

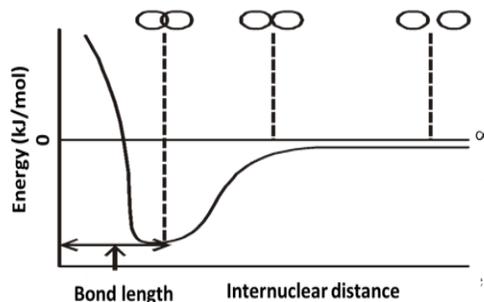


Chemical Bonding and Molecular Structure

Chemical bond is defined as the attractive force acting between two or more atoms in a molecule involving redistribution of electrons among them to hold them together in a stable configuration. This process accompanied by decrease in energy. Therefore, decrease in energy \propto strength of the bond.

Reasons for the formation of a Chemical Bond:

- **Minimum Energy concept:** When two atoms approach each other, both attraction and repulsion take place between the nucleus and electrons of atoms. When the attractive forces outweigh the repulsive forces, the potential energy of the system becomes minimum and the bond forms.



- **Octet rule (Lewis and Kossel theory):** Atoms tend to complete their outermost orbit to acquire the stable noble gas electronic configuration by transfer or sharing of electrons in their outermost orbit.

Lewis symbol:

Lewis symbol represents valence electrons of an element as a dot. The number of dots help to calculate the group valence of the element concerned. E.g., Li·, H·, He:

Exceptions of Octet Rule:

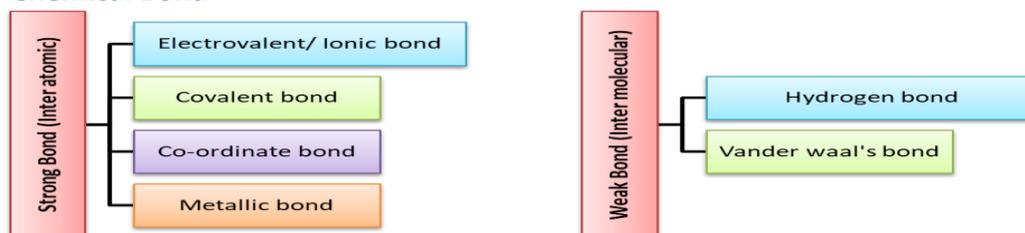
- **Electron Deficient Species:** The central atom of these molecules has less than 8 electrons in outermost shell. E.g.: BeCl_2 , BF_3 , AlCl_3
- **Odd Electron Species:** Molecules like NO_2 , NO , O_2^- , ClO_2^- etc. violate this rule as they have a non-bonding unpaired electron.
- Noble gases like Xe and Kr form a number of compounds with oxygen and fluorine such as XeF_2 , XeOF_2 , KrF_2 etc. Octet Rule does not account for the shape of these molecules.
- **Transition metal ions:** These have 9 to 18 electrons in outermost shell. Eg: Cr^{3+} , Mn^{2+} , Cu^+ .
- **Electron Efficient Species:** Molecules like PCl_5 , SF_6 , IF_7 , SF_4 , XeF_4 have more than eight electrons around the central atom. These compounds also known as hypervalent

Chemical Bonding and Molecular Structure

compounds.

Formal Charge: The charge assigned to an atom in a molecule, assuming that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity. It is given as: $FC = VE - [LPE - 1/2(BE)]$, where FC = formal charge, VE = number of valence electrons on the free atom, LPE = number of lone pair electrons on the atom in the molecule, and BE = number of bonding (bond pair) electrons.

Types of Chemical Bond



Ionic Bond or Electrovalent Bond:

- Involves complete transfer of e^- s from electropositive to electronegative element. Eg: NaCl, $MgCl_2$ etc.
- The number of electrons lost or gained during the formation of bond is termed as electro valency of the element.
- Metal is generally s-block having low ionization energy (IE) and non-metal is p-block having high electron affinity (EA).
- High lattice energy.
- Difference in electronegativity (EN) is >1.7 for the formation of ionic bond.
- Strongest bond is formed between elements of IA & VII A due to large EN difference.
- From IA \rightarrow Cs & from VIIA \rightarrow F form strongest ionic bond.

Covalent Bond:

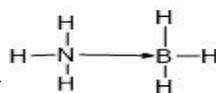
- Involves mutual sharing of one (single bond), two (double bond) or three (triple bond) electrons between the combining atoms. E.g.: CH_4 , N_2 , CO_2 etc.
- Number of electrons pairs an atom share in combination with other atoms in a molecule is called covalency. E.g.: covalency of H in $H_2O=1$, O in $CO_2=2$ etc.
- Combining atoms have high IE, high EA and zero or almost equal EN difference.
- Two types: polar covalent and non-polar covalent compounds.

Coordinate Covalent Bond or Dative Bond:

- Both electrons for sharing between two atoms are contributed by one atom only. In terms of orbital theory, it involves overlapping between empty and completely filled atomic orbitals.
- The donor atom donates electron pair whereas the acceptor accepts the electron pair.
- The bond is represented by an arrow (\rightarrow) pointing head towards the acceptor.

Chemical Bonding and Molecular Structure

E.g.: SO_2 , H_3O^+ , NH_3 and BF_3 form addition product

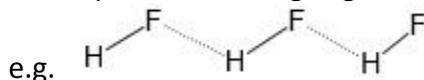


Metallic bond:

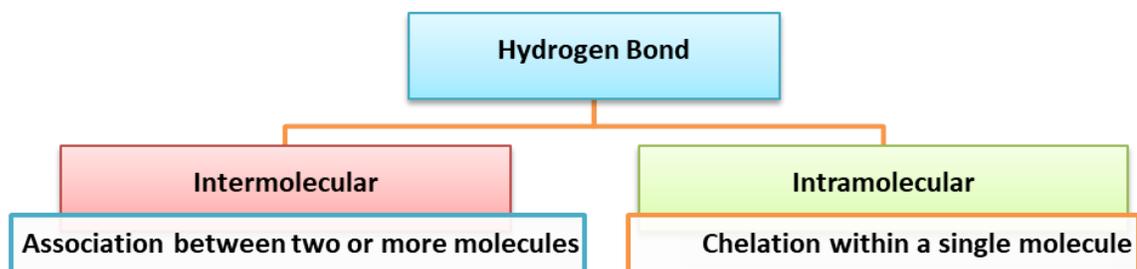
- The constituent particles are metals floating in a sea of electrons. Bond is formed by electrostatic force of attraction between conduction electrons and positively charged metal ions (Kernels). E.g.: Na(s) , Cu(s) etc.

Hydrogen Bond:

- Formed due to electrostatic attraction between hydrogen atom of one molecule and highly electronegative atom (F, O and N) of another molecule of the same or different species. It is represented as zig-zag chains with hydrogen bond shown by dotted lines.



- Depending on electronegativity of atom involved in H-bonding, the order of bond strength is $\text{H}\cdots\text{F} > \text{H}\cdots\text{O} > \text{H}\cdots\text{N}$



Vander Waal's Forces:

Attractive forces between uncharged molecules are known as van der Waals forces.

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory):

- Predict geometry of molecules based on the following repulsions between electrons pairs: lone pair - lone pair repulsion ($\text{lp} - \text{lp}$) $>$ lone pair - bond pair ($\text{lp} - \text{bp}$) $>$ bond pair - bond pair ($\text{bp} - \text{bp}$).

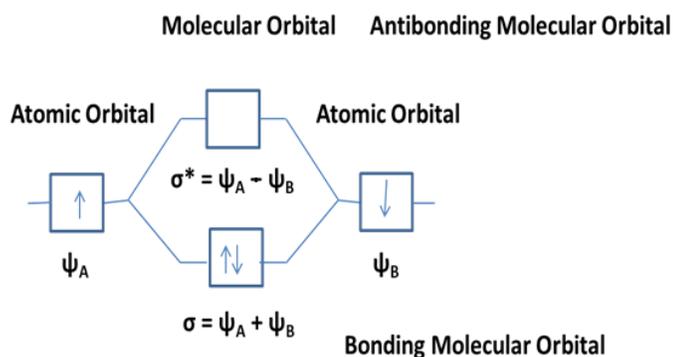
Valence Bond Theory:

- Overlapping of two half filled atomic orbitals having electrons with opposite spin results in covalent bond formation.
- Overlapping occurs either coaxially forming stronger sigma bond (σ -bond) or collaterally forming weaker pi - bond (π -bond).
- σ -bond involves overlap of atomic orbitals in 3 ways: s-s, s-p, p-p (axial).
- π -bond involves overlap of unhybridized p-p orbitals laterally (sideways).
- The strength of σ -bond depends upon the extent of overlapping between atomic orbitals. It follows the following order: $\text{p} - \text{p} > \text{s} - \text{p} > \text{s} - \text{s}$.

Chemical Bonding and Molecular Structure

Molecular Orbital Theory or Hund- Mulliken Theory:

- Atomic orbitals (A.O) combine to form the molecular orbitals (M.O).
- Number of M.O is equal to number of A.O involved.
- Formation of M.O is by LCAO method (linear combination of atomic orbitals) i.e. by addition or subtraction of wave functions of individual orbitals.
- M.O of lower energy is known as bonding M.O (BMO) and of higher energy is known as antibonding M.O (ABMO).
- Electron filling takes place according to Aufbau rule, Pauli's exclusion principle and Hund's rule.



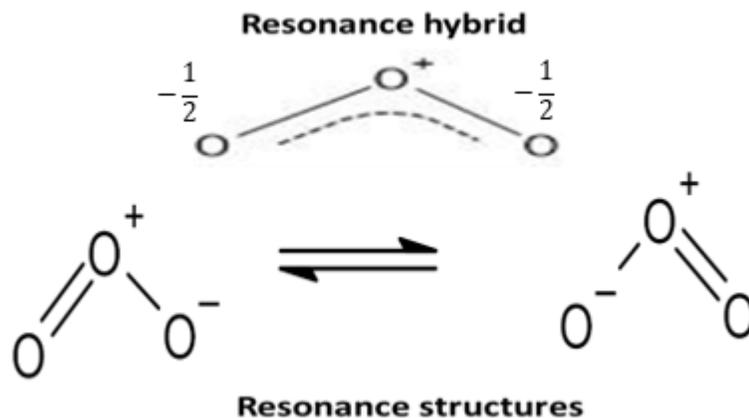
Hybridisation: Process in which redistribution of energy takes place by intermixing of atomic orbitals of slightly different energies resulting in the formation of same number of new atomic orbitals of equivalent energy and shape. The new atomic orbitals are termed hybrid atomic orbitals.

Types of hybridization with atomic orbitals involved, shape and examples

Hybridization	Atomic Orbitals	Shape	Example
sp	s+p	Linear	BeCl ₂
sp ²	s+p (2)	Trigonal planar	BCl ₃
sp ³	s+p (3)	Tetrahedral	H ₂ O
dsp ²	d+s+p (2)	Square planar	[Ni(CN) ₄] ²⁻ , [Pt(Cl) ₄] ²⁻
sp ³ d	s+p (3) +d	Trigonal bipyramidal	PF ₅ , PCl ₅
sp ³ d ²	s+p (3) +d (2)	Square pyramidal	BrF ₅
sp ³ d ² d ² sp ³	s+p (3) +d (2) d (2) +s+p (3)	Octahedral	SF ₆ , [CrF ₆] ³⁻ [Co (NH ₃) ₆] ³⁺

Resonance: Two or more alternative forms of a molecule represented by double headed arrow and showing the movement of valence electrons from one position to another. The actual structure is the resonance hybrid and its alternative forms are called resonating or canonical structures. E.g.:

Chemical Bonding and Molecular Structure



Bond parameters:

Bond length: Equilibrium distance between the nuclei of two bonded atoms in a molecule.

Bond angle: The angle between two adjacent bonds around the central atom in a molecule or complex ion.

Bond order: Number of shared electron pairs between two atoms in a molecule.

Bond enthalpy: Amount of energy required to break one mole of bonds of a particular type between two atoms in gaseous state.

Bond order \propto Bond enthalpy \propto 1/bond length