Pull your socks to get perfection

CHEMICAL BONDING AND MOLECULAR STRUCTURE

The beauty of chemistry lies in the understanding of chemical bond formation. Knowledge of chemical bonding helps in proper explanation of the facts. Modern day examinations trying to evaluate the understanding capacity of students in this topic. So students.. pull your socks to get perfection in this chapter.

RECAPITULATION

The force of attraction between atoms in a molecule or ions in a compound is known as "chemical bond". Whenever a bond is formed energy is released due to attractions, potential energy of bonded atom is less than that of isolated atom hence atoms gain extra stability.

- When a chemical bond is formed the forces of attraction is equal to forces of repulsion.
- Chemical bonds may be primary force of attraction like ionic bond, covalent bond or metallic bond and secondary force of attraction like H-bond, dipole-dipole attraction, etc.

Ionic bond [Electrovalent bond]

Complete loss of electrons to form ions, Electrostatic force of attraction between ions. Electrovalency is the total number of electrons lost or gained by one atom of element in the formation of ionic bond.

- Elements of s-block have fixed electro valency. Elements of "p" and "d" block may show variable electrovalency due to **1) Inert Pair effect, 2) Unstability of core.**
- Ionic bonds are Non directional in nature, do not exhibit space isomerism.
- Ionic compounds have high Melting points and Boiling points, soluble in polar solvents, conducts electricity in aqueous and molten state. Show isomorphism.
- $MgSO_4.7H_2O$, $FeSO_4.7H_2O$ and $ZnSO_4.7H_2O$ are Isomorphous.
- Isomorphous ionic compounds should have the cations and anions of both compounds isostructural relationship.
- **Solubility Orders:** Increase difference in radii ↑ solubility ↑ and vice-versa.

  Increasing solubility:
  $LiF \rightarrow LiI$; $NaF \rightarrow NaI$;
  $LiF \rightarrow CsF$; $LiOH \rightarrow CsOH$;
  $Be(OH)_2 \rightarrow Ba(OH)_2$
  Decreasing solubility:
  $CsF \rightarrow CsI$; $LiI \rightarrow CsI$;
  $BeSO_4 \rightarrow BaSO_4$;
  $LiClO_4 \rightarrow CsClO_4$

Covalent bond

Covalent bond formed by Sharing of electrons, overlapping of orbitals. Covalent bond formed may be single, double, triple, polar, nonpolar. Covalency is the total number of electron pairs shared by one atom of element in the formation of covalent compound.

- **Fajan's rules:** covalent character will be more if cation is more polarising and anion is easily polarisable.
- Increasing order of covalent character: i) $NaCl < MgCl_2 < AlCl_3$
  ii) $CaF_2 < CaCl_2 < CaBr_2 < CaI_2$
  iii) $AlF_3 < Al_2O_3 < AlN$
- Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.
- $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{+3} is smaller than Fe^{+2} and thus charge is more.
- As covalent character increases intensity of color increases. For example $AgCl$ is white $AgBr$, AgI, Ag_2CO_3 are yellow. $SnCl_2$ is white but SnI_2 is red. $PbCl_2$ is white but PbI_2 is yellow.
- Covalent bonds are directional in nature, show isomerism. Low melting point and boiling points.

Entrance Exams Questions

1. The species in which the N atom is in a state of sp hybridization is: **(JEE Main-2016)**
   1) NO_2^- 2) NO_3^- 3) NO_2 4) NO_2^+
2. The hybridizations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively: **(JEE Main-2016)**
   1) sp, sp^3 and sp^2 2) sp^2, sp^3 and sp
   3) sp, sp^2 and sp^3 4) sp^2, sp and sp^3
3. Which one of the following compounds shows the presence of intramolecular hydrogen bond? **(NEET-2016)**
   1) H_2O_2 2) HCN 3) Cellulose
   4) Concentrated acetic acid
4. The compound(s) with TWO lone pairs of electrons on the central atom is (are): **(JEE Adv-2016)**
   A) BrF_5 B) ClF_3 C) XeF_4 D) SF_4

Answers: 1) 4; 2) 3; 3) 3; 4) B, C

- Electrical conductivity of covalent compounds is due to auto-protolysis or self ionisation.
- Formation of covalent bond can be explained by: i) Lewis theory
  ii) Valence bond theory
  iii) Molecular orbital theory etc.

Valence Bond Theory

A covalent bond is formed by overlapping of half filled atomic orbitals of valence shell of the two atoms. Greater the extent of overlapping greater is the strength of covalent bond.

- A bond formed between two atoms by the overlap of single occupied orbitals along their axis is called sigma bond. π bonds are formed by the sidewise overlapping of p-orbitals or p–d (or) d–d orbitals.
- Strength of the bonds follows the order.. $\sigma_{p-p} > \sigma_{s-p} > \sigma_{s-s} > \pi$
  Triple bond > Double bond > Single bond.
- Co-ordinate covalent bond or dative bond is a special type of covalent bond where shared pair of electrons is contributed by one of the bonding atoms.

VSEPR Theory

Shape of the molecule is based on the number and nature of electron pairs in the valence shell of the central atom. Repulsion among different lone pairs are in the order:
L.P. – L.P. > L.P. – B.P. > B.P. – B.P.

- Presence of lone pairs cause deviation in shape and bond angle.
- 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.

Hybridization

The process of intermixing of the orbitals of nearly equal energies resulting in the formation of new set of orbitals of equivalent energies and shape is known as "hybridization". Hybridization of orbitals involves orbitals with single electrons or paired electrons or no electrons (empty orbital).

- **Drago rule:** Elements of 3rd period (p-Block) and lower than 3rd period do not allow hybridisation in molecule when they form compounds with less electronegative elements such as hydrogen.
  Ex: PH_3, SiH_4, AsH_3, H_2S.
- Steric number of any atom in a molecule or Number of hybrid orbitals = Number of sigma bonds + Non bonded pair of electrons.
- Number of non-bonded pairs = ½ × (Group number of central atom) – (σ + π).

Molecular Orbital Theory (MOT)

The molecular orbital formed by the addition of wave function of atomic orbitals is called the bonding molecular orbitals. The molecular orbital formed by the subtraction of wave function of atomic orbital is called anti-bonding molecular orbital.

- **The energy order:** Bonding orbitals < non bonding orbitals < antibonding orbitals.
- **Bond order** = ½ $(N_b - N_a)$.
- The extent of back bonding the much larger if the orbitals involved in the back bonding are of same size, for example back bonding in boron trihalides.
- **Dipole moment:** The product of the magnitude of the charge and the distance of separation between the charges. Dipolemoment $\mu = ql$ where, q is charge and l is bond length.
- 1 Debye = 10^{-18} esu × cm
  = 3.33×10^{-30} coloumb × metre.
- If the polar bonds of a molecule are separated by an angle of θ, then the net μ is obtained from the relation: $\mu_{net} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$
- $\% \text{ Ionic character} = \frac{\mu_{Experimental}}{\mu_{Theoretical}} \times 100$
- % Ionic character (Hanny-Smith equation) = $16\Delta + 3.5\Delta^2$ where, Δ = absolute difference of E.N. of bonded atoms.
- On pauling scale for 50% ionic character Δ = 2.1. But in many cases even a difference of 1.7 ionic character is observed is 50%.
- Resonance is the delocalisations of π electron cloud in between orbitals of various atoms in a molecule (provided all the atoms are in the same plane)
- Formal charge = Number of valence electrons in free atom – Number of nonbonding electrons – ½ [Number of bonding (shared) electrons].
- The formal charges help in selection of lowest energy structure from a number of possible Lewis structures for a given molecule or ion. Lowest energy structure is the one which has lowest formal charges on the atoms.
- **Bond length:** It is defined as the average distance between the nuclei of two bonded atoms in a molecule. Bond length depends on size of the bonded atoms, multiplicity of bonds and resonance.
- **Bond angle:** It is defined as the average angle between orbitals containing bonding electron pairs around the central atom in a molecule.
- **Bond dissociation energy:** It is defined as amount of energy required to break one mole of covalent bonds of a particular type of gaseous diatomic molecules.

Hydrogen bonding

"The weak electrostatic forces of attractions between a partially positively charged hydrogen atom of a polar molecule and a highly electronegative atom (of the same molecule or of a different molecule) is known as a hydrogen bond". Hydrogen bond is a weak electrostatic force as the energy of hydrogen bond varies from 2 to 10 K.cals/mole.

- Vanderwaals force < Hydrogen bond < Covalent bond.
- **Types of H-bonding:**
  i) Intermolecular
  ii) Intramolecular

Important Questions for IPE

LAQs (8 Marks)

1. Give an account of VSEPR theory and its applications
2. What do you understand by hybridisation? Explain different types of hybridisation ivolving s and p orbitals.
3. Give the molecular orbital energy diagram of a) N_2 b) O_2. Calculate the respective bond order. Write the magnetic nature of N_2 and O_2 molecules.

SAQs (4 Marks)

1. Explain hybridisation involved in PCl_5 molecule.
2. Explain hybridisation involved in SF_6 molecule.
3. What is hydrogen bond? Explain different types of hydrogen bonds with examples.