Bond characteristics: Bond length, Bond Enthalphy, Bond <u>angle, Bond order</u>

1. Bond Angles

- i. It is the angle between any two bonded atoms at central atom in a molecule.
- ii. Bond angles of molecule may (or) may not same.

iii. In a molecule if all Bond angles are not same then is unsymmetrical and less stable.

iv. Bond angles of molecules depend upon

- a. Electro negativity difference between two bonded atoms
- b. Size of central atom and size of surrounding atoms.

v. Bond angle decreases with increase in electronegative difference between central atom and bonded atoms



vi. Bond angle decreases with increase in size of central atom,

 $NH_3 > PH_3 > AsH_3 > SbH_3$

vii. Bond angle increases with increase in size of surrounding atoms



viii. In isoelectronic and isostructural Molecules the Bond angles are same

- **Ex:** CO_2, NO_2^+ are iso electronic & iso structural. So bond angles are same i.e (1)
 - ix. Greater the bondangle greater will be the stability of molecule.

Ex: Stability of $BeCl_2(180^\circ) > BCl_3(120^\circ)$

2. Bond Energy-or bond dissociation energy-"It is the energy required to convert one mole of a diatomic molecular substance in the gaseous state into its free constituent atoms."

Ex:
$$C_2H_5 - Br \xrightarrow{\text{hom olytic cleavage}} (C_2H_5^{\bullet}) + (Br^{\bullet});$$

Bond energy = $280.9 \text{ KJ mol}^{-1}$

$$C_2H_5 - Br \xrightarrow{heterolytic cleavage} (C_2H_5^+) + (Br: T_2)$$

Bond energ = 764.94KJ mol⁻¹

- *In homolytic cleavage free radicals are formed and in heterolytic clevage ions are formed.
 - i) As the bond energy increases, the stability of the bond increases and reactivity of the substance decreases.
- E.g.: O₂, N₂ etc. are stable gases in the atmosphere because their bond energies are high.

ii) σ^- bonds are stronger than π bonds.

Eg:-C-C- bond energy = 341.1 KJ mol⁻¹

- C= C - bond energy = $610.7 \text{ KJ mol}^{-1}$

www.sakshieducation.com

The bond strength values show that σ^- bond strength $>\pi^-$ bond strength.

- iii) As the number of bonds increases between the same atoms, the overall bond strength also increases.
- iv) In compounds of same group the bond energy of similar type of bonds gradually decreases down the group.

Eg: Bond H - F H - Cl H - Br H - I

B.E (kjmol⁻¹) 568.2 431.9 366.1 298.3

*Among the halogens, chlorine has highest bond energy. $Cl_2 > Br_2 > F_2 > I_2$

v) With increase in 'p' character of the hybrid orbitals, the energy of the σ -bond formed by it increases.

The increasing order of bond energies for hybrid orbitals is as follows.

sp < sp2 < sp3

%p 50 33 25

vi) As the number of lone pairs of electrons on bonded atoms increases, the bond energy decreases.

$$\begin{array}{c} -\overset{l}{C}-\overset{l}{C}-\overset{l}{C}-\overset{}{N}-\overset{}{N}-\overset{}{N}-\overset{}{N}-\overset{}{N}-\overset{}{\Omega}-\overset{}{}$$

- vii) The energy required for heterolytic cleavage of bond is higher than that required for homolytic cleavage.
- viii) As the bond energy increases, the stability of the bond also increases. The chemical reactivity of the substance decreases. N₂ is very stable gas in the atmosphere because the bond energy is high (944 kJ mol⁻¹)
 - ix) In case of polyatomic molecules the measurement of bond strength is complicated.
 The average bond energy of C–H bond in CH₄ is equal to one fourth of the energy

of dissociation of CH_4 into atoms (C + 4H). However, the bond energy of each C– H bond in CH_4 molecule is different.

 $CH_{4(g)}CH_{3(g)} + H_{(g)}$; H = 426 kJ mol⁻¹.

 $CH_{3(g)}CH_{2(g)} + H_{(g)}$; H = 439 kJ mol⁻¹.

 $CH_{2(g)} CH_{(g)} + H_{(g)}$; H = 451 kJ mol⁻¹.

 $CH_{(g)}C_{(g)} + H_{(g)}$; H = 347 kJ mol⁻¹.

 $CH_{4(g)}C_{(g)} + 4H_{(g)}$;H 1663 kJ mol⁻¹.

Hence, average C–H bond energy is calculated as 1663/4 = 416 kJ mol⁻¹

- x) Bond energy values are used to estimate the heat of a reaction.
- 3. Bond length: It is "The Equilibrium distance between the centres of the two nuclei of covalently bonded atoms in a molecule. It is measured in angstroms or nanometers or Pico meters."
- i. Bond length increases with an increase in the size of the bonded atoms.

Ex. F-F < Cl-Cl < Br-Br < I-I

H-F < H-Cl < H-Br < H-I

- ii. The bond length of a homonuclear diatomic molecule is twice the covalent radius. Covalent radius of H atom is 37 pm. H–H bond length is 74pm.
- iii. A double bond is shorter than a single bond. A triple bond is shorter than a double bond. This is because of an increase in the number of bonds. C–C bond length in ethane is 154 pm, C=C bond in ethylene is 134 pm and C=C bond in acetylene is 120 pm.
- iv. The bond length decreases with the increase in's' character or decrease in 'p' character in case of hybrid orbitals. The bond length of Csp3–H is 110 pm (25%, s character), Csp2–H is 109 pm (33% s character) and Csp–H is 106 pm (50% s character).

- v. Bond length of a polar bond is smaller than the theoretical bond length, calculated by the addition of covalent radii.
- iv. Bond energy and stability of molecule increases as the bond length decreases.
- vii. Bond length decreases due to resonance

E.g.In benzene molecule "C - C" bond length is 0.139nm.which is intermediate between C-C single (0.154nm) and C=C double bond (0.134 nm) due to resonance.

Bond Order In Some Molecular And Ions

Molecule	Specified	Total number	Number of	Bond order
or ion	bond	of bonds	canonical	
		(structures	
Ozone	0–0	3	2	1.5
Benzene	C–C	3	2	1.5
Graphite	C–C	4	3	1.33
Nitrate	N–O	4	3	1.33
Phosphate	P–O	5	4	1.25
Sulphite	S-O	4	3	1.33
Sulphate	S-O	6	4	1.5
Carbonate	• C–O	4	3	1.33
Chlorite	Cl–O	3	2	1.5
Chlorate	Cl–O	5	3	1.67
Perchlorate	Cl–O	7	4	1.75

Polarity of Bonds-Dipole Moment: It is defined as the product of magnitude of chargeon either of the two bonded atoms (e) and the distance (d) between them in a polar molecule.

www.sakshieducation.com

i. = exd .units of esu.cm or Debye.S.I units of dipole moment = columb.metre

1Debye=esu.cm = 3.33564×10^{-30} C.m

ii. The dipole moment of an electron seperated from unit positive charge by a distance of

 $1A^{0}$ is $4.8x10^{-10}$ esu $x10^{-8}$ cm = $4.8x10^{-18}$ esu cm=4.8 Debye

iii. Dipole moment is a vector quantity, it has both direction and magnitude. The total Dipole moment of a molecule is the vector sum all the bond moments.

a. Molecules having dipole moment $\mu = 0$ are called non polar molecules.

b. Molecules with $\mu > 0$ are polar.

c. Greater is μ , greater is the polarity.

Applications of dipole moment

1) Dipole moment is helpful in predicting the geometry of the molecule.

2) Dipole moment helps in determining the polarity

3) Dipole moment can distinguish between symmetrical and non symmetrical molecules

Eg. CO₂ has 0, dipole moment as it is symmetrical where as H_2O has a dipole

moment of 1.85 D.

$$c \xrightarrow{} c \xrightarrow{} 0$$

$$\mu = 0$$

$$H = 1.85$$

$$H$$

Net dipole moment of water = $1.85 \text{ D} = 1.85 \text{ x} 3.336 \text{ x} 10^{-30} \text{ C.m} = 6.17 \text{ x} 10^{-30} \text{ C.m}$ **E.g.**-Dipole moment of $< (0.8 \text{ x} 10^{-30} \text{ C.m})$ (4.9 x10⁻³⁰ C.m)

*In the bond pairs are moving opposite to lonepair and in NH³ the bond pairs are moving towards the lone pair.

4) Cis and Trans isomers can be distinguished by dipole moments; usually cis isomers have higher dipole moment and hence higher polarity



Note: If inductive effect of two groups is opposite then Tran's isomer will have greater dipole moment



6) Hybridisation can be determined by dipole moment for eg

i) If a molecule AB $_2$ has = 0, the orbitals used by A (z < 21) must be sp hybridized. **E.g.** BeF₂

ii) If a molecule AB_3 has = 0, the orbitals used by A (z < 21) must be sp² hybridised. **E.g.** BF₃

iii) If a molecule AB₄ has = 0, the orbitals used by A (z < 21) must be sp³ hybridised. **E.g.** CCl₄

7) Dipole moment for tri (or) polyatomic molecules is $\mu_R = 2 \times Bond \ moment \times \cos\theta/2$

www.sakshieducation.com

Polarity of a Covalent Bond

i) By electro negativity difference: - It is determined by the electronegativity difference of the participating atoms. The higher the electronegativity difference between the two atoms more is the percentage ionic character of a covalent bond. The mathematical equations for calculating, the % ionic character

a) Puling equation

$$= 100 \left[1 - \exp^{\frac{1}{4}(X_A - X_B)} \right]$$

% ionic character

b) Hannay and Smith equation

% ionic character = $16(X_A - X_B) + 3.5 (X_A - X_B)^2$

Where X_A and X_B are the electronegativities of atoms

From dipole moment -

% ionic character = $\frac{observed \ dipole \ moment \ of \ bond}{calculated \ dipole \ moment \ of \ bond} \times 100$

Eg: Calculate the percentage ionic character of HCl molecule. The bond length is 1.275 A^o and observed dipole moment is 1.03 D

A and observed upper momentals 1.05 D

Solution - For 100% ionic character the dipole moment should be

$$\mu = e \times d = 4.8 \times 10^{-10} \times 1.275 \times 10^{-8} = 6.12 D$$

The observed dipole moment is = 1.03 D. % ionic character

$$=\frac{1.03}{6.12}\times100=16.83\%$$