

Chemical Bonding and Molecular Structure

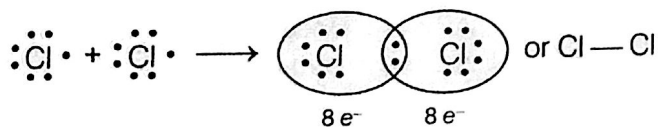
1. **Chemical Bond** It is defined as the force of attraction which holds various constituents (atoms, ions, etc.) together in different chemical species. The combining tendency of an element or ion is called its 'valency'.

2. Kossel-Lewis Approach to Chemical Bonding

According to Kossel and Lewis concept of bonding, an atom has a tendency to attain stable octet (inert gas configuration) by gaining, losing or sharing electrons.

3. **Covalent Bond** The bond formed by mutual sharing of electrons between the combining atoms of the same or different elements is called the covalent bond.

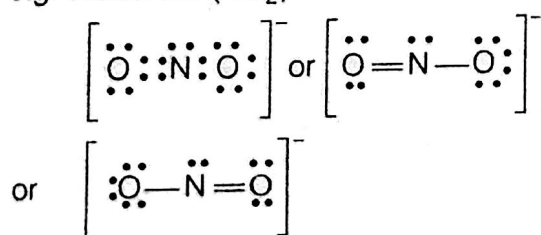
e.g. Formation of chlorine molecule.



4. Lewis Representation of Simple Molecules (Lewis Structures)

Representation of valence electrons is done by dots around the symbol of the element.

e.g. Nitrite ion (NO_2^-)



5. **Formal Charge on an Atom or an Ion** It is a factor which is based on a pure covalent view of bonding in which electron pairs are shared equally by neighbour atoms.

$$\text{FC} = \left[V - L - \frac{1}{2} S \right]$$

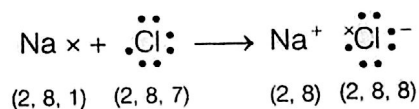
where,

FC = Formal charge on an atom in a Lewis structure
V = Total number of valence electrons in the free atom

L = Total number of non-bonding (lone pair) electrons

S = Total number of bonding (shared) electrons

6. **Ionic or Electrovalent Bond** It is formed by complete transfer of electrons from one atom to another. e.g. Formation of sodium chloride



Factors governing the formation of ionic bond are:

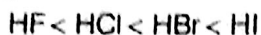
- (i) Low ionisation enthalpy of metal atom.
- (ii) High electron gain enthalpy of non-metal atom.
- (iii) High lattice enthalpy of the ionic compound formed which in turn depends upon
 - (a) charge on ions (greater is the charge, greater is the lattice enthalpy).
 - (b) size of the ion (smaller is the size, greater is the lattice enthalpy).

7. Bond Parameters

- (i) **Bond length** The equilibrium distance between the nuclei of two bonded atoms in a molecule is called the bond length.

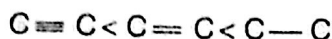
The various factors that affect bond length are as follows:

- (a) **Size of the atoms** The bond length increases with increase in the size of the atoms. Thus, the order of bond length of H—X bond is

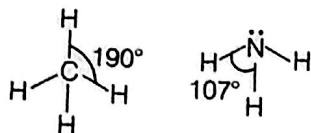


Similarly, C—C < Si—Si < Ge—Ge

- (b) **Bond multiplicity** The bond length decreases as the multiplicity of the bond increases. Thus, the carbon-carbon bond lengths follow the order



- (ii) **Bond angle** The angle between the orbitals containing bonded electron pairs around central atom in a molecule/complex ion is called the bond angle. e.g. C—H bond angle in CH₄, H—N—H bond angle in NH₃ are shown below:



- (iii) **Bond enthalpy** It is the amount of energy required to break one mole of bonds of a particular type between two atoms in gaseous state.

Its unit is kJ mol⁻¹.

$$\text{Bond enthalpy} \propto \frac{1}{\text{Size of atoms}}$$

$$\propto \frac{1}{\text{Number of lone pair(s) of electrons}}$$

$$\propto \text{Multiplicity of bond}$$

Greater the multiplicity of the bond, greater is the bond enthalpy.

e.g. H—H < O = O < N ≡ N.

- (iv) **Bond order** The number of bonds formed between the two atoms in a molecule is called the bond order.

e.g. The bond order of a few molecules are given below:

Molecule	H—H	O = O	N ≡ N	C ≡ O
Bond order	1	2	3	3
Bond order ∝ Bond enthalpy ∝	$\frac{1}{\text{Bond length}}$			

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

- (vi) **Dipole moment** It is a measurement of polarity in any molecule/compound/ion. It is defined as the product of charge (*q*) and distance between the charges (*r*). Dipole moment (μ) = *q* × *r*. Its unit is Debye (D). The dipole moment of symmetrical molecule is always zero.

8. Partial Ionic Character of Covalent Bond

- Electronegative difference between combining atoms = 1.7, then bond is 50% ionic and 50% covalent.
- Electronegativity difference > 1.7, ionic character in bond is more than 50%.
- Electronegativity difference < 1.7, ionic character in bond is less than 50%.

9. Partial Covalent Character in Ionic Bonds: Fajans' Rule

According to Fajans' rule, the covalent character will be favoured by

- small size of cation.
- large size of anion.
- high charge of cation and anion.
- the cation having 18-electrons shell.

10. Valence Shell Electron Pair Repulsion (VSEPR) Theory

According to this theory, all valence shell electron pairs surrounding the central atom arrange themselves in such a manner that they are as far away from each other as possible. There are two types of electron pairs around the central atom; bonding electron pairs, i.e. bond pair (*bp*) and non-bonding electron pairs, i.e. lone pair (*lp*). The strength of repulsion between the electron pairs varies as:

$$lp-lp > lp-bp > bp-bp$$

If central atom is linked to similar atoms and there are no lone pairs, the shape is symmetrical otherwise irregular. If A represents central atom, B bond pair, L lone pair, then AB₂ → linear, AB₃ → trigonal planar, AB₂L → V-shaped, AB₄ → tetrahedral, AB₃L → trigonal pyramidal, AB₅ → triangular bipyramidal, AB₄L → see-saw, AB₃L₂ → T-shaped, AB₂L₃ → Linear, AB₆ → octahedral, AB₅L → Square pyramidal, AB₄L₂ → square planar.

11. **Valence Bond Theory (VBT)** It explains bond formation in terms of overlapping of orbitals, e.g. the formation of H₂ molecule from two hydrogen atoms involves the overlapping of 1s-orbital of two H-atoms which are singly occupied. Because of orbital overlapping, the electron density between the nuclei increases which helps in bringing them closer. The overlapping of orbitals may result in two types of bonds, sigma (σ) and pi (π) bond.
12. **Concept of Hybridisation** (involving s, p, d and f-orbitals) Intermixing of orbitals of almost similar energy belonging to the same atom to form same number of orbitals of exactly equal energy is known as hybridisation.

The new orbital thus formed are known as hybrid orbitals. The hybridisation of the molecule can be determined by

$$H = \frac{1}{2} (V + Y - C + A)$$

Handwritten notes:
 σ or $\left[\begin{array}{l} \sigma \text{ bonds} \\ + \text{ lone pairs} \end{array} \right]$
 $+ \rightarrow \text{bond}$
 $+ \text{ single electron}$

where, V = valence shell electrons of the central metal atom
 Y = number of monovalent atom
 C = total positive charge
 A = total negative charge on the molecule

2	3	4	5	6	7
sp	sp ²	sp ³	sp ³ d	sp ³ d ²	sp ³ d ³

13. Geometry and Hybridisation of Molecules

Hybridisation	Number of electron pairs	Bond angle	Molecular geometry	Examples
sp	2	180°	Linear	BeCl ₂ , HgCl ₂ , ZnCl ₂
sp ²	3	120°	Trigonal planar	BF ₃ , AlF ₃
sp ³	4	109.5°	Tetrahedral	CH ₄ , NH ₄ ⁺ , CCl ₄
sp ³ d	5	90°, 120°	Trigonal bipyramidal	PCl ₅
sp ³ d ²	6	90°	Octahedral	SF ₆

14. Molecular Orbital Theory (MOT)

- (i) **Bonding molecular orbitals** The molecular orbitals obtained by the addition of atomic orbitals are called bonding molecular orbitals (BMOs) and are represented by σ and π .
- (ii) **Antibonding molecular orbitals** The molecular orbitals obtained by the subtraction of atomic orbitals are called antibonding molecular orbitals (AMOs) and are represented by σ^* and π^* .

The electronic configuration of molecular orbitals (MO) are written in the following manner:

In the case of O₂ and F₂,

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x \approx \pi 2p_y < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$$

However, the above sequence of energy levels is not true in case of remaining molecules, like Li₂, Be₂, B₂, C₂, N₂. For these molecules, the increasing order of energies of various molecular orbitals is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x \approx \pi 2p_y < \sigma 2p_z < \pi^* 2p_x \approx \pi^* 2p_y < \sigma^* 2p_z$$

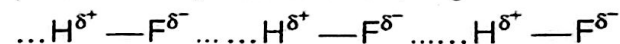
Stability and magnetic character of molecules/molecular ions

If BO is positive, molecule or ion is stable otherwise not. Greater the bond order, greater is the stability and shorter is the bond length. Further, if all electrons are paired, the species is diamagnetic and if some unpaired electrons are present, the species is paramagnetic.

$$\text{Bond order} = \frac{1}{2} (\text{Number of electrons in BMOs}) - (\text{Number of electrons in AMOs})$$

$$\text{BO} = \frac{1}{2} (N_b - N_a)$$

15. **Hydrogen Bonding** The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule, is called hydrogen bonding. It is represented by dotted lines, e.g.



Types of H-Bonds

There are two types of H-bonds:

- (i) **Intermolecular hydrogen bond** Such bond exists between two different molecules of the same or different compounds.
- (ii) **Intramolecular hydrogen bond** Such bond exists when hydrogen atom is internally bonded though H-bond with highly electronegative (F, O, N) atoms present within the same molecule.