl, NaCl, KCl, RbCl, CsCl, lithium chloride has maximum lattice energy while lattice energy of CsCl is minimum. It is due to small internuclear distance between cation (Li^+) and anion (Cl^-).

$$\text{Lattice energy} \propto \frac{1}{(\text{Nuclear distance between cation and anion})^2}$$

(3) **Size of negative ion:** For a common cation, the lattice energy decreases with increase in the size of negative ion. For example,



- The electrostatic force of attraction between two oppositely charged ions in air (vacuum) is governed by Coulomb's law, $F = \frac{q_1 \times q_2}{r^2}$, where q_1 and q_2 are the respective charges of the ions and 'r' is the distance between the ions.
- The nuclear distance between the ions is obtained by adding the radii of the two ions.

Characteristics of Electrovalent Compounds:

1. Ionic solids are well-defined crystalline solids. They are hard, but brittle solids. They are composed of charged atoms or group of atoms. As single ions of a metal are not associated with single ions of a non-metal, separate units of ionic compounds do not exist. Therefore, ionic compounds do not contain molecules. They have formula units. The formula only indicates the ratio of number of ions. Thus, NaCl is not the molecule of sodium chloride but represents its formula unit.

Hardness of ionic solids is due to the strong electrostatic forces of attraction between oppositely charged ions.

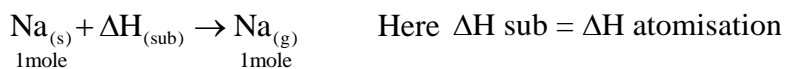
2. Ionic compounds have **high melting and boiling points**. There exist strong electrostatic forces of attraction between the ions in the crystal of an ionic compound. The ionic bond is very strong and hence a large amount of thermal energy (high temperature) is required to overcome these forces and break down the crystal lattice.
3. Ionic compounds are **generally soluble in water** and other polar solvents (solvents with high dielectric constant which separate ions). They are practically insoluble in organic solvents such as benzene, carbon tetrachloride, carbon disulphide, etc. as there is no attraction between ions

and the molecules of non-polar solvents. **When an ionic compound dissolves in water, the ions get hydrated; the energy evolved is hydration energy.**

- For dissolution of an ionic solid in water, the necessary condition is:
Hydration Energy > Lattice Energy
- Ionic compounds such as $\text{Ca}_3(\text{PO}_4)_2$, CaF_2 , BaSO_4 , CaCO_3 , etc. are insoluble in water due to their high lattice energies.
- 4. Ionic compounds do not conduct electricity in the solid state although they are composed of ions. It is because the ions are held by strong forces of columbic attraction, hence can not act as carrier of electric current. In aqueous solution or molten state, they become conductors of electricity because the attractive forces between the ions are cut off and the component ions become mobile. These free ions are capable of movement under the influence of electric field and thus act as carriers of electric current.
- 5. The chemical properties of an ionic compound are the properties of its constituent ions. Thus, all the chlorides respond to the reactions of the chloride ions. For example, they produce white ppt. of AgCl on reaction with AgNO_3 solution.
- In the solution of an ionic compound, the cations and anions behave independently.
- 6. In solution, ionic compounds show ionic reactions which are quite fast and are instantaneously completed.
- 7. Ionic compounds **do not show stereo isomerism** because ionic bond is **non-directional**. The electrostatic forces of attraction act in all directions, therefore, ionic compounds do not possess directional characteristics.
- Electrovalent bonds are more common in inorganic compounds. The hydrides, halides, oxides, sulphides, nitrides and carbides of alkali metals (IA) and alkaline earth metals (IIA) are ionic compounds.
- Ionic character \propto Difference of group number of metal and non-metal.

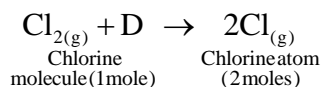
Born-Haber cycle (Energy changes involved in the formation of an ionic bond): The energy changes which take place in the formation of an ionic compound from its component elements can be studied with the help of a thermochemical cycle known as **Born-Haber cycle**. For example, in the formation of one mole of sodium chloride from sodium and chlorine the following steps are involved.

1. Conversion of metallic sodium (solid) into gaseous sodium atoms:



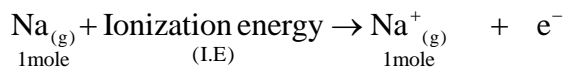
where ΔH_{sub} is the enthalpy of sublimation of sodium. It is the amount of energy required for converting one mole of solid sodium into gaseous sodium atoms.

2. Dissociation of chlorine molecules into chlorine atoms:

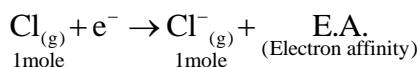


where D is the dissociation energy (bond energy) of Cl₂. It is clear that the energy needed for the formation of one mole of chlorine atoms is D/2.

3. Conversion of gaseous sodium atoms into gaseous sodium ions:

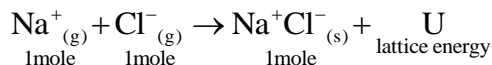


4. Conversion of gaseous chlorine atoms into gaseous chloride ions:

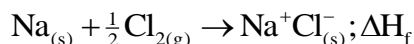


E.A., electron affinity is the energy released in the conversion of 1 mole chlorine atoms into one mole gaseous chloride ions.

5. Combination of gaseous sodium ions and gaseous chloride ions to give solid crystal.

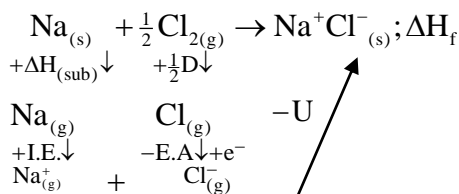


The overall formation of ionic solid may be represented as below:



Where ΔH_f is the heat of formation of 1 mole of Na⁺Cl⁻_(s).

The various steps may be represented in the form of Born-Haber cycle as follows:



Born-Haber cycle in the formation of Na⁺Cl⁻_(s).

Now, according to Hess law of constant heat summation, the heat of formation of one mole of Na⁺Cl⁻_(s) should be the same whether its formation takes place directly in a single step or through a number of steps.

Hence,

$$\Delta H_f = \Delta H_{sub} + IE + \frac{1}{2}D + (-EA) + (-U)$$

On substituting the respective values in the above expression, we get:

$$\Delta H_f = (+108.5) + 495.2 + \frac{1}{2}(243.0) + (-348.3) + (-758.7) = -381.8 \text{ kJ mole}^{-1}$$

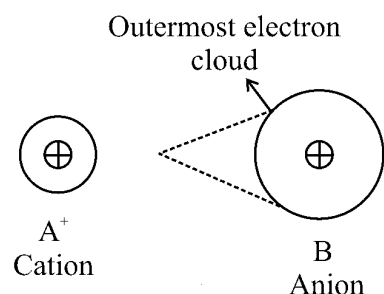
The negative sign in the values shows the energy released, while the positive signs indicate that the energy is absorbed.

It is now clear that in the formation of sodium chloride unit there is a *net fall* in the energy of the system hence $\text{Na}^+\text{Cl}^-_{(s)}$ is quite stable. Higher the negative values of heat of formation, greater will be the stability of the resulting ionic compound.

It is evident that the negative value of ΔH_f is due to the negative values of EA and U. It, therefore, becomes clear that higher the negative value of electron affinity of electronegative element and higher the value of lattice energy of the ionic solid, greater will the negative value of ΔH_f which gives higher stability and more chances of formation of ionic solid.

2. FAJAN'S RULES (covalent character in ionic compounds)

In an ionic solid there are cations and anions which are closely packed in the crystal in such a way that the forces of attraction in the oppositely charged ions overcome the forces of repulsion in the like ions. Let us consider two oppositely charged ions A^+ and B^- which are adjacently placed in an ionic crystal. Although the charge on the ions are equal, but charge densities are different. Charge density is higher on cation (due to smaller size) than anion and therefore the electron cloud of the outermost shell of anion is electrostatically attracted by the cation. As a result, the anion (B^-) is *polarized or deformed or distorted*. The outer electrons of B^- are attracted in the middle of the nuclei of A^+ and B^- . It seems as if the electron is shared between the two atoms, and hence imparts a slight covalent character to the ionic bond, *i.e.* ionic bond assumes some covalent nature due to polarization of anion by cation. Greater the polarization of anion, higher will be covalent character in ionic bond.

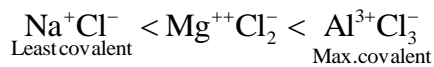


- Polarization of anion by adjacently placed cation.
- Covalent character in ionic bond \propto anion polarization.

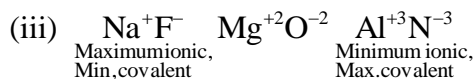
Fajan studied the development of covalent character in ionic bond and gave rules known as **Fajan's rules**. The following are the factors (Fajan's rules) on which covalent nature in ionic bond depends:

1. **High charge on cation, anion or both** favour covalent nature in ionic bond. The increase of positive charge on cation increases its polarizing power while the increase of negative charge on anion increases its polarizability. Thus, as the charge on both the ions increases, the electrostatic attraction between them also increases and hence the covalent character increases in ionic bond. For example,

(i) Among NaCl, MgCl₂ and AlCl₃ the covalent nature increases in the order



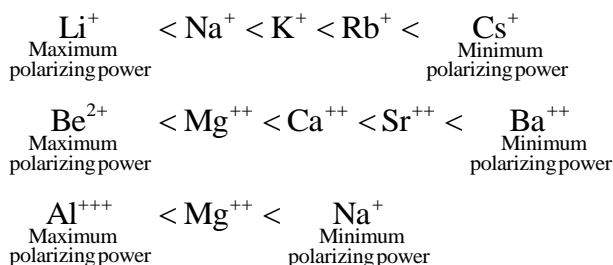
(ii) Among MgF₂, MgO and Mg₃N₂, Mg₃N₂ is maximum covalent (least ionic) because nitride ion has maximum negative charge.



2. **Small size of cation** favours covalent nature in ionic bond because the polarizing power of positive ion increases with decreasing ionic size, i.e. polarizing power of cation $\propto \frac{1}{\text{cation size}}$.

And thus, covalent nature in ionic bond $\propto \frac{1}{\text{cation size}}$.

• Increasing order of size of some cations is:



Hence, it is concluded that the covalent character in ionic bond increases with decreasing cation size. Therefore among:

LiCl— Max. covalent, Min ionic

NaCl

KCl

RbCl

CsCl—Max. ionic, Min. covalent

Similarly, among BeCl₂, MgCl₂, CaCl₂, SrCl₂ and BaCl₂,

BeCl₂ is maximum covalent (least ionic).

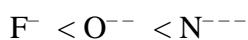
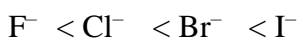
• Among BeCl₂ and LiCl, BeCl₂ is lesser ionic (more covalent).

3. **Large size of anion** favours covalent character in ionic bond.

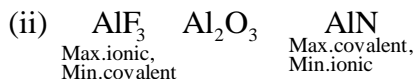
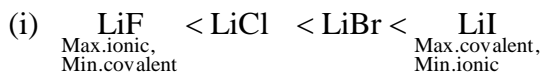
Polarizability of negative ion (anion) \propto size of anion.

So, covalent character in ionic bond \propto anion size.

• increasing order of size of some negative ions:

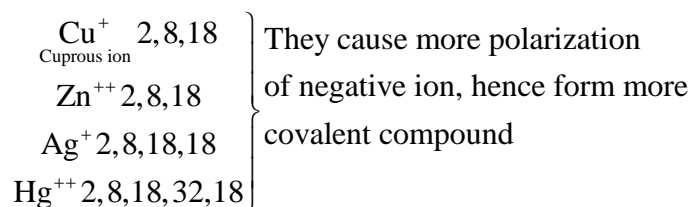


- Polarizability of negative ion by a cation increases with size because the nuclear attraction on the outermost electron cloud in anion decreases, and therefore covalent nature in an ionic bond increases. For example, (i) Increasing order of covalent nature among lithium halides is

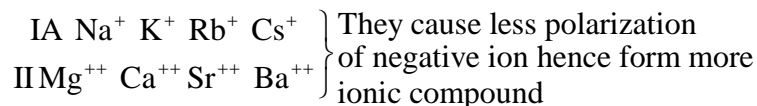


4. **Cation with a pseudo noble gas type structure** has high polarizing power because of its high nuclear charge but comparatively low screening effect. Cations with 8 electrons (inert gas type structure) cause less polarization of anion.

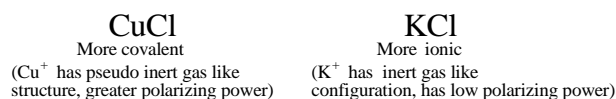
Cations having 18 electrons (pseudo noble gas type structure) are:



Cations having 8 electrons (Inert gas type structure) are:



For example,

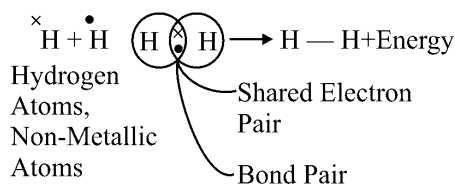


3. Covalent bond:

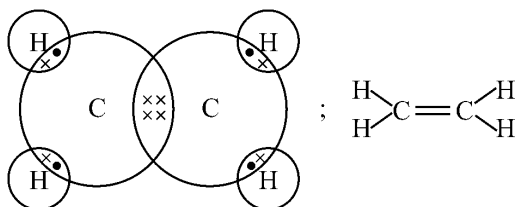
A covalent bond is formed between non-metallic atoms by mutual sharing of electrons. The number of electrons contributed by each atom depends upon its requirement for gaining stability, i.e. nearest inert gas like structure. The shared electrons contribute towards the stability of both the atoms. The number of electrons contributed by each atom for sharing is called its **covalency**.

When two electrons, one pair of electrons, one electron by each atom is shared between non-metallic atoms, a single covalent bond results between them. For example:

- (i) **Formation of H₂ molecule:**



(ii) **Formation of $\text{CH}_2 = \text{CH}_2$:** It involves the sharing of four electrons between the carbon atoms.



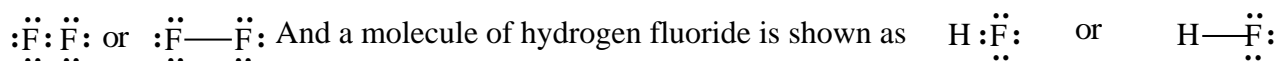
Characteristics of Covalent Compounds:

- (i) Under ordinary conditions, covalent molecules may exist in gaseous, liquid or solid state. For example, F_2 and Cl_2 are gases, Br_2 is a dark brown liquid while I_2 is a steel grey coloured crystalline solid. All these halogens form covalent molecule.
- (ii) Covalent molecules are molecular in nature in all the states. For example, solid methane, solid CO_2 etc. are molecular solids.
- (iii) Melting and boiling points of covalent compounds are much lower than electrovalent compounds. It is due to *weak Vander Waal's forces of attraction between covalent molecules*. Hence, less energy is needed to separate the molecules.
- (iv) Generally covalent molecules are insoluble in water but dissolve in organic (non-polar) solvents such as benzene, CCl_4 , CS_2 , etc.
 - Those covalent compounds which form hydrogen bonds with water molecules become fairly soluble in it. For example, NH_3 , lower alcohols, lower carboxylic acids, lower amines, etc.
- (v) Covalent molecules do not conduct electricity in aqueous solution or in molten state because they do not contain ions.
 - When a covalent molecule reacts with water, dissolves and produces ions, it begins to conduct electricity. For example, $\text{H}-\text{Cl}_{(g)}$ is a covalent molecule, but in aqueous solution it gives H^+ and Cl^- ions, $\text{HCl}_{(aq)}$ is a conductor of electricity.
- (vi) Covalent compounds show structural and space isomerism because covalent bonds are rigid and directional.
- (vii) Due to low melting and boiling points, covalent solids are more volatile than ionic solids and therefore have higher vapour pressure.
- (viii) Covalent compounds show molecular reactions which are quite slow and complex.

4. Lewis Structures of Molecules

The formula of a molecule shows the number of atoms of each element but does not show the bonding arrangement of the atoms. To represent the bonding pattern in a molecule, the electron dot

symbols of the elements are arranged such that the shared pairs and unshared pairs (called lone pairs) are shown and the octet rule (or duet for hydrogen) is satisfied. For example, a molecule of fluorine is shown as



And a molecule of hydrogen fluoride is shown as $\text{H}:\ddot{\text{F}}:$ or $\text{H}-\ddot{\text{F}}:$ Arrangement of dot symbols used to represent molecules are called as Lewis structures Lewis structure do not convey any information regarding the shape of the molecule. Usually, the shared pairs of electrons are represented by lines between atoms and any unshared pairs are shown as dot pairs.

Lewis structures are written by fitting the element dot symbols together to share electron pairs and to satisfy the octet rule. **For example.**

- (i) In water (H_2O), one H and two $\ddot{\text{O}}$ complete their duet and octet respectively as
$$\begin{array}{c} :\ddot{\text{O}}-\text{H} \\ | \\ \text{H} \end{array}$$
- (ii) In ammonia (NH_3), three H and one $\ddot{\text{N}}$ fit together and satisfy their duet and octet respectively as

Limitations of Lewis Theory of Drawing Structure

This method would be applicable to only those molecules/species, which follow octet rule except hydrogen.

There are three kinds of molecules/species, which do not follow octet rule:

- Molecules, which have contraction of octet. Such molecules are electron deficient. For example, BH_3 , BF_3 , BCl_3 , AlCl_3 , GaCl_3 etc.
- Molecules, which have expansion of octet. Such species have more than eight electrons in their outermost shell. This is possible in those molecules, which have vacant d-orbital, thus they can expanded their octet. For example, PCl_5 , SF_6 etc.
- Molecules containing odd number of electrons (in total) cannot satisfy octet rule. Such species are called odd electron species and are paramagnetic in nature due to presence of unpaired electron. For example, NO , NO_2 and ClO_2 .

Method of Drawing Lewis structures

To draw Lewis structure of polyatomic species, follow the given sequence.

- First calculate n_1 .

$$n_1 = \text{Sum of valence electron of all atoms of the species} \pm \text{no of } e^- \text{ s (contribution to charge) on the species.}$$

For a negatively charged species, electrons are added while for positively charged species, the electrons are subtracted. For an uninegatively charged species, add 1 to the sum of valence electrons and for a dinegatively charged species, add 2 and so on.
- Then calculate n_2 .

$$n_2 = (8 \times \text{number of atoms other than H}) + (2 \times \text{number of H atoms})$$

(iii) Subtract n_1 from n_2 , which gives n_3 .

$n_3 = n_2 - n_1 =$ number of electrons shared between atoms = number of bonding electrons

$\frac{n_3}{2} = \frac{n_2 - n_1}{2} =$ number of shared (bonding) electron pairs = number of bonds.

(iv) Subtracting n_3 from n_1 gives n_4 .

$n_4 = n_1 - n_3 =$ number of unshared electron or non – bonding electrons.

$\frac{n_4}{2} = \frac{n_1 - n_3}{2} =$ number of unshared electron pairs = number of lone pairs.

(v) Identify the central atom. Generally, the central atom is the one, which is least electronegative of all the atoms. When the other atoms are hydrogen only, then the central atom would be the more electronegative atom. However some exceptions are possible, for example Cl_2O .

(vi) Then calculate the formal charge on each atom of the species.

Formal charge on an atom = number of valence electrons - 2' no of lone pairs on that atom – no of bonds of that atom.

(viii) When two adjacent atoms get opposite formal charges, then charges can be removed by replacing the covalent bond between the atoms by a dative (co-ordinate) bond. This bond will have the arrowhead pointing towards the atom with negative formal charge. It is not mandatory to show the dative bonds unless required to do so.

(ix) The given Lewis structure account for the factual aspects of the molecule like resonance (delocalization), bond length, π – $d\pi$ back bonding etc.

Sometimes, there are more than one acceptable Lewis structure for a given species. In such cases, we select the most plausible Lewis structure by using formal charges and the following guidelines:

- For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one which where formal charges are present.
- Lewis structure with large formal charges (+2,+3 and/ or –2,–3 and so on) are less plausible than those with small formal charges.
- Among Lewis structure having similar distribution of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Example 1: Determine Lewis structure of NO_3^- ion.

Solution

(i) $n_1 = 5 + (6 \times 3) + 1 = 24$

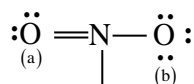
(ii) $n_2 = (4 \times 8) = 32$

(iii) $n_3 = n_2 - n_1 = 32 - 24 = 8$

$$\therefore \text{Number of bonds} = \frac{8}{2} = 4$$

(iv) $n_4 = n_1 - n_3 = 24 - 8 = 16$

(v) Nitrogen is the central atom (as it is less electronegative than O); Arranging three O atoms around it and distributing 4 bonds and 8 lone pairs as.



(vi) Calculating formal charge on each atom.

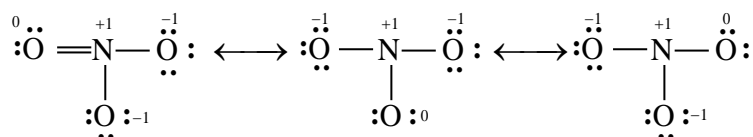
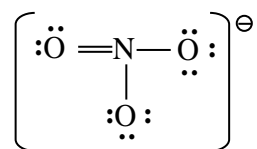
Formal charge on N = $5 - 4 = +1$

Formal charge on O(a) = $6 - 2 - 4 = 0$

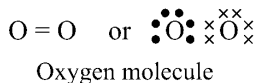
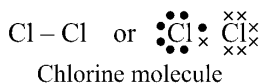
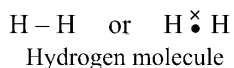
Formal charge on O(b) = $6 - 1 - 6 = -1$

Formal charge on (c) = $6 - 6 = 0$

Thus, the structure can now be shown as

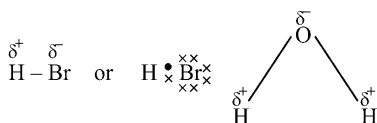
Final structure of NO_3^- is therefore shown asWhich even accounts for resonance in NO_3^- ion.

Polarity in a covalent bond: When two covalently bonded atoms have equal electronegativities, the bonded pair of electrons is equally shared between them, *i.e.*, shared pair of electrons remains in the middle of the nuclei of bonded atoms. Such a bond is **non-polar** covalent bond. For example,

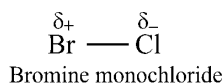


- Non-polar covalent bond is formed between identical non-metallic atoms or atoms having electronegativity difference equal to zero.
- Forces of attraction between non-polar molecules are weak, so their M.P and B.P. are low.

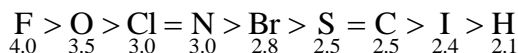
Polar covalent bond: When the two covalently bonded atoms are dissimilar, i.e., differ in their electronegativities, the bonded pair of electrons does not remain in between the bonded nuclei but is attracted towards the more electronegative atom resulting in the development of partial negative charge on this atom and equal but opposite (positive) charge on the other atom. The magnitude of charge produced on the bonded atoms is proportional to their electronegativity difference. Such a covalent bond formed between atoms with a difference in their electronegativities is called **polar covalent bond**. For example.



- For polar covalent bond electronegativity difference of bonded atoms $\neq 0$.
- Polarity of covalent bond \propto Electronegativity difference of bonded atoms.
- Forces of attraction between polar molecules are stronger dipole-dipole attractions.
- A diatomic molecule with a polar covalent bonds is called a dipole, for example,



- The relative order of electronegativities of few of the common elements is—



Dipole Moment (μ): The property which measures the extent of polarity in a bond is called dipole moment (μ). Molecules like $\begin{array}{c} \delta^+ \quad \delta^- \\ \text{A} - \text{B} \end{array}$ having two polar ends are known as **dipole** and possess dipole moment, which is 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 these two atoms, i.e., the bond length”. Thus:

Dipole moment (μ) = Magnitude of charge (e) \times distance (d).

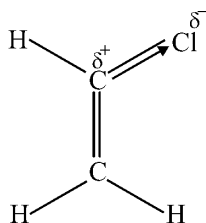
The dipole moment of any molecule may be determined experimentally. Its value provides a measure of the polar character of the molecule.

- $\mu = 0$, the molecule, is non-polar.

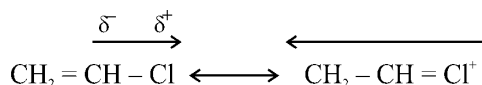
- A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule.
- Unsymmetrical molecules such as NH_3 , PCl_3 , H_2S , H_2O , $:\text{CH}_3-\text{Cl}$, CH_3-F , CH_3-OH , CH_3-SH , etc. possess dipole moments which are not cancelled.
- Dipole moments of CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 decrease in the order:
 $\text{CH}_3\text{Cl} > \text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$

(iii) Dipole moments of some organic compounds: (a) μ of $\text{CH}_2 = \text{CH}_2$ is zero due to its symmetrical planar structure but the following molecules will possess dipole moment:

(a) **Vinyl chloride (chloroethene).**



- The dipole moment of vinyl chloride is less than expected because it is resonance hybrid of two structures having bond polarities in different (opposite) directions.



So, the net dipole moment becomes less than expected from its structure.

- The ionic character of a bond can be calculated by using dipole moment data as follows:

% Ionic character

$$= \frac{\text{Observed dipole moment} \times 100}{\text{Dipole moment for pure or 100\% Ionic bond}}$$

The dipole moment for pure ionic bond is obtained by multiplying the electronic charge by distance between the atoms.

5. ORBITAL CONCEPT OF COVALENCY:

This concept was put forward by Heitler and London and modified by Pauling and Slater. According to this concept, “the formation of a covalent bond between two atoms results by coupling of electrons with opposite spins belonging to outermost shell orbitals to the two atoms.”

Thus, the presence of one or more unpaired electrons in the Valence shell of an atom is responsible for chemical bonding. Half filled atomic orbitals having electrons spinning in opposite directions overlap with each other to form a covalent bond. The overlapping results in the coupling (pairing) of electrons and thus leads to lowering of potential energy of the system.

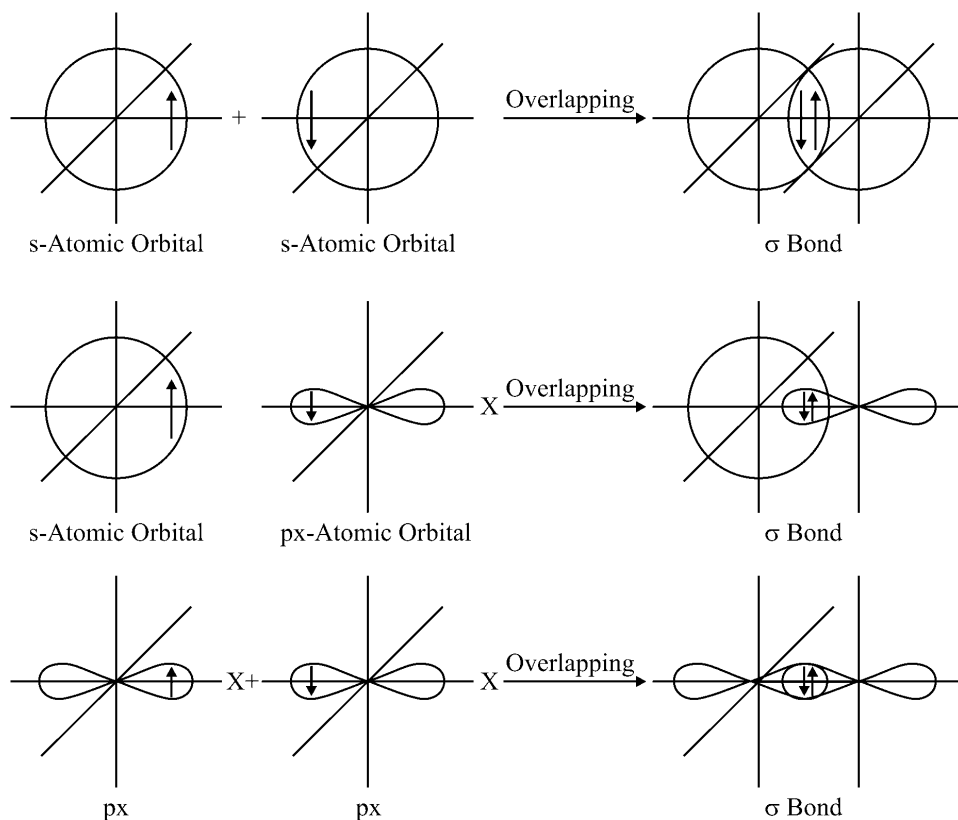
Noble gases do not take part in chemical bonding because they do not have unpaired electron(s) in their outermost shell. The combining capacity or covalency of an atom is equal to the number of unpaired electrons present in its ground or excited state. Important points of orbital theory of covalency are:

- Every atom has a tendency to get its unpaired electrons paired up with opposite spinning electrons of other atom. It results in lowering of energy of the system which is stabilized and hence atoms are chemically bonded.
- Atomic orbitals of the two atoms having unpaired electrons overlap with each other. Thus, overlapping of atomic orbitals of the outer shell of two atoms gives rise to a covalent linkage.
- Greater the extent of overlapping of the atomic orbitals, the stronger is the bond formed between the atoms.

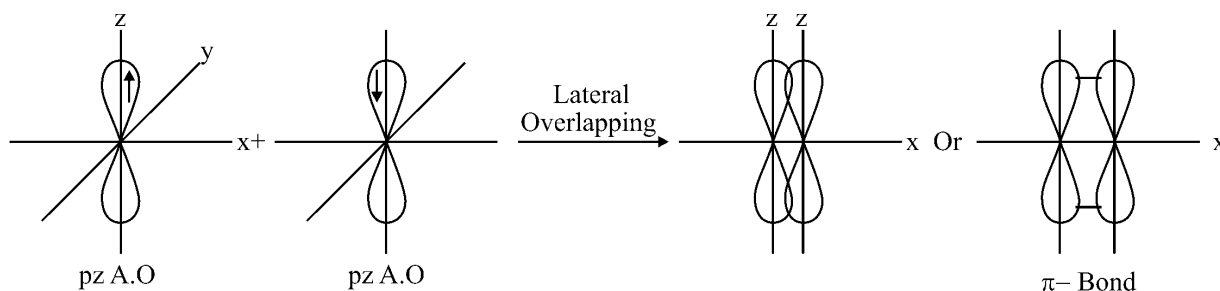
Covalent bonds are of two types:

(i) **Sigma σ bond:** This bond results by:

- Head on (end to end)
- Axial.
- Maximum overlapping of atomic orbitals along their inter-nuclear axis. It is a strong bond as the extent of overlapping is maximum. A sigma bond is formed by s—s, s— p_x , p_y or p_z and p_x — p_x overlapping.
- There can be only one sigma bond between two atoms.
- All single bonds are sigma (σ) bonds.
- The σ electrons are strongly held up between the bonded atoms.
- σ -electrons do not take part in mesomeric effect.
- σ C—H electrons are involved in hyperconjugation (σ — π conjugation).
- σ -bond is directional in nature and hence determines the shape or geometry of a molecule.
- There is free rotation of the molecule possible about a σ (single) bond.



(ii) Pi (π) bond: This bond is formed by the sidewise or lateral overlapping of two half filled parallel p -orbitals in direction perpendicular to the inter nuclear axis. It is a weaker bond than σ bond because the extent of overlapping of atomic orbitals is very small.



The half filled parallel p_y - p_y and p_z - p_z atomic orbitals undergo lateral overlapping to give π -bonds. It should be noted that whenever there are multiple bonds between any two atoms, one of them would be a σ bond and the other will be π -bonds. There can be a maximum of two π -bonds between two atoms.

- A π -bond is never formed alone. First a σ -bond is formed and then the formation of π -bond occurs.
- The electrons in a π -bond (π -electrons) are not so much under the influence of bonded nuclei, so they are easily polarizable.
- π -electrons take part in electromeric and mesomeric effect (resonance).
- Compounds containing π -bond give addition reactions, the weak π -bonds are converted into strong σ -bonds in addition reactions.

- π -bonds are not directional hence do not determine the shape of a molecule.
- Free rotation of atoms about a π -bond is not possible.
- A triple bond is made up of one σ and two π -bonds, while a double bond consists of one σ and one π -bond.
- Formation of a π -bond shortens the distance between the two atoms involved.
- Decreasing order of bond distance: single bond > double bond > triple bond.

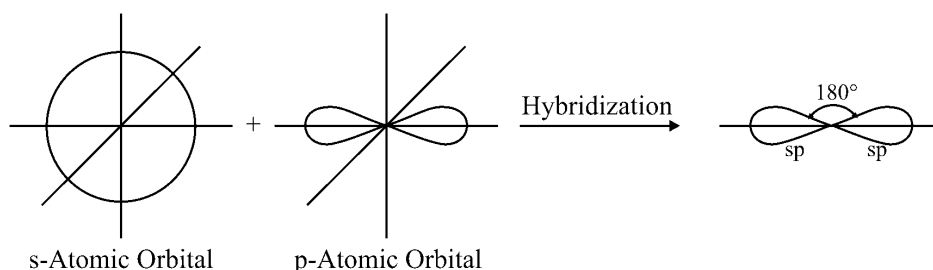
6. Hybridization :

The phenomenon of hybridization was introduced by **Pauling** to explain the equivalent nature of covalent bonds in molecules. It may be defined as, "Mixing or merging of atomic orbitals having slightly different energies, of outermost shell in an atom in such a way that there is a redistribution of shape and energy amongst themselves to give equivalent orbitals known as hybrid orbitals". The following points should be remembered in the study of hybridisation:

- Excitation of an atom is not a necessary condition for hybridization.
- Atomic orbitals of outermost shell slightly differing in their energies undergo hybridization.
- Both half-filled and fully filled orbitals can participate in hybridization.
- Hybridization never takes place in isolated atoms but occurs only at the time of covalent bond formation.
- Orbitals of a single atom are hybridized.
- The number of hybrid orbitals obtained is equal to the total number of pure atomic orbitals undergoing hybridization.
- Hybrid orbitals are quite identical in shape and energy.
- The hybrid orbitals are oriented in space as far apart as possible. Thus, they help in determining the shape or geometry of a molecule.
- Covalent bonds formed by overlapping between hybrid orbitals are stronger than those formed between pure atomic orbitals.

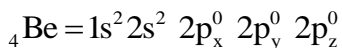
Types of Hybridizations:

- sp* or Diagonal hybridization:** It involves the combination (intermixing) of one *s*- and one *p*-atomic orbitals and gives two equivalent orbitals known as ***sp*-hybrid orbitals**. These *sp*-hybrid orbitals lie diagonally opposite to each other, *i.e.*, in a straight line subtending an angle of 180° between them. Each *sp*-hybrid orbital has 50% *s*-character and 50% *p*-character.



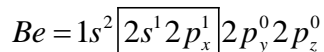
The effective size of sp -hybrid orbitals is smaller than sp^2 and sp^3 -hybrid orbitals. This type of hybridization takes place in the formation of alkynes ($C \equiv C$), CO_2 , BeF_2 , $BeCl_2$, BeH_2 , $HgCl_2$, $ZnCl_2$, $MgCl_2$, CS_2 etc. Let us consider the formation of BeH_2 .

Electronic configuration of $4Be$:



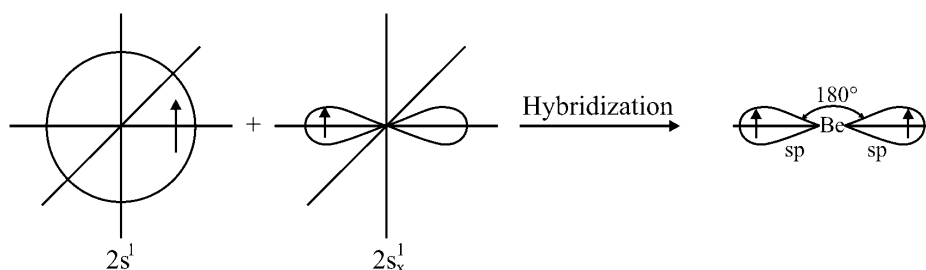
(Ground state)

(No unpaired e^- in the outermost shell, no covalency)

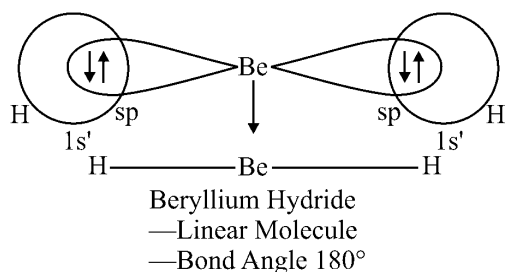


(In excited state) sp -hybridization

(One e^- is promoted from $2s$ to $2p_x$, two unpaired electrons, hence bivalent in its compounds)

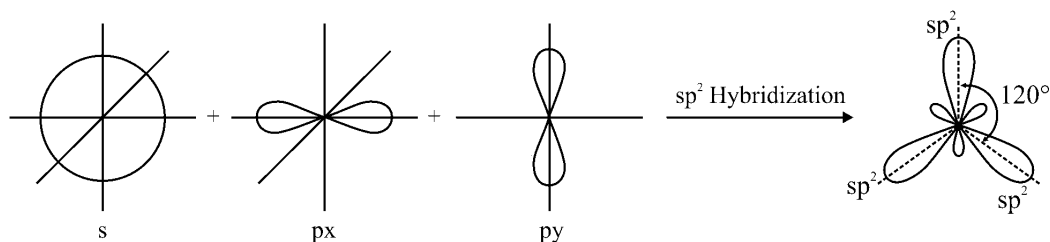


Each of sp -hybrid orbitals of Be overlaps with $1s^1$ orbitals of hydrogen to give BeH_2 .



- (ii) **sp^2 - or Trigonal hybridization:** When one s - and two p -atomic orbitals of outermost shell of an atom are mixed to give three new equivalent orbitals, the process is called sp^2 -hybridization. The three equivalent new orbitals (sp^2 -hybrid orbitals) lie in the same plane and are directed towards the three corner of an equilateral triangle. The angle between sp^2 -hybrid orbitals is 120° to have minimum repulsion. The effective size of sp^2 - hybrid orbitals is slightly greater than sp -hybrid orbitals. The s -character in sp^2 hybrid orbitals is $\frac{1}{3}$, i.e., (33%).

This type of hybridization takes place in the formation of alkenes ($> C = C <$), BF_3 , BCl_3 , CO_3^- , NO_3^- etc.,



Formation of BF_3 : Electronic configuration of boron atom in ground state is—

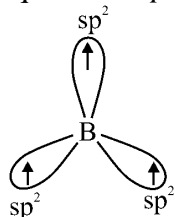
$${}_5\text{B} = 1s^2 2s^2 2p_x^1$$

There is one unpaired electron in this atom and hence boron can form only one covalent bond, but boron is trivalent in its compounds which is possible in its excited state. In the excited state, one electron from 2s orbital is promoted to 2p, atomic orbital:

$${}_5\text{B} = 1s^2 \boxed{2s^1 2p_x^1 2p_y^1} 2p_z^0$$

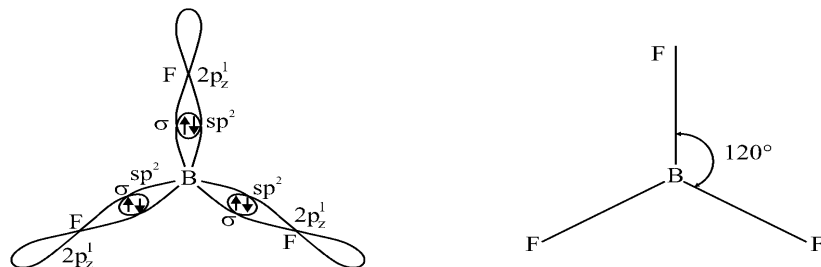
sp^2 hybridization

Now, the three atomic orbitals ($2s^1$, $2p_x^1$ and $2p_y^1$) undergo hybridization to give three equivalent sp^2 -hybrid orbitals.



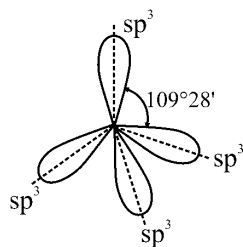
Each of these sp^2 -hybrid orbitals of boron overlaps with the unpaired electron in $2p_z$ orbital of each of the three fluorine atoms.

- The shape of BF_3 molecule is plane triangular with a bond angle 120° .
- The vacant $2p_z$ atomic orbital of boron is present on boron in BF_3 molecule in a plane perpendicular to the plane of molecule.

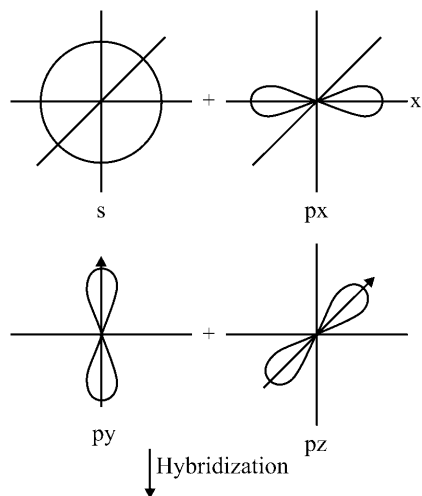


- Boron atom can accept one pair of electrons in this atomic orbital.

(iii) sp^3 or Tetrahedral hybridization: This hybridization involves the intermixing of one s - and three p -atomic orbitals of outermost shell of an atom. As a result, four equivalent orbitals known as sp^3 -hybrid orbitals are obtained. These sp^3 -orbitals are directed

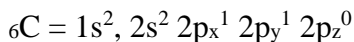


towards the four corners of a regular tetrahedron hence the name **tetrahedral hybridization**. The hybrid orbitals subtend an angle of $109^\circ 28'$ (tetrahedral angle) for minimum repulsion. The s-character in sp^3 hybrid orbital is $\frac{1}{4}$, i.e., 25%. The effective size of sp^3 - orbitals is greater than sp and sp^2 hybrid orbitals.

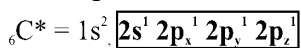


This type of hybridization takes place in carbon in saturated organic compounds such as methane, ethane, etc. In NH_3 , SiF_4 , $SiCl_4$, H_2O , SO_4^{2-} , ClO_2^- , ClO_3^- etc. also sp^3 hybridization of central atom takes place.

Formation of methane: Ground state electronic configuration of carbon is:

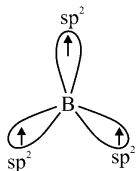


(Two unpaired electrons hence 'C' can form two covalent bonds only)

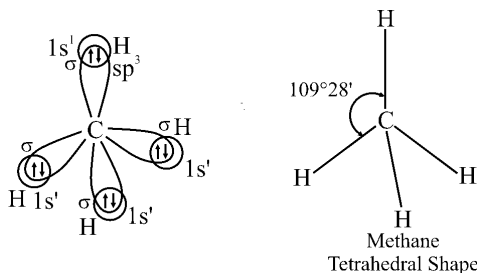


(In excited state) sp^3 hybridization

(Four unpaired electrons, hence 'C' can form four covalent bonds)

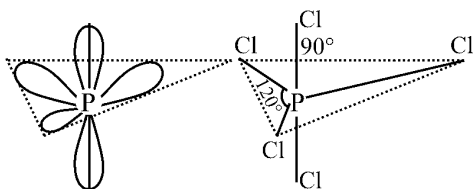


These sp^3 -orbitals overlap with the $1s^1$ -orbitals of hydrogen atoms to form four σ -bonds.



(ii) **$sp^3 d$ -Hybridization** (Trigonal bipyramidal hybridization): In this hybridization, there is mixing of one s, three p and one dz^2 orbital of outermost shell. Five equivalent $sp^3 d$ -hybrid orbitals are obtained which form a trigonal bipyramidal geometry.. Three $sp^3 d$ -orbitals lie in a

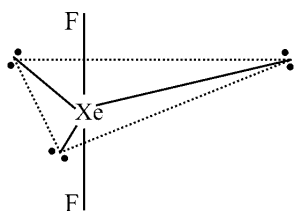
plane subtending an angle of 120° and the rest two lie in a perpendicular plane, one above the plane and other below the plane, i.e., making an angle of 90° .



Hybridization of phosphorus atom in PCl_5 is sp^3d .

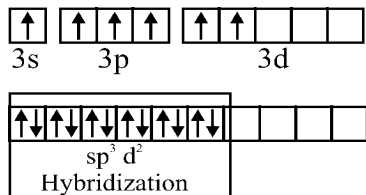
Trigonal bipyramidal shape introduces dis-symmetry in the molecule. It is not completely a regular structure as its some bond angles are 90° and others are 120° . Therefore, such compounds are less stable and more reactive. PCl_5 molecule splits in the solid state into PCl_4^+ and PCl_6^- ion having tetrahedral and octahedral structures respectively.

'Xe' atom in XeF_2 , also has trigonal bipyramidal hybridization. It has a linear shape because three equatorial positions are occupied by three lone pairs of electrons.



(iii) sp^3d^2 or octahedral hybridization: One s , three p and two d -orbitals ($d_{x^2-y^2}$ and d_{z^2}) in the

outermost shell of an atom mix up to give size new equivalent hybrid orbitals known as sp^3d^2 hybridization. These six hybrid orbitals form a *regular octahedral* geometry with the bond angles of 90° each. Four sp^3d^2 orbitals lie in the same plane and the remaining two are perpendicular to this plane, (i.e., one above the plane and the other below the plane). For example, hybridization of S in SF_6 is sp^3d^2 :

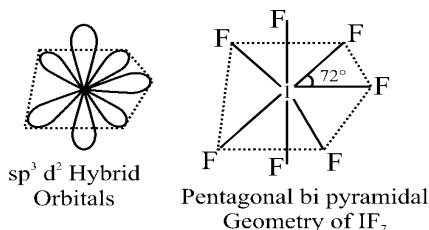


The $2p_z^1$ atomic orbitals of $9F$ atom overlap with each of six sp^3d^2 orbitals of sulphur to give SF_6 molecule. Other examples of which central atom is in sp^3d^2 hybridization are IF_5 , XeF_4 , etc. Octahedral geometry is symmetrical, hence is quite stable. That is why SF_6 molecule is quite stable and a less reactive compound.

(iv) sp^3d^3 or pentagonal bipyramidal hybridization: One s , three p and three d -orbitals (d_{xy} , d_{xz} and d_{yz}) of the outermost shell of an atom undergo mixing to give seven sp^3d^3 hybrid orbitals in this type of hybridization. Out of these seven atomic orbitals, five are co-planar pointing towards the five corners of a regular pentagon and the remaining two are perpendicular to this plane (one above and the other below the pentagonal plane). The angle between any two sp^3d^3 orbitals in the pentagonal plane is 72° and the remaining two subtend an angle of 90° with the plane. An example of sp^3d^3 hybridization is in the molecule IF_7 . Other example of sp^3d^3 hybridized state, the geometry of this molecule is distorted octahedral.

Pentagonal bipyramidal geometry is dis-symmetrical. Therefore, such a molecule is less stable and hence more reactive.

VESEPR Theory and Geometry of molecules: The theory known as *valency shell electron pair repulsion theory* determines the shape or geometry of a molecule. In a polyatomic molecule, there is a central atom covalently



bonded to other atoms, *i.e.* it is surrounded by bonding electron pairs or lone pairs and shared pairs of electrons in its valency shell. These electron pairs exert a repulsive force on one another and so lie as far apart from one another as possible so that the forces of repulsion are minimized. The repulsive forces between various types of electron pairs are in the order: *lone pair—lone pair* > *lone pair—bond pair* > *bond pair—bond pair*.

Thus, the geometry of a molecule is determined by the number and nature of pairs of electrons surrounding the central atom. If there are only bond pairs in the valency shell around the central atom it has a **regular geometry**, but when there are lone pairs also in the valency shell, the geometry becomes irregular. This is due to increasing force of repulsion between lone pairs and bond pairs of electrons about the central atom. Geometry corresponding to number of bonds about the central atom is given in the following table :

Total No. of bond pairs about the central atom	Type of hybridization	Geometry of the Molecule	Bond Angle(s)	Example
2	sp	Linear	180°	$BeH_2, BeF_2, BeCl_2, HgCl_2, ZnCl_2, CO_2, Cs_2, CO, H-C \equiv C-H$, etc.
3	sp^2	Plane triangular	120°	$[BeF_3]^-$, BF_3 , BCl_3 , NO_3^- , CO_3^{2-} , C_2H_4 , etc.
4	sp^3	Tetrahedral	$109^\circ 28'$	$CH_4, CCl_4, NH_4^+, SiF_4, [BF_4]^-$, $[BeF_4]^{2-}$, SO_4^{2-} , ClO_4^- , PO_4^{3-} , etc.
4	dsp^2	Square planar	90°	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Cu(H_2O)_4]^{2+}$
5	$sp^3 d$	Trigonal bipyramidal	$120^\circ, 90^\circ$	PF_5, PCl_5
6	$sp^3 d^2$	Octahedral	$90^\circ, 90^\circ$	SF_6
7.	$sp^3 d^3$	Pentagonal bipyramidal	$72^\circ, 90^\circ$	IF_7

As has been mentioned before that the presence of one or more lone pairs of electrons on the central atom makes the shape of the molecule irregular. In the following table are listed the compounds with different geometries with different number of bond pairs and lone pairs.

Shape of some Common Molecules and Ions

Total no. of electron pairs about the central atom	No. of bond Pairs	No. of lone Pairs	Hybridization of the central atom	Geometry of the molecule	Examples
2	2	0	sp	Linear	HgCl ₂ , ZnCl ₂ , etc
3	3	0	sp ²	Plane triangular	BF ₃ , BCl ₃ , etc
	2	1	sp ²	V-shaped	SnCl ₂ (gas)
4	4	0	sp ³	Tetrahedral	CH ₄ , SiF ₄
	3	1	sp ³	Pyramidal	$\ddot{\text{N}}\text{H}_3, \ddot{\text{P}}\text{H}_3, \ddot{\text{P}}\text{Cl}_3$ etc
4	2	2	sp ³	Bent or V-shape	H ₂ O: , F ₂ O:
5	5	0	sp ³ d	Trigonal bipyramidal	PF ₅ , PCl ₅
	4	1	sp ³ d	Irregular tetrahedron	SCl ₄ , TeBr ₄ , etc.
	3	2	sp ³ d	T-shape	ClF ₃ , ICl ₃ , BrF ₃ , etc
	2	3	sp ³ d	Linear	I ₃ ⁻ , ICl ₂ ⁻ , XeF ₂
6	6	0	sp ³ d ²	Octahedral	SF ₆ , [PCl ₆] ⁻ , etc
	5	1	sp ³ d ²	Square pyramidal	IF ₅ , ClF ₅ , XeOF ₄
	4	2	sp ³ d ²	Square planar	XeF ₄ , ICl ₄ ⁻ , etc

7. CO-ORDINATE BOND, DATIVE BOND, SEMIPOLAR BOND:

This type of bond is formed by one sided sharing of one pair of electrons between two atoms, i.e., electron pair of one atom is contributed between two atoms. The necessary condition for the formation of co-ordinate bond is that octet of one atom should be complete having at least one lone pair of electrons. The other atom should have a deficiency of at least one pair of electrons. If the atom 'X' has its octet already complete and the atom "Y" has only six electrons in its valency shell, a co-ordinate bond is formed as below:

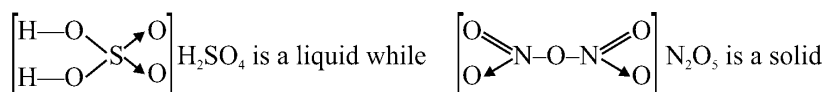


The atom having completed octet which provides the electron pair for sharing is known as **donor** and the other which accepts the electron pair is called **acceptor atom**. For the same reason, the co-ordinate bond is also known as **donor-acceptor** or the **dative bond**. A co-ordinate bond is represented by a arrow (\rightarrow) pointing from donor atom to acceptor.

Example 11. Formation of ammonium NH_4^+ ion:

Characteristics of Co-ordinate Compounds:

(i) They may be gaseous, liquids or solids. For example, N_2O , SO_2 , etc. are gases,

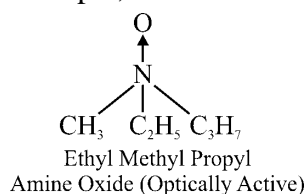


(ii) Their melting and boiling points are lower than electrovalent but higher than covalent compounds.

(iii) Generally they are poor conductors of electricity but some of them are good conductors also.

(iv) Generally dative compounds are insoluble in water but soluble in organic solvents. However, some of them become soluble in water.

(v) Co-ordinate compounds show stereo isomerism because this bond is directional in nature. For example,



8. Bond Length, Bond Angle and Bond Energy:

(i) **Bond length:** In a molecule, the constituent atoms vibrate with respect to each other, hence their positions in a molecule are not fixed. *The average distance between the nuclei of bonded atoms is called bond lengths.*

When a covalent molecule is made up of identical non-metallic atoms, the bond lengths is equal to double of the covalent radius of the atom. *In ionic compounds, the bond length is the sum of ionic radii of component cation and anion.* Bond lengths of some common di-atomic molecules are given in the following table:

Bond Lengths (Å) of Some Common Covalent Bonds

Bond	Bond length	Bond	Bond length	Bond	Bond length
H—F	0.47	$\text{N}\equiv\text{N}$	1.094	H—N	1.014
F—F	1.435	H—F	0.926	C—C	1.543

Cl—Cl	2.002	H—Cl	1.284	C = C	1.34
Br—Br	2.286	H—Br	1.423	C ≡ C	1.20
I—I	2.667	H—I	1.615	O—O	1.48
N—N	1.47	H—O	0.957	O = O	1.207
		H—S	1.334	C—O	1.42
				C = O	1.22

It becomes clear from the study of the table that multiple bonds are of smaller bond length than single bonds. As the involvement of p -orbital increases, the C—H bond distance increases. For example,

≡ C—H bond distance 1.08Å

(sp)

= C—H bond distance 1.10Å

(sp²)

$\begin{array}{c} | \\ \text{—C—H bond distance } 1.110\text{Å} \\ | \\ (\text{sp}^3) \end{array}$

- Bond lengths decrease in the order:

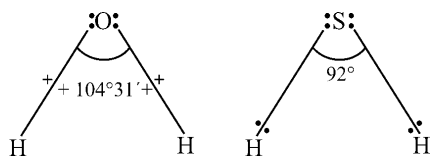
$$sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$$

- Bond length between atoms are changed if a molecule shown resonance.
- If the covalently bonded atoms possess lone pair or pairs of electrons, the bond length becomes greater than the sum of their covalent radii.

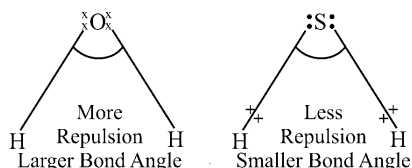
Bond angle: Bond angle is the internal angle between the orbitals having bond pair of electrons in the valency shell of central atoms in a molecule. For example, the bond angle in H₂O (H—O—H), NH₃ (H—N—H bond angle) and, CH₄ (H—C—H bond angle) are 104°31', 107° and 109°28' respectively. The following factors affect bond angles:

(i) **Hybridization of central atom**, (ii) **Lone pair repulsions**, (iii) **Electronegativity of central atom**.

- Bond angle increases with increasing s -character in a hybrid orbital, e.g.,
Bond angle (H—C—H) in sp^3 carbon < H—C—H in sp^2 carbon < H—C—H in sp carbon.
- In H₂O: molecule, although central 'O' atom is sp^3 hybridised, H—O—H bond angle should have been 109° 28', but the angle is 104°31'. It is (the decrease in bond angle) due to repulsion between the lone pairs present on the oxygen atom, lone pair–lone pair repulsion > bond pair–bond pair repulsion.
- The increase in electronegativity of central atom increase the bond angle. For example,



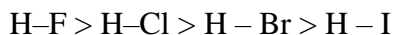
Sulphur is lesser electronegative element than oxygen. The bond pairs in H_2S are more away from the central 'S' atom, the repulsive forces between bond pairs are smaller and bond angle is small.



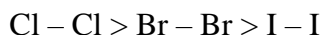
Bond angles can be measured by X-ray analysis or by some other spectroscopic methods such as Infra red spectroscopy.

Bond energy or bond strength: It is the amount of energy required to break one mole of a chemical bonds of a type in gaseous state. Bond energy is expressed in kJ mol^{-1} (in SI units) or in kcal. mol^{-1} . Bond energy is inversely related to bond length. Bond energy depends upon the following factors:

- 1. Electronegativity of Bonded atoms (Bond polarity):** Greater the electronegativity difference, greater is the bond polarity so, greater is the bond strength, *i.e.*, stronger the bond. For example, bond strength of hydrogen halides decreases in the order.

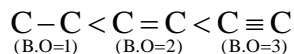


- 2. Atomic size of bonded atoms:** Bond distance \propto Atomic size of bonded atoms so, small atoms form shorter bonds and the bond energy is large. For example, bond energy of halogens is in the order.

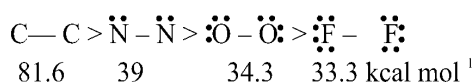


Because their atomic sizes are in the order $\text{Cl} < \text{Br} < \text{I}$.

- 3. Extent of overlapping of atomic orbitals :** A larger extent of overlapping of component atomic orbitals imparts great strength to the bond.
- 4. Hybridization:** Hybrid orbitals form stronger bonds because they provide more extent of overlapping than pure atomic orbitals. Thus, $sp^3 - sp^3$ overlapping results in a stronger bond than $p-p$ overlapping.
- 5. Bond order:** Bond energy \propto Bond order. Thus the increasing order of bond energy is:



- 6. Repulsion between the lone pairs of electrons of bonded atoms:** As the number of lone pairs of electrons on the bonded atoms increases, the bond energy decreases because repulsion between these lone pairs of electrons increases. For example, the bond energies of the following single bonds having zero, one, two and three lone pairs of electrons are in the order:



8. Molecular orbital theory:

This theory was developed by Hund and Mulliken. This theory gives the molecular orbital picture of a molecule in the same way as atomic orbitals describe an atom. According to this theory, the outer electrons as well as the inner orbitals of the bonding atoms lose their identity and belong to the molecule as a whole. Molecular orbitals (M.O) are formed by the combination of atomic orbitals. Molecular orbitals are polycentric. The M.O. in which the electron pair remains under the influence of two nuclei only is called a **localized M.O.**, that in which electrons embrace three or more nuclei are known as **delocalized molecular orbitals**. Energy of a **delocalized molecular orbital**.

The following are the main points of the theory:

1. The number of M.O. formed is equal to the number of atomic orbitals undergoing combination. Thus, if 'n' atomic orbitals take part in bonding, the number of M. O's is n. Out of these half (n/2) will be **bonding molecular orbitals (BMO)** and n/2 will be **anti bonding molecular orbitals (ABMO)**.
2. The orbitals participating in bonding (combination) are of nearly equal energies. This is 1s-atomic orbital of one atom combines with 1s of other atom.
3. Those orbitals of comparable energy, only take part in overlapping to which symmetry gives permission for example, if z- is the molecular axis, s-A.O. can combine with p_z but not with p_x or p_y or p_z can combine with p_z but not with p_x or p_y to form molecular orbitals.
4. Greater the extent of overlapping, stronger is the bond formed.
5. The ionic nature of the bond is decided by the difference in the energy of atomic orbitals undergoing overlapping.
6. Electrons in the resulting molecular orbitals are filled according to Aufbau's Principle, *i.e.* M.O. of lower energy is filled up first with electrons.
7. Each M.O can accommodate a maximum of two electrons with antiparallel spins.
8. M.O of equal energies are filled according to Hund's rule, *i.e.*, M.O having equal energies are first singly occupied by electrons having parallel spins and only after that pairing of electrons starts.
9. The shapes of M.O. formed depend upon the type of combining A.O.'s.

Bonding Molecular Orbitals (BMO): According to the principle of linear combination of atomic orbitals (LCAO), it is formed by the addition of wave-function of atomic orbitals. If Ψ_A and Ψ_B are the wave functions of atomic orbitals of A and B, then the B.M.O wave function

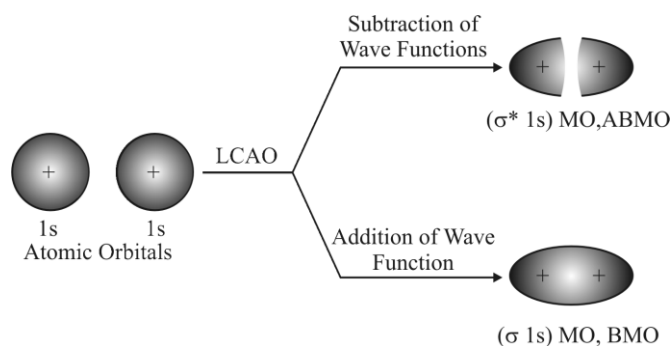
$$\Psi' = \Psi_A + \Psi_B$$

The energy of BMO is lower than both of the two participating atomic orbitals. The electron density is maximum between the nuclei of bonded atoms. Thus, formation of BMO's leads to the formation of stable chemical bonds. BMO formed by the axis overlapping of two atomic orbitals is designated by σ M.O.

Antibonding Molecular Orbitals (ABMO) : It is formed by the subtraction of wave function of participating atomic orbitals.

Thus, the wave function of ABMO (Ψ) is given by $\Psi = \Psi_A - \Psi_B$

The energy of ABMO is higher than both of the atomic orbitals participating in bond formation. The electron density is minimum between the nuclei leading to repulsion between them. It decreases the stability of the bond. It is designated as σ^* (sigma star) M.O.



Difference between BMO and ABMO

Bonding M.O	Antibonding M.O
1. BMO is formed by addition of wave functions of atomic orbitals	1. ABMO results by the subtraction of wave functions of atomic orbitals.
2. In BMO, there is greater electron density in the region between the two nuclei of bonded atoms	2. In ABMO, the electron density is much lesser between the nuclei of bonded atoms.
3. The forces in BMO have a tendency of bring the nuclei together, <i>i.e.</i> , electrons in BMO contribute to bonding between the atoms	3. The forces in ABMO, push the nuclei apart, <i>i.e.</i> , the electrons in these MO's contribute to repulsion between the nuclei hence to non-bonding between the atoms.
4. It has lower energy than both of the atomic orbitals.	4. It possesses higher energy than both of the two participating atomic orbitals.

Component Atomic Orbitals	Designation of BMO	Designation of ABMO
1s and 1s	σ 1s	σ^* 1s
2s and 2s	σ 2s	σ^* 2s
2p _z and 2p _y	π 2p _y	π^* 2p _y

$2p_x$ and $2p_x$	$\pi 2p_x$	$\pi^* 2p_x$
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- σ -type of MO will be formed when:
 - (i) s-Atomic orbital of one atom overlaps with s or p_z orbital of another atom.
 - (ii) p_z orbital of one atom overlaps with s or p_z orbital of another atom.
- π -type of MO will be formed when:
 - (i) p_y -orbital of one atom combines with p_y -orbital of another atom (both p_y are parallel hence give lateral overlapping).
 - (ii) p_x orbital of one atom combines with p_x orbital of another atom (Both p_x and p_x AO are parallel). The order in which these molecular orbitals can be arranged according to their energy, is as follows:

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

$$= \pi 2p_x < \pi^* 2p_y = \pi^* 2p_x < \sigma^* 2p_z$$
- $\pi 2p_x$ and $\pi 2p_x$, and $\pi^* 2p_x$ and $\pi^* 2p_x$ are degenerate molecular orbitals, i.e., they are of equal energies.
- For molecules like B_2 , C_2 , and N_2 , the energy of the molecular orbitals is as follows:

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

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

For these molecules, the energy of $\sigma 2p_z$ is higher than $\pi 2p_y$ and $\pi 2p_x$ orbitals.

The main reason for the difference in the sequence of energy of M.O is the interaction of 2s and $2p_z$ atomic orbitals.

For the molecules Li_2 , B_2 , C_2 and N_2 , the difference in energies of 2s and $2p_z$ orbitals is small and hence these can undergo interaction. On the other hand, the difference in energy for 2s and $2p_z$ atomic orbitals for O_2 , F_2 and Ne_2 is large and so these cannot interact.

Bond order (B.O): Bond order is a quantity introduced to estimate the relative stability of a molecule. It is defined as the , “half of the difference between the number of electrons in Bonding Molecular orbitals and Antibonding Molecular Orbitals.

$$\text{i.e., B. O.} = \frac{1}{2}(N_b - N_a)$$

where N_b = number of electrons in BMO's

N_a = number of electrons in ABMO's

More about bond order

- A molecular species is non-existent if $N_b = N_a$, i.e., B.O is zero.
- For stability of a molecule, $N_b > N_a$.
- B.O may have integral or non- integral (fractional) values.
- Integral bond order of one, two or three indicates single, double or triple bonds between atoms.
- Stability of a molecule \propto Bond order.
- Bond strength \propto Bond order.

$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

- The addition of an electron in the bonding molecular orbital makes the molecule more stable where as that in the antibonding molecular orbital makes it less stable.

The removal of an electron from the B.M.O. makes the molecule less stable and from antibonding M.O. makes it more stable.

- Stability order is $O_2^+ > O_2 > O_2^-$.
- Decreasing order of bond length is $O_2^- > O_2 > O_2^+$.
- Decreasing order of bond energy: $O_2^+ > O_2 > O_2^-$.

Bond order of Iso-electronic species: All the isoelectronic species have the same bond order.

Example (i) : He_2^+ and H_2^- are isoelectronic. Their B.O. = $\frac{1}{2}$.

Example (ii) : O_2^{2+} , N_2 , CN^- , CO , NO^+ are isoelectronic species. Their B.O. is 3.

Example (iii) : O_2^+ , NO , N_2^-

$$B. O = 2.5.$$

9. Molecular orbital configurations of heteronuclear diatomic species:

Bond order, and magnetic properties of some important heteronuclear diatomic molecules and their ions are summarized in the table below :

Molecule/ion	Molecular orbital (M.O.) Configuration	Bond order	No. of unpaired Electrons	Magnetic character
CN(13e ⁻)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2(\sigma 2p_z)^1$	$\frac{7-2}{2} = 2.5$	1	Paramagnetic
CN ⁻ (14e ⁻)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $(\pi 2p_y)^2(\sigma 2p_z)^2$	$\frac{8-2}{2} = 3.0$	Nil	Diamagnetic
NO (15e ⁻)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2(\sigma 2p_z)^2\pi^*(2p_x)^1$	$\frac{8-3}{2} = 2.5$	1	Paramagnetic
NO ⁺ (14e ⁻)	$KK\sigma(2s)^2\sigma^*(2s)^2\pi(2p_x)^2$ $\pi(2p_y)^2(\sigma 2p_z)^2\pi^*(2p_x)^0$	$\frac{8-2}{2} = 3.0$	Nil	Diamagnetic

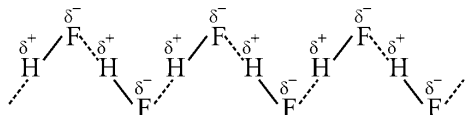
$$\propto \frac{1}{\text{Atomic size of Z}}$$

- The strength of H-bond varies from 2 to 10 kcal/ mole.
- $\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{N}}\cdots\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{F}}$, H bond is the strongest and $\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{N}}\cdots\overset{\delta^+}{\text{H}}-\overset{\delta^-}{\text{N}}$; H-bond is the weakest bond.

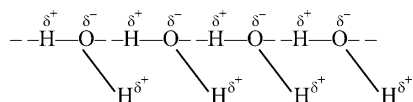
Types of hydrogen bonds: It is mainly of two types:

(1) **Intermolecular H-bonding:** Hydrogen bond formation between two or more molecules of either the same or different compounds is known as intermolecular H-bonding. Examples are:

(a) **Hydrogen Fluoride (H-F):** It exists as a polymeric molecule, (HF)_n.



(b) **H₂O:** It is a polar molecule. One molecule of H₂O can form hydrogen bonds with four other H₂O molecules.



- Degree of association between H₂O molecules decreases as:*

Ice > water > steam. Two ice cubes when pressed against each other become one unit due to the formation of hydrogen bonds.

- (c) Ammonia (NH₃), All primary amines (R-NH₂ or Ar NH₂), all secondary amines are intermolecularly H-bonded.
- (d) All alcohols (R-OH) contain H-bonding.
- (e) All carboxylic acids are H-bonded.

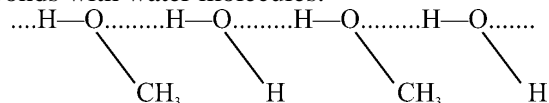
(2) **Intramolecular H-bonding:** It takes place within the same molecule. It results in ring formation (chelation). For example, o-Nitrophenol, o-Fluorophenol, etc.

Effect of H-bonding on properties: Almost all the physical properties undergo a change when there is hydrogen bonding in a molecule. Chemical properties may or may not be altered.

1. Effect of H-bonding on solubility:

(a) Intermolecular H-bonding: It results in association of a large number of molecules of a substance. Water molecules are also intermolecularly H-bonded. So, when a substance having intermolecular H-bonding is added to water, it breaks the H-bond water molecules and itself becomes associated with them and thus gets intermixed. i.e., gets dissolved.

For example: (i) Lower alcohols are miscible with water in every proportion because they can form H-bonds with water molecules.



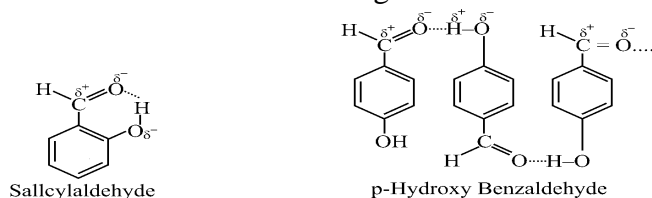
- The solubility of alcohols in water decreases with increasing molecular weight because the hydrocarbon character in alcohols increases which prevents H-bond formation with water molecules.
- Decreasing order of solubility among isomeric alcohols is:
t-alcohol > sec-alcohol > prim-alcohol

(ii) Similarly lower carboxylic acids, lower amines, sugars, etc., are soluble in water. In general, any substance which has a tendency to form H-bond with water, will become soluble in it.

(b) Intramolecular H-bonding : It gives rise to ring formation (chelation). It decreases solubility of a substance in water because intramolecularly H-bonded molecule can not form H-bond with water molecules hence remains insoluble.

For example :

(i) Salicylaldehyde (o-Hydroxybenzaldehyde) does not dissolve in water while p-Hydroxybenzaldehyde is fairly soluble. Salicylaldehyde contains intramolecular H-bonding, hence does not form H-bonds with water. p-Hydroxybenzaldehyde having intermolecular H-bonding, forms H-bonds with water molecules and so gets dissolved.



2. Effect on melting and boiling point:

The presence of intermolecular H-bonding gives rise to association among molecules. As a result a large amount of energy is required to separate the molecules. So, the boiling point of the compound increase.

SOLVED EXAMPLES

Ex.1 Why H_2^+ is less stable than H_2 molecule?

Sol. Stability of a molecule \propto Bond order.

$$\text{Bond order of } H_2 (\sigma 1s)^2 (\sigma^* 1s^0) = \frac{2-0}{2} = 1$$

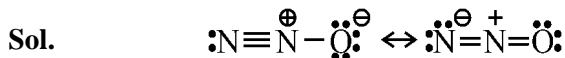
$$\text{Bond order of } H_2^+ (\sigma 1s^1) (\sigma^* 1s^0) = \frac{1-0}{2} = \frac{1}{2}$$

$\therefore H_2$ is more stable than H_2^+ .

Ex.2 How many sigma and π -bonds are present in benzene molecule?

Sol. There are twelve (12) sigma (σ) and three (3) pi (π) bonds in benzene molecule.

Ex.3 Give the resonance structure of nitrous oxide.

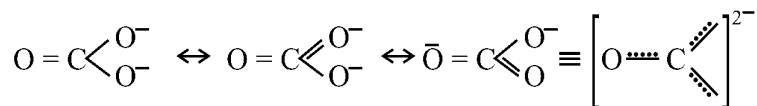


Ex.4 Among CH_3OH , CH_4 , CF_4 , CO_2 and CH_3F , which has the highest dipole moment?

Sol. CH_4 , CF_4 (both tetrahedral), and CO_2 (linear) are symmetrical molecules. Their dipole moment is zero. Since fluorine is more electronegative than oxygen, the dipole moment of CH_3F is higher than that of CH_3OH . Thus, among CH_3OH , CH_4 , CO_2 and CH_3F , CH_3F has the largest dipole moment.

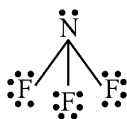
Ex.5 Carbon-oxygen bond lengths are equal in Na_2CO_3 , why?

Sol. In carbonate ion (CO_3^{2-}), the three C—O bond lengths are equal due to resonance. Carbonate ion is a resonance hybrid of following three canonical structures.



Ex.6 In the formation of SF_6 molecule which d-orbitals undergo hybridization?

- Sol.** $d_x^2 - y^2$ and dz^2 .
- Ex.7** State the hybridization of iodine in I_3^+ and ICl_2^- . What are their shapes?
- Sol.** In both of these molecules, iodine is in sp^3d state of hybridization. Both the molecules are linear.
- Ex.8** Which of the following substances are paramagnetic?
 N_2 , O_2 , F_2 , $K_3[CoF_6]$, NO_2 , $K_4[Fe(CN)_6]$
- Sol.** The following substances are paramagnetic, O_2 , (Two unpaired e^-); $K_3 [CoF_6]$ and NO_2 .
- Ex.9** Write the molecular geometry of each of the following:
- (i) H_2O , (ii) $[PCl_4]^+$, (iii) NCl_3 ,
 (iv) $HgCl_2$, (v) $[SiF_6]^{2-}$
- Sol.**
- | Molecule | Geometry |
|--------------------|-----------------|
| (i) H_2O | Angular or Bent |
| (ii) $[PCl_4]^+$ | Tetrahedral |
| (iii) NCl_3 | Pyramidal |
| (iv) $HgCl_2$ | Linear |
| (v) $[SiF_6]^{2-}$ | Octahedral |
- Ex.10** Explain the difference in the nature of bonding in LiF and LiI .
- Sol.** LiF is more ionic while LiI is more covalent because I^- ion being of much bigger size, is polarized by small Li^+ ion more than the F^- ion.
- Ex.11** Assign the possible hybridization to the central atom of the following species:
- (i) ClF_3 (ii) NO_3^- (iii) ClO_4 (iv) ClO_2^-
- Sol.**
- (i) ClF_3 → sp^3d hybridization of Cl atom,
 (ii) NO_3^- → sp^2 hybridization of N atom,
 (iii) ClO_4^- → sp^3 hybridization of Cl atom,
 (iv) ClO_2^- → sp^3 hybridization of Cl atom.
- Ex.12** What types of bonding are present in H_3O^+ ?
- Sol.** Covalent and co-ordinate.
- Ex.13** Arrange the following as indicated:
- (a) O, F, S, Cl, N in the order of increasing strength of hydrogen bonding (X.....H—X).
 (b) NO_2^+ , NO_2^- , NO_3^- in the order of increasing N—O bond length.
- Sol.**
- (a) $S < Cl < N < O < F$,
 (b) $NO_2^+ < NO_2^- < NO_3^-$.
- Ex.14** The N—F bond length in NF_3 molecule is greater than the sum of covalent radius of N and F atoms why?
- Sol.** It is due to repulsive forces acting between the lone pairs present on N and F atoms in NF_3 molecule.



Pyramidal shape of NF_3

Ex.15 Which out of B_2 and C_2 has higher bond dissociation energy?

Sol. Bond dissociation energy of C_2 is higher than that of B_2 . Bond order of C_2 is 2, while that of B_2 is one.

Ex.16 Among Co^{3+} , Zn^{2+} , Cu^+ , Ni^{2+} and Mn^{3+} ions, which are attracted in a magnetic field?

Sol. Co^{3+} , Ni^{2+} and Mn^{3+} ions are attracted in a magnetic field as these ions contain unpaired electrons.

Ex.17 In the formation of N_2^+ molecule, from which molecular orbital an electron is removed?

Sol. The electron is removed from $\sigma 2p_z$ molecular orbital.

EXERCISE # 1

- Q.1** The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement(s) about the nature of HCl is/are:
(a) HCl is 17% ionic (b) 83% ionic (c) 50% (d) 100%.
- Q.2** The order of strength of hydrogen bond is:
(a) $\text{Cl}-\text{H}\cdots\text{Cl} > \text{N}-\text{H}\cdots\text{N} > \text{O}-\text{H}\cdots\text{O} > \text{F}-\text{H}\cdots\text{F}$
(b) $\text{N}-\text{H}\cdots\text{N} > \text{Cl}-\text{H}\cdots\text{Cl} > \text{O}-\text{H}\cdots\text{O} > \text{F}-\text{H}\cdots\text{F}$
(c) $\text{O}-\text{H}\cdots\text{O} > \text{N}-\text{H}\cdots\text{N} > \text{Cl}-\text{H}\cdots\text{Cl} > \text{F}-\text{H}\cdots\text{F}$
(d) $\text{F}-\text{H}\cdots\text{F} > \text{O}-\text{H}\cdots\text{O} > \text{N}-\text{H}\cdots\text{N} > \text{Cl}-\text{H}\cdots\text{Cl}$
- Q.3** The electronegativity of O,F,N, Cl and H are 3.5, 4.0, 3.2, 3.0 and 2.1 respectively. The strongest bond will be:
(a) F—O (b) O—Cl (c) N—H (d) O—H.
- Q.4** The carbonyl group has following resonating structures:
(I) $>\overset{+}{\text{C}}-\overset{-}{\text{O}}$ (II) $>\overset{-}{\text{C}}-\overset{+}{\text{O}}$ (III) $>\text{C}=\text{O}$
The correct order of stability of these structures is:
(a) I > II > III (b) III > I > II (c) I > III > II (d) III > II > I.
- Q.5** Which combination will give the strongest ionic bond?
(a) Na^+ and Cl^- (b) Mg^{2+} and Cl^- (c) Na^+ and O^{2-} (d) Mg^{2+} and O^{2-} .
- Q.6** Number of bonding pairs and lone pairs around the central atom in the I_3^- ion are:
(a) 2,2, (b) 3,2 (c) 2,3 (d) 4,3.
- Q.7** The formal charge on the central oxygen atom in O_3 molecule is:
(a) 0 (b) +1 (c) -1 (d) -2.
- Q.8** Match **List I** (species) and **List II** (bond orders) and select the correct answer:
- | List I | List II |
|------------------|----------|
| A N_2 | 1 1.0 |
| B O_2 | 2 2.0 |
| C F_2 | 3 2.5 |
| D O_2^+ | 4 3.0 |
- (a) A → 4, B → 2, C → 1, D → 3 (b) A → 1, B → 3, C → 4, D → 2
(c) A → 1, B → 2, C → 4, D → 3 (d) A → 4, B → 3, C → 1, D → 2.
- Q.9** Which of the following have identical bond order?
(I) CN^- (II) O_2^- (III) NO^+ (IV) CN^+
(a) I, III (b) I, II (c) II, IV (d) I, II, III.
- Q.10** The ratio of σ and π bonds in meistyrene is:
(a) 3 (b) 7 (c) 5 (d) 6.
- Q.11** Both BF_3 and NF_3 are covalent compounds. BF_3 is a non-polar compound but NF_3 is polar. The reason is that:
(a) boron is a solid and nitrogen is a gas in free state (b) BF_3 is planar but NF_3 is pyramidal in shape

(c) boron is a metalloid while nitrogen is a non-metal (d) atomic size of boron is smaller than that of nitrogen.

Q.12 Which of the following sets of species does not follow octet rule?

(a) CO, PCl₅, PCl₃, AlCl₃ (b) CO, B₂H₆, NH₃, H₂O (c) AlCl₃, BF₃, PCl₅, SF₆ (d) H₂O, NH₃, CO₂, AlCl₃.

Q.13 Which of the following species is diamagnetic in nature?

(a) He₂⁺ (b) H₂ (c) H₂⁺ (d) H₂⁻.

Q.14 The number and type of bonds between two carbon atoms in calcium carbide are:

(a) one sigma, one /8pi (b) one sigma, two pi (c) two sigma, one pi (d) two sigma, two pi.

Q.16 In Ag (CN)₂]⁻, the number of π -bonds is:

(a) 2 (b) 3 (c) 4 (d) 6.

Q.17 Which of the following molecules/ions does not contain unpaired electrons?

(a) O₂²⁻ (b) B₂ (c) N₂⁺ (d) O₂.

Q.18 In which of the following molecule/ions are all the bonds not equal?

(a) SF₄ (b) SiF₄ (c) XeF₄ (d) BF₄⁻.

Q.19 H₂, Li₂, B₂ each has bond order equal to 1, the order of their stability is:

(a) H₂ = Li₂ = B₂ (b) H₂ > Li₂ > B₂ (c) H₂ > B₂ > Li₂ (d) B₂ > Li₂ < H₂.

Q.20 Which of the following pair is expected to have the same bond order?

(a) O₂, N₂ (b) O₂⁺, N₂⁻ (c) O₂⁻, N₂⁺ (d) O₂⁻, N₂⁻.

Q.21 Pick out the incorrect statement :

- (a) in PCl₅, P atom is sp³d hybridized and has trigonal bipyramidal geometry
- (b) PCl₅ on hydrolysis forms oxychloride
- (c) PCl₅ acts as a Lewis acid
- (d) in PCl₅, the axial chlorine atoms are closer to central P atom than equatorial chlorine atoms.

Q.22 Among of the following molecules, which is the most ionic?

(a) CaCl₂ (b) SnCl₂ (c) NaCl (d) CuCl

Q.23 Among of the following, the molecule with the highest dipole moment is

(a) CH₃Cl (b) CH₂Cl₂ (c) CHCl₃ (d) CCl₄

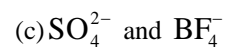
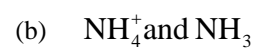
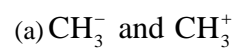
Q.24 Orthonitrophenol is steam volatile but paranitrophenol is not because

- (a) Orthonitrophenol has intermolecular hydrogen bonding while paranitrophenol has intermolecular hydrogen bonding
- (b) Both ortho – and paranitrophenol intermolecular hydrogen bonding.
- (c) Orthonitrophenol has intermolecular hydrogen bonding and paranitrophenol has intermolecular hydrogen bonding
- (d) Van der Walls force are dominant in orthonitrophenol.

Q.25 The shape of PCl₄⁺, PCl₄⁻ and AsCl₅ are respectively

- (a) Square planer, tetrahedral and see-saw. (b) Tetrahedral, see-saw and trigonal bipyramidal
- (c) Tetrahedral, square planer and pentagonal bipyramidal (d) Trigonal bipyramidal, tetrahedral and square pyramidal

Q.26 Which of the following pairs are isostructural?



EXERCISE # 2

- Q.1** The formal charge of the O-atoms in the ion $[\ddot{\text{O}} = \text{O} = \ddot{\text{O}}]^{+}$ is:
- (a) -2 (b) -1
(c) 0 (d) +1.
- Q.2** Among the following compounds the one that is polar and has the central atom with sp^2 hybridization is:
- (a) H_2CO_3 (b) SiF_4
(c) BF_3 (d) HClO_2 .
- Q.3** Which of the following hydrocarbons has the lowest dipole moment?
- (a) $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \\ \text{H} \end{array}$ (b) $\text{CH}_3 \equiv \text{CCH}_3$
(c) $\begin{array}{c} \text{H} \\ \diagdown \\ \text{CH}_3\text{CH}_2\text{C} \\ \diagup \\ \text{CH} \end{array} \equiv \text{CH}$ (d) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$.
- Q.4** CO_2 is isostructural with:
- (a) HgCl_2 (b) SnCl_2
(c) C_2H_2 (d) NO_2 .
- Q.5** Which one of the following arrangements of molecules is correct on the basis of their dipole moments?
- (a) $\text{BF}_3 > \text{NH}_3 > \text{NF}_3$ (b) $\text{BF}_3 > \text{NF}_3 > \text{NH}_3$
(c) $\text{NH}_3 > \text{BF}_3 > \text{NF}_3$ (d) $\text{NH}_3 > \text{NF}_3 > \text{BF}_3$.
- Q.6** Which of the following have undistorted octahedral structures?
1. SF_6 2. PF_6^- 3. SiF_6^{2-} 4. XeF_6 .
- Select the correct answer using the codes given below:
- (a) 2,3 and 4 (b) 1,3 and 4 (c) 1,2 and 3 (d) 1,2 and 4
-

