CHAPTER 3

THEORIES OF COVALENT BONDS AND SHAPES OF MOLECULES

* OLD CONCEPT

Chemical bond results from attraction between oppositely charged particles.

LIMITATION

Bond formation in molecules like H_2, N_2, organic compounds cannot be explained by above concept

* LEWIS CONCEPT

Lewis gave octet theory, according to which
" In chemical bond formation atoms interact by sharing of electrons to attain noble gas electronic configuration"

LIMITATION

This theory fails to explain geometry of molecules.

SHAPES OF MOLECULES

Nyholm and Gillespie put forward VSEPR theory to explain shape and geometry of molecule.

*VSEPR THEORY

Main Postulate:

"The valence electron pairs (Lone pairs and the bond pairs) are arranged around the central atom to remain at maximum distance to keep repulsio minimum".

POSTULATES

1. Both lone pair and bond pair determine the geometry of molecules.
2. Lone pair occupies more space than a bond pair
3. The magnitude of repulsion is in the following order:

   Lone Pair - Lone Pair > Lone Pair - Bond Pair > Bond Pair - Bond Pair
4. Double bond and triple bond behaves like a single bond in determining the geometry of the molecule.
5. The effect of a bonding electron pair decreases with increasing electronegativity of an atom forming a molecule.

LIMITATION

→ VSEPR Theory predicts and explains the shape of molecules but doesnot give reasons for the formation of bonds.

→ Complexes donot form this Theory

* Crystal Field Theory and Ligand Field Theory are applied to describe the geometry of complexes.

* lone pair → present on Central Atom

* DETERMINATION OF CENTRAL ATOM

The element in a molecule with the lowest electronegativity - other than hydrogen - acts as the central atom for the Lewis structure. Hydrogen can never form more than one bond which precludes it from serving as central atom.

SHAPES OF MOLECULES

A : Central Atom
X : Attached Atoms

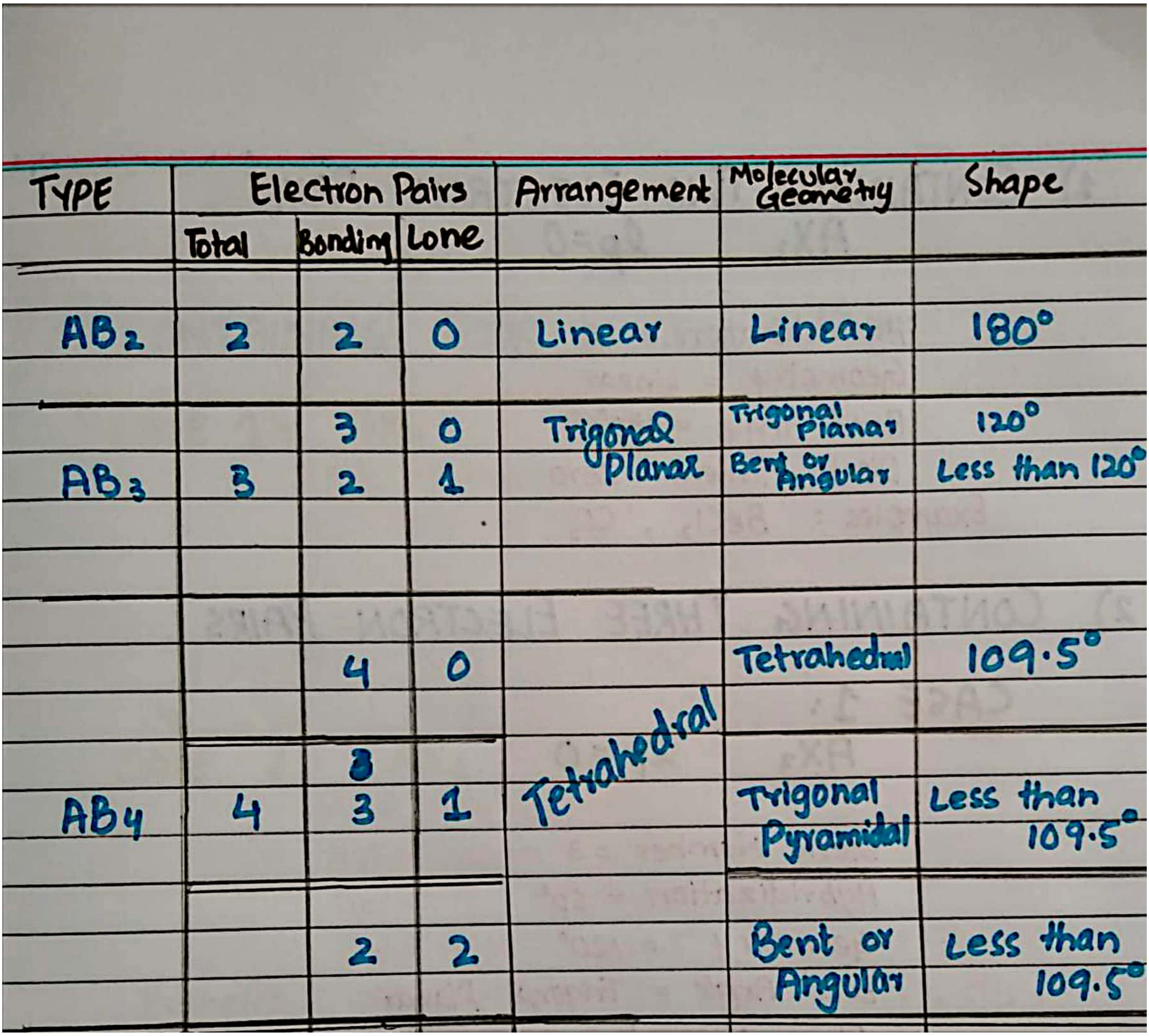
STERIC NUMBER:

Steric Number = Attached Atoms (X) + Lone Pair

Steric Number	Hybridization
2	sp
3	sp^2
4	sp^3
5	sp^3d
6	sp^3d^2

AB TYPE ELEMENTS

e.g HF, HCl, CO have no central atom. They must have some dipole moment.



TYPE	Electron Pairs			Arrangement	Molecular Geometry	Shape
	Total	Bonding	Lone			
AB_2	2	2	0	Linear	Linear	180°
AB_3	3	3	0	Trigonal Planar	Trigonal Planar	120°
		2	1		Bent or Angular	Less than 120°
AB_4	4	4	0	Tetrahedral	Tetrahedral	109.5°
		3	1		Trigonal Pyramidal	Less than 109.5°
		2	2		Bent or Angular	Less than 109.5°

1) CONTAINING TWO ELECTRON PAIRS

AX_2 $lp = 0$

Hybridization = sp
Geometry = Linear
Bond Angle = 180°
Dipole Moment = zero
Examples : $BeCl_2$, CO_2

2) CONTAINING THREE ELECTRON PAIRS

CASE 1:

AX_3 $lp = 0$

Steric Number = 3
Hybridization = sp^2
Geometry = 120°
Bond Angle = Trigonal Planar
Dipole Moment = zero
Examples: BF_3 , AlF_3 , $AlCl_3$, BCl_3 , $\overset{+}{C}H_3$, SO_3
(All of these are electrophiles)

CASE 2:

AX_2 $lp = 1$

Steric Number = 3
Hybridization = sp^2
Geometry = Angular
Bond Angle = Less than 120°

Dipole Moment > Zero

Examples : $SnCl_2$, SO_2

3) CONTAINING FOUR ELECTRON PAIRS

CASE 1 : AX_4 $lp = 0$

Steric Number = 4

Hybridization = sp^3

Geometry = Tetrahedral

Bond Angle = 109.5°

Examples : H_2O , NH_3 , CH_4

CASE 2 : AX_3 $lp = 1$

Steric Number = 4

Hybridization = sp^3

Geometry = Pyrimidal

Bond Angle < 109.5° (NH_3 : 107.5°)

Examples : NH_3 , NF_3 , NCl_3 , PH_3 , PF_3 , PCl_3 , H_3O^+ , $\bar{C}H_3$

CASE 3 : AX_2 $lp = 2$

Steric Number = 4

Hybridization = sp^3

Geometry = ~~Tetrahedral~~ Angular

Bond Angle < 109.5° (H_2O : 104.5°)

Dipole Moment > Zero

Examples : H_2O , H_2S, OF_2

* CONTAINING FIVE ELECTRON PAIRS

AX_5 lp = 0

Steric Number = 5

Hybridization = sp^3d

Geometry = Trigonal Bipyrimidal

Examples : PCl_5, PBr_5

* CONTAINING SIX ELECTRON PAIRS

AX_6 lp = 0

Steric Number = 6

Hybridization = sp^3d^2

Geometry = Octahedral

Example : SF_6

NOTE:

The actual angle of sp^2 is 120° but due to lone pair it becomes less than 120°

The actual angle of sp^3 is 109.5° but due to lone pair it becomes less than 109.5°

SHAPES :	Angular	Pyrimidal	Tetrahedral
	↓	↓	↓
GEOMETRY:	Tetrahedral	Tetrahedral	Tetrahedral

* If E.N of central atom increases, bond angle increases but lone pair should not be zero e.g

$H_2O > H_2S$

$NH_3 > PH_3$

As we go down the group bond angle decreases bcz E.N decreases.

* With increase in lone pair, bond angle increases and vice versa.

* Angle :

$sp > sp^2 > sp^3$

$180° \quad 120° \quad 109.5°$

RESONANCE

- * Ingold → Mesomerism (an intermediate structure)
- * Heisenberg → Resonance → from Quantum mechanics

PROPERTIES:

1. Same position of nuclei
2. Different position of π-electrons
3. Same number of unpaired electrons

ACTUAL STRUCTURE

Resonance Hybrid

POSSIBLE STRUCTURES

→ Resonance Structures
→ Canonical Structures

More Stable Molecules have:

1. More Resonating structures
2. Greater Resonance Energy
3. Greater Bond Energy

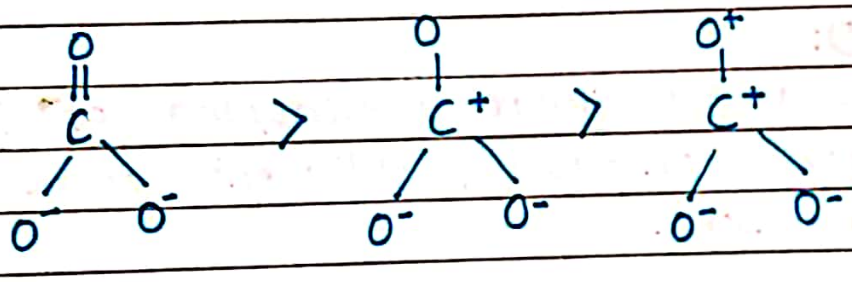
* STABILITY OF RESONATING STRUCTURES

To compare stability of resonating structures we'll see :

1. More electrons involved in bonding, more the stability (This will be most stable)

2. Negative charge on electronegative element and positive charge on electropositive element (This will be second in stability)

3. Positive charge on electronegative element (This will be least stable)



VALENCE BOND THEORY

- VBT explains how bond is formed.
- Bond is formed by the overlapping of half filled orbitals
- The spin of two electrons in a covalent bond have to be opposite.

TYPES OF BONDS :

1. Sigma Bond
2. π - Bond

SIGMA BOND:

1. A bond formed by linear overlapping of two half filled atomic orbitals . of adjacent atoms is called a sigma bond.

2. Electron density is concentrated around the bond axis

3. It has only one lobe of electron density between the nuclei.

4. Only one sigma bond can exist between two atoms.

5. The sigma bonds present in the molecule determines its shape.

In sigma bond, s-s overlap is stronger than s-p or p-p overlap.

* PI-BOND

1. A bond formed by the sidewise overlapping of two half filled parallel atomic orbitals of adjacent atoms is called a π-bond.
2. Electron density lies above and below the bond axis.
3. It has two lobes of electron density on opposite sides of bond axis.
4. π- bond has no effect on the shape of the molecule.

* CALCULATION OF π-BONDS (OR DOUBLE BONDS) IN OPEN CHAIN OLEFINIC HYDROCARBONS

$$P = \frac{2X - Y}{2} + 1$$

P : No. of π-bonds
X : No. of Carbon atoms
Y : No. of Hydrogen atoms

* CALCULATION OF SIGMA BONDS IN OPEN CHAIN OLEFENIC HYDROCARBONS

$$S = X + Y - 1$$

S : No. of δ-bonds
X : No. of Carbon atoms
Y : No. of Hydrogen atoms

* CALCULATION OF π-BOND IN CYCLIC OLEFINIC HYDROCARBONS

$$P = \frac{2X - Y}{2}$$

* CALCULATION OF δ-BONDS IN CYCLIC OLEFINIC HCs

$$S = X + Y$$

HYBRIDIZATION

A process in which atomic orbitals of different energies and shapes are mixed together to form a new set of equivalent orbitals of the same energy and same shape is called hybridization.

→ Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.

→ The number of hybrid orbitals is always equal to the number of orbitals which are mixed.

→ Once an orbital has been ~~formed~~ used to form hybrid orbitals, it become stable and lowered in energy than atomic orbitals.

sp^3 HYBRIDIZATION

→ mixing of one s and three p-orbitals

→ s-character : 25%

→ p-character : 75%

→ Bond Angle : 109.5°

Examples: CH_4, NH_3, H_2O, H_2S, CCl_4, SO_4^{-2}, C_2H_6 etc

sp^2 HYBRIDIZATION

→ Mixing of one s and two p-orbitals

→ S-character : 33%

→ p-character : 66%

→ Bond Angle : 120°

Examples: Ethene (C_2H_4), BF_3, $AlCl_3$, SO_3, SO_2, BH_3

SP HYBRIDIZATION

- → Mixing of one s and one p-orbital
- → s-character : 50%
- → p-character : 50%
- → Bond Angle : 180°

Examples : Acetylene (C_2H_2), CO_2, CO, CS_2, $BeCl_2$, C_2H_2

FORMULA FOR HYBRIDIZATION

$$H = \frac{1}{2}(V + M - C + A)$$

V : Number of valence electrons
M : Monovalent atoms bonded to central atom
C : cationic charge (+)
A : Anionic charge (-)

For

$H = 2 \rightarrow sp$
$H = 3 \rightarrow sp^2$
$H = 4 \rightarrow sp^3$
$H = 5 \rightarrow sp^3d$
$H = 6 \rightarrow sp^3d^2$
$H = 7 \rightarrow sp^3d^3$

EXAMPLE : $BeCl_2$

$V = 2$
$M = 2$
$C = 0$
$A = 0$

So $H = \frac{1}{2}(2+2-0+0)$

$= \frac{1}{2}(4)$

$H = 2$

So sp hybridization

EXAMPLE 2 : SO_4^{-2}

Central Atom : Sulphur

$V = 6$
$M = 0$ (No. of monovalent electrons)
$C = 0$
$A = 2$

$H = \frac{1}{2}(6+0-0+2)$

$H = \frac{8}{2} = 4$

So sp^3 hybridization

* Monovalent atoms mean hydrogen, alkali, metals and halogens.

MOLECULAR ORBITAL THEORY

→ Explains magnetic properties of molecules.

→ The number of molecular orbitals formed is equal to the number of atomic orbitals overlapped.

* Bonding Molecular Orbital :

→ Lower in Energy

→ Denoted by σ or π

* Antibonding Molecular Orbital :

→ Higher energy orbital

→ Denoted by σ^* or π^*

→ Electrons are filled in molecular orbitals according to Aufbau and Pauli exclusion principle.

RELATIVE ENERGIES

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

BOND ORDER

Number of bonds formed between two atoms is called bond order.

$$\text{Bond Order} = \frac{N_B - N_A}{2}$$

N_B : No. of electrons present in bonding molecular orbital
N_A : No. of electrons present in anti bonding molecular orbitals

* Bond order is zero if :

$$N_B = N_A$$

* Bond Order > Zero if :

$$N_B > N_A$$

→ All even electron species have bond order in whole number.

→ All odd electron species have bond order in fractions and paramagnetic

→ All even electron species are diamagnetic except:

$16e^-$, $10e^-$
O_2 B_2

→ All iso-electron species have same bond order, magnetic behaviour.

→ $14e^-$ species N_2 , O_2^{+2}, NO^+ , CN^{-1} have bond order $= 3$ and are diamagnetic

→ $16e^-$ species : O_2 , N_2^{-2} , NO^{-1} have bond order $= 2$ and are paramagnetic.

* FINDING BOND ORDER

1. MOLECULES AND IONS HAVING TOTAL NO. OF ELECTRONS IN RANGE 1-2

$$B.O = \frac{n}{2}$$

n : Total number of electrons.

e.g H_2

Total Electrons = 2

$$B.O = \frac{2}{2} = 1$$

2. TOTAL ELECTRONS = 3-6

$$B.O = \frac{|4-n|}{2}$$

'| |' indicates mod function i-e value of bond order is always positive.

e.g Li_2^+ (5 electrons)

$$B.O = \frac{|4-5|}{2}$$

$$= \frac{1}{2}$$

$$= 0.5$$

3. TOTAL ELECTRONS : 7 - 14

$$B.O = \frac{|8-n|}{2}$$

e.g CO

Total electrons = 6+8 = 14

$$B.O = \frac{|8-14|}{2} = 3$$

4. TOTAL ELECTRONS : 15 - 20

$$B.O = \frac{|20-n|}{2}$$

e.g NO

Total electrons = 15

$$B.O = \frac{|20-15|}{2} = 2.5$$

* PARAMAGNETIC

Paramagnetic means attracted to magnetic field. Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted to magnetic field.

* DIAMAGNETIC

Diamagnetic substances are repelled by magnetic field. These substances are characterized by paired electrons. There are no unpaired electrons.

→ No He molecule will exist according to MOT. There are two electrons in each of the bonding and antibonding orbitals giving zero bond order.
He is more stable than He_2.

→ O_2 is more paramagnetic than O_2^+

SIGNIFICANCE OF MOT

1. Predicts bond feasibility
2. If $N_B > N_A$, molecule is stable
3. Greater bond order, greater bond dissociation energy
4. Bond length is inversely proportional to bond order.

BOND ENERGIES

→ The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy

→ Unit of Bond Energy is kJ/mol

* NON-POLAR BOND ENERGY

When sharing of electrons is between two same atoms (e.g H_2) each atom contributes half of bond energy

* POLAR BOND ENERGY

If the sharing of electrons is between two different atoms (e.g in HCl) the bond energy gives higher than calculated value. This shows that with unequal sharing of electrons, there comes an additional binding energy.

Greater the charge difference between the bonded atoms, greater will be additional bond energy.

RELATIVE STRENGTH

Polar bonds are stronger than non-polar bonds bcz the bond energy of polar bonds is greater than non-polar bonds.

* FACTORS AFFECTING BOND ENERGY

1. ELECTRONEGATIVITY DIFFERENCE

Greater E.N difference, greater bond energy

$H-F > H-Cl > H-Br > H-I$

2. ATOMIC SIZE

Larger atomic size, smaller bond energy

3. BOND LENGTH

Shorter bond length, higher bond energy

e.g

$C \equiv C > C=C > C-C$

* Bond energy may be positive or negative

→ Bond Breaking is endothermic

→ Bond formation is exothermic

* VALUES :

1. Bond energy of H_2 (For one mole) :

436 kJ/mol

2. Bond energy of H_2 molecule :

$= 436\ kJ\ mol^{-1} \div N_A$

$= 72 \times 10^{-23}\ kJ/bond$

BOND LENGTH

"The distance between the nuclei of two atoms forming a covalent bond is called bond length".

***UNITS:** A°, nm, pm

*DETERMINATION OF BOND LENGTH

1. Electron Diffraction
2. X-Ray Diffraction (XRD)
3. Spectral studies

* FACTORS AFFECTING BOND LENGTH

1. Greater the E.N difference between bonded atoms, shorter will be bond length.
   order of bond length in HX is:
   H-I > HBr > H-Cl > H-F

2. Ionic character shortens bond length.

3. Involvement of π- bond reduces bond length.

4. Greater s- character in the hybrid orbital results in shortening of bond length.

5. Along a period, bond length decreases.
   Down the group, bond length increases.

* $\text{Bond length} \propto \frac{1}{\text{Bond Energy}}$

* FOR HOMO ATOMIC MOLECULES

Bond length equals to sum of atomic radii.

* FOR HETERONUCLEAR DIATOMIC MOLECULES

Bond length for heteronuclear diatomic molecules is shorter than the sum of their atomic radii. This is due to an increase in electronegativity.

VALUES

H-H : 74 pm
Cl-Cl : 198 pm

Covalent Bond Radius of H : 37 pm (74÷2)
Bohr's Radius for H : 53 pm

IONIC BOND

Difference in E.N > 1.7

COVALENT BOND

ΔE.N < 1.7

Polar covalent : ΔE.N b/w 0.9 - 1.7
Non-Polar Covalent : ΔE.N < 0.9