CHEMICAL BONDING AND MOLECULAR STRUCTURE

BOND PARAMETERS

❖ 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 distance between the nuclei of two atoms bonded together is termed bond length or bond distance. It is expressed in angstrom (A) or picometre (pm) units:

$$[1\ \text{Å}=10^{-8}\text{cm};\ 1\ \text{pm} = 10^{-12}\ \text{m}]$$

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 N-O N=O	1.35 1.36 1.22

Important features:

(i) The bond length of the hormonic 1ear diatomic molecules are twice the covalent radii. Bond length increases with the increase in the size of atoms.

H_2	C-H	C-Cl
0.74 Å	1.09 Å	1.77 Å

(ii) The lengths of double bonds are less than the lengths of single bonds between the same two atoms and triple bonds are even shorter than double bonds.

Single bond > Double > Triple bond

(iii) Bond length decreases with increase in s-character since 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) Bond length of polar bond is smaller than the theoretical non-polar bond length.

(v) Bond length is affected by resonance and hyperconjugation.

The internuclear distance between the two single covalently bonded atoms is called bond length or bond distance.

(i) If the electronegativities of both the atoms are equal, then the bond length is equal to the sum of the covalent radii of two bonded atoms.

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

(ii) If the electronegativities of two bonded atoms differ, then the bond length is smaller 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 increases, 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 are changed if a molecule shows resonance.

2) BOND ANGLE

Angle between two adjacent bonds at an atom in a molecule made up of three or more atoms is known as the bond angle.

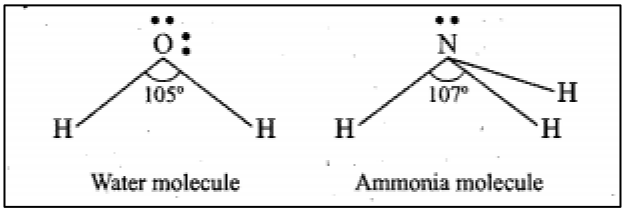
Bond angles mainly depend on the following three factors:

(i) Hybridization: Bond angle depends on the state of hybridization of the central atom.

Hybridization	Sp^3	Sp^2	Sp
Bond angle	109°28	102°	180°
Example	CH_4	BCl_3	$BeCl_2$

It is observed that as s-character increases in the hybrid bond, the bond angle increases.

(ii) Lone pair repulsion: Bond angle is affected by the presence of lone pair of electrons at the central atom. A lone pair of electrons at the central atom always tries torepel the shared pair (bond. edpair) of electrons. Due to this, the bonds are displaced slightly inside resulting in a decrease of bond angle. The bond angle in NH3 is 107° and bond angle in H20 is 105° inspite of the fact that N-atom and O-atom undergo sp3 hybridization.



(iii) Electronegativity: If the electronegativity of the central atom decreases, bond angle decreases. In case the central atom remains the same, bond angle increases with decrease ill 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 electron.

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: When compounds having same hybridisation state of central atom and some number of lone pair of electrons, then bond angle depends on 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 or bond strength is defined as the amount of energy required to break a bond in a molecule. Each bond has a characteristic value of this energy and is measure of the strength of the bond. It is generally observed that shorter the bond length, greater is the bond strength or bond energy of the bond.

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

(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)

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

(Bond length = 1.27 Å)

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

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

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

Similarly, the average bond energy of C-H bond in CH4 is equal to one-fourth of the energy of dissociation of CH4 into (C + 4H). However, the bond energy of each C-H bbnd in CH4is different.

$$CH_4(g) \rightarrow CH_3(g) + H(g); \qquad \triangle H = 242\ KJ\ moj^{-1}$$

$$CH_3(g) \rightarrow CH_2(g) + H(g); \qquad \triangle H = 239\ KJ\ moj^{-1}$$

$$CH_2(g) \rightarrow CH(g) + H(g); \qquad \triangle H = 451\ KJ\ moj^{-1}$$

$$CH(g) \rightarrow C(g) + H(g); \qquad \triangle H = 347\ KJ\ moj^{-1}$$

$$CH_4(g) \rightarrow C(g) + 4H; \qquad \triangle H = 1663\ KJ\ moj^{-1}$$

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

Thus, the bond energy of C-H bond depends on the order in which the particular hydrogen atom is lost from the molecule. A similar situation exists for all molecules with more than two atoms. The strengths of the bonds depend on the order in which they are broken. Average bond energies of some common bonds are listed below:

BOND ENERGIES IN kJ mol^{-1}

Bond	Bond energy	Bond	Bond energy
H – H	436	$Cl - Cl$	242

Bond	Bond energy	Bond	Bond energy
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 (in C_2H_4)	598

Important features:

(i) The magnitude of the bond energy depends on the type of bonding. Most of the covalent bonds have energy between 50 to 100 kcal mol-l (200-400 kJ mol-I). Strength of sigma bond is more than that of a 1t-bond.

(ii) A double bond in a diatomic molecule has a higher bond energy than a sirigle bond and" triple bond has a higher bond energy than a double bond between the same atoms.

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

(iii) The magnitude of the bond energy depends on the size of the atoms forming the bond, i.e., bond length. Shorter the bond length, higher is the bond energy.

(iv) Resonance in the molecule affects the bond energy.

(v) The bond energy decreases with increase in number of lone pairs on the bonded atom. This is due to electrostatic repulsion of lone pairs of electrons on the two bonded toms.

(vi) Homolytic and heterolytic fission involve different amounts of energies. Generally, the values are low for homolytic fission of the bond in comparison to heterolytic fission.

(vii) Bond energy decreases down the group in case of similar molecules.

(viii) Bond energy increases in the following order:

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

$$\mathrm{C-C > N-N > 0-0}$$

$$\underset{\text{(No lone pair)}}{346} \quad \underset{\text{(One lone pair)}}{163} \quad \underset{\text{(Two lone pairs)}}{146.4\ kJ\ mol^{-1}}.$$

(ix) Bond energy of covalent molecule can be calculated using Pauling's formula.

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

where EA- B, EA-A and EB- B are the bond energies of the molecules A-B, A2 and B2 respectively and xA and xB are the electronegativity of A and B.

(i) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state are known as 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:** As the EN difference of the bonded atoms increase the bond energy increases because the ionic nature of the bond increases.

Ex. Bond strength of hydrogen halides decreases in the order

$$\mathrm{H-F > H-Cl > H-Br > H-I}$$

(b) **Bond Order:** Bond energy $\propto$ Bond order, therefore the increasing order of bond energy is $\mathrm{C-C < C=C < C\equiv C}$

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

Ex. $\mathrm{-C-H < -C=H < -C\equiv H}$

$$\mathrm{sp^3 \quad sp^2 \quad sp}$$

(d) **Atomic Size of Bonded Atoms:** Atoms with small atomic radii form stronger bonds because the extent of overlapping of atomic orbitals is more

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 larger extent of overlapping of component atomic orbitals impart great 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.

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

4) **Bond order**:

Bond order is defined as the number of bonds or number of shared electron pairs between two atoms in a molecule.

$H - H$ or $H : H$ Bond order $= 1$

$O = O$ or $O ::$ Bond order $= 2$

$N \equiv N$ or $N \vdots\vdots N$ Bond order $= 3$

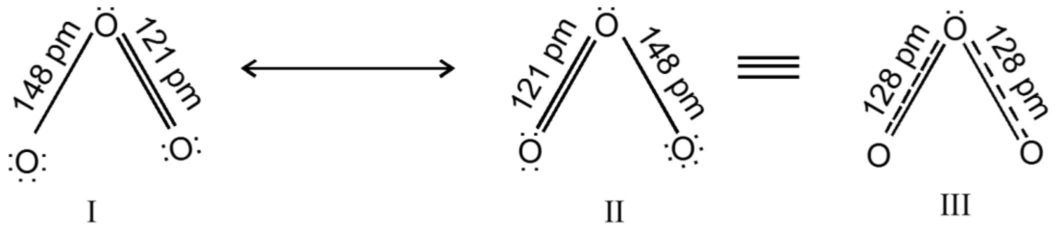
$C \equiv O$ or $C \vdots O$ Bond order $= 3$

Isoelectronic molecules or ions have same bond order.

For example, F2 and O~- (18 electrons), have bond order 1. N2, CO and NO+ (14 electrons) have bond order 3. It is observed that with increase in bond order, bond enthalpy increases while bond length decreases.

RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below:



Resonance in The O_3 Molecule

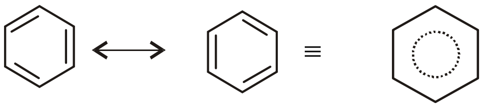
(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O – O single bond and a O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus, the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3 . According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Thus, for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3, more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

Definition: Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound

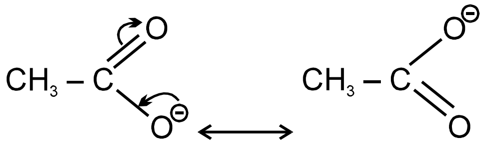
Resonance Hybrid: It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



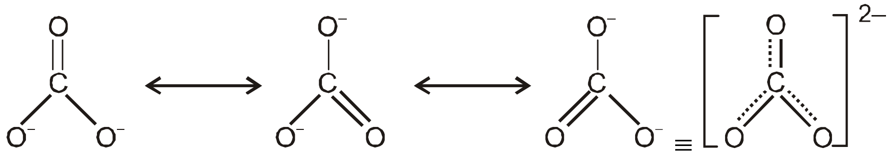
Resonance hybrid

Ex.

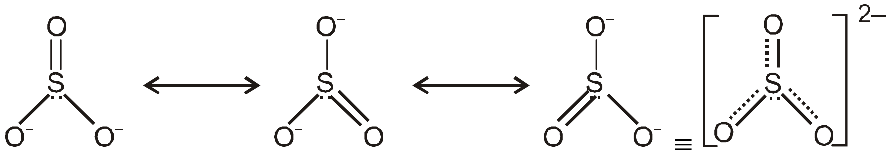
(i)



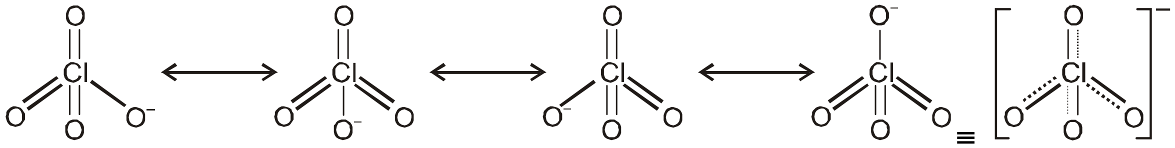
(ii)



(iii)

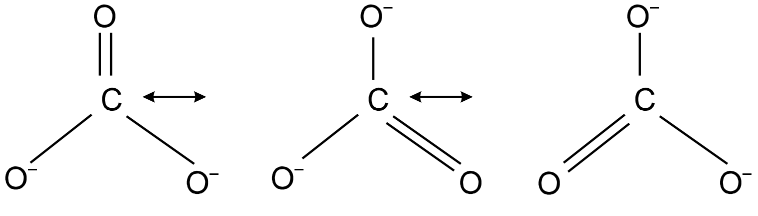


(iv)



- Bond order = $\dfrac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}}$

Ex.



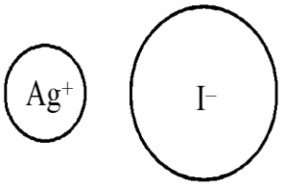
Bond order = $\dfrac{2+1+1}{3} = 1.33$

- Resonance energy = Actual bond energy – Energy of most stable resonating structure.
- Stability of molecule α resonance energy.
- More is the number of covalent bonds in molecule more will be its resonance energy.
- Resonance energy α number of resonating structures.

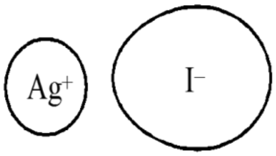
POLARITY OF COVALENT BOND

TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

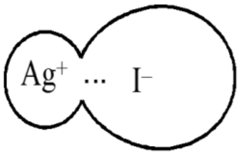
(a) Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



separate ions



distorted ion



covalent character in ionic bond

(b) Factors Influencing Ion – Deformation or Increasing Covalent Character

(i) Large Charge on the Ions

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminum chloride is a covalent compound whereas NaCl, AlF_3, AgF are ionic.

(ii) Small Cation and Large Anion

For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover, a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighboring cation. Hence there will be increased covalent character with a small cation and a large anion, as in AgI.

(iii) Cation with a Pseudo-Inert Gas Type of Electronic Configuration

A cation with a 18 electron in outermost shell such as Ag^+ ([Kr] $4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+. The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+. Thus, AgI is more covalent than KI, although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors, which influence covalent character, are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

Polarization power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi(\text{phi}) = \frac{\text{Charge on cation}}{\text{Size of cation}}$$