CHEMICAL BONDING Content

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4.1 Introduction:

Molecules and chemical bond

Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g.

$H_2, O_2, P_4, S_8, H_2O.$

A group of atoms existing together as one species and having characteristic properties is called a **molecule.**

Obviously, there must be some force which holds these atoms together within the molecules. This force which holds the atoms together within a molecule is called a **chemical bond.**

Different theories have been put forward from time to time. These are:

Kossel-Lewis approach

- Valence Shell Electron Pair Repulsion (VSEPR) theory
- Valence Bond Theory
- Molecular Orbital Theory.

A number of attempts were made to explain the formation of chemical bonds in terms of electrons, but it was only in 1916 when **Kossel** and **Lewis** succeeded independently in giving a satisfactory explanation. Since their theory was based on the electronic concept of atom, so it is referred to as **Electronic Theory of Valency**

4.2 Electronic Theory Of Valency

The theory of valency explains chemical combination in terms of electrons. The theory was developed independently by **W. Kossel** and **G.N. Lewis** (1916) and extended by **Irving Langmuir (in 1919).**

The chemical behaviour of an atom is determined to a large extent by the number and arrangement of electrons in the outer orbitals of the atom. Only these electrons are involved in chemical combination and so these are called the valence electrons.

Completed Electron Octet Or Duplet

Group 0 of the periodic table contains the noble gases. With the exception of helium which has a $1s^2$ electron arrangement others have ns^2 configuration in the outer orbitals.

He **1s²**

Ne 1s² 2s²2p⁶

Ar 1s² 2s²2p⁶ **3s² 3p⁶**

Kr 1s² 2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶

Xe 1s² 2s²2p⁶3s²3p⁶3d¹⁰4s²4p⁶4d¹⁰5s²5p⁶

Since the atoms of the noble gases were not known to form chemical bonds, it was argued that the presence of 8 electrons (an electron octet) in the valence shell makes the atom stable. Therefore all other atoms must undergo bonding by gaining or losing or sharing electrons so as to acquire the electronic configuration of the nearest inert gas. The presence of 8 electrons gives the number octet rule to this concept. In the case of the first few elements such as hydrogen, lithium and beryllium and atoms combine in such a way to attain the stable structure of helium with 2 electrons (duplet) in its only one valence shell. There are, however, many exceptions to the octet rule. Also compounds of noble gases, especially xenon, have been synthesized. The various types of chemical bonds are discussed below.

4.3 Ionic Bond

The transfer of electrons results in the formation of the ionic bond.

[Ne]3s¹ [Ne]3s²3p⁵ [Ne] [Ar]

4.3.1. Conditions For The Formation Of Ionic Bond

- (1) The difference between the electronegativity of two combining atoms must be greater than two.
- (2) Low ionization energy of the metal: Low ionization energy means that the metal atom requires only a small amount of energy to release its valence electron. For example, sodium, which has a low I.E. readily gives up its loosely held electron and forms Na⁺ ion. Metals of s-block have low ionization energies and so readily form the corresponding cations.
- (3) High electron affinity of the non-metal: An atom with a high electron affinity releases a lot of energy when it takes up an electron and forms an anion. For example, chlorine which has a high electron affinity readily takes up an electron from the Na atom and forms Cl⁻ ion. Non-metals of groups VI A and VII A have high electron affinity and can form ionic bonds.
- (4) High lattice energy of the crystal: In the formation of sodium chloride crystal, the Na⁺ ion attracts the Cl⁻ ion to form an ion-pair Na⁺Cl⁻. Since the electrostatic force of attraction is present in all directions, this ion-pair will attract other ion-pairs and build up into a crystal lattice. A crystal lattice is three dimensional basic pattern of points, in which each point corresponds to unit of the crystal, say an ion (atom or molecule). As the lattice builds up, energy is released. The energy released when sufficient number of cations and anions come together to form 1 mole of the compound is called the lattice energy of the compound.

Therefore, an ionic compound is formed when the energy released in (3) and (4) exceeds the energy absorbed in (2).

The formation of O²⁻ ion is accompanied by considerable absorption of energy. O(g) + 2e⁻ \rightarrow O²⁻; $\Delta H = + 844$ kJ Still MgO is readily formed. Explain.

Examples:

• **Formation of sodium chloride.** Sodium (atomic number = 11) has electronic configuration 2,8,1. By losing one electron of its outermost shell, it acquires the inert gas configuration of neon and changes into ion.

Na
$$\rightarrow$$
 Na⁺ + e⁻ (cation formation)

$$(1s^2, 2s^2, 2p^6, 3s^1)$$
 $(1s^2, 2s^2, 2p^6)$

On the other hand, chlorine (atomic number = 17) having electronic configuration 2,8,7 accepts one electron released by sodium to complete its octet by attaining stable configuration of argon. In this process, chlorine is converted into chloride ion.

$$Cl + e^- \rightarrow Cl^-$$
 (anion formation)

 $(1s^2, 2s^2, 2p^6, 3s^2 3p^5)$ $(1s^2, 2s^2, 2p^6, 3s^2 3p^6)$

Now, we have two species, one is positively charged sodium ion and the other is negatively charged chloride ion. As they approach each other, they are held together by strong electrostatic forces of attraction. Thus, formation of sodium chloride takes place.

 $Na^+ + Cl^- \rightarrow NaCl$ (molecule formation)

The above steps may be represented directly as follows:

The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

Coordination number of an ion may be defined as the number of oppositely charged ions present as the nearest neighbours around that ion in an ionic crystal.

4.3.2 Factors Governing the Formation of Ionic Bonds

The formation of ionic bond involve

- The formation of a positive ion by loss of electrons from one kind of atoms.
- The formation of a negative ion by gain of electrons from another kind of atoms.
- Holding the positive and negative ions by electrostatic forces of attraction.

The formation of ionic bond depends upon the following factors:

(i) Ionisation Enthalpy (Ionization Energy).

Ionisation enthalpy of any element is the amount of energy required to remove an electron from the outermost shell of an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.

It is clear that lesser the ionization enthalpy, easier will be the removal of an electron, i.e., formation of a positive ion and hence greater the chances of formation of an ionic bond, Ionisation enthalpy (I.E.) of alkali metals (i.e., group I elements) is low, hence they have more tendency to form positive ions in case of sodium, the I.E., is 495 kJ/mole while in case of magnesium, it is 743 kJ/mole. So the formation of positive ion of sodium is easier than that of magnesium.

Na (g)
$$\xrightarrow{495 \text{ kJ mol}^{-1}}$$
 Na⁺ (g) + e^{-1}
Mg(g) $\xrightarrow{743 \text{ kJ mol}^{-1}}$ Mg⁺ (g) + e^{-1}

The energy required for the removal of second electron from Mg^+ ion (second ionization enthalpy) is very high (because after the removal of the first electron, the effective nuclear charge increases. It may thus be concluded that lower the values of ionisation enthalpies, greater the chances of ionic bond formation.

(ii) Electron Gain Enthalpy (Electron Affinity)

Electron affinity or Electron gain enthalpy of an element is the enthalpy change that takes place when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stabler will be negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced.

Cl (g) +
$$e^- \rightarrow$$
 Cl⁻ + 348 kJ/mol
or E.A. = + 348 kJ mol⁻¹

Hence, the halogens can form negative ions easily on the other hand, elements of group 16, form divalent negative ions; this is because the second electron affinity in case of these elements is negative

O (g) +
$$e^-$$
 → O⁻ (g),
EA₁ = +142 kJ mol⁻¹
O (g) + e^- → O⁻ (g),
EA₂ = -693 kJ mol⁻¹

It may be concluded from the above discussion that ionic bonds are generally formed between the atoms of the elements placed on the left and on the right side of the periodic table.

(iii) Lattice Enthalpy Energy. In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$$A^+(g) + B^-(g) \rightarrow A^+B^-(s)$$

The energy released when the requisite number of gaseous positive and negative ions combines to form one mole of the ionic compound is called lattice enthalpy.

The higher the value of lattice enthalpy of the resulting ionic compound, the greater will be the stability of the compound and hence greater will be the ease of its formation.

The value of lattice enthalpy depends upon the following two factors:

- (iv) Charge on the ions
- (v) Size of the ions

4.3.3. General Characteristics Of Ionic Compounds

- (i) Generally ionic compounds are hard solids. As single ions of a metal are not associated in the solid with single ions of a non-metal, separate units of ionic compounds do not exist. (Thus in NaCl crystal each Na⁺ ion is surrounded by 6Cl⁻ ions and vice versa (in an octahedral arrangement). The attraction between Na⁺ and Cl⁻ ions is quite large.
- (ii) As a good deal of thermal energy is required to overcome the large electrostatic forces of attraction in an ionic crystal, ionic compounds have high melting and boiling points.
- (iii) Ionic compounds are commonly soluble in water and other polar solvents (which separate the ions). They are practically insoluble in organic solvents such as benzene, carbon tetrachloride, etc., as there is no attraction between ions and the molecules of the non-polar liquids.
- (iv) Ionic compounds are electrolytes. In the presence of an ionizing solvent such as water, the electrostatic forces between the ions are so greatly reduced that the ions get separated. The free ions in solution conduct electricity and on passing a current, the ionic compound undergoes chemical decomposition (called electrolysis). When an ionic compound is melted, the crystal lattice structure is broken and free ions are produced. It is the free movement of ions, which makes an ionic compound a conductor and to undergo electrolysis in the molten condition.
- (v) When an ionic compound dissolves in water, the ions get solvated (in this case hydrated). The energy requested is called salvation energy. This energy counters wholly or in part the high lattice energy of the ionic compound. Insoluble ionic compounds (eg., sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and the salvation energy of the constituent ions is insufficient to counteract the high lattice energies and make them soluble.
- (vi) The chemical properties of an ionic compound are the properties of its constituent ions. Thus all chlorides give the characteristic reactions of the chloride ion (reaction with conc. H₂SO₄, AgNO₃ solution, etc). All acids, which contain H⁺ ions give the same reactions (change blue litmus to red, effervesce with a carbonate, etc).

(vii) Reactions between solution of ionic compounds are almost instantaneous, because they are reactions between ions (and do not involve the breaking up of bonds as in covalent compounds, q.v.). For example, when silver nitrate solution is added to sodium chloride solution, silver chloride is immediately precipitated. The reaction may be represented thus:

 $Na^{+} + Cl^{-} + Ag^{+}NO_{3}^{-} \rightarrow AgCl + Na^{+} + NO_{3}^{-}$

4.4 Covalent Bond

A covalent bond is formed by the sharing of a pair of electrons between two atoms, each atom contributing one electron to the shared pair. The shared pair of electrons should have opposite spins and they are localized between the two nuclei concerned.

Note that the covalent bond consists of a pair of electrons shared between two atoms, and occupying a combination of two stable orbitals, one of each atom; the shared electrons of each covalent bond are counted for each of the two atoms connected by the covalent bond.

Langmuir, in 1919 improved the Lewis concept by suggesting that when both the atoms taking part in a chemical combination is short of electrons than the nearest noble gas configuration.

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called **covalent bond** or covalent linkage and the number of electrons contributed by each atom is known as **covalency**.

- **I.** The number of electrons needed by an atom to acquire its octet (C-4, N-3, O-2, Cl-1) is equal to the number of covalent bonds commonly formed.
- II. When two pairs of electrons are shared between two atoms, there is a double bond as in ethylene, C_2H_4



III. When three pairs of electrons are shared between two atoms, there is a triple bond as in acetylene, C₂H₂.

$$H \cdot \cdot C \stackrel{:}{:} C \cdot \cdot H$$
 or $H - C \equiv C - H$

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

An example is phosphorus pentachloride PCI₅. In this molecule phosphorus atom is surrounded by 5 chlorine atoms, with each of which it forms a covalent bond (with some ionic character, about which we shall learn later). In this compound the phosphorus atom seems to use 5 of the nine orbitals of the M shell (rather than only 4 of the most stable orbitals). It seems likely that of the nine or more orbitals in the M, N and O shells, four are especially stable, but one or more others may be occasionally utilized.



Examples to illustrate the formation of covalent bond. Let us examine the formation of chlorine molecule. in this case, two chlorine atoms combine to produce chlorine molecule. Each chlorine atom is short of one electron to attain stable

configuration of argon. Each of them contributes one electron to form a common shared pair. By doing so, both them complete their orbits and acquire argon structure. The completed octets are generally represented by enclosing the dots around the symbol by a circle or elipse. Thus,

$$\begin{array}{c} \vdots \vdots \vdots & + \cdot \vdots \vdots \\ 2,8,7 & 2,8,7 \end{array} \longrightarrow \begin{array}{c} \vdots \vdots \vdots \vdots \vdots \\ \text{shared pair} \end{array} \text{ or Cl-Cl}$$

Multiple covalent bonds. In the example cited above, each atom contributes one electron. Hence, the covalency of chlorine and hydrogen is

- The bond formed is called single covalent bond and is represented by single line

 (-) between two atoms. Covalent bond may also be formed by the contribution
 of two or three electrons by each of two atoms. The bond then formed is called
 double or triple bond and are represented by a double line (=) and a triple line
 (=) respectively.
- Formation of Oxygen molecule

$$: \overrightarrow{O}: + : \overrightarrow{O}: \longrightarrow : \overrightarrow{O}:: \overrightarrow{O}: \overrightarrow{O}:$$

• Formation of Nitrogen molecule

$$:N: +:N: \longrightarrow (N:N: or:N \equiv N:$$

Bond Pairs and Lone Pairs: The shared pairs of electrons present between the atoms are called bond pairs. On the other hand, the valence electrons not involved in bonding (i.e., sharing) are shown as such and are called **non-bonding electrons** *or* **lone pairs** *or* **unshared pairs**.

4.4.1. Formal Charge (F.C.) on an atom in a molecule/ion:

The formal charge on an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in the free state and the number of electrons assigned to that atom in the Lewis structure, assuming that in each shared pair of electrons,

The atom has one electron of its own and the lone pair on it belongs to it completely. Thus it

Can be calculated as follows:



i.e., FC = A - L +
$$\frac{1}{2}$$
 S

Example: Calculate formal charge on each O-atom of O_3 molecule.

Solution: Lewis structure of O_3 is as follows:

$$:0^{1}$$

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

Formal charge on central O-atom numbered 2

$$= 6 - 2 - \frac{1}{2}(6) = +1$$

Formal charge on end O-atom numbered 3

$$= 6 - 6 - \frac{1}{2} (2) = -1$$

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

4.4.2 General Characteristics Of Covalent Compounds

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

4.4.3 Types of Covalent Bonds-Sigma and Pi Bonds

Depending upon the type of overlapping, the covalent bonds are mainly of two types:

4.4.3.1 Sigma (σ) bond: When a bond is formed between two atoms by the overlap of their atomic orbitals along the internuclear axis (end to end or head on overlap), the bond formed is called sigma (σ) bond.

The overlapping along the internuclear axis can take place in any one of the following ways:

(i) **s-s overlapping:** This type of overlapping takes place between atoms having halffilled s-orbitals in their outermost energy shell. For example, in the formation of hydrogen molecule, 1s orbital of one hydrogen atom overlaps with 1s orbital of other hydrogen atom thus forming a sigma bond.

- (ii) **s-p overlapping:** In this case, half-filled s-orbital of one atom overlaps with the half-filled p-orbital of another atom. A simple example of this type is the formation of hydrogen fluoride. Here, 1s orbital of hydrogen overlaps with 2p_z orbital of fluorine.
- (iii) **p-p overlapping:** The type of overlapping occurs when p-orbital of one atom overlaps with the p-orbital of the other as in case fluorine molecule. The electronic configuration of fluorine is $1s^2 2s^2 2p^2_s 2p^2_y 2p^1_z$ (i.e., it has a half-filled $2p_z$ orbital). The molecule of fluorine is produced by the overlapping of $2p_z$ orbitals of the two fluorine atoms
- **Note:** If Z-axis is chosen as the internuclear axis, no overlapping can take place between s and P_s or P_y orbital, or p_s and p_y , orbitals, i.e., there is zero overlap.

4.4.3.2 Pi (π) **Bond:** Pi-bond is formed by lateral (sideways) overlapping of p-orbitals, i.e., by overlapping of p-orbitals in a direction at right angles to the internuclear axis.

A $\pi\text{-bond}$ is seldom formed between atoms unless accompanied by a $\sigma\text{-bond}.$ For example,

In case of oxygen molecule (each oxygen atom having electronic configuration, $1s^2 2s^2 2p^2_s 2p^1_y 2p^1_z$), the two atoms are held together by one σ -bond and one π -bond.

Strength of σ **and** π **bonds.** The strength of a bond depends upon the extent of overlapping. Since in the formation of σ -bond, overlapping is along the internuclear axis, therefore there is considerable overlapping. Hence, the σ -bond is a strong bond. On the other hand, in case of the formation of a π -bond, side-way overlapping takes place which is only to a small extent. Hence, π -bond is a weak bond.

Further, as p-orbitals undergo greater overlapping than s-orbitals, the expected order of the strength of sigma bonds is:

p - p > p - s > s - s

Symmetry of σ and π electron clouds. Another important aspect about the σ and π - bonds is that whereas in case of σ -bond, the electron cloud is symmetrical about the internuclear axis, in case of π -bond, it is unsymmetrical.

Comparison of Sigma and Pi Bonds, Some important points of difference between sigma and pi bond are listed in Table

Table: Comparison	of sigma and pi bonds
Sigma (σ) Bond	Pi (π) Bond
 (i) This bond is formed by overlap of orbitals along their internuclear axis (end to end overlap). 	(i) This is formed by sideway overlapping of orbitals (lateral overlapping)
(ii) This is formed by overlapping between s-s, s-p or p-p orbitals.	(ii) This is formed by the overlap of p-p orbitals only.
(iii) Overlapping is quite large and hence sigma bond is a strong bond.	(iii) Overlapping is to a small extent. Hence, π -bond is a weak bond.
(iv) Electron cloud in this case is symmetrical about the line joining the two nuclei.	(iv) Electron cloud of π -bond is unsymmetrical.
(v) Sigma bond consists of only one electron cloud, symmetrical about the internuclear axis.	(v) Pi (π) bond consists of two electron clouds, one above the plane of atomic nuclei and the other below it.
(vi) Free rotation about a σ-bond is possible.	(vi) Free rotation about a π -bond is not possible because on rotation, overlapping vanishes and so the bond breaks.

4.4.4 Some Important Bond Characteristics

(1)Bond Length: The equilibrium distance between the centers of the nuclei of the two bonded atoms is called its bond length.

Factors affecting bond length:

- (i) Size of the atoms
- (ii) Multiplicity of bond
- (iii) Type of hybridization
- (2)Bond Enthalpy (Bond Energy): The amount of energy required to break one mole of bonds of a particular type so as to separate them into gaseous atoms is called bond dissociation enthalpy or simply bond enthalpy.

Factors affecting bond enthalpy:

- (i) Size of the atoms
- (ii) Multiplicity of bond
- (iii)Number of lone pair of electrons present.
- (3)Bond Angle: The angle between the lines representing the directions of the bonds, i.e., the orbitals containing the bonding electrons is called the bond angle.

A covalent bond is a space-directed bond and it may exhibit isomerism.

4.5 Polar Covalent Bonds – Electronegativity

The shared pair of electrons may be shared equally between two atoms; then the covalent bond is said to be non-polar. Equal sharing occurs between identical atoms, as in H – H or Cl – Cl (i.e., in homonuclear molecules) or between identical atoms with identical neighbours as in H_3C-CH_3 . When the two bonded atoms are dissimilar (i.e., in heteronuclear molecules) the sharing is unequal. For example a chlorine atom has a greater electron attracting power than a hydrogen atom; so in H – Cl, the shared pair of electrons are drawn more towards chlorine and away from hydrogen. The result is separation of charges within the molecule, the chlorine end acquiring a slight negative charge and the hydrogen end a slight but equal positive charge:

Such covalent bonds are said to be polar (i.e., bonds formed by sharing a pair of electrons between two atoms but displaced towards the nucleus of one of the bonded atoms).

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

Table of	⁵ Electronegativities	(Pauling)
----------	----------------------------------	-----------

Н							
2.1							
Li	Be	В	С	Ν	0	F	
1.0	1.5	2.0	2.5	3.0	3.5	4.0	
Na	Mg	Al	Si	Р	S	Cl	
0.9	1.2	1.5	1.8	2.1	2.5	3.0	
K	Ca			As	Se	Br	
0.8	1.0			2.0	2.4	2.5	
Rb	Sr			Sb	Те	I	
0.8	1.0			1.9	2.1	2.5	

To assess the tendency of an atom of a given element to attract electrons towards itself in a covalent bond, relative electronegativity values are used. Table gives the relative

electronegativity values of atoms calculated by Pauling (adopting arbitrarily the value of 4 units for the electronegativity of fluorine).

- (i) Electronegativity values increases across a period and decrease down a group.
- (ii) Smaller atoms have greater electronegativity than larger ones and so they attract electrons more towards them than larger ones. Alkali metals have low electronegativities and halogens high electronegativities.
- (iii) Atoms with nearly filled shells of electrons (e.g., halogens) have greater electronegativity than those with sparsely occupied shells.
- (iv) Elements with low electronegativity values such as Cs (0.8) and Rb (0.8) tend to form positive ions, i.e., these are metals. Elements with high electronegativity values such as F (4.0) and O(3.5) tend to form negative ions, i.e., these are non-metals.
- (v) Electronegativity value may be used to make rough predictions of the type of bonding to be found in a compound. The larger the difference between electrongativity values of two combining atoms, the more polar the covalent bond. If the difference is greater than 2, the greater the chance for ionic bonding (i.e., the chance 'of covalent bond assuming 100% ionic character) From this point of view ionic bond may be considered to be an extreme case of a polar bond (with total separation of charges.)

If the difference between the electronegativities of the combining atoms is to be an extreme case of polar bond (with total separation of charges).

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

C—H	N — H	О—Н	F-H
4%	19%	39%	60%
C-F	C-CI	C—Br	C-1
43%	11%	3%	0%

 Table : % Ionic Character of Bonds

Example: Calculate the electronegativity of chlorine from the bond energy of Cl-F bond (61 kcal mol⁻¹), F-F bond (38 kcal mol⁻¹) and Cl-Cl bond (58 kcal mol⁻¹) and electronegativity of fluorine 4.0 eV.

Plane based on Pauling's scale:

 $(EN)_F - (EN)_{Cl} = k\sqrt{\Delta} = 0.208 \sqrt{\Delta}$

Where Δ is resonance energy and k is the conversion factor (Which is 0.208 of reconverting kcal into eV).

Solution:
$$\Delta = (BE)_{Cl-F} - \sqrt{(BE)_{Cl-Cl}(BE)_{F-F}}$$

 $= 61 - \sqrt{58 \times 38}$ = 61-46.95 = 14.05 kcal $(EN)_{Cl} = (EN)_F - 0.208\sqrt{\Delta}$ = 4.0 - 0.208 $\sqrt{14.05}$ = 4.0 - 0.78 = 3.22 eV

4.6 Dipole Moments

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



If the charge is in SI units (Coulombs) and d in metre, μ will be coulomb-metre (C.m) units.

1D = 3.336×10⁻³⁰ C.m.

Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compounds containing such bonds will have dipole moments, for the polatity of the molecule as a whole is the vector sum of the individual bond moments. For example, CO_2 has zero dipole moment, although the C = O bond is a polar bond. This shows that CO_2 is linear molecule, O = C = O, so that the dipole moments of the two C = O bonds cancel out. The $C \rightarrow CI$ bond has a definite polarity and a definite dipole moment but carbon tertrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4C – CI bond moments is zero. On the contrary CH_3CI , CH_2CI_2 and $CHCI_3$ have definite dipole moments.

(B) Organic substances

(i) Methane and CCl₄ have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.



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



Benzene

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

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



(i) Dipole moment in aromatic ring system

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



In those cases where X = Y, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) are electron pushing and the other (NO₂) is electron withdrawing while in aminophenol, both the groups (OH and NH₂) attached is electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment. Then calculation of dipole moment follows as:

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

Let the bond dipole of C-X bond is represented by μ_1 and that of C-Y bond by μ_2 . Now let us assume that the electron pushing groups have +ve bond moment and the electron withdrawing groups have -ve bond moment. The net dipole moment is the resultant of two bond dipoles at different orientations.

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

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

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

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

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

$$\therefore \quad \mu_p = \mu_1 - \mu_2$$

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

Case (ii): When X is electron pushing and Y is electron withdrawing or vice versa. Let the bond moment of C-X dipole is μ_1 and that of C-Y dipole is μ_2 .

$$\begin{split} \mu_0 &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)cos60^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - 3\mu_1\mu_2} \\ \mu_{meta} &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)cos120^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - \mu_1\mu_2} \\ \mu_{para} &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)cos180^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} \end{split}$$

 $= \mu_1 + \mu_2$

Looking at the expressions of $\mu_0 = \mu_{m_r}$ and $\mu_{p'}$ it is clear that the para isomer has the highest dipole moment and ortho has the least.

4.6.1 Dipole Moment And Percentage Ionic Character

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

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

 $1D = 1 \times 10^{-18}$ e.s.u-cm.

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

Example: Calculate the percent ionic character of HCl. Given that the observed dipole moment is 1.03 D and bond length of HCl is 1.275 Å.

Solution: If HCl were 100% ionic, each end would carry charge equal to one unit, viz,

4.8 x 10^{-10} esu. As bond length of HCl is 1.275 Å, its dipole moment for 100% ionic character would be

^µionic = q x d = 4.8 x 10⁻¹⁰ esu
x 1.275 x 10⁻⁸ cm
^µobserved = 1.03 D (given)
∴ % *ioniccharacter* =
$$\frac{\mu_{observed}}{\mu_{ionic}}$$
 ×100
= $\frac{1.03}{6.12}$ ×100 = 16.83%

4.6.2 Transition From Ionic To Covalent Bond – Fajans' Rule

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

certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



4.6.3 Factors Influencing Ion – Deformation Or Increasing Covalent Character

(i) Large charge on the ions:

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al³⁺ can distort Cl⁻ ion more than Na⁺ ion. So aluminium chloride is a covalent compound whereas NaCl, AlF₃, AgF are ionic.

(ii)Small cation and large anion:

For a small cation, the electrostatic force with which its nucleus will attract the anion will be large. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalence with a small cation and a large anion, as in AgI.

(iii) Cation with a non-inert gas type of electronic configuration:

A cation with a 18 electron outermost shell such as Ag^+ ([Kr]4d¹⁰) polarizes anions more strongly than a cation with a 8 electron arrangement as in K⁺. The 'd' electrons in Ag⁺ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K⁺. Thus AgI is more covalent than KI, although Ag⁺ and K⁺ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors, which influence covalent character, are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

Example: Which of the compounds MgCO₃ and ZnCO₃ is thermally more stable?

Solution: Mg²⁺:[Ne]

Zn²⁺: [Ar]3d¹⁰

 Mg^{2+} has noble-gas electron configuration while Zn^{2+} has an 18-electron configuration of the valence-shell. Thus, polarizing power of Zn^{2+} on an anion is larger than a cation of the same size and charge. Thus, lattice energy of $ZnCO_3$ is greater than that of $MgCO_3$ and thus, $ZnCO_3$ is thermally more stable.

4.7 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 $H: \vec{F}:$ or $H \longrightarrow \vec{F}:$

Arrangement of dot symbols used to represent molecules is called Lewis structures. Lewis structures 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 structure is written by fitting the element dot symbols together to show shared electron pairs and to satisfy the octet rule. For example,

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: Ö—Н

- (ii) In ammonia (NH₃), three \dot{H} and one \dot{N} fit together and satisfy their duet and octet respectively as
- (iii)In carbon tetrachloride (CCl₄), four ici and one .c. complete their octet as

: Ċŀ-Ċ-Ċ!: : Ċŀ :

For the given molecules, we have adopted hit & trial method to fit the dot symbols together and satisfy the octet rule. But remember that hydrogen form one bond, oxygen forms two bonds, nitrogen three bonds and carbon forms four bonds. For simple molecules, the hit & trial method works perfectly but for slightly complicated polyatomic species, this may give us more than one possible structure. Thus, a systematic approach is needed to design the Lewis structures of such polyatomic species. But before proceeding further, let us understand the limitation of this approach.

4.7.1 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.

- (a) Molecules, which have contraction of octet. Such molecules are electron deficient. For example, BH₃, BrF₃, AlCl₃, GaCl₃ etc.
- (b) 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-orbitals, thus they can expand their octet. For example, PCI_5 , SF_6 etc.
- (c) 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, NO₂ and ClO₂.

4.8 Co-ordinate Covalent Bond Or Dative Bond

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

(i) Formation of ammonium ion

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

н	[н]		[4]	+
H : Ŋ : + H →	н: ё:н	or	H−Ņ→H	
Н	Lн		ĽμΊ	

Nitrogen atom is called the donor and H⁺, the acceptor. The arrow-head in N \rightarrow H shows that N-atom is electron donor and H-atom is electron acceptor. NH₃ is a neutral molecule. H⁺ carries a unit positive charge; so NH_4^+ ion carries a unit positive charge. Once the NH_4^+ ion is formed, all the N-H bonds become identical.

(i) Hydronium ion, H₃O⁺



(ii) Aluminium chloride, Al₂Cl₆



(iii) Nitromethane, CH₃NO₂

4.8.1 General Characteristics Of Coordinate Covalent Compounds

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

- (i) The nuclei in coordinate covalent compounds (such as in NH_4^+) are held firmly by shared electrons and so do not form ions in water.
- (ii) Their covalent nature makes them sparingly soluble in water and more soluble in organic solvents.
- (iii) The coordinate bond is also rigid and directional, Just like covalent bonds.

4.8.1.1 Resonance

Carbon dioxide may be represented by Lewis dot formula as

$$: 0 :: C :: 0 : or 0 = C = 0$$

The bond length of C=O is 1.22Å, but the actual measured value is 1.15Å. Further CO₂ is quite stable and does not show the characteristic reactions of the carbonyl group, as shown by aldehydes and ketones. Without shifting, the relative positions of atoms of CO₂ can be represented by two more Lewis formulae:

In (ii) and (iii), the two bonds between C and O are different, one being a triple bond and the other a single bond. Both the C-O bonds in CO_2 are identical. It is now obvious that none of these structures actually represents CO_2 . To explain this difficulty the concept of resonance was introduced, according to which CO_2 cannot be accurately depicted by any Lewis formula. The actual structure of CO_2 is a resonance hybrid of the three structures:

$$0 = C = 0 \longleftrightarrow 0 \Longrightarrow C \rightarrow 0 \longleftrightarrow 0 \longleftrightarrow C \rightleftarrows 0$$

These different structures are called the canonical or contributing structures. The actual structure of CO_2 is different from the canonical structures although it is closely related to them, the actual structure cannot be represented on paper using the symbols. All the molecules of CO_2 have the same structure. Usually, a double-headed arrow \leftrightarrow is used between the canonical structures.

Example: Draw two resonance structures for diazomethane (CH_2N_2). Show formal charges. **Solution:** The skeletal structure of CH_2N_2 is,

Two resonance structures are:

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$$H - C = N = N^{-} \longleftrightarrow H - C = N \equiv N^{-}$$

Example: Draw three resonance structures for the molecule N₂O in which the atoms are arranged in the order NNO. Also indicate formal charges.

Solution: Resonance structures are shown below:

$$-\mathbf{N} = \mathbf{N} = \mathbf{O} \longleftrightarrow \mathbf{N} = \mathbf{N} - \mathbf{O} = \mathbf{O} \longleftrightarrow \mathbf{N} = \mathbf{O}$$

Note: Calculation of bond order for molecules showing resonance. In case of molecules or ions having resonance, the bonds order changes and is calculated as follows:

Bond order = $\frac{\text{Total no. of bonds between two atoms in all the structures}}{\text{Total no. of bonds between two atoms in all the structures}}$

Total no.of resonating structures

(Any two bonded atoms may be selected and a double bond will mean 2 bonds and a triple bond will mean 3 bonds)



4.9 Valence shell electron pair repulsion (VSEPR) theory:-

Valence shell electron pair repulsion (VSEPR) theory (1957) is a model in chemistry, which is used for predicting the shapes of individual molecules, based upon their extent of electron-pair electrostatic repulsion, determined using steric numbers. The theory is also called the **Gillespie-Nyholm theory** after the two main developers. The premise of VSEPR is that a constructed Lewis structure is expanded to show all lone pairs of electrons alongside protruding and projecting bonds, for predicting the geometric shape and lone-pair behaviour of a compound through consideration of the total coordination number.

VSEPR theory is based on the idea that the geometry of a molecule or polyatomic ion is determined primarily by repulsion among the pairs of electrons associated with a central atom. The pairs of electrons may be bonding or nonbonding (also called lone pairs). Only valence electrons of the central atom influence the molecular shape in a meaningful way.

Basic assumptions

- 1. Pairs of electrons in the valence shell of a central atom repel each other.
- 2. These pairs of electrons tend to occupy positions in space that minimize repulsions and maximize the distance of separation between them.
- 3. The valence shell is taken as a sphere with electron pairs localizing on the spherical surface at maximum distance from one another.
- 4. 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.
- 5. Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.

Three types of repulsion take place between the electrons of a molecule:

• The lone pair-lone pair repulsion

- The lone pair-bonding pair repulsion
- The bonding pair-bonding pair repulsion.

A molecule must avoid these repulsions to remain stable. When repulsion cannot be avoided, the *weaker repulsion* (i.e. the one that causes the smallest deviation from the ideal shape) is preferred.

The lone pair-lone pair (lp-lp) repulsion is considered to be stronger than the lone pairbonding pair (lp-bp) repulsion, which in turn is stronger than the bonding pair-bonding pair (bp-bp) repulsion. Hence, the weaker bp-bp repulsion is preferred over the lp-lp or lp-bp repulsion.

VSEPR theory is usually compared (but not part of) and contrasted with valence bond theory, which addresses molecular shape through orbitals that are energetically accessible for bonding. Valence bond theory concerns itself with the formation of sigma and pi bonds. Molecular orbital theory is another model for understanding how atoms and electrons are assembled into molecules and polyatomic ions.

VSEPR theory has long been criticized for not being quantitative, and therefore limited to the generation of "crude", even though structurally accurate, molecular geometries of covalent molecules. However, molecular mechanics force fields based on VSEPR have also been developed.

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

(a) Molecules having general formula AB₂

BeCl₂ is representing the general formula AB₂. The Lewis structure of beryllium chloride in the gaseous state is



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

(b) Molecules having general formula AB₃

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



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

(c) Molecules having general formula AB4

Methane (CH₄) represents the best example of this class of molecules. The Lewis structure of CH₄ is



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

In a tetrahedral molecule, the central atom (carbon) is located at the centre of the tetrahedron and the other four atoms (H) are at the corners. The HCH bond angles are all 109°28'.



(d)Molecules with general formula AB₅

The general formula AB_5 is represented by the molecule PCI_5 . The Lewis structure of PCI_5 (in gas phase) is



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

The central atom (P) is at the centre of the common triangular with the surrounding atoms positioned at the five corners of the trigonal bipyramid. The atoms that are above and below the triangular plane are said to occupy axial positions and those, which are in the triangular plane, are said to occupy equatorial positions. The angle between any two equatorial bonds is 120°, that between an axial bond and an equatorial bond is 19° and that between two axial bonds is 180°.



(e) Molecules having general formula AB_{6.}

The molecule SF₆ exhibits the general formula AB₆. The Lewis structure of SF₆ is



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



4.9.1 Molecules In Which The Central Atom Has One Or More Lone Pairs

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

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

To keep track of total number of bonding pairs and lone pairs, we designate molecules with lone pairs and bonding pairs.

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

(a) Molecules with general formula AB₂E

Example of this is SO₂. The Lewis structure of SO₂ is $\dot{O} = \overset{\circ}{S} - \dot{O} \overset{\circ}{S}$

VSEPR theory treats double bond and triple bonds as though they were single bonds. Thus, SO₂ molecule can be viewed as having three electron pairs on the central atoms, of which, two are bonding pairs and one is a lone pair. The overall arrangement of three electron pairs is trigonal planar. But since one of the electron pair is a lone pair, the SO₂ molecule looks like



This shape is referred as bent or angular. The shape is determined only by the bonding pairs and not by lone pairs. Since lone pair repel the bonding pairs more strongly, the SO bonds are pushed together slightly the OSO angle is less than 120°

(b) Molecules having general formula AB₃E

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



(c) Molecules with general formula AB₂E₂ Example of such a molecule is H₂O.A water molecules has 2 bonding pairs and

two lone pairs . $H - \ddot{O} - H$

The overall arrangement of the four electron pairs in water is tetrahedral. However, unlike NH_3 , H_2O has 2 lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each

other and H_2O shows even greater deviation from tetrahedral angle than in NH_3 . The shape of H_2O is referred as bent or angular with HOH bond angle of 104.5°.



(D) Molecules having general formula AB₄E Example to this class of molecule is SF₄. The Lewis structure of SF₄ is

The S atom in SF₄ has 5 electron pairs, which can be arranged as trigonal bipyramidal. In SF₄ since one of the electron pair is a lone pair, so the molecule can have any one of the following geometries:



In (a), the lone pair occupies an equatorial position and in (b), it occupies an axial position. Repulsion between the electron pairs in bonds only 90° apart are greater than repulsion between electron pairs in bond 120° apart. Each axial bond has three electron pairs 90° away while each equatorial bond has only two electron pairs 90° away. Thus axial bonds (electron pairs) experience greater repulsion than the equatorial bonds. Thus, atoms at the equatorial positions are closer to the central atom than atoms at the axial positions i.e. equatorial bond lengths are smaller than axial bond length. Thus, when the central atom also has lone pairs alone with the bonding pairs, it will occupy a position where the repulsions are less, so lone pairs in trigonal bipyramidal are more comfortable at equatorial positions. Thus, (a) is the appropriate structure of SF₄. It is referred as see-saw shaped or irregular tetrahedron.

(E) Molecules with general formula AB₃F₂

Example of this type is CIF₃. The Lewis structure of CIF₃ is



The Cl atom in CIF_3 has 5 electron pairs, of which 2 are lone and 3 are bonding pairs. The molecule can have any of the following three geometries:



In structure (a), there are 6 lone pair-bond pair repulsions at 90° and one lone pair – lone pair repulsion at 180°. In structure (b), 1 lone pair – lone pair repulsion is at 90° and there are 3 lone pair-bond repulsions at 90°, 2 at 120° and 1 at 180°. While in structure (c), there are 4 lone pair-bond pair repulsions at 90°, 2 at 120° and one lone pair-lone pair repulsion at 120°. The structure (b) is tightly rules out since the lone pair-lone pair repulsion is of highest magnitude. Among structures (a) and (c),

each structure has 4 lone pair-bond pair repulsions at 90°. Apart from these repulsions, (a) has 1 lone pair-lone pair repulsion at 180° and 2 lone pair-bond pair repulsions at 90° while (c) has 1 lone pair-lone pair repulsion at 120° and 2 lone pair-bond pair repulsions also at 120°. So, the structure (c) has overall lesser repulsions than (a). Thus, (c) has the appropriate structure of CIF₃. It is called T-shaped structure.

4.9.2 Prediciting Geometry Of Species Using VSERP Theory

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

- i. Identify the central atom and count the number of valence electrons on the central atom.
- **ii.** Add to this, the number of other atoms (which from single bonds only). Here, oxygen atoms are not added as they form two bonds.
- **iii.** If the species is an anion, add negative charges and if it is a cation, subtract positive charges.
- **iv.** This gives us a number, which we refer as N.
- **v.** Divide N by 2 and we get the sum of bonding and non-bonding electron pairs. $\frac{N}{2}$ = Number of other atoms + number of lone pairs.
- **vi.** Compare the result $(\frac{N}{2} value)$ with the value given in table, corresponding to the given number of lone pairs.

N/2 Value	No. of lone pairs	Shape of the species	Example
2	0	Linear	HgCl ₂ , BeCl ₂
2	0	Trigonal planar	BF ₃ , AICI ₃ , BH ₃ , <i>NO</i> ₂ ⁻ , SO ₃
5	1	Angular or bent	SnCl ₂ , SO ₂ , <i>NO</i> ₂ ,
0		Tetrahedral	CCl ₄ , BeF ₄ ²⁻ , BF ₄ ⁻ , NO ₂ ⁻ , PCl ₄ ⁺ , ClO ₄ ⁻
4	1	Trigonal pyramidal	NH ₃ , PCI ₃ , PF ₃ , <i>ClO</i> ₃ ⁻
	2	Angular or bent	H ₂ O, H ₂ S, OF ₂ , ClO ₂ ⁻
3		Linear	CIO-
	0	Trigonal bipyramidal	PCI ₅ , PF ₅
5 1		See-saw or irregular tetrahedron	SF4, <i>IF</i> ₄ ⁺
	2	T-shaped	CIF ₃ ,BrF ₃
3		Linear	I ₃ , Br ₃ , XeF ₂
0		Octahedral or square bipyramidal	SF ₆ , <i>PCl</i> ₆
Ö	1	Square pyramidal	BrF ₅ , IF ₅
	2	Square planer	ICl ₄ , XeF ₄ , IF ₄
7	0	Pentagonal bipyramidal	IF ₇

In addition to all this, VSEPR theory can also used to determine the geometry of other covalently bonded molecules and their bond angles. In order to predict these, following generalizations would be helpful.

1. Repulsions exerted by bond pair's decrease as the electronegativity of the bonded atom increases. For example,

 $OH_2 (104.5^\circ) > OF_2 (103.2^\circ)$ $NH_3 (107.3^\circ) > NF_2 (102^\circ)$ $PI_3 (102^\circ) > PBr_3 (101.5^\circ) > PCI_3 (100^\circ)$ $AsI_3 (101^\circ) > AsBr_3 (100.5^\circ) > AsCl_3 (98.4^\circ)$

- Repulsion between bonded electron pairs in filled shells is greater than those between electron pairs in incompleted shells. OH₂ (104.5°) >> SH₂ (92°) > SeH₂ (91°) > TeH₂ (89.5°) NH₃ (107.3°) >> PH₃ (93.3°) > AsH₃ (91.8°) ≥ SbH₃ (91.3°) N (CH₃)₃, 109°> P(CH₃)₃, 102.5° > As(CH₃)₃, 96°
- **3.** When in an atom the filled valence shell and one or more lone pairs is bonded to an atom with an incomplete valence shell, or a valence shell that can become complete by electron shifts, there is a tendency for the lone pairs to be partially transferred from the filled to the unfilled shell.

 PH_3 (93.3°) < PF_3 (104°)

AsH₃ (91.8°) < AsF₃ (102°)



 $Cl_2O(111^\circ) > H_2O(104.5^\circ) > F_2O(103.2^\circ)$



4. The size of a bonding electron pair decreases with increasing electronegativity of the ligand. Also, the two electron pairs of a double bond (or the three electron pairs of a triple bond) take up more room than does the one electron pair of a single bond. Using above facts one can rationalize size and the trends which are given below:

Molecule		An	gles
	XCX	XCO	XCC
F ₂ CO	108°	126°	-
Cl ₂ CO	111°	124°	-
(NH ₂) ₂ CO	118°	121°	-
F ₂ SO	93°	107°	-
$H_2C=CF_2$	110°	-	125°
OPF ₃	103°	-	-
OPCI ₃	104°	-	-
$H_2C=CCI_2$	114°	-	123°

AXE Method

The "AXE method" of electron counting is commonly used when applying the VSEPR theory. The *A* represents the central atom and always has an implied subscript one. The *X* represents how many sigma bonds are formed between the central atoms and outside atoms. Multiple covalent bonds (double, triple, etc) count as one X. The *E* represents the number of lone electron *pairs* present outside of the central atom. The sum of *X* and *E*, sometimes known as the steric number, is also associated with the total number of hybridised orbitals used by valence bond theory.

Steric No.	Basic Geometry 0 Ione pair	1 lone pair	2 lone pairs	3 lone pairs
1	A—X			
2	X—A—X	E—A—X		
3			E X E Trigonal planar	
4	X I X Tetrahedral	E A Manual A trigonal pyramid	E E A MARK	
5	$\begin{array}{c} X \\ \downarrow \\ X \\ \downarrow \\ X \\ \downarrow \\ X \\ X \\ \\ X \\$	E A A X X X X X X X X X X X X X	E A X X A Chemistry) E E E E	-×
6	$X X \text{ in the second secon$	$\begin{array}{c} & X \xrightarrow{\mu_{H}} \\ & X \xrightarrow{\mu_{H}} \\$	N X Y X	







When the substituent (X) atoms are not all the same, the geometry is still approximately valid, but the bond angles may be slightly different than the ones where all the outside atoms are the same. For example, the double-bond carbons in alkenes like C_2H_4 are AX_3E_0 , but the bond angles are not all exactly 120°. Similarly, SOCl₂ is AX_3E_1 , but because the X substituents are not identical, the XAX angles are not all equal.

Examples

The methane molecule (CH₄) is tetrahedral because there are four pairs of electrons. The four hydrogen atoms are positioned at the vertices of a tetrahedron, and the bond angle is $\cos^{-1}(-1/3) \approx 109^{\circ}28'$. This is referred to as an AX₄ type of molecule. As mentioned above, A represents the central atom and X represents all of the outer atoms.

The ammonia molecule (NH₃) has three pairs of electrons involved in bonding, but there is a lone pair of electrons on the nitrogen atom. It is not bonded with another atom; however, it influences the overall shape through repulsions. As in methane above, there are four regions of electron density. Therefore, the overall orientation of the regions of electron density is tetrahedral. On the other hand, there are only three outer atoms. This is referred to as an AX₃E type molecule because the lone pair is represented by an E. The overall shape of the molecule is a trigonal pyramid because the lone pair is not "visible." The shape of a molecule is found from the relationship of the atoms even though it can be influenced by lone pairs of electrons.

A steric number of seven is possible, but it occurs in uncommon compounds such as iodine heptafluoride. The base geometry for this is pentagonal bipyramidal.

Conclusion:

The above concept leads to the following results (called the basic assumptions of the VSEPR theory) which help to find the shape of a molecule:

- (1) The shape of a molecule containing only two atoms is always linear.
- (2) For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.
- (3) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar. As a result, the shape of the molecule is *symmetrical* and the molecule is said to have a *regular geometry*.
- (4) If the central atom are linked to different atoms or is surrounded by bond pairs as well lone pair of electrons, the repulsions between them are different. As a result, the molecule has an irregular or distorted geometry. The order of repulsions between electron pairs is as follows :

Lone pair – lone pair > lone pair-bond pair > bond pair-bond pair.

- (5) The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.
- (i) Total no. of electron pairs around the central atom

 $=\frac{1}{2}$ (No. of valence electrons of central atom + No. of atoms linked to central

atom by single bonds)

Example: On the basis of VSEPR theory, predict the shapes of the following:

(i) ClF_3 (ii) $H_3 O^+$

Solution: (i) Shape of ClF_3

No. of valence electrons of the central Cl atom = 7

No. of atoms linked to it by single bonds = 3

: Total no. of electron pairs around Cl

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

No. of bond pairs = No, of atoms linked to CI = 3

 \therefore No. of lone pairs = 5 - 3 = 2

Thus, the molecule is of the type $AB_3 L_2$

Hence, it is T-shaped.

(ii) Shape of $H_3 O^+$ ion

No. of valence electrons of central 'O' atom = 6 - 1 (due to one unit + ve charge) = 5No. of atoms linked to 'O' atom = 3

:. Total no. of electron pairs around 'O'

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

No. of bond pairs = 3

\therefore No of bonds pairs = 4 - 3 = 1

Thus, the ion is of the type AB_3L . Hence, its shape is trigonal pyramidal.

Example: The tri-iodide 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.

- **Solution:** F_3^- and I_3^- are of same group. I 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.
- **Example:** Predict whether the following molecules are iso-structural or not. Justify your answer.

(i) NMe₃ (ii) N(SiMe₃)₃

Solution: N(Me)₃ and N(SiMe₃)₃ are not isostructural because N(Me)₃ is trigonal pyramidal shape

 $N(SiMe_3)_3$ is trigonal planar because in it silicon uses its vacant d-orbital for back bonding with lone pair electrons of central N-atom, so it is trigonal planar in shape.

4.9.3 Limitations of VSEPR Theory and Advent of Valence Bond

No doubt, VSEPR theory is able to explain the shapes of simple molecule but is unable to predict the shape in a number of cases. Thus, it had a limited application only.

Lewis approach as well as VSEPR theory had a number of limitations.

To explain the above limitations, two important theories called **modern theories** of covalent bond formation have been put forward. These are based on quantum mechanical principles. These are:

- (1) Valence Bond (VB) Theory
- (2) Molecular Orbital (MO) Theory

4.10 Valence Bond Theory

The valence bond theory was put forward by **Heitler** and **London** in 1972 and was extended by **Pauling** and **Slater** in 1931. The theory can be summarized as:

- **1.** A covalent bond is formed when the orbital of one atom overlaps with the orbital of another atom, each of the orbital containing one unpaired electron.
- **2.** The two atomic orbital in such a case, merge to form a single bond orbital or a localized molecular orbital, which is occupied by both the electrons.
- **3.** The two electrons occupying the bond orbital must have opposite spins.
- 4. Each electron may be considered to belong to both the atomic nuclei.

- **5.** As a result of overlapping, there is maximum electron density somewhere between the two atoms. The electrostatic attraction between the nuclei and the accumulated electron clouds between them provides a large part of the binding force of covalent bond.
- **6.** The neutralization of spin magnetic moments of the two electrons taking part in the bond formation also contributes to the binding force.

Valence bond theory explains that a covalent bond is formed by the overlapping of the electron clouds of the atomic orbitals of the constituent atoms. The greater the overlap, the stronger the bond.

(a) Formation of hydrogen molecule:

Hydrogen $(1s^1)$ has only one electron in its 1s-orbital. When two hydrogen atoms come together, overlap of their s-orbitals takes place (s-s overlap), energy is released (bond energy) and a covalent bond called the σ bond is formed.



The electrons shared between the two atoms are to a large extent located in the region of space between the two nuclei. So the region of overlap is the region of high electron density. The electron density (or electron cloud) is distributed symmetrically about the bond axis, i.e., the line joining the nuclei. Such a bond formed by the axial overlapping of the orbitals is called a sigma (σ) bond.

(b)Formation of hydrogen fluoride molecule:

H1s₁ F 1s²2s²2p⁵

The 1s-orbital of the hydrogen atom and one of the 2p-orbitals of the fluorine atom contain only one electron each. The 1s-orbital of the hydrogen atom and the partly filled p-orbital of the fluorine atom overlap axially and form a σ bond (s-p overlap).



(c) Formation of chlorine molecule:

Cl 1s²2s²2p⁶3s²3p⁵

One of the 3p-orbitals of the chlorine atom contains only one electron. The half-filled p-orbital of a chlorine atom overlaps axially with the half-filled p-orbital of the other chlorine atom and forms a σ bond (p-p overlap).



(d) Formation of nitrogen molecule:

N 1s²2s $2p_x^1 2p_y^1 2p_z^1$

There are three unpaired electrons in the 2p-obitals of a nitrogen atom. When two nitrogen atoms combine the three 2p-orbitals of one atom mutually overlap with those of the other atom and form three bonds.



Suppose the orbitals approach along the x-axis the p_x -orbitals overlap axially and form a σ bond (p – p overlap). the p_y and p_z -orbitals of the N atoms cannot overlap axially and so make a lateral (side to side) overlap forming the Pi (π) bonds



Generally in any multiple bond between two atoms one bond is a σ bond and a π bond and a triple bond will consist of a σ bond and two π bond formed between two p-orbitals, the upper lobe overlaps the upper lobe and the lower lobe overlaps the lower lobe. Together they constitute π bond. The π electron cloud will lie above and below the plane of the bond.

4.11 Hybridization of Atomic Orbitals and the Shape of Molecules

If the four hydrogen atoms in a methane molecule (CH₄) were bound to the three 2p orbitals and the 2s orbital of the carbon atom, the H-C-H bond angles would be 90° for 3 of the hydrogen atoms and the 4th hydrogen atom would be at 135° from the others. Experimental evidence has shown that the bond angles in methane are not arranged that way but are 109.5° giving the overall shape of a tetrahedron. The tetrahedral structure makes much more sense in that hydrogen atoms would naturally repel each other due to their negative electron clouds and form this shape. Experimental evidence has also shown that the H-N-H bond angles in ammonia (NH₃) are 107° and the H-O-H bond angles in water are 105°. It is clear from these bond angles that the non-bonding pairs of electrons occupy a reasonable amount of space and are pushing the hydrogen atoms closer together compared to the angles found in methane.

The valence shell electron-pair repulsion model (VSEPR) was devised to account for these molecular shapes. In this model, atoms and pairs of electrons will be arranged to minimize the repulsion of these atoms and pairs of electrons. Since the non-bonded electron pairs are held somewhat closer to the nucleus than the attached hydrogen atoms, they tend to crowd the hydrogen atoms. Thus ammonia exists as a distorted tetrahedron (trigonal pyramidal) rather than a trigonal plane and water also exists as a distorted tetrahedron (bent) rather than a linear molecule with the hydrogen atoms at an 180° bond angle.

This concept proposes that since the attached groups are not at the angles of the p orbitals and their atomic orbitals would not have maximum overlap (to form strong bonds) the s and p orbitals will be hybridized to match the bond angles of the attached groups.

The number of these new hybrid orbitals must be equal to the numbers of atoms and non-bonded electron pairs surrounding the central atom!

In the case of methane, the three 2p orbitals of the carbon atom are combined with its 2s orbital to form four new orbitals called "sp³" hybrid orbitals. The name is simply a tally of all the orbitals that were blended together to form these new hybrid orbitals. Four hybrid orbitals were required since there are four atoms attached to the central carbon atom. These new orbitals will have energy slightly above the 2s orbital and below the 2p orbitals as shown in the following illustration. Notice that no change occurred with the 1s orbital.



These hybrid orbitals have 75% p-character and 25% s-character, which gives them a shape that is shorter and fatter than a p-orbital. The new shape looks a little like...



A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)



A space-filling model of methane would look like...



In the case of ammonia, the three 2p orbitals of the nitrogen atom are combined with the 2s orbital to form four sp³ hybrid orbitals. The non-bonded electron pair will occupy a hybrid orbital. Again we need a hybrid orbital for each atom and pair of non-bonding electrons. Ammonia has three hydrogen atoms and one non-bonded pair of electrons when we draw the electron-dot formula. In order to determine the hybridization of an atom, you must first draw the electron-dot formula.



A stick and wedge drawing of ammonia showing the non-bonding electrons in a probability area for the hybrid orbital...



A space-filling model of ammonia would look like...(Note the non-bonded electron pair is not shown in this model.)



In the case of water, the three 2p orbitals of the oxygen atom are combined with the 2s orbital to form four sp³ hybrid orbitals. The two non-bonded electron pairs will occupy hybrid orbitals. Again we need a hybrid orbital for each atom and each pair of non-bonding electrons. Water has two hydrogen atoms and two non-bonded pairs of electrons when we draw the electron-dot formula.



A stick and wedge drawing of water showing the non-bonding electron pairs in probability areas for the hybrid orbital...



A space-filling model of water would look like...(Note the non-bonded electron pairs are not shown in this model.)

Now let's look at something a bit different. **In the boron trifluoride molecule**, only three groups are arranged around the central boron atom. In this case, the 2s orbital is combined with only two of the 2p orbitals (since we only need three hybrid orbitals for the three groups...thinking of groups as atoms and non-bonding pairs) forming three hybrid orbitals called sp² hybrid orbitals. The other p-orbital remains unhybridized and is at right angles to the trigonal planar arrangement of the hybrid orbitals. The trigonal planar arrangement has bond angles of 120°.



In the following stick model, the empty p orbital is shown as the probability area...one end shaded blue and the other is white...there are no electrons in this orbital!





A space-filling model of boron trifluoride would look like...



Finally let's look at beryllium dichloride. Since only two groups are attached to beryllium, we only will have two hybrid orbitals. In this case, the 2s orbital is combined with only one of the 2p orbitals to yield two sp hybrid orbitals. The two hybrid orbitals will be arranged as far apart as possible from each other with the result being a linear arrangement. The two unhybridized p-orbitals stay in their respective positions (at right angles to each other) and perpendicular to the linear molecule.



In the following stick model, the empty p orbitals are shown as the probability areas...one gray and one black.



A space-filling model of beryllium dichloride would look like...



Hybridization Involving d-Orbitals

As we discussed earlier, some 3rd row and larger elements can accommodate more than eight electrons around the central atom. These atoms will also be hybridized and have very specific arrangements of the attached groups in space. The two types of hybridization involved with d orbitals are sp^3d and sp^3d^2 .

The groups will be arranged in a trigonal bipyramidal arrangement with $sp^{3}d$ hybridization...bond angles will be 120° in the plane with two groups arranged vertically above and below this plane.



There will be an octahedral arrangement with sp^3d^2 hybridization...all bond angles are at 90°.

Non-bonded electron pairs are always placed where they will have the most space...in the trigonal plane for sp³d hybridization.

Try drawing the 3-dimensional electron-dot picture for each of the following molecules...First draw an electron-dot formula. Remember to put all the extra electrons on the central atom as pairs when drawing this initial electron-dot formula. Now count the groups around the central atom. If there are six groups (Remember to count non-bonding electron pairs as groups.) it will have $sp^{3}d^{2}$ hybridization. If it has five groups it will have $sp^{3}d$ hybridization.

SF₆ sulfur hexafluoride

PF5 phosphorus pentafluoride

SF4 sulfur tetrafluoride

CIF3 chlorine trifluoride

XeF2 xenon difluoride

4.11.1 Summary of Hybridization. In the following summary, groups are considered to be atoms and/or pairs of electrons and hybrid orbitals are the black lines and wedges. When the octet of an element is exceeded, then hybridization will involve d-orbitals. Unhybridized p-orbitals are shown as probability areas in black and gray for sp hybridization and carbon black for sp² hybridization. A single electron as found in a radical would occupy an unhybridized p-orbital.

Number of Groups Attached to a Cental Atom	Description and 3-Dimensional Shape
Two Groupssp	2 groups = sp hybridization 180 degree bond angle linear electron-pair geometry
Three Groupssp ²	3 groups = sp ² hybridization 120 degree bond angles trigonal planar electron-pair geometry
Four Groupssp ³	4 groups = sp ³ hybridization 109.5 degree bond angles tetrahedral electron-pair geometry
Five Groupssp ³ d	5 groups = sp ³ hybridization 120 and 90 degree bond angles trigonal bipyramidal electron-pair geometry
Six Groupssp ³ d ²	6 groups = sp ³ hybridization 90 degree bond angles octahedral electron-pair geometry

Hybridization Involving Multiple Bonds

Only a maximum of two electrons can occupy any orbital whether it is an atomic orbital or a molecular orbital due to electron-electron repulsion. When we draw a double or a triplebond between two atoms, we imply that either four or six electrons are directly between these two atoms. Since this is impossible, we must have these extra electrons off to the side in what we refer to as pi bonds. Therefore, all multiple bonds are composed of two different kinds of molecular bonds called pi-bonds and sigma-bonds.

The sigma-bond is defined as the linear overlap of atomic orbitals (hybrids except for hydrogen) in which two electrons are directly between the two bonded nuclei.

Pi-bonds are defined as the parallel overlap of p-orbitals. A double bond has one sigmabond and one pi-bond. A triple bond thus consists of a sigma-bond and two pi-bonds with the pi-bonds in different planes. In the molecule C_2H_4 , ethene, both carbon atoms will be sp^2 hybridized and have one unpaired electron in a non-hybridized p orbital.



These p-orbitals will undergo parallel overlap and form one pi bond with bean-shaped probability areas above and below the plane of the six atoms. This pair of bean-shaped probability areas constitutes one pi-bond and the pair of electrons in this bond can be found in either bean-shaped area.



The 3-dimensional model of ethene is therefore planar with H-C-H and H-C-C bond angles of 120°..the pi-bond is not shown in this picture.



Now let's look at H_2C_2 (acetylene). Both carbon atoms will be sp hybridized and have one electron in each of two unhybridized p orbitals.



These p orbitals will undergo parallel overlap to form two pi-bonds at right angles to each other.



The 3-dimensional model of acetylene is therefore linear...the pi-bonds are not shown in this picture.



4.11.2 Electron-Pair Geometry and Molecular Geometry

Now for a discussion about the shape of molecules! Why should you learn two ways to describe the geometry?

When we experimentally look at molecules, we see how the atoms are arranged but don't see the non-bonded electron pairs. Therefore inorganic chemists tend to use molecular geometry since they deal a lot with solid ionic compounds.

When we think about the character of molecules and how they interact, those non-bonded electron pairs and their orientation in space become very important. Thus organic chemists tend to use electron-pair geometry.

The various shapes for electron-pair geometry are linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral. Remember a "group" is either an atom or a non-bonded pair of electrons.

Some of the common shapes for molecular geometry are linear, bent, trigonal pyramidal, tetrahedral, T-shaped, seesaw and octahedral.

4.12 Molecular orbital theory

Molecular orbital theory was developed by **F. Hund** and **R.S. Mulliken** in 1932. The basic idea of molecular orbital theory is that atomic orbitals of individual atoms combine to form molecular orbitals. The electrons in molecules are present in the molecular orbitals which are associated with several nuclei. These molecular orbitals are filled in the same way as the atomic orbitals in atoms are filled.

Salient Features of Molecular Orbital Theory

The salient features of the molecular orbital theory are :

- 1. Just like an atom, molecule has orbital's of definite energy levels. Like electrons of atoms are present in atomic orbital's, electrons of a molecule are present in different molecular orbital's.
- Molecular orbital's are formed by the combination of atomic orbital's of proper symmetry and comparable energies. The atomic orbital's of these atoms merge into molecular orbital's.
- **3.** An electron in an atomic orbital is under the influence of only one nucleus. However, an electron in a molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
- **4.** Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- 5. The number of molecular orbital's formed is equal to the number of combining atomic orbital's. When two atomic orbital's combine they form two molecular orbital and antibonding molecular orbital's. These are called **bonding** molecular orbital and antibonding molecular orbital.
- **6.** The bonding MO has lower energy and hence greater stability whereas corresponding antibonding MO has more energy and hence lesser stability.
- **7.** The molecular orbital's are filled in same way as atomic orbital's are filled in accordance with Aufbau principle, Pauli exclusion principle and Hund's rule. Molecular orbital's are formed by the combination of atomic orbital's of bonded atoms. We have learnt that according to wave mechanics, the atomic orbital's can be expressed by wave functions (Ψ^{s}) . The wave functions represent the amplitude of

the electron waves. These are obtained from the solutions of Schrodinger wave equation. Similarly, we can write Schrodinger wave equation for the whole molecule. However, it is very difficult to solve the wave equation for molecules. To overcome this problem, scientists have used an approximate method known as **linear combination of atomic orbital's abbreviated as LCAO method. Formation of Molecular orbitals**

According to LCAO method, the orbitals are formed by the linear combination (addition or subtraction) of atomic orbitals of the atoms which form the molecule. Let us apply this theory to hydrogen molecule. Consider that hydrogen molecule consists of two atoms A and B. Each of these atoms has 1s-orbital of lowest energy. The

atomic orbital's of these atoms may be represented by the wave functions Ψ_{A} and

 $\psi_{B}~$ for hydrogen atoms A and B respectively. Now, when these atomic orbital's are

brought closer, they combine to form molecular orbital's. According to LCAO method, the linear combination of atomic orbital's can take place by addition and by subtraction of wave functions of atomic orbital's.

i.e.,
$$\psi_{MO} = \psi_A \pm \psi_B$$

These two types of combinations give rise to two molecular orbital's as described below :

(i) Molecular orbital obtained by **addition of wave functions** of atoms may be represented as;

$$\psi(MO) = \psi_A + \psi_B$$

or $\sigma = \psi_A + \psi_B$

This molecular orbital is called **bonding molecular orbital**.

(ii) Molecular orbital obtained by **subtraction of wave functions** of atoms may be represented as:

$$\psi^*(MO) = \psi_A - \psi_B$$

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

The molecular orbital is called **antibonding molecular orbital**.

The physical picture of bonding and antibonding molecular orbital's can be obtained by considering the atomic orbital's. To illustrate this, we may take the combination of 1s-orbital of one hydrogen atom with 1s-orbtial of second hydrogen atom to form two molecular orbital's in hydrogen molecule. As discussed above, there are two ways of combining atomic orbital's. The molecular orbital formed by the addition of overlapping of two 1s-orbtials is shown in Fig. It is clear from the figure that the region between the two nuclei where the two 1s-atomic orbital's overlap has high electron density. Such a molecular orbital is called **bonding molecular orbital**. It is designated as σ 1s (called sigma 1s) orbital. The sigma (σ) signifies that the orbital is symmetrical about the molecular axis and the script `1s' indicates that it is formed by the combination of 1s-atomic orbital's.



The molecular orbital formed by the subtraction of overlapping of two 1s-orbtials is shown in Fig.



It is clear from the figure that the electron density in between the two nuclei is practically zero and is concentrated in regions away from each nucleus. In this case, the electron probability densities of two atomic orbital's get cancelled in the centre (by subtraction) so that there is no probability of finding the electron in the region of overlap i.e. between the nuclei. This situation does not favour the bond formation. Such an orbital is called **antibonding molecular orbital**.

Thus, the bonding molecular orbital is designated as σ 1s (called sigma bonding) and antibonding molecular orbital is designated as σ^* 1s (called sigma antibonding).

Table: Differences between atomic and molecular orbital's

The important differences between atomic and molecular orbital's are:

Atomic orbital	Molecular orbital
 An electron in atomic orbital is under the influence of only one positive nucleus of the atom. 	An electron in molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.
2. Atomic orbital's are inherent property of an atom.	Molecular orbital's are formed by the combination of atomic orbital's.
3. They have simple shapes.	They have complex shapes.

The formation of bonding and antibonding molecular orbital's can be explained in terms of constructive interference (or additive effect) and destructive interference (or subtractive effect) of the electron waves of the combing atoms.

Amplitude a + b Amplitude a ΨΑ+ΨΒ Constructive interference Amplitude b (Wave are added up) Two waves in phase Amplitude a Amplitude a - b Amplitude b Ψ_A - Ψ_B (a > b) Amplitude a $\Psi_A - \Psi_B (a = b)$ Amplitude b Destructive interference (Waves are subtracted) Two waves out of phase

(i) **During constructive interference**, the two waves are in phase and the amplitudes of the waves get added up. Therefore, the resulting wave function has more electron density in between the nuclei. This corresponds to bonding MO.

Fig : Constructive and destructive interference of waves.

(ii) On the other hand, when the two waves are out of phase, there is **destructive** interference and the amplitudes of the waves get subtracted or cancelled. Therefore, the resulting wave function has less electron density between the nuclei. This also gives rise to nodal plane between two nuclei. This corresponds to wave function of antibonding MO.

The probability density in boding and antibonding MOs can also be shown by simple mathematics. We know that the probability density is given by square of wave function (Ψ^2).

For bonding MO,

$$\psi = \psi_A + \psi_B$$
, so that
 $\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B$

Thus, Ψ^2 is greater than $\psi_A^2 + \psi_B^2$ (sum of the probability densities of individual atoms) by an amount equal to $2\psi_A \quad \psi_B$. Therefore, the probability of finding electros in the bonding MO is greater than in either of atomic orbital's (ψ_A or ψ_B).

For antibonding MO,

$$\psi^* = \psi_A - \psi_B$$
, so that
 $\psi^{*2} = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A \psi_B$

Thus, ψ^{*^2} is less than $\psi_A^2 + \psi_B^2$ by an amount equal to $2\psi_A \ \psi_B$. Therefore the probability of finding the electrons in antibonding MO is less than that in either of the atomic orbital's ($\psi_A \ or \ \psi_B$).

4.13 Relative energies of bonding and antibonding molecular orbitals

We have learnt that in the case of bonding molecular orbital, the attraction of both the nuclei for both the electrons is increased. This results in lowering of energy. In the case of antibonding molecular orbital, the electrons try to go away from the nuclei and this corresponds to repulsive state. The energy of this orbital will be higher. The relative energies of bonding and will be higher. The relative energies of bonding and antibonding molecular orbital's along with atomic orbital's can be represented as shown in Fig.



Thus, the bonding molecular orbital is stabilized relative to the energy of the isolated atoms and antibonding molecular orbital is destabilized relative to the individual atoms. Further, it may be noted that the boding MO is stabilized to the same extent as the antibonding MO is destabilized.

TABLE PITCICICCO DECACCI POTATIA ANA //ILE DOTATIA TOTECATAL OTDICAL	Table:	Differences	between	Bonding	and Ant	i-bondina	Molecular	Orbital's
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	Bonding MO	Anti-bonding MO
1.	Bonding molecular orbital is formed by the addition of overlapping of atomic orbital's. The wave function of the bonding MO may be written as: $\psi(MO) = \psi_A + \psi_B$	Anti-bonding molecular orbital is formed by the subtraction of overlapping of atomic orbitals. The wave function for the ant-bonding MO may be written as: $\psi^*(MO) = \psi_A - \psi_B$
2.	They are formed when the lobes of the combining atomic orbitals have same sign.	They are formed when the lobes of the combining atomic orbitals have opposite sign.
3.	It has greater electron density in the region between the two nuclei of bonded atoms.	It has lesser electron density in the region between the two nuclei of the atoms.
4.	The forces in this orbital tend to bring the two nuclei of the atoms together. Therefore, the electrons in the bonding MO contribute to attraction between the two atoms.	The forces in this orbital push the nuclei apart. Therefore, the electrons in antibonding MO contribute to repulsion between the atoms.
5.	It possesses lower energy than the isolated atomic orbitals.	It possesses higher energy than the isolated atomic orbital's.

4.14 Combination of 2s and 2p atomic orbitals to form molecular orbitals

Combination of 2s atomic orbital's. Like 1s- orbital's, 2s-orbitals combine by addition and subtraction, of overlapping to form bonding and antibonding molecular orbital's. These are labeled as σ 2s and σ *2s. These molecular orbital's have exactly the same shapes as σ 1s and σ * 1s MOs but they are slightly larger in size.

Combination of 2p atomic orbital's. There are three p-orbital's namely $2p_x$, $2p_y$ and $2p_z$ which are directed in space along the x, y and z coordinate axes respectively. By convention, we can assume z-axis then be perpendicular to the **internuclear axis.** The combination of 2p-orbitals forms two types of MOs; sigma (σ) MOs and pi (π) MOs as discussed below:

- (i) Formation of σ -molecular orbital's. When the two $2p_z$ orbital's are brought closer along the internuclear axis, they overlap head on forming σ -bond (Fig). When the two orbital's overlap by the addition of electron waves (i.e., with proper sings, ++ lobes overlap), bonding molecular orbital is formed. This may be designated as $\sigma 2p_z$. On the other hand, when the two wave functions are subtracted, an designated as $\sigma^* 2p_z$. Thus, two $2p_z$ atomic orbital's combine to form two molecular orbital's, i.e. a bonding M.O. ($\sigma^2 2p_z$).
- (ii) Formation of π -molecular orbital's. When a 2p_x atomic orbital of one atom approaches the 2p_x atomic orbital of another atom, the overlapping occurs sidewise and not end-to-end. The molecular orbital formed by sidewise or lateral overlap is known as pi (π) molecular orbital. The molecular orbital formed is not symmetrical about the internuclear axis. The molecular orbital formed by overlapping of two 2p_x atomic orbital's by the addition of electron waves is called bonding pi molecular orbital designated as π 2p_x while the molecular orbital by the subtraction of electron waves is called antibonding molecular orbital labeled as π *2p_x. These are shown in Fig.



Atomic orbitals

Molecular orbitals

Fig : Bonding and antibonding molecular orbitals from 2p_z atomic orbitals.



Similarly, when a $2p_y$ orbital of one atom overlaps with a $2p_y$ orbital of another atom, they also overlap sidewise forming two molecular orbitals $\pi 2p_y$ and $\pi^* 2p_y$. These are exactly similar to $\pi 2p_x$ and $\pi^* 2p_x$ MOs.

σΜΟ	πΜΟ
1. It is formed by the head to head	It is formed sidewise overlap of AOs
overlap of AOs along internuclear	perpendicular to internuclear axis.
axis.	
2. The overlap region is maximum.	The overlap region is minimum.
3. The orbital is symmetrical to	The orbital is not symmetrical to
rotation about internuclear axis.	rotation about internuclear axis.
4. It leads to the formation of a	It leads to the formation of a weak
strong bond.	bond.

	Table: Differences	between	Sigma and	Pi Molecular	Orbitals
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4.15 Conditions for the combination of atomic orbitals

Molecular orbital's are formed by the combination of atomic orbital's. cannot combine with each other. The following are the main conditions for effective combination of atomic orbital's:

- **1.** The combining atomic orbital's must have same or nearly the same energies. For example, in case of homonuclear diatomic molecules of the type A₂, 2s-orbital of one atom can combine with 2s-orbital of another atom but 1s-orbital of one atom cannot combine with 2s-orbital of another atom.
- 2. The extent of overlapping between the atomic orbital's of two atoms should be large.

3. The combining atomic orbital's must have the same symmetry about the molecular axis.

For example, 2s- orbital of one atom can combine with 2s-orbital of another atom but it cannot overlap with $2p_x$ or $2p_y$ orbital of another atom.

For example, when 2s-orbital of one atom A overlaps with $2p_x$ orbital of another atom B (Fig), ++ overlap is canceled by the +- overlap. As a result, no molecular orbital is formed. In other words, such a combination (2s with $2p_x$ or 2s with $2p_y$) is not possible.



However, it may be noted that 2s-orbital of one atom can also combine with 2pz orbital of another atom because both have same symmetry about the internuclear z-axis (i.e., + + overlap can occur). This is shown in Fig.



Fig Possibility of combination of 2s and 2p_z atomic orbitals.

4.16 Energy level diagram for molecular orbitals

The relative energies of molecular orbital's depend upon the following two factors:

- (i) The energies of the AOs combining to form MOs.
- (ii) The extent of overlapping between the atomic orbital's. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs. For example, the extent of overlapping in case of σ -orbital is more than that in π -orbital. Consequently, the energy of $\sigma 2p_z$ is lower than the energy of bonding $\pi 2p_x$ or $2p_y$ MOs.

Now, 1s AOs of two atoms form two MOs designated as σ 1s and σ *1s. The 2s and 2p and 2p orbital's (eight AOs on two atoms) from four bonding MOs and four anti-bonding MOs as:

Bonding MOs: σ2s, σ2pz, π2px, π2py**Anti-bonding: MOs** : σ*2s, σ*2Pz, π*2Px, π*2Px, π*2Px, π*2Py

The energy levels of these molecular orbital's have been determined experimentally by spectroscopic methods. The order of increasing energy of molecular orbital's obtained by the combination of 1s, 2s and 2p orbital's of two atoms is:

σ1s, σ*1s, σ2s, σ*2s, σ2p_z, π2p_x = π2p_y, π*2p_x = π*2p_y, σ*2p_z

Energy Increases

However, experimental evidence for some diatomic molecules have shown that above sequence of energy levels of MOs is not correct for all molecules. For example, for homonuclear diatomic molecules of second row elements such as Li₂, Be₂, B₂, C₂, N₂, **the** σ **2p_z MO is higher in energy than** π **2p_x and** π **2p_y MOs.** The order of MOs for these molecule is

σ1s, σ*1s, σ2s, σ*2s, $π2p_x = π2p_y$, $σ2p_z$, $π*2p_x = π*2p_y$, $σ*2p_z$

Energy Increases

But for molecules O_2 onwards ($\mathsf{O}_2,\,\mathsf{F}_2),$ the first order of energies of MOs is correct

Thus, for diatomic molecules of second period (Li₂ to Ne₂), there are two types of energy levels of MOs as shown in Fig. For molecules Li₂, Be₂, B₂, C₂ and N₂ the molecular orbital energy level diagram is shown in Fig. (a). On the other hand, for the molecules O₂, F₂ and Ne₂ the molecular orbital energy level diagram is shown in Fig. (b). The main difference between the two types of sequences is that for molecules O_2 , F_2 and Ne_2 , the $\sigma 2p_2$ MO is lower in energy than $\pi 2p_x$ and $\pi 2p_y$ MOs while in the case of molecules Li₂, Be₂, B₂, C₂ and Ne₂, $\sigma 2p_2$ MO has higher energy than $\pi 2p_x$ and $\pi 2p_y$ MOs.



(For O₂, F₂,Ne₂ Molecules) Fig : (b) Molecular orbital energy level diagram for O₂, F₂ and Ne₂ molecules.

The main reason for the difference in sequences is the interaction of 2s and $2p_z$ AOs. For the molecules Li₂, Be₂, B₂ C₂ and N₂, the differences in energies of 2s and $2p_z$ orbital's is small and, therefore, they can interact. While the energies of 2s and $2p_z$ AOs for O₂, F₂ and Ne₂ is large and therefore, they cannot interact.

4.17 Rules for filling molecular orbitals

The following rule are followed for filling up molecular orbitals with electrons in order to write molecular configurations:

- 1. The molecular orbital having the lowest energy is filled first. This is in accordance with **Aufbau principle** as already discussed for atoms.
- 2. Each molecular orbital can accommodate maximum of two electrons having opposite spins. This is in accordance with **Pauli's exclusion principle.**
- 3. If there are two molecular orbitals of the same energy, the pairing of electrons will occur only after each orbital of same energy has one electron. This is in accordance with **Hund's rule.**

4.18 Electronic configurations and molecular behaviour

The distribution of electrons among various molecular orbitals is called the **electronic configuration of the molecules.** The electronic configuration of the molecule or the molecular orbital energy level diagram gives very valuable information regarding the behavior of molecules. The important informations conveyed by electronic conveyed by electronic configuration of molecules are:

- (a) **Stability of a molecule.** We have learnt that the electrons in bonding molecular orbitals contribute the formation of bond. ON the other hand, the electrons in anti-bonding molecular orbitals contribute to repulsion between the atoms and, therefore, oppose the formation of bond. Thus, the electrons in bonding molecular orbitals will give stability to the molecule whereas those in antibonding molecular orbitals will decrease the stability. Thus, if N_b represents the number of electrons in bonding molecular orbitals and N_a represents the number of electrons in anti-bonding molecular orbitals, then the following generalization can be made:
 - (i) The molecule is stable if $N_b > N_a$. (ii) The molecule is unstable if $N_b < N_a$. (iii) The molecule is unstable if $N_b = N_a$.
- According to (i) more bonding molecular orbitals are occupied and therefore, the bonding influence is stronger and therefore, a stable molecule is formed.
- In (ii) the anti-bonding influence is stronger and hence the molecule is unstable.
- According to (iii), even if the number of electrons in bonding MOs are same, the atoms do not combine to form molecules. This is because of the fact that the effect of anti-bonding electrons is slightly more than that of bonding electrons.
- (b) **Bond order.** The relative stability of a molecule can be determined on the basis of bond order. It is defined as the number of covalent bonds in a molecule. It is equal to one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.

Bond order

$$=\frac{\begin{bmatrix} No. \ of \ electrons \\ in \ bodning \ Mos \end{bmatrix} - \begin{bmatrix} No. \ of \ electrons \\ in \ anti-bodning \ Mos \end{bmatrix}}{2}$$

$$or = \frac{N_{b} - N_{a}}{2}$$

The bond order of 1, 2 3 corresponding to single, double or triple bond. But bond order may be fractional also in some cases.

Information Conveyed by Bond Order

The bond order conveys the following important informations:

- (i) If the value of bond order is positive, it indicates a stable molecule and if the value of bond order is negative or zero, it means that the molecule is unstable.
- (ii) The stability of a molecule is measured by its bond dissociation energy. But the bond dissociation energy is directly proportional to the bond order. Greater the bond order, greater is the bond dissociation energy. For example, nitrogen molecule with bond order equal to 3 has larger bond dissociation energy (945 kJ mol⁻¹) than oxygen molecule (bond dissociation energy 495 kJ mol⁻¹) with a bond order equal to 2.

(iii)Bond order is inversely proportional to the bond length. The higher the bond order value, smaller is the bond length. For example, the bond length in nitrogen molecule is shorter than in oxygen molecule as shown below.

Molecule	Bond order	Bond Dissociation	Bond length
		energy	
Oxygen	2	495 kJ mol ⁻¹	121 pm
Nitrogen	3	945 kJ mol ⁻¹	110 pm

(c) Magnetic character. If all the electrons in the molecule of a substance are paired, the substance is diamagnetic (repelled by the magnetic field). On the other hand, if there are unpaired electrons in the molecule, the substance is paramagnetic (attracted by the magnetic field.)

4.19 Bonding in some diatomic molecules

Let us discuss bonding in some homonuclear diatomic molecule of the elements of first and second rows of the periodic table.

1. **Hydrogen molecule (H₂).** It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electrons in 1s-orbtial and, therefore, there are two electrons in hydrogen molecule. Both these electrons are to be accommodated in the lowest energy molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins. The molecular orbital energy level diagram for H₂ molecule is shown in Fig.



The molecular orbital electronic configuration of H₂ molecule is:

$$H_2: (\sigma \ 1s)^2$$

The bond order in H_2 is:

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

This means that two hydrogen atoms are bonded together by a **covalent bond**. The bond. dissociation energy of hydrogen molecule has been found to be 438 kJ mol⁻¹ and bond length equal to 74 p,. Moreover, since no unpaired electron is present in hydrogen molecule, it is **diamagnetic.**

2. Hydrogen molecule ion (H_2^+) . This is formed by the combination of hydrogen atoms containing one electron and hydrogen ion having no electron. Therefore, this ion has only one electron. The molecular orbital diagram is given in Fig.



The electronic configuration of the molecule is:

$$(H_2^+): (\sigma \ 1 \ s)^1$$

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

The positive value of bond order indicates that the molecule is stable. The presence of unpaired electron in the molecule indicates that is **paramagnetic** molecule. The stability of the ion as well as its paramagnetic character have been confirmed experimentally.

The bond length of H_2^+ ion is larger than that of H2 molecule (bond length $H_2^+ = 104 \text{ pm}$; H₂ = 74 pm) while its bond dissociation energy is less than that of H₂ molecule (bond dissociation energy $H_2^+ = 269 \text{ kJ mol}-1$, H₂ = 458 kJ mol⁻¹) This clearly supports the fact that bond in H_2^+ ion is weaker than that in H₂ molecule.

3 Hypothetical helium molecule (He₂): Each helium atom has two electron single 1s-orbtial, and therefore, there are four electron sin He₂ molecule. These electrons will be accommodated in σ 1s and σ * 1s Mos as shown in Fig. The electronic configuration for helium molecule may be written as:



The zero bond order value indicates that there is no net bonding and He2 molecule should not be formed. In fact, there is no experimental evidence for the existence of this molecule.

4. Helium molecule ion (He_2^+). This molecule contains three electrons, two form one helium atom and one from the other (He⁺ ion). The molecular orbital electronic configuration of the molecule is

 $He_{2}^{+}:(\sigma \ 1s)^{2} \ (\sigma * \ 1s)^{1}$

Bond order =
$$\frac{2-1}{2} = \frac{1}{2}$$

The value of bond order indicates that He_2^+ is stable. Its bond dissociation energy has been found to be 242 kJ mol⁻¹. The molecule is expected to be **paramagnetic** and same has been experimentally observed also.

5. Lithium molecule (Li₂). The electronic configuration of lithium is 1s² 2s¹. These are six electrons in lithium molecule. The electronic configuration of Li₂ molecule may be written as:

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

The above configuration may also be written as:

$$KK(\sigma 2s)^2$$

where KK represents fully filled inner K shells in two atoms i.e. $(\sigma 1s)^2 (\sigma^* 1s)^2$ From the electronic configuration of Li₂ molecule it is clear that there are 4 electrons is bonding MOs and 2 electrons in antibonding MOs.

Therefore, its bond order is:

Bond order =
$$\frac{N_b - N_a}{2} = \frac{4 - 2}{2} = 1$$

Thus, there is one Li-Li sigma bond. The bond energy of the molecules is quite low, being about 110 kJ mol⁻¹. The bond length of the molecule is 265 pm. Since it has no unpaired electrons, it should be diamagnetic. Indeed diamagnetic Li_2 molecules are known to exist in the vapour phase.

Comparison of Li-Li and H-bonds. The comparison of Li-Li and H-H bonds reveals that the sigma bond in Li2 molecule is weaker and much longer than σ -bond in H₂ molecule. This may be attributed to the following reasons:

- The 2s orbital of lithium is bigger in size than the 1s orbital. Therefore, the overlapping of 2s-2s atomic orbitals is less effective than the overlapping of 1s-1s orbitals.
- (ii) In lithium molecule, the outer electrons in $(\sigma 2s)$ molecular orbital are shielded by the inner 1s electrons. Therefore, the attraction between the nuclei and the electrons in $(\sigma 2s)$ molecular orbital is less.

Moreover, the inner $1s^2$ electrons of two lithium atoms cause repulsion between the atoms. Therefore, they do not allow them to come closer.

6. Beryllium molecule, (Be₂). Beryllium (Z= 4) has electronic configuration $1s^22s^2$. In the formation of a diatomic molecule, evidently, two outer electrons of each atom, i.e., four in all, have to be accommodated of each atom, i.e., four in all, have to be accommodated in molecular orbital's. Two of these go into the bonding (σ 2s) orbital while the other two have to go into the antibonding (σ *2s) orbital.

The molecular orbital electronic configuration is;

$$Be_2 : KK(\sigma 2s)^2 (\sigma * 2s)^2$$

bond order = $\frac{1}{2}(2-2) = 0$

The zero **bond order** suggests that Be₂ molecule does not exist.

7. Boron molecule, (B₂). The electronic configuration of boron is $1s^2 2s^2 2p^1$. The outermost shell of each atom contains 3 electrons. When two B atoms combine to form molecule B₂, there are 6 electrons which need to be accommodated in the molecular orbitals of B₂. The molecular orbital electronic configuration is:

*B*₂: KK
$$(\sigma 2s)^2 (\sigma * 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$$

bond order = $\frac{1}{2}(4-2) = 1$

The molecule has only one bond. The electrons which contribute towards bonding are the $\pi 2p_x$ and $\pi 2p_y$ MOs. This indicates that the molecule is formed by a weak π -bond. The bond dissociation energy of B₂ molecule has been found to be 290 kJ mol⁻¹ and bond length equal to 159 pm.

Since each $\pi 2px$ and $\pi 2py$ MO contains single electron, the molecule B₂ is **paramagnetic.**

8. Carbon molecule, (C₂). The electronic configuration of carbon is $1s^2 2s^2 2p^2$. The outer shell of each atom contains 4 electrons. In the formation of C₂ molecule, there will be evidently 8 electrons to be accommodated in the outer molecular orbitals of C₂. The molecular orbital electronic configuration is:

$$C_2 : \text{KK} (\sigma 2s)^2 (\sigma 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$$

bond order =
$$\frac{1}{2}(6-2)=1$$

Thus, the C₂ molecule has tow bonds. The bond dissociation energy of C₂ molecule has been found to be 620 kJ mol⁻¹ and bond length equal to 131 pm. Further, since C₂ molecule does not have any unpaired electron, it is **diamagnetic.** The diamagnetic C₂ molecule has been detected in vapour phase.

It may be noted that double bond in C_2 molecule consists of both the pi bonds because of the presence of 4 electrons in tow pi MOs. In most of the other molecules, a double bond is made up of a sigma bond a pi bond.

9. Nitrogen molecule (N₂). The electronic configuration of nitrogen atom is $1s^2 2s^2 2p_x^1 2p_z^1$ and N₂ molecule has 14 electrons. The M.O. diagram is shown in Fig.

The molecular orbital electronic configuration of the molecules is:

$$N_{2}: KK (\sigma 2s)^{2} (\sigma * 2s)^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\sigma 2p_{z})^{2}$$

Bond order = $\frac{8-2}{2} = 3$.

Thus, nitrogen molecule has **three bonds**, one σ and two π -bonds. This is in accordance with very high bond dissociation energy (945 kJ mol⁻¹) and small bond length (110 pm) of the molecule. The molecule is **diamagnetic** because there are no unpaired electrons.

Comparison of N₂ and N_2^+ ion

 N_2^+ ion is formed by the removal of one electron from N₂ molecule. This electro will be lost from 2pz M.O. Hence the electronic configuration of N_2^+ ion will be

$$\begin{split} N_{2}^{+} &: \text{KK} (\sigma 2 \text{s})^{2} (\sigma * 2 \text{s})^{2} (\pi 2 \text{p}_{x})^{2} (\pi 2 \text{p}_{y})^{2} (\sigma 2 \text{p}_{z})^{1} \\ Bond \ order &= \frac{7 \cdot 2}{2} = 2\frac{1}{2} \end{split}$$



Since bond order of N_2^+ ion (2.5) is less than the bond order of N₂ (3) molecule, therefore, the bond strength of N_2^+ will be less than that of N₂ molecule and bond length of N_2^+ will be more than that of N₂ molecule.

10. Oxygen molecule (O₂). The electronic configuration of oxygen atom is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$. Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbital, the electrons in the inner shells are expressed as KK denoting $(\sigma 1s)^2 (\sigma * 2s)^2$. The remaining 12 electrons are filled in molecular orbitals as shown in Fig.

The electronic configuration of the molecule is:

O₂: KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^1$

Bond order =
$$\frac{8-4}{2} = 2$$

Thus, oxygen molecule has **two bonds** (one σ and one π). Further, in accordance with Hund's rule, the last two electrons in π^*2p_x and π^*2p_y orbitlas will remain unpaired. Therefore, the molecule has **paramagnetic character** due to the presence of two unpaired electrons. These facts are in accordance with experimental observations. The bond dissociation energy in O₂ molecule has been found to be 498 kJ mol⁻¹ and bond length 121 pm.

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Comparison of O₂, O_2^+ and O_2^- species

Oxygen molecule ion (O_2^+ **).** This ion is formed by the removal of one electron form O_2^- molecule as:

$$O_2 \longrightarrow O_2^+ + e^-$$

it is clear from Fig. that the electron will be lost from anti-bonding MO i.e., $\pi * 2p_y$ and electronic configuration of O_2^+ is:



g : Molecular orbital energy level diagram for C molecule

Since the bond order of O_2^+ ion is greater than the bond order of O₂ molecule, therefore, the bond strength of O_2^+ will be more than that of O₂ molecule and bond length of O_2^+ will be less than that of O₂ molecule.

Superoxide ion (O_2^-) . This ions is formed by the addition of one electron as:

 $O_2 + e^- \longrightarrow O_2^-$

According to Fig. the electron will be added to either of the antibonding MO (s) $(\pi^* 2p_x \text{ or } \pi^* 2p_y)$. The electronic configuration of O_2^- is

$$O_{2}^{-}: \text{KK} (\sigma 2s)^{2} (\sigma * 2s)^{2} (\sigma 2p_{z})^{2} (\pi 2p_{x})^{2} (\pi 2p_{y})^{2} (\pi * 2p_{x})^{2} (\pi * 2p_{y})^{1}$$

Bond order
$$=$$
 $\frac{8-5}{2} = \frac{3}{2} = 1\frac{1}{2}$

Since the bond order of O_2^- ion is less than that of O_2 molecule, therefore, **the bond in** O_2^- will be weaker than in O_2 and bond length of O_2^- will be larger than that of O_2 molecule.

Peroxide ion (O_2^{2-} **).** This ion is formed by the addition of two electrons to O₂ molecule.

$$O_2 + 2e^- \longrightarrow O_2^{2-}$$

The additional electrons enter the two half-filled π -anti-bonding MOs. The electronic configuration of $O_2^{2^-}$ ion is:

$$O_2^{2-} : \text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^2$$

Bond order =
$$\frac{8-6}{2} = 1$$

Since bond order of $O_2^{2^-}$ ion is less than that of molecule, therefore, the bond $O_2^{2^-}$ will be weaker that in O2 and bondlength of $O_2^{2^-}$ will be larger than that of O2 molecule. therefore, the bond $O_2^{2^-}$ will be weaker that in O2 and bond length of $O_2^{2^-}$ will be larger that of O2 molecule.

The experimental bond dissociation energies and bond lengths for O₂, O_2^{2+} and O_2^{2-} are given below:

Species	Bond order	Bond dissociation energy (kJ mol ⁻¹)	Bond length
O_2^+	2.5	625	112 pm
O ₂	2	495	121 pm
O_2^-	1.5	395	130 pm

The species O_2, O_2^+, O_2^- and O_2^{2-} can be arranged as:

Bond dissociation energy : $O_2^+ > O_2 > O_2^- > O_2^{2-}$ Bond length: $O_2^{2-} > O_2^- > O_2 > O_2^+$

11. **Fluorine molecule (F₂).** The electronic configuration of fluorine atom is $1s^2 2s^2 2p^5$ and therefore, there are 14 electrons in the valence shell of F₂ molecules. The molecular orbital electronic configuration of the molecule is:

$$F_{2}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi * 2p_{x})2(\pi * 2p_{y})^{2}$$

Bond order = $\frac{8-6}{2} = 1$.

Thus, there is one σ -**bond** in the molecule. Since all the electrons in the molecular orbital's are paired, it is **diamagnetic**. The single bonding the molecule is also in agreement with bond dissociation energy of 159 kJ mol⁻¹ and bond length equal to 118 pm.

12. Hypothetical neon molecule. The electronic configuration of neon molecule. The electronic configuration of neon atom is $1s^2 2s^2 2p^6$ and the molecular orbital electronic configuration of neon molecule is $F_2: KK(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_*)^2 (\pi 2p_*)^2 (\pi 2p_*)^2 (\pi^* 2p_*)^2 (\sigma^* 2p_*)^2$

Bond order =
$$\frac{8-8}{2} = 0$$
. Thus, Ne₂ molecule **does not exist**.

Example:- Arrange the following species in the decreasing order of their bond dissociation energies:

$$O_2, O_2^+ and O_2^-$$
.

Solution :- The bond dissociation energy of a molecule is related to its bond order. the larger the bond order, the greater will be the bond dissociation energy. We shall first calculate the bond orders for the various species from their electronic configurations.

$$O_{2}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{1}(\pi * 2p_{y})^{1}$$

$$\therefore Bond \ order = \frac{8 \cdot 4}{2} = 2.$$

$$O_{2}^{+}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{1}$$

$$\therefore Bond \ order = \frac{8 \cdot 3}{2} = 2\frac{1}{2}$$

$$O_{2}^{-}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{2}(\pi * 2p_{y})^{1}$$

$$\therefore Bond \ order = \frac{8 \cdot 5}{2} = 1\frac{1}{2}$$

Now, O_2^+ has the highest bond order, it will have largest bond dissociation energy. The bond dissociation energies will decrease in the order

$$O_2^+ > O_2 > O_2^-$$
.

- **Example :-** With the help of M.O. theory, predict which of the following species is diamagnetic: H_2^+, O_2, O_2^{2+}
- **Solution :-** The diamagnetic species are those which contain only paired electrons. This can be predicted from the molecular orbital electronic configurations as given below:

$$H_{2}^{+}: (\sigma ls)^{1}$$

$$O_{2}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{1}(\pi * 2p_{y})^{1}$$

$$O_{2}^{2+}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}$$

Since O_2^{2+} contain all paired electrons, it will be diamagnetic.

Example :- Explain why N₂ has greater bond dissociation energy than N_2^{2+} whereas O₂ has lesser bond dissociation energy than O_2^+ .

Solution: The M.O. electronic configurations are :

 N_2 : KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$

Bond order =
$$\frac{8 - 2}{2} = 3$$

 N_2^+ : KK $(\sigma 2s)^2 (\sigma * 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^1$
Bond order = $\frac{7 - 2}{2} = 2\frac{1}{2}$

Since bond order of N₂ is larger than that of N_2^+ , N₂ has grater bond dissociation energy than N_2^+ .

$$O_{2}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{1}(\pi * 2p_{y})^{4}$$

Bond order = $\frac{8 - 4}{2} = 2$
 $O_{2}^{+}: KK(\sigma 2s)^{2}(\sigma * 2s)^{2}(\sigma 2p_{z})^{2}(\pi 2p_{x})^{2}(\pi 2p_{y})^{2}(\pi * 2p_{x})^{1}$
Bond order = $\frac{8 - 3}{2} = 2\frac{1}{2}$

Since bond order of O₂ is less than that of O_2^+ , O₂ has lower bond dissociation energy than O_2^+ .

Example :- Which of the two: peroxide ion or superoxide ion has larger bond length ?

Solution :- The bond length of a molecule is related to its bond order. The larger the bond order, the smaller will be the bond length.

Superoxide ion, O_2^- :

$$O_2^{2-}$$
: KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^1$

Bond order =
$$\frac{8-5}{2} = 1\frac{1}{2}$$

Peroxide ion, O_2^{2-} :

 $O_2^{2-} \text{ KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^2$ Bond order = $\frac{8-6}{2} = 1$

Now, superoxide ion (O_2^{-}) has larger bond order than peroxide ion (O_2^{2-}), therefore, bond length of peroxide ion will be larger.

M.O. occupancy and molecular properties of homonuclear diatomic molecules of second period.

σ2p* _z						σ*2p _z			^
$\pi 2p_X^\star$, $\pi 2p_Y^\star$ [π [*] 2p _χ , π [*] 2p _γ	<u>+</u> +	† ↓ † ↓	
σ2p _z					¢↓	π2p _x . π2p _y	↑↓ ↑↓	↑↓↑↓	1
π2р _χ , π2р _у			† †	↑ ↓ ↑ ↓	↑ ↓ ↑ ↓	σ2p _z		^	^
σ2s '		^	↑ ↓	₽	↑ ↓	σ*2s	^	↑ ↓	≜ ↓
025	↑ ↓	^	≜	₽	≜ ↓	σls.	↑↓	•	† ↓
Molecule	Li ₂	Be ₂	B ₂	C ₂	Ng	and the second	02	F ₂	Ne ₂ ,
Bond order	1.000	0	1	2	3	1.1.1.1	2	and a	ó
Bond energy (kJ mol ⁻⁵)	110	(Person) Synthesis	290	620	945		498	159	na ann an Talas
Bond length (pm)	265		159	131	110	States a	121	143	-
Paramagnetic (P) Diamagnetic (D)	D	-	P	D	D		P	D	

Molecular orbital electronic configurations of some common hetero nuclear molecules

The configurations of heteronuclear molecules (containing different atoms) can be written in a similar manner as in case of homonuclear molecules.

(i) NO : Total number of electrons = 7 + 8 = 15
NO : KK(
$$\sigma 2s$$
)² ($\sigma * 2s$)²($\pi 2p_x$)² ($\pi 2p_y$)²($\sigma 2p_z$)²($\pi * 2p_x$)¹
Bond order = $\frac{8 \cdot 3}{2} = 2\frac{1}{2}$
(ii) NO⁺ : KK($\sigma 2s$)² ($\sigma * 2s$)²($\pi 2p_x$)² ($\pi 2p_y$)²($\sigma 2p_z$)²
Bond order = $\frac{8 \cdot 2}{2} = 3$
(iii) CN : Total number of electrons = 6+7= 13
CN : KK($\sigma 2s$)² ($\sigma * 2s$)²($\pi 2p_x$)² ($\pi 2p_y$)²($\sigma 2p_z$)¹
Bond order = $\frac{7 \cdot 2}{2} = 2\frac{1}{2}$
(iv) CN⁻ : KK($\sigma 2s$)² ($\sigma * 2s$)²($\pi 2p_x$)² ($\pi 2p_y$)²($\sigma 2p_z$)²
Bond order = $\frac{8 \cdot 2}{2} = 3$
(v) CO : Total number of electrons = 6 + 8 = 14

Bond order =
$$\frac{8-2}{2} = 3$$

Table: Summary of MO electronic configurations for some heteronuclear diatomic molecules.

Valence electrons	Species	MO electronic configuration	Bond order	Bond dissociati on energy (kJ mol ⁻¹)	Bond length (Å)
8	BN	KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$	2	358	128 pm
9	BO CN *CO ⁺	KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_z)^1$	2.5	773 786	120 PM 117 pm 111 pm
10	*CO NO ⁺	KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$	3	1067	113 pm 106 pm
11	NO	KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2 (\pi^* 2p_x)^1$	2.5	667	115 pm

* It may be noted that in CO and CO+, σ *2s MO is higher in energy than

 $\pi 2 p_x$, $\pi 2 p_y$ and $\sigma 2 p_z$ MOs.

4.20 Comparison of Valence Bond and Molecular orbital theories Points of resemblance

- (i) According to both the theories, the bond results from the overlap of atomic orbitals.
- (ii) According to both the theories, the atomic orbitals overlapping each other must be of the same energy and must have same symmetry.
- (iii) According to both theories, the electron charge resides in the region between the atomic nuclei.
- (iv) Both the theories account for directional nature of the bond.
- (v) Both the theories predict the non-existence of helium molecule (He₂) and neon molecule (Ne₂)
- (vi) Both the theories are approximate.

Table: Points of difference-

	Valence Bond Theory		Molecular Orbital Theory
i.	The atomic orbitals of the combining atoms retain a large amount of their individual	i.	Atomic orbitals of the combining atoms lose their individual identity in the resulting molecular
	character.		orbital.
ii.	Resonance plays an important role in this theory.	ii.	Resonance has no role in this theory.
iii.	It fails to explain paramagnetism of O_2	iii.	It explains easily the paramagnetism of O ₂
iv.	Mathematically, it is simple to	iv.	It is difficult to apply.
	apply.	ν.	It explains the possibility and
v.	It fails to explain the possibility and existence of H_2^+		existence of H ₂ ⁺

Molecular bonding

There are four basic types of bonds that can be formed between two or more (otherwise non-associated) molecules, ions or atoms. Intermolecular forces cause molecules to be

attracted or repulsed by each other. Often, these define some of the physical characteristics (such as the melting point) of a substance.

- A large difference in electronegativity between two bonded atoms will cause **dipoledipole interactions**. The bonding electrons will, on the whole, be closer to the more electronegative atom more frequently than the less electronegative one, giving rise to partial charges on each atomic center, and causing electrostatic forces between molecules.
- A **hydrogen bond** is effectively a strong example of a permanent dipole. The large difference in electronegativities between hydrogen and any of fluorine, nitrogen and oxygen, coupled with their lone pairs of electrons cause strong electrostatic forces between molecules. Hydrogen bonds are responsible for the high boiling points of water and ammonia with respect to their heavier analogues.
- The **London dispersion force** arises due to instantaneous dipoles in neighbouring atoms. As the negative charge of the electron is not uniform around the whole atom, there is always a charge imbalance. This small charge will induce a corresponding dipole in a nearby molecule; causing an attraction between the two. The electron then moves to another part of the electron cloud and the attraction is broken.
- A **cation-pi interaction** occurs between the negative charges of pi bonds above and below an aromatic ring and a cation.

4.21 Hydrogen bonding:

The attractive electrostatic force between a hydrogen atom (which is already covalently attached to a strong electronegative atom i.e., any of F, O, N and Cl upto least extent) and an electronegative atom (any out of F, O, N and Cl) is known as hydrogen bond. The hydrogen bond is of two types mainly: (1) Intramolecular H-bonding, (2) Intermolecular H-bonding.

Hydrogen bond is formed when a slightly positive hydrogen atom, attached covalently to strong electronegative atom A (*e.g.*, F, O or N) is held by a non-bonded electron pair of another atom B. The coordination number of hydrogen becomes two and it acts as a bridging atom between A and B.

Generally hydrogen bond is formed with only F, O and N atoms. Sometimes less electronegative atoms such as Cl, S etc., also take part in the formation of hydrogen bond. Hydrogen bond is denoted by dotted lines (.....). It can be defined as:

The attractive force that binds a hydrogen atom, which is already covalently attached with strongly electronegative atom of gain element, is known as hydrogen bond. The bond energy of hydrogen bond is 3--10 kcal/mole.

4.21.1 Types of Hydrogen Bonding

Three types of hydrogen bonding exist:

(i) Intermolecular hydrogen bonding (ii) Intramolecular hydrogen bonding

(iii) π -Hydrogen bonding

(i) Intermolecular hydrogen bonding. Intermolecular hydrogen bonding exists between two or more molecules of the same or different compounds.

(a) Homo-intermolecular hydrogen bonding. It is also termed as self-association. It refers to the association of two or more identical molecules e.g., association in alcohol, association in water, association in NH₃, association in HF etc.

(b) Hetero-intermolecular hydrogen bonding. It refers to the association of two different species. One which donates the lone pair of electrons is called electron donor or hydrogen acceptor, while the other which donates proton is called proton donor. Examples of hetero-intermolecular hydrogen bonding are as follows:



Due to intermolecular hydrogen bonding the molecules are associated together to form a cluster, which results in the increase in melting point and boiling point of the compound.

(ii) Intramolecular hydrogen bonding. When hydrogen bonding exists within the molecule it is called intramolecular hydrogen bonding. In such type of hydrogen bonding two groups of the same molecule link through hydrogen bond, forming a stable five or six membered ring structure **e.g.**, salicylaldehyde, *o*-chlorophenol, acetylacetone, ethylacetoacetate etc.



This intramolecular hydrogen bonding was first called chelation (after the Greek word "Chela" meaning, claw) because in the same molecule the formation of a ring hydrogen bonding is a pincer like action resembling the closing of a Crab's claw. Some more examples of intramolecular hydrogen bonding are:



(iii) π -Hydrogen bonding. Sometimes π -electrons of an olefin or aromatic system act as proton acceptor in hydrogen bonding. Such type of hydrogen bonding is called π -Hydrogen bonding. These are again of two types:

(a) Intermolecular π -hydrogen bonding. It occurs between two or more molecules of the same or different compounds. For example,

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(b) Intramolecular π -hydrogen bonding. This occurs between the groups of the same molecule. Hydrogen of a group (*e.g.*, -- OH) forms hydrogen bond with π -electrons of an aromatic ring or an olefin bond. For example,



4.21.2 Properties of Hydrogen Bond

(i) Hydrogen bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms.

(ii) Bond energy of hydrogen bond is in the range of 3-10 kcal/mole. Thus hydrogen bond is a weaker bond than a covalent bond (bond energy of a covalent bond is 50-100 kcal/mole). But it is stronger than Van der Waal's forces (1 kcal/mol).

(iii) In the formation of hydrogen bond electron pair is not shared. In this respect it is different from the covalent bond.

(iv) The strength of hydrogen bond depends upon the electro negativity of the atom A to which hydrogen atom is attached with a covalent bond. As the electronegativity increases, strength of hydrogen bond increases. Thus HF will form most strong hydrogen bond as fluorine is the most electronegative atom.

(v) Typical hydrogen bond is linear. Angular hydrogen bonds exist in solids or in intermolecular hydrogen bonding.

(vi) The bond length A -- H and B -- H are generally different except $HF_2^{-}(F -- H -- F)$ which is a symmetrical ion.

4.21.3 Significance of hydrogen bonding in biological systems.

Water present in plants and animals (which is more than 50% by weight) is attached to the proteins by hydrogen bonding. Similarly, the structures of proteins and nucleic acids are stabilized by hydrogen bonding.

Example: Arrange the following as stated.

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"Increasing strength of hydrogen bonding (X-H-X)."

O, S, F, Cl, N

Solution: Increasing strength of hydrogen bonding

(X-H-X) is as:

S < Cl < N < O < F

H-bond strength increases with increasing electron affinity and decreasing atomic size.

Additional Useful Information

Born-Haber Cycle For Lattice Enthalpies

Born and Haber (1919), proposed a method to relate the lattice enthalpy of an ionic crystal to other thermodynamic data. This is known as **Born –Haber cycle.** We have learnt that

the formation of bond takes place only if there is decrease in enthalpy. As an example, let us consider the energy changes during the formation of sodium chloride from metallic sodium and chlorine gas and the formation of a Born-Haber cycle.

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

The overall process is thought to take place in the following steps:

(i) **Conversion of metallic sodium into gaseous sodium atoms.** The sodium atom can lose its electron only in the gaseous state and has to be sublimated. The energy required for the conversion of one mole of metallic sodium into gaseous sodium is called **enthalpy of sublimation.** It is represented by **`S'.**

 $Na(s) + S \longrightarrow Na(g); S =$ Enthalpy of Sublimation

(ii) Dissociation of chlorine molecules into chlorine atoms. Each chlorine molecule consists of two atoms of chlorine. The amount of enthalpy required for the conversion of gaseous chlorine molecule into atoms, is known as enthalpy of dissociation. It is represented by 'D'

$$Cl_2(g) + D \longrightarrow 2Cl(g); D = \text{Enthalpy of Dissociation}$$

 1 mole 2 mole

Thus, the enthalpy required for producing one mole of gaseous chlorine atoms is D/2.

$$\frac{1}{2}Cl_2(g) + \frac{D}{2} \longrightarrow Cl(g)$$

(iii) Conversion of gaseous sodium atoms into sodium ions. The amount of enthalpy required to convert one mole of gaseous sodium atoms into sodium ions in the gaseous state is called ionization enthalpy. It is denoted by I.E.

$$Na(g) + IE \longrightarrow Na^+(g) + e^-(g)$$

(iv) Conversion of gaseous chlorine atoms into gaseous chloride ions. The amount of enthalpy released during the conversion of one mole of gaseous chlorine atoms into chloride ions is known as **electron gain enthalpy**. It is denoted by Δ_{eg} H.

$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g) + \Delta_{\rho g}H$$

(v) Combination of oppositely charged ions to form a solid crystal. The oppositely charged Na⁺ and Cl⁻ ions attract each other to form solid NaCl crystal. This leads to the release of energy. The amount of energy released when one mole of solid crystalline compound is obtained from gaseous ions of opposite charges is called lattice enthalpy. It is denoted by 'U'.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) + U = Lattice enthalpy$$

The overall energy change may be expressed as:

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

The enthalpy change for this reaction is called enthalpy of formation and it may be denoted as $\Delta_f H$.

The various steps may be represented in the form of Born-Haber cycle, as shown in the figure.

According to Hess's law, the enthalpy of formation of one mole sodium chloride should be the same irrespective of the fact whether it takes place directly in one step or though a number of steps as shown above. Thus,

$$\begin{split} \Delta_f H &= S + \frac{1}{2} D + IE + \Delta_{eg} H + U \\ or \qquad U &= \Delta_f H - S - \frac{1}{2} D - IE - AE \end{split}$$

Thus, lattice enthalpy can be calculated by knowing the values of different quantities. While using the above relation for lattice enthalpy, **a special care should be taken for the signs of various quantities**. Positive sign is used for enthalpies absorbed and negative sign is used for enthalpies released. For NaCl, the various values are given below:

Enthalpy of sublimation of sodium (S) = 108.5 kJ mol⁻¹ Enthalpy of dissociation of Cl₂ (D) = 243.0 kJ mol⁻¹ Ionisation enthalpy of sodium (IE) =495.2 kJ mol⁻¹ Electron gain enthalpy of chlorine ($\Delta_{eg}H$) = -348.3 mol⁻¹ Enthalpy of formation of NaCl ($\Delta_{f}H$) = -381.8 kJ mol⁻¹ Substituting the various values, we get $U = (-381.8) - 108.5 - \frac{1}{2}(243.0) - 495.2 - (-348.3)$ = -758.7 kJ mol⁻¹ \therefore Lattice enthalpy of NaCl crystal =-758.7 kJ mol⁻¹

In general, Born-Haber cycle for a simple ionic solid such as MX may be represented as:

Here ΔH_1° , ΔH_2° , ΔH_3° , ΔH_4° and ΔH_5° are enthalpy changes respectively for

- (i) sublimation of M (s) to M(g)
- (ii) ionization of M(g) to $M^+(g)$
- (iii) dissociation of X_2 (g) to X (g)
- (iv) electron gain by X (g) to $X^{-}(g)$ and
- (v) lattice formation from M^+ (g) and X^- (g)

According to Born-Haber cycle,

$$\Delta_{f}H^{\circ} = \Delta H_{1}^{\circ} + \Delta H_{2}^{\circ} + \Delta H_{3}^{\circ} + \Delta H_{4}^{\circ} + \Delta H_{5}^{\circ}$$

Applications of Born-Haber Cycle

In addition to calculation of lattice enthalpies, Born-Haber cycle has been used for the calculation of many properties. Some of the important uses are given below:

1. Calculation of enthalpy of formation.

Enthalpies of formation of unknown compounds can be easily calculated by making a Born-Haber cycle. The enthalpy of formation tells us about the stability of the compound. If the enthalpy of formation comes out to be negative, i.e., the reaction is exothermic, the compound formed, will be stable. On the other hand, if enthalpy of formation comes out to be positive, i.e., the reaction is endothermic, the formation of the compound will be highly unfavourable energetically. For example, it can be explained why NaCl₂ is not formed, though it is expected to have higher lattice enthalpy than NaCl. The enthalpy of formation for NaCl₂ by using Born-Haber cycle comes out to be highly positive.

2. Calculation of electron gain enthalpies.

The Born-Haber cycle can be used for the calculation of electron enthalpies of some elements which are otherwise very difficult to measure. Enthalpy of formation of a compound may be expressed as:

$$\Delta_f H = S + D + IE + \Delta_{eg} H + U$$

It may be rearranged as:

$$\Delta_{eg}H = \Delta_f H - S - D - IE - U$$

Using the above equation, electron affinity may be calculated.

Example : The thermo chemical data for the formation of argon chloride (ArCl) are given below:

$$Ar(g) + \frac{1}{2}Cl_2(g) \longrightarrow ArCl(g)$$

(i) Enthalpy of dissociation of chlorine = -243.0 kJ

(ii) Electron gain enthalpy of chlorine = -348.3 kJ

(iii) Ionisation enthalpy of argon= 1526.3 kJ

(iv) Lattice enthalpy of argon chloride = -703.0 kJ

Predicate, whether the formation of argon chloride is favorable or unfavorable?

Solution . The formation of argon chloride may be represented by the Born-Haber cycle:



The heat of formation, $\Delta_f H$ may be expressed as:

$$\Delta_f H = \Delta H_1 + \Delta H_2 + \Delta H_3 + U_0$$

Where $\Delta H_1 = 1526.3 \text{ kJ}$

$$\Delta H_2 = \frac{243.0}{2} = 121.5 \text{ kJ}$$

$$\Delta H_3 = -348.3 \text{ kJ}$$

$$U_0 = -703.0 \text{kJ}$$

$$\Delta_f H = 1526 + 121.5 - 348.3 - 703.0$$

= 596.5 kJ

Thus, the formation of hypothetical argon chloride is endothermic and therefore, it is **unfavorable.**

Born Lande Equation for Lattice Enthalpy

The lattice enthalpy of ionic solids can be calculated theoretically on the basis of Coulombic interaction between all of its ions present in the crystal. The first theoretical interpretation of lattice enthalpy was given by Born Lande known as **Born Lande equation**

$$U_{0} = -\frac{N_{A} \cdot AZ^{+} Z^{-} e^{2}}{4\pi\varepsilon_{0} r_{0}} \left(1 - \frac{1}{n}\right)$$

where $U_0 =$ lattice enthalpy,

 N_A = Avogadro constant,

- A = Madelung constant (which takes into account interactions with all other ions besides the nearest neighbours and depends upon the geometry of the crystal),
- **Z**⁺= charge on positive ion,
- **Z**⁻ = charge on negative ion,
- \mathbf{e} = charge on the electron,
- **n** = Born exponent (takes into account repulsive terms),
- $\pi = \text{constant} (3.14159),$
- ϵ_0 = vacuum permittivity and r_0 = interionic distance.

Quick Chapter Recap

- The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is called a **chemical bond**.
- The man cause of chemical combination is (i) tendency to acquire noble gas configuration and (ii) tendency to acquire minimum energy.

- The electrostatic force which holds the oppositely charged ions together is known as **ionic bond** or **electrovalent bond**.
- The number of electrons which an atom loses or gains is called electrovalency.
- The ionic compound is a three dimensional aggregation of positive and negative ions in an ordered arrangement called the **crystal lattice**. The crystal lattice is stabilized by the **enthalpy of lattice formation**.
- The bond formed by mutual sharing of electrons between combining atoms of the same or different elements is called **covalent bond**.
- A covalent bond in which both the electrons in the shared pair come from one atom is called **coordinate or dative bond.**
- The relative arrangement of the bonded atoms in a molecule is called **geometry of the molecule.**
- Valence Shell Electron Pair Repulsion Theory (VSEPR) helps to predict the geometry of molecule.
- According to **quantum theory of covalent bond**, the bond is formed by the overlapping of half filled atomic orbitals having electrons with opposite spins. The greater the overlapping. the stronger is the bond formed between two atoms.
- The hybridisation also helps to know the geometry of molecules.
- The tendency of an atom to attract the shared pair of electrons towards itself is called **electronegativity.**
- **Dipole moment.** A vector quantity defined as the product of charge developed on any of the atom in a bond and distance between the atoms.
- The molecules having dipole moment ($\mu > 0$) are called **polar molecules** while those having no dipole moment ($\mu = 0$) are called **non-polar molecules.** Even a non-polar molecule may have individual polar bonds in it.
- The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies and to give new set of orbitals of equivalent energies and shape is called **hybridisation**.
- When a molecule cannot be represented by a single structure but its characteristic properties can be described by two or more than two structures, then the actual structure is said to be resonance hybrid of these structures. This phenomenon is called **resonance**. The various contributing structures are called **resonating structures**.
- **Canonical form.** The contributing structures taken together contribute the resonating hybrid which represents the molecule or ion.
- The difference between the actual bond energy and the most stable of the resonating structures is called resonating structures is called **resonance energy**.
- MOs are formed by the combination of atomic orbitals of same symmetry and of nearly same energy.
- If z-axis is internuclear axis $2p_z$ orbitals combine to form σ MOs while $2p_x$ and $2p_y$ can combine to form π MOs.
- 2s orbitals may combine with $2p_z$ orbital but it cannot combine with $2p_x$ or $2p_y$ orbitals.
- Larger the bond order of a molecule, greater will its bond dissociation energy and smaller will be its bond length.
- Bond order and bond dissociation energy follow the order :

$$N_2 > N_2^+$$

$$O_2^+ > O_2^- > O_2^- > O_2^{2-}$$

• B₂ molecule is paramagnetic because of its MO electronic configuration : KK $(\sigma 2s)^2 (\sigma * 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$. In this case $\pi 2p_x$ and $\pi 2p_y$ MOs have lower

energy than $\sigma 2 p_z$ MO.

• Hydrogen bonds are formed in molecules in which hydrogen is bonded to slightly electronegative elements (such as F, O or N).

 C_2^{2-} (diamagnetic), O_2^- (paramagnetic) N_2^+ (B.O = $2\frac{1}{2}$) is more stable than O_2^- (B.O = $1\frac{1}{2}$). Both are paramagnetic.