BOND PARAMETERS

Covalent bonds are characterized by the following four parameters:

1) Bond length
2) Bond Energy
3) Bond Angle
4) Bond Order

1) BOND LENGTH

The separation between the nuclei of two bonded atoms is referred to as bond length or bond distance. It is expressed in angstrom (A) or picometre (pm) units:

[1 Å=10^{-8}cm; 1 pm = 10^{-12} m]

BOMD LENGTHS

Bond	Bond length (Å)	Bond	Bond length (Å)
H-H (in H_2)	0.74	H-H (in HF)	0.92
Cl-Cl (in Cl_2)	1.99	H-Cl (in H Cl)	1.27
Br-Br (in Br_2)	2.28	H-Br (in HBr)	1.41
I-J (in I_2)	2.67	H-I (in HI)	1.61
F-F	1.42	O-H (in H_2O)	0.96
C-C	1.54	O=O (in O_2)	1.21
Bond	Bond length (Å)	Bond	Bond length (Å)
C=C (in C_2H_4)	1.34	C-O (in alcohols)	1.43
C=C (in C_2H_2)	1.21	C-O (in aldehydes)	1.22
C-N (in amines)	1.47	N-H	1.03
C-H (in organic Molecules)	1.08	S-H	1.35
		N-O	1.36
		N=O	1.22

Important features

(i) The bond length of harmonic linear diatomic molecules is double the covalent radii. As the size of atoms increases, the bond length also increases.

H_2	C-H	C-Cl
0.74 Å	1.09 Å	1.77 Å

(ii) Double bonds exhibit shorter lengths than single bonds between the same two atoms, and triple bonds are even shorter than double bonds.

Single bond > Double > Triple bond

(iii) The decrease in bond length is associated with an increase in s-character, given that the s-orbital is smaller than a p-orbital.

Sp^3 C-H=1.112 Å (25% 5-character as in alkanes)	Sp^2 C-H=1.103 Å (33.3% 5-character as in alkanes)

Sp C-H=1.108 Å
(50% 5-character as in alkanes)

(iv) The bond length of a polar bond is shorter than the theoretically calculated bond length for a non-polar bond.

(v) Bond length is influenced by resonance and hyperconjugation. The bond length, or bond distance, represents the internuclear distance between two covalently bonded atoms.

(i) In the case where the electronegativities of both atoms are equal, the bond length is equal to the sum of the covalent radii of the two bonded atoms:

$$d_{A-A} = r_A + r_A$$

(ii) Conversely, when the electronegativities of the two bonded atoms differ, the bond length is shorter than the sum of their covalent radii:

$$d_{A-B} < r_A + r_B$$

Factors Affecting Bond Length

(i) **Size of Atoms**

$$HI > HBr > HCl > HF$$

$$H_2Te > H_2Se > H_2S > H_2O$$

(ii) **Hybridization State of The Bonded Atoms:** If the s-character in hybridization state of the bonded atoms increase, the C–H bond distance decreases.

Ex. In C – C single bond.

$sp^3 - sp^3$ single bond length = 1.54 Å

$sp^3 - sp^2$ single bond length = 1.52 Å

$sp^2 - sp^2$ single bond length = 1.51 Å

$sp^3 - sp$ single bond length = 1.46 Å

$sp^2 - sp$ single bond length = 1.45 Å

$sp - sp$ single bond length = 1.37 Å

Bond length decreases in the order $sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$

(iii) **Resonance or Delocalization of Electrons of The Bond:** Bond length between atoms is changed if a molecule shows resonance.

2) Bond Angle

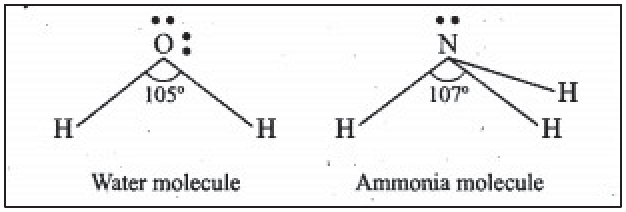
The bond angle, in a molecule consisting of three or more atoms, refers to the angle between two adjacent bonds at an atom. Bond angles mainly depend on the following three factors:

(i) Hybridization: The bond angle is contingent upon the hybridization state of the central atom.

Hybridization	Sp^3	Sp^2	Sp
Bond angle	109°	102°	180°
Example	CH_4	BCl_3	$BeCl_2$

It is noted that an increase in s-character within the hybrid bond corresponds to an increase in the bond angle.

(ii) Lone pair repulsion: The bond angle is influenced by the presence of a lone pair of electrons at the central atom. A lone pair of electrons at the central atom tends to repel the shared pair (bonded



pair) of electrons, causing the bonds to shift slightly inward, resulting in a reduction of the bond angle.

For instance, the bond angle in NH^3 is 107°, and the bond angle in H^2O is 105°, despite both nitrogen (N) and oxygen (O) atoms undergoing sp3 hybridization.

(iii) Electronegativity: A decrease in the electronegativity of the central atom leads to a decrease in the bond angle. Alternatively, if the central atom remains constant, the bond angle increases with a decrease in the electronegativity of the surrounding atoms. The angle between two bonds is known as bond angle.

Factors Affecting Bond Angle

(i) **Hybridisation State of Central Atom:** Compounds having different hybridization have different bond angle.

Ex.	BeH_2	BH_3	CH_4
Hybridisation	sp	sp^2	sp^3
Bond angle	180º	120º	109º28'

(ii) **Lone Pair of Electron:** If compounds have same hybridization states, then bond angle depends on lone pair of electrons.

Ex.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
Lone pair e^-	zero	one	two
Bond angle	109º28'	107º	105º

The different in bond angle is explained on the basis of following repulsion sequence

The repulsion between:

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

(iii) **Electronegativity:** In compounds with the same hybridization state of the central atom and a similar number of lone pairs of electrons, the bond angle is contingent upon electronegativity.

Bond angle $\propto$ electronegativity

Ex.

$$H_2O > H_2S$$

$$NH_3 > PH_3$$

E.N. of oxygen is more than sulphur therefore the bond angle in H_2O will be more than H_2S.

(iv) **Size of Terminal Atoms:** When size of terminal atoms increases, bond angle increases.

Ex.

$$OF_2 < Cl_2O < Br_2O$$

$$PF_3 < PCl_3 < PBr_3$$

3) Bond Energy

Bond energy, also known as bond strength, is the energy needed to break a bond within a molecule. Each bond possesses a specific energy value, serving as a measure of its strength. It is commonly observed that the bond strength or bond energy increases with a shorter bond length.

$$\text{H-H(g)} \rightarrow \text{2H(g)} \qquad \triangle H = 436\ KJ\ moj^{-1}$$

(Bond length = 0.74 Å)

$$\text{Cl-Cl(g)} \rightarrow \text{H(g)+Cl(g)} \qquad \triangle H = 242\ KJ\ moj^{-1}$$

(Bond length = 1.99 Å)

$$\text{H-O-H(g)}\rightarrow\text{2H(g)+O(g)};\ \triangle H = 242\ KJ\ moj^{-1}$$
$$\text{(Bond length = 1.27 Å)}$$

Consider the dissociation of water molecule which consists of two O-H bonds.

$$\text{H-O-H(g)}\rightarrow\text{2H(g)+O(g)};\qquad \triangle H = 926\ kJ\ mol^{-1}$$

$$\text{The average bond energy of O-H bond} = \frac{926}{2} = 463\ \text{KJ}$$

Likewise, the mean bond energy of the C-H bond in CH^4 is equivalent to one-fourth of the dissociation energy required for the separation of CH^4 into (C+4H). However, it's important to note that the bond energy of each individual C-H bond in CH^4 differs.

$$CH_4(g) \rightarrow CH_3(g) + H(g);\ \triangle H = 242\ KJ\ moj^{-1}$$
$$CH_3(g) \rightarrow CH_2(g) + H(g);\ \triangle H = 239\ KJ\ moj^{-1}$$
$$CH_2(g) \rightarrow CH(g) + H(g);\ \triangle H = 451\ KJ\ moj^{-1}$$
$$CH(g) \rightarrow C(g) + H(g);\ \triangle H = 347\ KJ\ moj^{-1}$$
$$CH_4(g) \rightarrow C(g) + 4H;\ \triangle H = 1663\ KJ\ moj^{-1}$$

$$\text{Hence, average bond energy C-H} = \frac{1663}{4} \simeq 416\ \text{KJ mol}^{-1}$$

Hence, the bond energy of a C-H bond is contingent on the sequence in which the specific hydrogen atom is detached from the molecule. This scenario is applicable to all molecules comprising more than two atoms. The resilience of the bonds is determined by the sequence in which they are disrupted. The average bond energies for some common bonds are provided below:

Bond Energies in Kj Mol^{-1}

Bond	Bond energy	Bond	Bond energy
$H-H$	436	$Cl-Cl$	242
$O=O$	497	$Br-Br$	193
$N=N$	945	$I-I$	151
$F=F$	158	$H-F$	563
$H-Cl$	431	$N-H$ (in NH_3)	389
$H-Br$	366	$O-H$ (in water)	464
$H-I$	299	$C-C$	346
$C-H$ (in methane)	416	$C=C$ $\left(\text{in } C_2H_4\right)$	598

Important features

(i) The bond energy's magnitude is influenced by the type of bonding, with most covalent bonds having energies ranging between 50 to 100 kcal mol^{-1} (200-400 kJ mol^{-1}). Sigma bonds exhibit greater strength than pi bonds.

(ii) In a diatomic molecule, a double bond possesses higher bond energy than a single bond, and a triple bond has higher bond energy than a double bond between the same atoms.

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

(iii) The bond energy's magnitude depends on the size of the atoms forming the bond, i.e., the bond length. A shorter bond length corresponds to higher bond energy.

(iv) Resonance in a molecule has an impact on the bond energy.

(v) Bond energy decreases with an increase in the number of lone pairs on the bonded atom, owing to electrostatic repulsion between lone pairs of electrons on the two bonded atoms.

(vi) Homolytic and heterolytic fission involve different amounts of energies, with homolytic fission generally having lower values compared to heterolytic fission.

(vii) Down a group, the bond energy decreases for similar molecules.

(viii) The bond energy increases in the following order:

$$s < p < sp < sp^2 < sp^3$$

$$C - C > N - N > 0 - 0$$

346 163 146.4 kJ mol^{-1}
(No lone pair) (One lone pair) (Two lone pairs) .

(ix) The bond energy of a covalent molecule can be calculated using Pauling's formula,

$$E_{A-B} = 1/2[E_{A-A} + E_{B-B}] + 23(x_A - x_B)^2$$

where EA - B, EA-A and EB- B are the bond energies of the molecules A-B, A^2 and B^2 respectively and x_A and x_B are the electronegativity of A and B.

(i) The energy required to break one mole of a bond and separate the bonded atoms in the gaseous state is termed the bond energy of that particular bond.

(ii) B.E. is expressed in KJ mol^{-1} (in SI units) or in Kcal mol^{-1}.

Factors Affecting Bond Energy

(a) **Electronegativity Difference of The Bonded Atoms:** An increase in the electronegativity difference of the bonded atoms results in an increase in bond energy due to the heightened ionic nature of the bond.

Ex. Bond strength of hydrogen halides decreases in the order

$$H – F > H – Cl > H – Br > H – I$$

(b) **Bond Order:** Bond energy ∝ Bond order, therefore the increasing order of bond energy is:

$$C – C < C = C < C \equiv C$$

(c) **Hybridisation State of The Bonded Atoms:** Bond energy ∝ s-character

Ex. $–C – H < –C = H < – C \equiv H$

sp^3 sp^2 sp

(d) **Atomic Size of Bonded Atoms:** Atoms with smaller atomic radii form stronger bonds due to increased overlapping of atomic orbitals.

Ex. B.E. of halogens is of the order

$$Cl – Cl > Br – Br > I – I$$

because their atomic sizes are in the order Cl < Br < I.

(e) **Extent of Overlapping of Atomic Orbitals:** A greater extent of overlapping of component atomic orbitals imparts greater strength to the bond.

(f) **Repulsion Between the Lone Pairs of Electrons of Bonded Atoms:**

$$\text{Bond energy} \propto \frac{1}{\text{No. of lone pair of electron on the bonded atoms}}$$

Ex. the bond energies of the following single bonds having zero, one, two and three lone pair of electrons are in the order.

$$C - C > \ddot{N}\_ > \ddot{N}_{>}:\ddot{O}\_ > \ddot{O}: >: \ddot{F}:\_ > \ddot{F}::$$

Bond Enthalpy

Bond enthalpy is the energy needed to break one mole of bonds of a specific type between two atoms in the gaseous state. It is expressed in kJ mol and is typically measured at 298 K.

Breaking a bond is an endothermic operation, meaning it requires input energy. Consequently, the bond enthalpy associated with this process is assigned a positive sign.

The magnitude of bond enthalpy tends to increase with the multiplicity of the bond, even when the atoms participating in the bond formation remain the same. This increase in magnitude can be attributed to the heightened attractive force between the nuclei and electrons, which intensifies with the formation of multiple bonds.