

Chemical Bonding and Molecular Structure

Chemical bond:

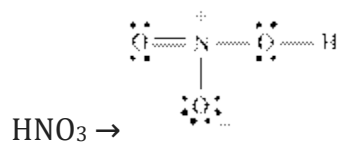
Chemical bond is the attractive force, which holds various constituents (such as atoms, ions) together in different chemical species.

Octet rule:

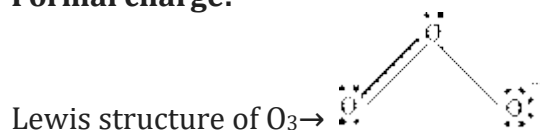
Atoms tend to gain, lose, or share electrons so as to have eight electrons in their valence shells.

Lewis dot Structure:

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



Formal charge:



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

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

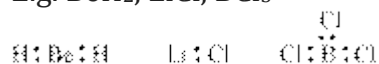
$$\text{F.C. on the O}^{-2} = 6 - 4 - \frac{1}{2}(4) = 0$$

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

Limitations of the octet rule:

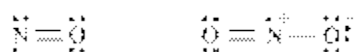
- Incomplete octet of the central atom

E.g. BeH_2 , LiCl , BCl_3



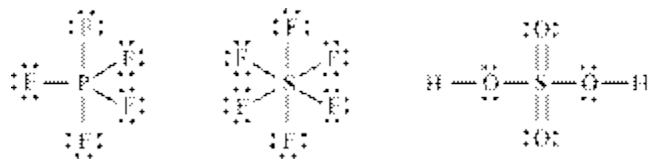
- Odd electron molecules

E.g. NO, NO₂



- 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 ($\Delta_{eg} H$):

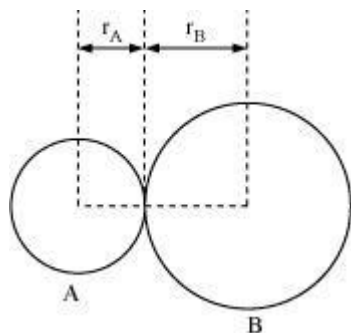
The ionisation enthalpy is the enthalpy change when a gas phase atom in its ground state loses an electron and the electron gain enthalpy is the enthalpy change when a gas phase atom in its ground state gains an electron.

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.

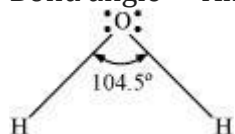
Bond parameters:

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

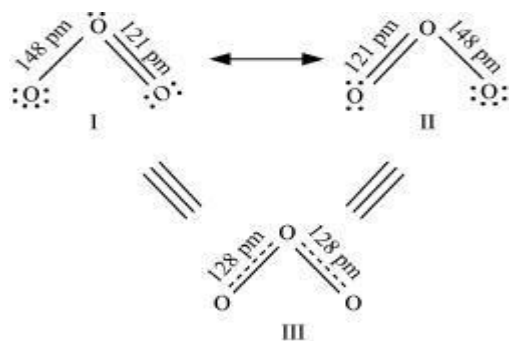


$$\text{Bond length (R)} = r_A + r_B$$

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



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



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

- Polarity of bonds →
Dipole moment (μ) = Charge (Q) \times Distance of separation (r)
Dipole moment is usually expressed in Debye units (D).
 $1D = 3.33564 \times 10^{-30} \text{ C m}$

VSEPR Theory:

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

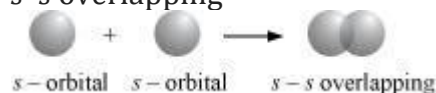
Valence bond theory:

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

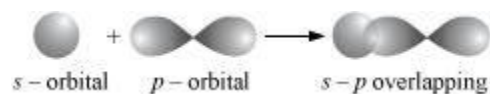
Types of overlapping and nature of covalent bonds:

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

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



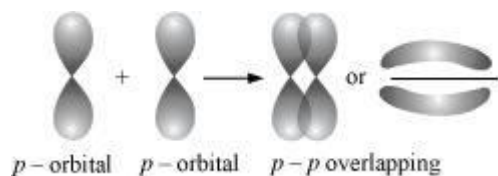
- $s-p$ overlapping



- $p-p$ overlapping



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



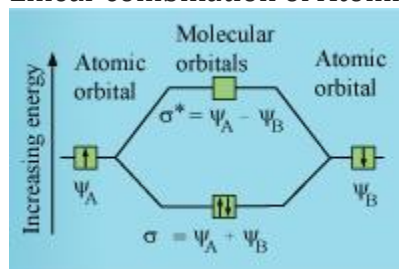
Sigma (σ) bond is stronger than Pi (Π) bond.

Hybridisation: 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)

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

- Bond order

Helium Molecule (He₂)

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

Lithium Molecule (Li₂)

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

Beryllium Molecule (Be₂)

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

Carbon Molecule (C₂)

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

Oxygen Molecule (O₂)

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

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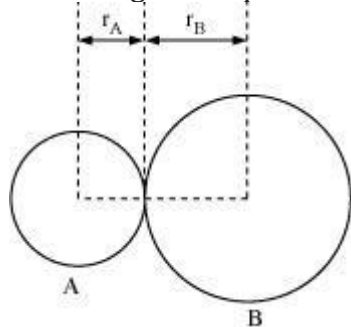
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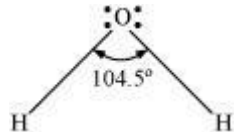
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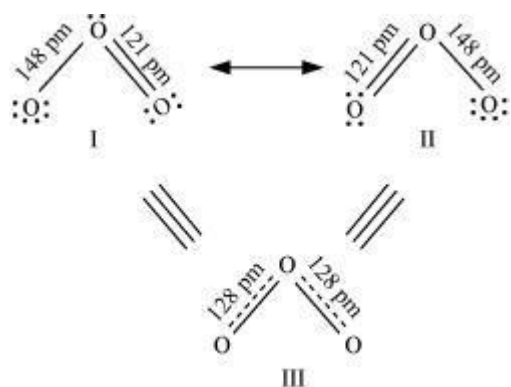


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