

8. Nature of Chemical Bond

Chemical bond:

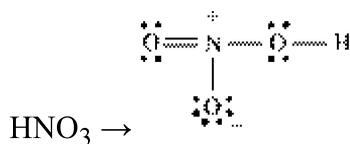
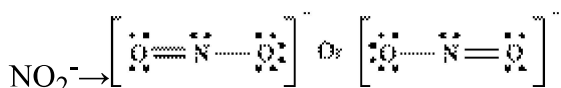
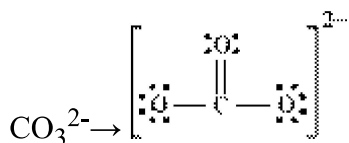
Chemical bond is the attractive force, which holds various constituents (such as atoms, ions) together in different chemical species.

Octet rule:

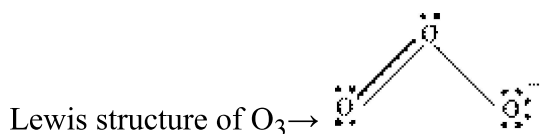
Atoms tend to gain, lose, or share electrons so as to have eight electrons in their valence shells.

Lewis dot Structure:

Representation of molecules and ions in terms of the shared pairs of electrons and the octet rule



Formal charge:



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



$$\text{F.C. on the O}^{-1} = 6 - 2 - \frac{1}{2}(6) = +1$$

$$\text{F.C. on the O}^{-2} = 6 - 4 - \frac{1}{2}(4) = 0$$

$$\text{F.C. on the O}^{-3} = 6 - 6 - \frac{1}{2}(2) = -1$$

Limitations of the octet rule:

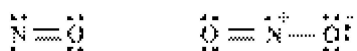
- Incomplete octet of the central atom

E.g. BeH_2 , LiCl , BCl_3



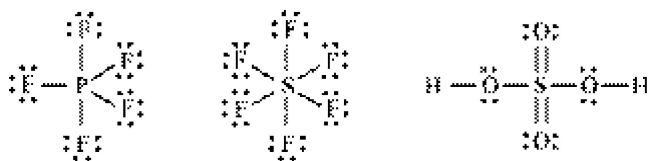
- Odd electron molecules

E.g. NO , NO_2



- Expanded octet

E.g. PF_5 , SF_6 , H_2SO_4



- Some other drawbacks:

1. It is based upon chemical inertness of noble gases. However, some noble gases can combine to form compounds such as XeF_2 , KrF_2 , XeOF_2 , etc.
2. Does not account for the shape of molecules

3. Does not explain the relative stability of molecules

Conditions for Formation of Covalent Bond

- Presence of four or more electrons in the outermost shell of an atom (exception H, Be, B and Al)
- High electronegativity of both the atoms
- High electron affinity for both the atoms
- High ionisation energy of both the atoms
- Electronegativity difference between combining atoms should be zero or very low

Ionic or Electrovalent Bond: Formation of ionic compound depends upon ease of formation of positive and negative ions

and also on arrangement of positive and negative ions.

Ionisation enthalpy ($\Delta_i H$) and electron gain enthalpy ($\Delta_{eg} H$):

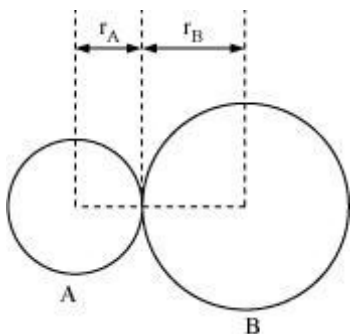
The ionisation enthalpy is the enthalpy change when a gas phase atom in its ground state loses an electron and the electron gain enthalpy is the enthalpy change when a gas phase atom in its ground state gains an electron.

Lattice enthalpy:

The energy required to separate completely one mole of a solid ionic compound into gaseous constituent ions is called the lattice enthalpy of the solid.

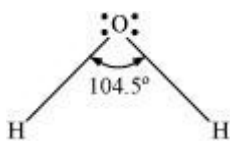
Bond parameters:

- Bond length → Equilibrium distance between the nuclei of two bonded atoms in a molecule

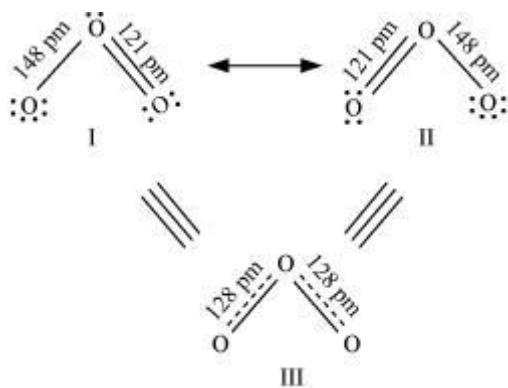


$$\text{Bond length (R)} = r_A + r_B$$

- Bond angle → Angle between the bonds around the central atom in a molecule/complex ion



- Bond enthalpy → Energy required to break one mole of a particular type of bond between two atoms in gaseous state
- Bond order → Number of bonds between two atoms in a molecule
- Resonance structures → Equivalent Lewis structures (example: ozone)



Here, I and II are resonance structures while III is the resonance hybrid.

- Polarity of bonds →

$$\text{Dipole moment } (\mu) = \text{Charge } (Q) \times \text{Distance of separation } (r)$$

Dipole moment is usually expressed in Debye units (D).

$$1\text{D} = 3.33564 \times 10^{-30} \text{ C m}$$

- The bonds that are formed by sharing electrons are known as **covalent bonds**. Covalently bonded molecules have strong intermolecular forces, but intramolecular forces are weak.
- Carbon has four valence electrons and requires four more electrons to complete its octet. Therefore, it is capable of bonding with four other atoms of carbon or atoms of other elements having a valency of 1.
- Some properties of covalent compounds are:
 - Covalent compounds are non-conductors of electricity.
 - They also have low melting and boiling points.
 - These compounds mostly exist as liquids or gases at room temperature.
- Polar covalent compounds: A covalent bond formed between two different atoms, with different electronegativities is known as **polar covalent bond**. For example, hydrogen chloride molecule
- $\text{H}^{\delta+} \text{---} \text{Cl}^{\delta-}$
- Non-polar covalent compounds: A covalent bond formed between two like atoms, is known as **Non-polar bond**. For example, hydrogen molecule
- $\text{H} \text{-----} \text{H}$
- **Coordinate bond**: It is formed when the shared pair of electrons is provided by one of the two atoms and shared by both.
- Conditions for formation of coordinate bond:
 - Presence of at least one lone pair of electrons on any of the two atoms. This atom acts like a donor.
 - Shortage of a lone pair of electron on the second atom. This atom acts like an acceptor.

VSEPR Theory:

The repulsive interaction of electron pairs decrease in the order:

$$\text{Lone pair (lp) - Lone pair (lp)} > \text{Lone pair (lp) - Bond pair (bp)} > \text{Bond pair (bp) - Bond pair (bp)}$$

Valence bond theory:

It considers the formation of a chemical bond by the overlapping of atomic orbitals of the participating atoms.

Types of overlapping and nature of covalent bonds:

There are two types of covalent bonds – Sigma (σ) and Pi (Π).

- Sigma (σ) bond (formed by head-on overlapping)

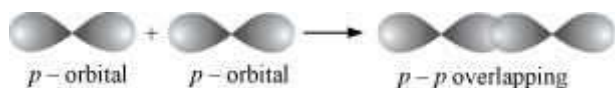
s-s overlapping



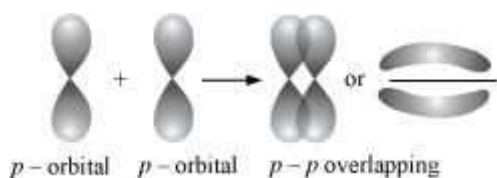
- *s-p* overlapping



- *p-p* overlapping



- Pi (Π) bond (formed by sidewise overlapping)



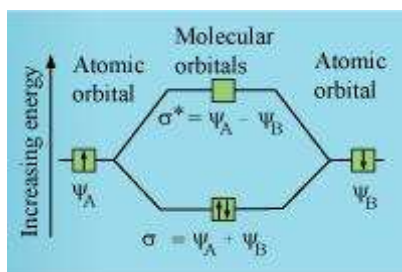
σ bond is stronger than Pi (Π) bond.

1: Process of intermixing of the orbitals of slightly different energies

Hybridisation type	Shape of molecules/ions	Example
sp	Linear	BeCl_2
sp^2	Trigonal planar	BCl_3
sp^3	Tetrahedral	CH_4
dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$
sp^3d	Trigonal bipyramidal	PCl_5
sp^3d^2	Square pyramidal	BrF_5
d^2sp^3	Octahedral	SF_6

Molecular orbital theory

Linear combination of Atomic Orbitals (LCAO)



Energy levels for molecular orbitals -

- Increasing order of energies of various molecular orbitals for O_2 and F_2 :

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

- Increasing order of energies of various molecular orbitals for Li_2 , Be_2 , B_2 , C_2 , and N_2 :

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

Where,

N_b = Number of electrons occupying bonding orbitals

N_a = Number of electrons occupying antibonding orbitals.

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

- The bond length decreases as bond order increases.
- If all the molecular orbitals in the molecule are doubly occupied, then the molecule is diamagnetic; and if one or more of the molecular orbitals are singly occupied, then the molecule is paramagnetic.

Hydrogen Molecule (H_2)

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

Helium Molecule (He_2)

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

Lithium Molecule (Li_2)

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

Beryllium Molecule (Be_2)

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4 - 4}{2} = 0$$

Carbon Molecule (C_2)

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

Oxygen Molecule (O₂)

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

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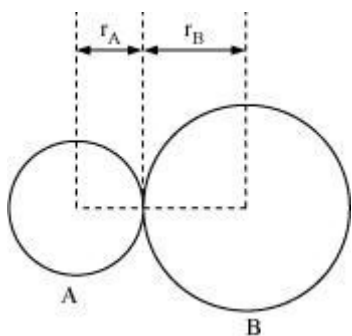
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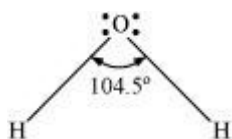
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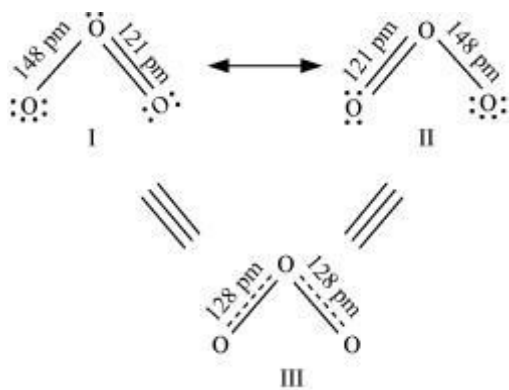


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