CHEMICAL BONDING AND MOLECULAR STRUCTURE

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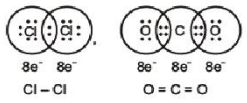
Chemical Bonding and Molecular Structure

Chemical bond

- The attractive force which holds various constituents (atoms, ions etc) together in different chemical species is called a chemical bond.
- Lewis postulated that atoms achieve the stable octet when they are linked with chemical bonds.
- Simple notation to represent valence electrons in an atom is called **Lewis symbols** e.g. Li, Be, B
- The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the **electrovalent bond or ionic bond**.
- **Octet rule** – According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells.
- Covalent bond – When two atoms share electron pair(s) they are said to be joined by covalent bonds.
- It two atoms share one electron pair, the covalent bond between them is called single bond, if two electrons pairs then double bond e.g.



- **Formal charge** = [Total number of valence electrons in free atom] − [Total number of non-bonding electrons] − $\frac{1}{2}$ [Total number of non-bonding electrons]

Ionic bond or electrovalent bond

- Ionic bonds will be formed more easily between elements with comparatively low ionisation enthalpies and elements with comparatively high negative value of electron gain enthalpy.
- **Lattice enthalpy** of an ionic solid is defined as the energy required to completely seperate one mole of a solid ionic compound into gaseous constituent ions.

Bond parameters

- Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.
- The **Covalent Radius** is measured approximately as the radius of on atom's core which is in contact with the core an adjacent atom in a bonded situation.
- The **vander Walls Radius** represents the overall size of atoms which included the valence shell in a non-bonded situation.
- **Bond Angle** is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/ ion.
- **Bond Enthalpy** is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. For polyatomic molecules the term mean or average bond enthalpy is used.
- **Bond Order** is given by the number of bonds between the two atoms in a molecule.
- Isoelectronic molecules and ions have identical bond orders for example F_2 and O_2^{2-} have bond order 1, N_2 CO and NO^+ have bond order 3.
- With increase in bond order, bond enthalpy increases and bond length decreases.

Hydrogen bonding

- Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule or within the same molecule. Types of H-bond
- Intermolecular hydrogen bond is formed between the atoms of two different molecules e.g. H_2O, NH_2, HF, C_2H_5OH etc.
- Intramolecular hydrogen bond is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule eg. orthonitrophenol.

Limitation of octet rule

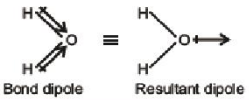
- In some compounds, the number of electrons surrounding the central atom is less than eight eg. LiCl, BeH_2.
- Molecules with an odd number of electron e.g. NO and NO_2
- In number of compounds there are more than eight valence electrons around the central atom. eg. PF_5, SF_6, H_2SO_4 etc
- Some noble gases also combine with oxygen and fluorine eg. XeF_2
- Does not account for the shape of molecules.

Polarity of bonds

- In non-polar covalent bonds electron pair is situated exactly between the two identical nuclei.
- In polar covalent bond electron pair between the two atoms gets displaced more towards more electronegative atom.
- Dipole moment is the product of the magnitude of the charge and the distance between the centres of positive or negative charge and denoted by μ
- Dipole moment is a vector quantity and represented by crossed arrow
- eg H→F
- Unit of μ is Debye (1D = 3.33564×10^{-30} C m)
- In polyatomic molecules, the dipole moment depend upon individual dipole moments of individual bonds and spatial arrangement of bonds eg.

Fajan's rule

- The smaller the size of cation and larger the size of the anion, the greater is the covalent character of an ionic bond.
- Greater the charge on the cation greater is the covalent character.
- For cations of the same size and charge, the one having d-electrons is more polarising, thus its salts have greater covalent character.



Valence shell electron pair repulsion (vsepr) theory

- The model used for predicting the geometrical shapes of molecules is based on the assumption that electron pairs repel each other therefore try to remain as far apart as possible
- The order of electron pair repulsion is lp – lp > lp – bp > bp – bp.
- Shape (geometry)

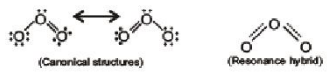
Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs	Shape	Example
2	0	B-A-B	Linear	BeF2
3	0		Trigonal planar	BF_3
2	1		Bent	SO_2
4	0		Tetrahedral	CH_4
3	1		Pyramidal	NH_3
2	2		Bent	H_2O
5	0		Trigonal bipyramidal	PCl_5
4	1		See saw	SF_4
3	2		T-shape	CIF3
6	0		Octahedral	SF_6
5	1		Square pyramid	BrF_5
4	2		Square Planar	XeF_4

Molecular orbital theory

- LCAO method is used for the formation of molecular orbitals.
- For two atomic orbitals having wave function ψ_A and ψ_B the molecular orbital (MO) are given as $\psi_A \pm \psi_B$
- MO formed by the addition of atomic orbitals is called Bonding Molecular Orbital (BMO) or σ and π while formed by the subtraction of atomic orbitals is called anti bonding molecular orbital (ABMO) or σ* and π*.
- Increasing order of energies for diatomic molecules upto 14 electrons is
  $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p = \pi 2p) < \sigma 2p_z < (\pi^*2p = \pi^*2p_y) < \pi^*2p_z$
- Increasing order of energies for diatomic molecules with more than 14 electrons is
  $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$
- Bond order $= \frac{1}{2}(N_B - N_A)$
- Bond order ∝ Bond strength $\propto = \frac{1}{\text{Bond length}}$
- If all the molecular orbitals in a molecule are doubly occupied then the substance is diamagnetic else paramagnetic.

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, position of nuclie, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.



- **Misconceptions** with resonancem
- The cannonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms.
- There is no such equilibrium between the cannonical forms.

Valence bond theory

- Discusses bond formation in terms of overlap of orbitals
- In case of the formation of H_2 molecule from two H-atoms involves overlap of s orbitals of two H-atoms which are singly occupied. The potential energy of the systems gets lowered as the two H-atoms come near to each other.
- Types of overlapping.
  Sigma (σ) bond is formed by the end to end overlap of bonding orbitals along the internuclear axis.
  Pi (π) bond is formed in such a way that atomic orbital axes remain parallel to each other and perpendicular to the internuclear axis.
  Hybridisation – Atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals and this phenomenon is known as hybridisation.
- Number of hybridised orbitals formed is equal to number of atomic orbitals intermixed.
- Hybridised orbitals only form sigma bond.
- Various types of hybridisations are *sp* sp^2, sp^3, sp^3d, dsp^2 etc.