CHAPTER 4

Chemical Bonding and Molecular Structure

Chemical Bond

The force of attraction which hold atoms together, molecule or ions within chemical species.

It is always exothermic process.

Type of Interactions in Molecules

8 kJ/mol | 42 kJ/mol

- Vander Waal's force
  1. Dipole-Dipole (Keesome)
  2. Dipole-induce dipole (Debye)
  3. Instantaneous dipole-induce dipole
  4. Ion-dipole
  5. Ion-induced dipole
- Hydrogen Bond
  1. Intermolecular hydrogen bond
  2. Intramolecular hydrogen bond
- Chemical bond or Strong bond
  1. Ionic bond
  2. Covalent bond
  3. Co-ordinate bond
  4. Metallic bond

Types of Intermolecular Forces

Types of Intermolecular Forces

- Ion - Dipole
- Ion - Induced dipole
- Dipole - dipole
- Hydrogen bonding
- Dipole - Induced dipole
- Dispersion (London force)

Force

Table: Relative strength of forces

Force	Relative strength	Interaction energy
Ion-ion (Cation-anion)	Very strong	Interaction energy $\propto r^{-1}$
Covalent bonds	Strong, (140–523 KJ/mole)	Interaction energy $\propto r^{-1}$
Ion-dipole	Moderate	Interaction energy $\propto r^{-2}$
Hydrogen bond	Moderate to weak (10–100 kJ/mol)	Interaction energy $\propto r^{-1}$
Dipole-dipole	Weak (5–25 kJ/mol)	Interaction energy $\propto r^{-3}$ (for stationary polar molecules) Interaction energy $\propto r^{-6}$ (for rotating polar molecules)
London force or dispersion force	Very weak (0.05–20 kJ/mol)	Interaction energy $\propto r^{-6}$

Hybridisation

Table : Hybridisation and geometry

S.No.	Type or orbital	No. of hybrid orbital	3D orientation	Example
1.	one s + one p	2; sp	Linear	BeH_2, $BeCl_2$
2.	one s + two p	3; sp^2	Triangular	BCl_3, BF_3
3.	one s + three p	4; sp^3	Tetrahedral	CH_4, CCl_4
4.	one s + three p + one d	5; sp^3d	Triangular bipyramidal	PCl_5
5.	one s + three p + two d	6; sp^3d^2	Octahedral	SF_6
6.	one s + three p + three d	7; sp^3d^3	Pentagonal bipyramidal	IF_7

Type of Hybridisation & Possible Structure

Table : Hybridisation and Shape

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridisation	2	-	Linear	BeF_2, CO_2, CS_2, $BeCl_2$
2. (a) sp^2-hybridisation	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridisation	2	1	V-shape, Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridisation	4	0	Tetrahedral	CH_4, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-1}, SO_4^{-2}, $AlCl_4^-$,
(b) sp^3-hybridisation	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridisation	2	2	V-shape Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O_2, SF_2, I_3^+
4. (a) sp^3d-hybridisation	5	–	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See-Saw, folded square distorted tetrahedral	SF_4, PF_4^-, AsF_4^- SbF_4^-, XeO_2F_2
			almost T-shape	
(c) sp^3d-hybridisation	3	2	Linear	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3		I_3^-, Br_3^-, ICl_2^-, XeF_2

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
5. (a) sp^3d^2-hybridisation	6	–	Square bipyramidal/octahedral	PCl_6^-, SF_6
(b) sp^3d^2-hybridisation	5	1	Square pyramidal/distorted octahedral	$XeOF_4$, ClF_5, SF_5^-,
(c) sp^3d^2-hybridisation	4	2	Square planar	XeF_5^+, XeF_4
6. (a) sp^3d^3-hybridisation	7	–	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridisation	6	1	Pentagonal pyramidal/ distorted octahedral/capped octahedral	XeF_6
(c) sp^3d^3-hybridisation	5	2	Pentagonal planar	XeF_5^-

Molecular Orbital Theory

Formation of molecule or orbitals from atomic orbitals ($\psi_A \pm \psi_B$)

$\psi_{MO} = \psi_A \pm \psi_B$

$\sigma = \psi_A + \psi_B$ (Bonding molecular orbital)

$\sigma^* = \psi_A - \psi_B$ (Antibonding molecular orbital)

Relative energies of M.O having

Less than or equal to 14 electrons.

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < [\pi^* 2p_x = \pi^* 2p_y] < \sigma^* 2p_z$

For more than 14 electrons

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < [\pi 2p_x = \pi 2p_y] < [\pi^* 2p_x = \pi^* 2p_y] < \sigma^* 2p_z$

Bond order

Bond order = $\frac{1}{2}$ [Number of bonding electrons – Number of antibonding electrons]

or, $= \frac{N_b - N_a}{2}$

$\text{B.O} \propto \text{B.E} \propto \frac{1}{\text{B.L}} \propto \text{Stablity}$

Properties of Ionic Salt

General Properties

Hard, Solid, Brittle (strong electrostatic attraction between ions)

Non directional nature (ionic compound do not exhibit stereo isomerism)

Higher Melting Point / Boiling Point

Isomorphism: $MgSO_4 . 7H_2O$; $ZnSO_4 . 7H_2O$; $FeSO_4 . 7H_2O$

Specific Properties

Conductivity | Solubility | Covalent Character

Conductivity:

Molten state

$\text{Ionic conduction} \propto \frac{1}{\text{Ionic radius}}$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl

Ionic Radius: $Li^+ <<< Cs^+$

Conductance: CsCl < RbCl < KCl < NaCl < LiCl

Aqueous medium

$\text{Ionic mobility} \propto \frac{1}{\text{Ionic radius}}$

Hyd. radius: $Cs^+ <<< Li^+(aq)$

conductance: LiCl < NaCl < KCl < RbCl, CsCl

Table: Hybridisation of following species in specified state

Species	Cationic part	Anionic part
PCl_5	PCl_4^+ (sp^3)	PCl_6^- (sp^3d^2)
PBr_5	PBr_4^+ (sp^3)	Br^-
XeF_6	XeF_5^+ (sp^3d^2)	F^-
N_2O_5	NO_2^+ (sp)	NO_3^- (sp^2)
I_2Cl_6 (liquid)	ICl_2^+ (sp^3)	ICl_4^- (sp^3d^2)
Cl_2O_6	ClO_2^+ (sp^2)	ClO_4^- (sp^3)
I_2 (molten state)	I_3^+ (sp^3)	I_3^- (sp^3d)

Table: Magnetic behaviour of odd electron species

	Hybridisation	Shape	Magnetic behaviour
NO_2	sp^2	V shape	Para
ClO_2	sp^2	V shape	Para
ClO_3	sp^3	Pyramidal	Para
$^\bullet CH_3$	sp^2	Trigonal planar	Para
$^\bullet CH_3/^\bullet CHF_2/CH_2F$	sp^3	Pyramidal	Para

Odd e⁻ species: Total number of electron or valence electron in odd number.