

Chemical Bonding

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CHEMICAL BONDING

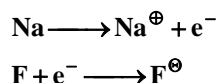
C1 INTRODUCTION

A molecule will only be formed if it is more stable, and has a lower energy than the individual atoms. Normally only electrons in the outermost shell of an atom are involved in forming bonds. We divide elements into three classes :

- (A) Electropositive elements, whose atoms give up one or more electrons easily. They have low ionisation potentials.
- (B) Electronegative elements, which can gain electrons. They have higher value of electronegativity.
- (C) Elements which have little tendency to lose or gain electrons.

C2A Ionic Bonding

An ionic bond is formed when a **metal atom** transfers one or more electrons to a **nonmetal atom**.



As a result of this transfer the metal atom becomes **cation** and the nonmetal the **anion**.

Cations and anions attain noble gas configuration with outer shell octet of electrons. In some cases cations may not have octet but different outershell.

Properties of Ionic solids

They are good conductor of electricity in fused state and in aq. solution. They are soluble in polar solvents and insoluble in non polar solvents. They have high m.p. and b.p. They have strong force of attraction

between cation and anion (Coulombic force) $F = \frac{z_1 z_2 e^2}{Dr^2}$

Practice Problems :

- Which of following elements has the strongest tendency to form electrovalent compound ?
 (a) Li (b) Na (c) Be (d) Mg
- Which of the following is more ionic ?
 (a) NaCl (b) KCl (c) MgCl₂ (d) CaCl₂

[Answers : (1) b (2) b]

C2B Solubility of Ionic Solids :

By the Coulombic force of attraction $F = \frac{z_1 z_2 e^2}{Dr^2}$. We can study the solubility of ionic solids in different

solvents. Greater the force of attraction between ions, smaller the tendency of the ions to go into solution and thus smaller the solubility.

For a given solute, greater the value of D then smaller the force of attraction between positive and negative ions, hence greater the solubility.

$$D(\text{H}_2\text{O}) > D(\text{CH}_3\text{CH}_2\text{OH}) > D(\text{CH}_3\text{OCH}_3)$$

hence solubility of ionic solid (say NaCl) in $\text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{OCH}_3$

Practice Problems :

- MgSO₄ is soluble while BaSO₄ is insoluble in H₂O. This is because
 (a) lattice energy of BaSO₄ is greater than MgSO₄
 (b) BaSO₄ is more covalent than MgSO₄
 (c) hydration energy of Mg²⁺ is greater than Ba²⁺
 (d) lattice energy of MgSO₄ is greater than BaSO₄

[Answers : (1) c]

C3A Covalent Bonding : If duplet (2) or octet (8) is completed by sharing of electrons between two electronegative elements, the bond formed is called **covalent bond**.

C3B The Octet Rule : For many light atoms a stable arrangement is attained when the atom is surrounded by eight electrons – the octet rule. (In case of H_2 , duplet is completed)

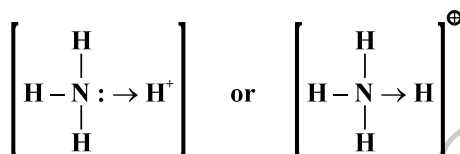
Exceptions to the Octet Rule : In so many cases, the octet rule is violated :

In BeF_2 , octet of Be is not complete, in BF_3 , octet of B is not complete. Other examples are PCl_5 , SF_6 , IF_7 where centre atom is having more than eight electrons.

C3C Coordinate Bonding

A covalent bond results from the sharing of pair of electrons between two atoms where each atom contributes one electron to the bond. It is also possible to have an electron pair bond where both electrons originate from one atom and none from the other. Such bonds are called **coordinate bonds** or **dative bonds**. Since in coordinate bonds, two electrons are shared by two atoms, they differ from normal covalent bonds. It is represented as \rightarrow . Atom/ion/molecule donating electron pair is called **DONOR** or **LEWIS BASE**. Atom/ion/molecule accepting electron pair is called **ACCEPTOR** or **LEWIS ACID** (\rightarrow) points donor to acceptor.

NH_4^+ : NH_3 has three (N — H) bonds and one lone pair. In NH_4^+ formation this lone pair is donated to H^+ (having no electron).



C4A Valence Shell Electron Pair Repulsion (VSEPR) Theory (Gillespie Theory)

The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.

Repulsion is in order : (lp – lp) > (lp – bp) > (bp – bp)

The magnitude of repulsion between pairs of electrons depends on the electronegativity difference between the central atom and the other atom. Double bond cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.

C4B The Effect of Bonding and Lone Pairs of Geometry and Bond Angles

Example	Orbitals on Central Atom	Theoretical Shape	Bond Angle	Distorted Geometry due to Repulsion
$BeCl_2$	2	Linear	180°	Linear
BF_3	3	Plane triangle	120°	Plane triangle
SO_2	3	Plane triangle	119°	Angular
CH_4	4	Tetrahedral	$109^\circ 28'$	Tetrahedral
NH_3	4	Tetrahedral	$107^\circ 48'$	Trigonal pyramidal
NF_3	4	Tetrahedral	$102^\circ 30'$	Pyramidal
H_2O	4	Tetrahedral	$104^\circ 27'$	Angular
F_2O	4	Tetrahedral	102°	Angular
H_2S	4	Tetrahedral	90°	Angular
PCl_5	5	Trigonal bipyramidal	120° and 90°	Trigonal bipyramidal
SF_4	5	Trigonal bipyramidal	$101^\circ 36'$ and $86^\circ 33'$	Irregular tetrahedral
ClF_3	5	Trigonal bipyramidal	$87^\circ 40'$	T-shaped
I_3^-	5	Trigonal bipyramidal	180°	Linear
SF_6	6	Octahedral	90°	Octahedral
BrF_5	6	Octahedral	$84^\circ 30'$	Square pyramidal
XeF_4	6	Octahedral	90°	Square planar

Practice Problems :

1. Molecular shapes of SF_4 , CF_4 and XeF_4 are
- the same, with 2, 0 and 1 lone pair of electrons respectively.
 - the same, with 1, 1 and 1 lone pair of electrons respectively.
 - different, with 0, 1 and 2 lone pairs of electrons respectively.
 - different, with 1, 0 and 2 lone pairs of electrons respectively.

[Answers : (1) d]

- C5 Isoelectronic Principle :** Isoelectronic species usually have the same structure. This may be extended to species with the same number of valence electrons.

Species	Structures
CH_4 , NH_4^+ , BF_4^-	tetrahedral
CO_3^{2-} , NO_3^- , SO_3	planar triangle
CO_2 , N_3^- , NO_2^+	linear

- C6A Valence Bond Theory :** The covalent bond is a region of high electron charge density (high electron probability) that results from the overlap of atomic orbitals between two atoms. In general, the greater the amount of overlap between two orbitals, the stronger the bond. For each bond there is a condition of maximum atomic orbital overlap leading to maximum bond strength at a particular internuclear distance (bond length). This is called **Valence Bond Approach**.

- This is a localised electron model of bonding.
- Most of the electrons retain the same orbital locations as in a separated atoms, and the bonding electrons are localised (fixed) in the region of atomic orbital overlap.
- In H_2 molecules, H – H σ bond is by s – s overlapping
- In F_2 molecule : F – F σ bond is by axial overlapping of two p-orbitals.
- In O_2 molecule : One σ bond is by axial overlap of p-orbitals and π bond is by lateral overlap of p-orbitals.
- In N_2 molecule : One σ bond is by axial overlap of p-orbitals and two π bonds are by lateral overlap of p-orbitals.

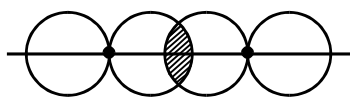
- C6B Hybridisation :** Hybridisation is defined as the concept of intermixing of orbitals of same energy or of slightly different energy to produce entirely new orbitals of equivalent energy, identical shapes and symmetrically disposed in plane. New orbitals formed are called hybrid orbitals.

- Only the orbitals of an isolated single atom can undergo hybridisation.
- The hybrid orbitals generated are equal in number to that of the pure atomic orbitals which mix up.
- A hybrid orbitals, like the atomic orbitals, cannot have more than two electrons of opposite signs.

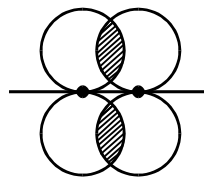
- C6C Sigma and Pi Bond** There can be following types of overlapping along the axes (end to end) :

- (s - s) overlapping when s-orbital overlapping with another s-orbital
- (s - p) overlapping, (p can be p_x or p_y or p_z)
- ($p_x - p_x$) overlapping
- any of the hybrid orbitals overlaps with another hybrid orbitals or s or p orbital.

Bond formed in the manner is called **sigma** (σ) bond in which electron **density** is concentrated in between the two atoms, and on a line joining the two atoms.



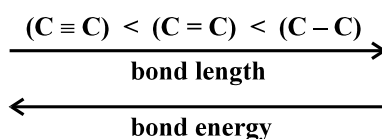
Sigma overlap (lobes point along nuclei)



Pi overlap (lobes are at right angles to the line joining the nuclei)

Double or triple bonds occur by sideways overlap of orbitals (like $(p_y - p_y)$ and $(p_z - p_z)$ orbitals) giving **pi** (π) bonds in which electron density also concentrates between the atoms, but on either side of the line joining the atoms.

The shape of the molecule is determined by the σ bonds (and lone pairs) but not by the π bonds. Pi bonds merely shorten bond length. Thus



Practice Problems :

- In which of the following molecules would you expect the nitrogen to nitrogen bond to be the shortest ?
 - N_2H_4
 - N_2
 - N_2O_4
 - N_2O
- Allyl cyanide has
 - 9 σ bonds and 4 π bonds
 - 9 σ -bonds, 3 π bonds and one lone pair
 - 8 σ bonds and 5 π bonds
 - 8 σ -bonds, 3 π bonds

[Answers : (1) b (2) b]

C6D Hybrid Orbitals and their Geometric Orientation

Hybrid Orbitals	Orientation	Example	Predict Bond Angle	Actual Shape
sp (two)	linear	$\text{BeCl}_2, \text{CO}_2, \text{C}_2\text{H}_2$	180°	linear
sp^2 (three)	trigonal planar	$\text{BF}_3, \text{C}_2\text{H}_4, \text{SO}_2, \text{SO}_3$	120°	trigonal planar
sp^3 (four)	tetrahedral	CH_4	$109^\circ 28'$	tetrahedral
		NH_3	$107^\circ 48'$	trigonal pyramidal (due to lp-bp repulsion)
		H_2O	$104^\circ 27'$	angular (V-shaped) due to lp-lp and lp-bp repulsion
sp^3d (five)	trigonal bipyramidal	PCl_5	120° and 90°	trigonal pyramidal
	pyramidal	SF_4	$101^\circ, 36'$ and $86^\circ 33'$	irregular tetrahedral
		I_3^-	180°	linear
sp^3d^2	octahedral	SF_6	90°	octahedral

Practice Problems :

- The hybridisation of atomic orbitals of N in NO_2^+ , NO_3^- and NH_4^+ are, respectively
(a) sp, sp^2, sp^3 (b) sp, sp^3, sp^2 (c) sp^2, sp, sp^3 (d) sp^2, sp^3, sp
- If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M are
(a) pure p (b) sp hybrids (c) sp^2 hybrids (d) sp^3 hybrids
- The shape of sulphate ion is
(a) hexagonal (b) square planar
(c) trigonal bipyramidal (d) tetrahedral
- The hybridisation of atomic orbitals of carbon in CH_4 , C_2H_4 , C_2H_2
(a) sp, sp^3 and sp^2 respectively (b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively (d) sp^2, sp^3 and sp respectively
- Specify the coordination geometry around and hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3
(a) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3 (b) N : pyramidal, sp^3 ; B : pyramidal, sp^3
(c) N : pyramidal, sp^3 ; B : planar, sp^2 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

[Answers : (1) a (2) c (3) d (4) d (5) a]

- C7 Dipole Moment :** In H_2 , there is no displacement of the electric charge due to same electron affinity of both H-atoms and the bond is **non-polar**. In HCl, the Cl atom has a more electron affinity than does the H atom. Electronic charge distribution is shifted towards the Cl atom. The **H-Cl bond is said to be polar**.



The magnitude of the charge displacement in a polar covalent bond is measured through a quantity called the **dipole moment** μ . It is the product of the magnitude of charges (δ) and the distance separating them (d). (Here the symbol (δ) suggests a small magnitude of charge, less than the charge on an electron)

$$\mu = \delta \times d$$

If $\delta = 4.8 \times 10^{-10}$ esu and $d = 1 \text{ \AA} = 1 \times 10^{-8}$ cm

then $\mu = 4.8 \times 10^{-10} \times 1 \times 10^{-8} = 4.8 \times 10^{-18}$ esu cm

In S.I. unit, 1 D = 3.33×10^{-30} coulomb meter (when charge $\delta = 3.33 \times 10^{-20}$ C and $d = 1 \times 10^{-10}$ m).

In diatomic molecule, $\mu = \delta \times d$

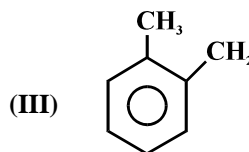
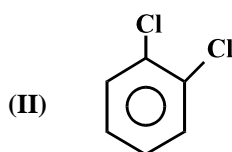
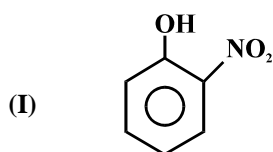
but in polyatomic molecule with angle θ , resultant dipole moment is the vector summation of the vector

moments. Also $\mu_{\text{resultant}} \propto \cos\left(\frac{\theta}{2}\right)$, $\mu \propto \frac{1}{\theta}$. Symmetrical molecules without lone pair will have $\mu = 0$.

$$\% \text{ ionic character in a molecule} = \frac{\text{observed value of } \mu}{\text{theoretical value of } \mu} \times 100$$

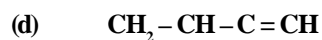
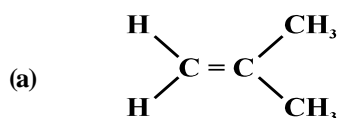
Practice Problems :

- A molecule possessing dipole moment is
(a) CH_4 (b) H_2O (c) BF_3 (d) CO_2
- Correct order of dipole moment for the following molecule is

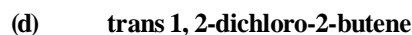
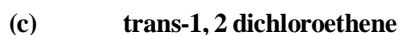


- (a) I = II = III (b) I < II < III (c) I > II > III (d) II < III < I

3. Which of the following hydrocarbons has the lowest dipole moment ?



4. Dipole moment is exhibited by



[Answers : (1) b (2) d (3) b (4) b]

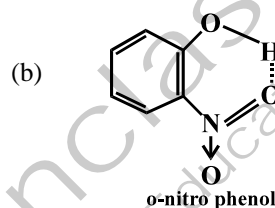
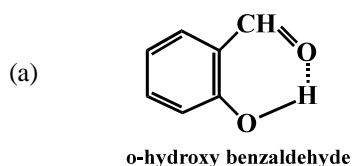
C8A Hydrogen Bonding : Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O, is held with weak electrostatic forces by the non-bonded pair of electrons of another atom. The coordination number of hydrogen in such cases is two. It acts as a bridge between two atoms, to one of which it is covalently bonded, and to the other attached through electrostatic forces, also called **Hydrogen Bond**.

Of all the electronegative donor atoms, only F, N and O atoms enter into stable hydrogen bond formation.

The weak electrostatic interaction leading to the hydrogen bond formation is shown by dott (...) lines. Thus $\text{X}-\text{H}\cdots\text{Y}$ represent hydrogen bonding between hydrogen and Y atom.

C8B Intramolecular H-Bonding :

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.

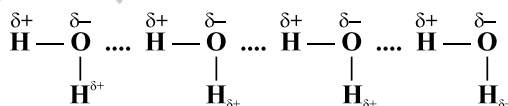


C8C Intermolecular H-Bonding :

This type of H-bonding takes place between H and electronegative element present in the different molecules of the same substance (as in between H_2O and H_2O) or different substances (as in between H_2O and NH_3)

e.g. **In water molecules :**

Due to polar nature of H_2O , there is association of water molecules giving a liquid state of abnormally high b.p.



C9A Molecular Orbital Theory (MOT) : According to Valence Bond Theory only the half-filled orbitals of one atom overlaps with the half filled orbitals of other atom to form the covalent bond. According to MOT, on the other hand, the all atomic orbitals of one atom overlap with the all the atomic orbitals of the other atom provided the overlapping orbitals are of the same symmetry and of similar energy. The resulting polynuclear molecular orbitals contain the all electrons of the molecule.

C9B The basic principles of the MOT :

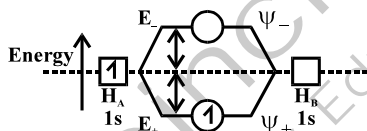
- When nuclei of two atoms come close to each other, their atomic orbitals interact leading to the formation of molecular orbital. The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of molecular orbital.
- Each molecular orbital is described by a wave function Ψ , known as molecular orbital wave function.

- The molecular orbital wave function Ψ is such that Ψ^2 represents the probability density or electron charge density.
- Each molecular orbital wave function (Ψ) is associated with a set of quantum numbers which determine the energy and shape of the molecular orbital.
- Each Ψ is associated with definite energy value.
- Electrons fill the molecular orbitals in the same way as they fill the atomic orbital following the aufbau principle, Pauli's exclusion principle, and the Hund's rule of maximum multiplicity.
- Each electron in a molecular orbital belongs to all the nuclei present in the molecule.
- Each electron moving in a molecular orbital has a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$.

The basic difference between an atomic orbital and molecular orbital is that while an electron in an atomic orbital belongs to or influenced by one positive nucleus only, an electron in a molecular orbital is influenced by all nuclei of atoms contained in a molecule.

Linear combination of Atomic orbitals (LCAO) in case of H_2^+

- A linear combination of two atomic orbitals Ψ_A and Ψ_B leads to the formation of two molecular orbitals Ψ_+ and Ψ_-
- The energy E_+ of molecular orbital Ψ_+ is lower than either of E_A and E_B (energies of isolated atoms). It is therefore designated as bonding molecular orbital (BMO).
- The energy E_- of molecular orbital Ψ_- is higher than either of E_A and E_B . It is therefore designated as antibonding molecular orbital (ABMO)
- The extent of lowering of energy of the bonding molecular orbital is equal to the extent of increase of energy of antibonding molecular orbital.



Energies of bonding and antibonding molecular orbitals.

The order of energy of molecular orbital for lighter elements like boron, carbon and nitrogen are as follows : $\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi 2py = \pi 2pz < \sigma 2px < \pi^* 2py = \pi^* 2pz < \sigma^* px$

The order of energy of molecular orbitals for heavier elements after nitrogen are :

$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma 2px < \pi 2py = \pi 2pz < \pi^* 2py = \pi^* 2pz < \sigma^* 2px$

Practice Problems :

- Which of the following molecular orbital in N_2 has least energy ?

- (a) π_{2p_y} (b) σ_{2p_z} (c) σ_{2s} (d) $\pi^*_{2p_z}$

[Answers : (1) c]

- C10 Heteronuclear Diatomic Molecule :** The same principle apply when combining atomic orbitals from two different atoms as applied when atoms are identical that is

- only atomic orbitals of about same energy can combine effectively
- They should have maximum overlap.
- They must have the same symmetry

Since the two atoms are different, the energies of their atomic orbitals are slightly different.

C11 Electronic Configuration of Molecules : While discussing the electronic configuration of molecules, we shall frequently make use of a term called bond order.

$$\text{B.O.} = \frac{1}{2} [N_b - N_a] \quad N_b \rightarrow \text{number of bonding electrons}$$

$$N_a \rightarrow \text{number of anti-bonding electrons}$$

If B.O. = 0, 1, 2, 3 so on it means that no bond is formed, one bond is formed, two bonds or three bonds are formed between the atoms respectively.

1. B.O. \propto Bond dissociation energy and $\text{B.O.} \propto \frac{1}{\text{Bond Length}}$

2. Electronic configuration helps to predict the magnetic character of the molecule.

If all the electrons in a molecule are paired they are diamagnetic and if unpaired electron is present they are paramagnetic.

Practice Problems :

- Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ , unpaired electron is present in
 - KO_2 only
 - NO_2^+ and BaO_2
 - KO_2 and AlO_2^-
 - BaO_2 only
- When N_2^+ is formed from N_2 , bond order and when O_2^+ is formed from O_2 , bond order
 - increases
 - decreases
 - increases, decreases
 - decreases, increases
- Which of the following has longest bond length ?
 - O_2
 - O_2^+
 - O_2^-
 - O_2^{2-}
- Which of the following has identical bond order ?

(I) CN^-	(II) O_2^-	(III) NO^+	(IV) CN^+
(a) I, III	(b) II, IV	(c) I, II, III	(d) I, IV

[Answers : (1) a (2) d (3) d (4) a]