# Chemical Bonding

## Chemical Bond Definition

A chemical bond is the attractive force that holds atoms, ions, or molecules together in a chemical species. It results from the transfer or sharing of valence electrons between atoms to achieve stability.

## Octet Rule

The octet rule states that atoms tend to combine in such a way that they each have eight electrons in their valence shell, achieving a stable electronic configuration similar to noble gases. This can occur through electron transfer or sharing.

## Limitations of Octet Rule

- Elements in and beyond the third period can have expanded octets with more than eight valence electrons, e.g., $PF_5$, $SF_6$.

- Molecules with an odd number of electrons, such as NO and $NO_2$, cannot satisfy the octet rule.
- Some molecules have central atoms with less than eight electrons, e.g., LiCl, $BeCl_2$, $BCl_3$.
- Some noble gases like Xenon and Krypton form compounds, e.g., $XeF_2$, $KrF_2$, $XeOF_2$, which do not follow the octet rule.

## Ionic Bond

An ionic bond is formed by the electrostatic attraction between oppositely charged ions, typically formed by the transfer of electrons from a metal to a non-metal. The electrovalence equals the charge on the ion.

## Properties of Ionic Compounds

- High melting and boiling points.
- High enthalpies of fusion and vaporization.
- Hard and brittle solids.
- Conduct electricity when molten or dissolved in water.
- Good electrical insulators in solid state.
- Ionic bonds are non-directional due to uniform distribution of surrounding ions.

## Covalent Bond

A covalent bond involves the sharing of electron pairs between atoms, resulting in a stable balance of attractive and repulsive forces. It forms molecules where atoms share electrons to complete their octets.

## Properties of Covalent Compounds

- Low melting and boiling points due to weak intermolecular forces.
- Do not conduct electricity as they lack free ions or electrons.

- Generally insoluble in polar solvents like water but soluble in non-polar solvents such as benzene and toluene.
- Reactions are generally slower due to molecular nature.

## Formal Charge

Formal charge on an atom in a molecule is calculated as:

FC = V - L - 1/2 S

where FC = formal charge, V = valence electrons in free atom, L = lone pair electrons, S = shared electrons.

## Bond Parameters

**Bond Length:** The equilibrium distance between the nuclei of two bonded atoms.

**Bond Angle:** The angle between two bonds at the central atom in a molecule.

**Bond Enthalpy:** The energy required to break one mole of bonds in gaseous state, measured in kJ molB9.

**Bond Order:** Number of bonds between two atoms; higher bond order means stronger and shorter bonds.

## Types of Covalent Bonds

- **Non-polar Covalent Bond:** Formed between atoms of the same element sharing electrons equally, e.g., $H_2$, $O_2$.

- **Polar Covalent Bond:** Formed between atoms with different electronegativities, resulting in unequal sharing and partial charges, e.g., HF, HCl.

### Dipole Moment

Dipole moment (⊠) is the product of the magnitude of charge (Q) and the distance of separation (r):

⊠ = Q D r

Expressed in Debye units (D), where 1 D = 3.33564 D7 10B0B3 C m.

## Solved Examples

## Practice Set

- **Level 1:** Define ionic and covalent bonds with examples.
- **Level 2:** Explain the limitations of the octet rule with suitable examples.
- **Level 3:** Calculate the formal charge on nitrogen in the nitrate ion (NO⊠3B1).

## Answer Key

- **Level 1:** Ionic bond is formed by transfer of electrons from metal to non-metal, e.g., NaCl. Covalent bond is formed by sharing of electrons between atoms, e.g., H⊠2.
- **Level 2:** Limitations include expanded octets in PF⊠5, odd electron molecules like NO, incomplete octets in BeCl⊠2, and noble gas compounds like XeF⊠2.
- **Level 3:** Formal charge on N in NO⊠3B1 = V - L - 1/2 S = 5 - 0 - 1/2(8) = 5 - 4 = +1.

## Resonance and VSEPR

## Resonance

Resonance occurs when a molecule cannot be represented by a single Lewis structure but by multiple canonical forms. The actual structure is a resonance hybrid with properties averaged over these forms.

### Conditions for Resonance Structures

- Same atomic positions and number of unpaired electrons.
- Negative charges on electronegative atoms and positive charges on electropositive atoms.
- No adjacent like charges.

### Resonance Energy

Resonance energy is the difference between the actual bond energy and the energy of the most stable canonical structure.

## Valence Shell Electron Pair Repulsion (VSEPR) Theory

VSEPR theory explains molecular shapes based on repulsions between electron pairs in the valence shell of the central atom. Electron pairs arrange themselves to minimize repulsion, determining molecular geometry.

### Postulates of VSEPR

- Molecular geometry depends on total valence electron pairs (bonding and non-bonding).
- Electron pairs repel each other and arrange to maximize distance.
- Multiple bonds are treated as single electron pairs.
- Applicable to resonance structures.

### Electron Pair Repulsion Order

Lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion.

## Solved Examples

## Practice Set

- **Level 1:** What is resonance? Give an example.
- **Level 2:** State the postulates of VSEPR theory.
- **Level 3:** Predict the shape and bond angle of ammonia ($NH_3$) using VSEPR theory.

## Answer Key

- **Level 1:** Resonance is the representation of a molecule by multiple structures; example: ozone ($O_3$).
- **Level 2:** Postulates include electron pair repulsion, arrangement to minimize repulsion, multiple bonds treated as single pairs, and applicability to resonance structures.
- **Level 3:** $NH_3$ has 3 bonding pairs and 1 lone pair; shape is trigonal pyramidal with bond angle approximately 107B0.

## Valence Bond Theory and Hybridisation

### Valence Bond Theory

Covalent bonds form by the overlap of half-filled atomic orbitals containing unpaired electrons. Greater overlap leads to stronger bonds.

## Types of Overlapping

- s-s overlapping: between two s orbitals.
- s-p overlapping: between s and p orbitals.
- p-p overlapping: between two p orbitals.

## Types of Covalent Bonds

- Sigma (σ) bond: formed by end-to-end overlap along internuclear axis.
- Pi (π) bond: formed by sidewise overlap of p orbitals perpendicular to internuclear axis.

## Hybridisation

Hybridisation is the mixing of atomic orbitals of similar energies to form new equivalent hybrid orbitals that determine molecular geometry.



## Types of Hybridisation

- sp: one s and one p orbital; linear shape, 180B0 angle.
- spB2: one s and two p orbitals; trigonal planar, 120B0 angle.
- spB3: one s and three p orbitals; tetrahedral, 109.5B0 angle.
- spB3d: one s, three p, one d orbital; trigonal bipyramidal.
- spB3dB2: one s, three p, two d orbitals; octahedral, 90B0 angle.
- spB3dB3: one s, three p, three d orbitals; pentagonal bipyramidal.

# Solved Examples

# Practice Set

- **Level 1:** Define sigma and pi bonds.
- **Level 2:** Describe spB3 hybridisation with an example.
- **Level 3:** Explain the hybridisation and shape of $PCl_5$ molecule.

## Answer Key

- **Level 1:** Sigma bond is formed by head-on overlap; pi bond by sidewise overlap of p orbitals.
- **Level 2:** spB3 hybridisation involves one s and three p orbitals forming four equivalent orbitals arranged tetrahedrally; example: methane ($CH_4$).
- **Level 3:** $PCl_5$ has spB3d hybridisation with trigonal bipyramidal shape.

## Molecular Orbital Theory

### Basic Concepts

Molecular orbitals (MOs) form by the combination of atomic orbitals (AOs) of similar energy and symmetry. Electrons in MOs belong to the entire molecule rather than individual atoms.

### Types of Molecular Orbitals

- Bonding molecular orbitals: formed by constructive interference, lower energy, stabilize molecule.
- Antibonding molecular orbitals: formed by destructive interference, higher energy, destabilize molecule, denoted by an asterisk (*).
- Non-bonding molecular orbitals: do not affect bonding.

### Energy Ordering

For molecules like $O_2$ onwards, the order is:

□ 1s < □* 1s < □ 2s < □* 2s < □ 2p_z < □ 2p_x = □ 2p_y < □* 2p_x = □* 2p_y < □* 2p_z

For lighter diatomic molecules (Li□2 to N□2), the □ 2p_z orbital is higher in energy than the □ 2p_x and □ 2p_y orbitals.

### Bond Order

Bond order = 1/2 (number of electrons in bonding MOs - number in antibonding MOs). Positive bond order indicates stability.

### Paramagnetism and Diamagnetism

Unpaired electrons in MOs cause paramagnetism; paired electrons cause diamagnetism.

## Solved Examples

## Practice Set

- **Level 1:** Define bonding and antibonding molecular orbitals.
- **Level 2:** Calculate bond order of O□2 molecule.
- **Level 3:** Explain why O□2 is paramagnetic using MO theory.

## Answer Key

- **Level 1:** Bonding MOs result from constructive overlap and stabilize molecules; antibonding MOs result from destructive overlap and destabilize molecules.
- **Level 2:** O□2 has 10 electrons in bonding and 6 in antibonding MOs; bond order = (10-6)/2 = 2.

- **Level 3:** $O_2$ has two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals, making it paramagnetic.

## Hydrogen Bonding

### Definition

Hydrogen bonding is a weak bond formed when a hydrogen atom covalently bonded to a highly electronegative atom (F, O, or N) interacts with a lone pair of electrons on another electronegative atom.

### Types of Hydrogen Bonds

- **Intermolecular:** Between molecules, e.g., hydrogen bonding in water and HF.
- **Intramolecular:** Within the same molecule, e.g., ortho-nitrophenol.



### Applications

- High melting and boiling points of water due to extensive hydrogen bonding.
- Lower density of ice compared to water because of hydrogen-bonded tetrahedral structure.
- Volatility differences in nitrophenol isomers due to intramolecular hydrogen bonding.

## Solved Examples

## Practice Set

- **Level 1:** What is hydrogen bonding? Give an example.
- **Level 2:** Differentiate between intermolecular and intramolecular hydrogen bonding.
- **Level 3:** Explain why water has a higher boiling point than $H_2S$.

## Answer Key

- **Level 1:** Hydrogen bonding is a weak bond between H and electronegative atoms like F, O, N; example: water ($H_2O$).
- **Level 2:** Intermolecular occurs between molecules; intramolecular occurs within the same molecule.
- **Level 3:** Water has stronger hydrogen bonds due to O-H bonds, leading to higher boiling point than $H_2S$.

## Quick Reference Table

## Common Mistakes and Misconceptions

## Glossary