

CHEMICAL BONDING

Chemical Bond :

In the process each atom attains a stable outer electronic configuration of inert gases.

Ionic or Electrovalent Bond :

The formation of an ionic compound would primarily depends upon :

* The ease of formation of the positive and negative ions from the respective neutral atoms.

* The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

Conditions for the formation of ionic compounds :

- (i) Electronegativity difference between two combining elements must be larger.
- (ii) Ionization enthalpy ($M(g) \rightarrow M^+(g) + e^-$) of electropositive element must be low.
- (iii) Negative value of electron gain enthalpy ($X(g) + e^- \rightarrow X^-(g)$) of electronegative element should be high.
- (iv) Lattice enthalpy ($M^+(g) + X^-(g) \rightarrow MX(s)$) of an ionic solid must be high.

Lattice Enthalpy :

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

Factors affecting lattice energy of an ionic compound :

- (i) Lattice energy $\propto \frac{1}{r_+ + r_-}$ where $(r_+ + r_-)$ = Inter-ionic Distance.
- (ii) Lattice energy $\propto Z_+, Z_-$
 $Z_+ \Rightarrow$ charge on cation in terms electronic charge.
 $Z_- \Rightarrow$ charge on anion in terms electronic charge.

Determination of lattice energy :

Born-Haber Cycle :

It inter relates the various energy terms involved during formation of an ionic compound.

It a thermochemical cycle based on the Hess's law of constant heat summation.



Hydration :

All the simple salts dissolve in water, producing ions, and consequently the solution conduct electricity. Since Li^+ is very small, it is heavily hydrated. This makes radius of hydrated Li^+ ion large and hence it moves only slowly. In contrast, Cs^+ is the least hydrated because of its bigger size and thus the radius of the Cs^+ ion is smaller than the radius of hydrated Li^+ , and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Hydrolysis :

Hydrolysis means reaction with water molecules ultimately leading to breaking of O-H bond into H^+ and OH^- ions.

Hydrolysis in covalent compounds takes place generally by two mechanisms

(a) By Coordinate bond formation : Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbitals.

(b) By H-bond formation : For example in Nitrogen trihalides

General properties of ionic compounds :

(a) **Physical state** : At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.

(b) Simple ionic compounds do not show isomerism but isomorphism is their important characteristic.



(c) **Electrical conductivity** :

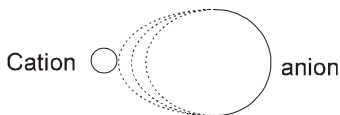
All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

(d) **Solubility of ionic compounds** :

Soluble in polar solvents like water which have high dielectric constant

Covalent character in ionic compounds (Fajan's rule) :

Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.



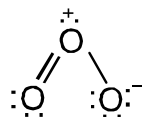
More distortion of anion, more will be polarisation then covalent character increases.



Formal Charge :

Formal charge (F.C.)
On an atom in a Lewis
structure

$$= \left[\begin{array}{l} \text{Total number of valence} \\ \text{electron in the free atom} \end{array} \right] - \left[\begin{array}{l} \text{Total number of non bonding} \\ \text{(lone pair) electrons} \end{array} \right] - \left(\frac{1}{2} \right) \left[\begin{array}{l} \text{Total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$



Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

Limitations of the Octet Rule :

1. The incomplete octet of the central atom

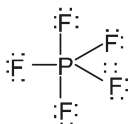
LiCl, BeH₂ and BCl₃, AlCl₃ and BF₃.

2. Odd-electron molecules

nitric oxide, NO and nitrogen dioxide. NO₂

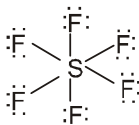


3. The expanded octet



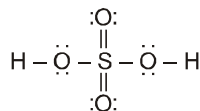
PF₅

10 electrons around
the P atom



SF₆

12 electrons around
the S atom



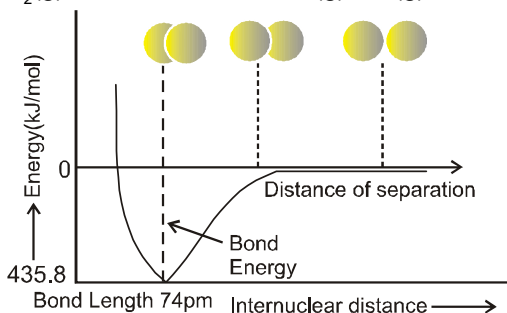
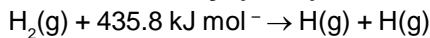
H₂SO₄

12 electrons around
the S atom

4. Other drawbacks of the octet theory

- (i) some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF₂, KrF₂, XeOF₂ etc.,
- (ii) This theory does not account for the shape of molecules.
- (iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Valence bond theory (VBT) :



Orbital Overlap Concept

according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present, in the valence shell having opposite spins.

Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping :

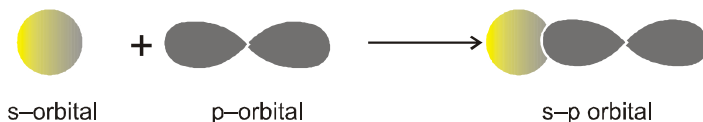
(i) sigma (σ) bond, and (ii) pi (π) bond

(i) **Sigma (σ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.

● s-s overlapping



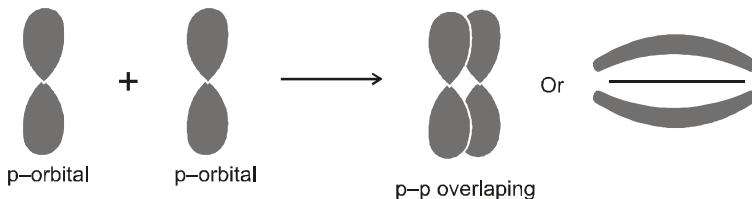
● s-p overlapping:



● p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



- (ii) **pi(π) bond** : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.



Strength of Sigma and pi Bonds :

In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent.

Valence shell electron pair repulsion (VSEPR) theory :

The main postulates of VSEPR theory are as follows:

- (i) The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- (ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- (iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- (iv) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- (v) 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.
- (vi) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :
lone pair (ℓ p) - lone pair (ℓ p) > lone pair (ℓ p) - bond pair (bp) > bond pair (bp) - bond pair (bp)

Hybridisation :

Salient features of hybridisation :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is the orbital that undergo hybridization and not the electrons.

Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.

Table-3

Steric Number	Types of Hybridisation	Geometry
2	sp	Linear
3	sp ²	Trigonal planar
4	sp ³	Tetrahedral
5	sp ³ d	Trigonal bipyramidal
6	sp ³ d ²	Octahedral
7	sp ³ d ³	Pentagonal bipyramidal

Hybridization Involving d-orbital :

Type of 'd' orbital involved

sp ³ d	d _{Z²}
sp ³ d ²	d _{x²-y²} & d _{Z²}
sp ³ d ³	d _{x²-y²} , d _{Z²} & d _{xy}
dsp ²	d _{x²-y²}

Molecular Orbital Theory (MOT) :

developed by F. Hund and R.S. Mulliken in 1932.

- (i) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (ii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**
- (iii) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- (iv) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

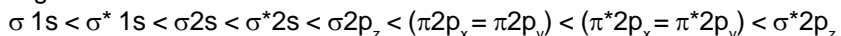


Conditions for the combination of atomic orbitals :

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

Energy level diagram for molecular orbitals :

The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :



The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

Bond Order

$$\text{Bond order (b.o.)} = \frac{1}{2} (N_b - N_a)$$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the Bond :

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

Bond-Length :

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic Nature :

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule.

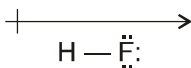
Dipole moment :

Dipole moment (μ) = Magnitude of charge (q) \times distance of separation (d)
Dipole moment is usually expressed in Debye units (D). The conversion factors are

○ $1 \text{ D} = 3.33564 \times 10^{-30} \text{ Cm}$, where C is coulomb and m is meter.

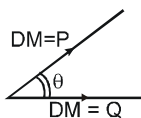
○ $1 \text{ Debye} = 1 \times 10^{-18} \text{ e.s.u. cm}$.

For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow (\rightarrow) above the Lewis structure to indicate the direction of the shift.

a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.



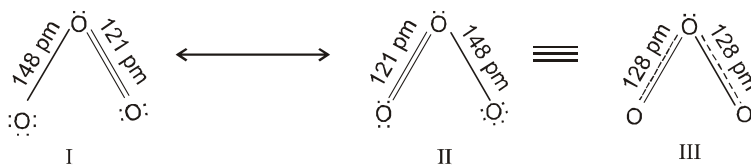
$$R = \sqrt{P^2 + Q^2 + 2PQ \cos \theta}$$

where R is resultant dipole moment.

Resonance :

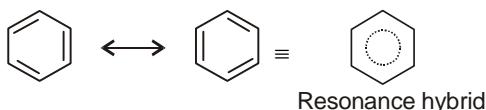
Definition : Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound.

For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below :



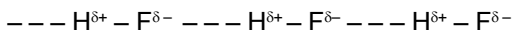
Resonance in the O_3 molecule

Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of maximum covalence for the atoms.



Resonance hybrid

Hydrogen Bond :

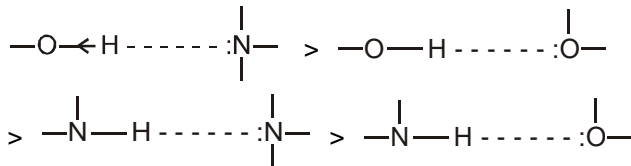


Conditions required for H-bond :

- (i) Molecule should have more electronegative atom (F, O, N) linked to H-atom.
- (ii) Size of electronegative atom should be smaller.
- (iii) A lone pair should be present on electronegative atom.



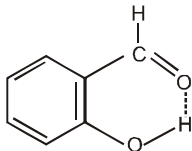
- Order of H-bond strength



TYPES OF H-BONDS :

(A) Intramolecular H-Bonding :

it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.



o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative

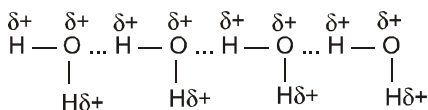
Necessary conditions for the formation of intramolecular hydrogen-bonding:

- the ring formed as a result of hydrogen bonding should be planar.
- a 5- or 6- membered ring should be formed.
- interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

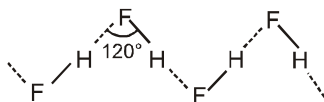
(B) Intermolecular H-Bonding :

it is formed between two different molecules of the same or different compounds.

(a) In water molecules



- The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(\text{HF})_n$ in both the solid and also in the liquid.



Intermolecular forces (Vander Waal's Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

- (a) Ion-dipole attraction
- (b) Dipole-dipole attraction
- (c) Ion-induced dipole attraction
- (d) Dipole-induced dipole attraction
- (e) Instantaneous dipole- Instantaneous induced dipole attraction : (Dispersion force or London forces)

- Strength of vander waal force \propto molecular mass.
- van der Waal's force \propto boiling point.

Metallic bond :

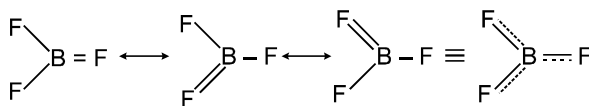
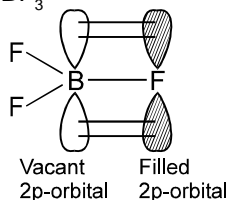
Two models are considered to explain metallic bonding:

- (A) Electron-sea model
- (B) Band model

Some special bonding situations :

(a) Electron deficient bonding: There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds. These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6 , $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

(b) Back Bonding : Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair (generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3



the extent of back bonding in boron trihalides.

