Unit 4: Chemical Bonding and Molecular Structure

Comprehensive Study Notes

Class 11 Chemistry - NCERT Based EXAM SPRINT - Complete Coverage for NEET and Board Examinations

Introduction

Chemical bonds are the attractive forces that hold atoms together in molecules and compounds. Understanding chemical bonding is fundamental to explaining the formation, structure, and properties of chemical compounds. This unit covers various theories that explain bonding: Kössel-Lewis approach, VSEPR theory, Valence Bond theory, and Molecular Orbital theory.

4.1 Kössel-Lewis Approach to Chemical Bonding

Historical Background

1916: Kössel and Lewis independently explained chemical bonding based on the inertness of noble gases.

Key Concepts

Lewis Symbols

- **Definition**: Simple notations representing valence electrons in atoms
- **Representation**: Dots around element symbols
- **Significance**: Number of dots = number of valence electrons

Examples of Lewis Symbols (Second Period):

- Li• Be•• •B• •C•• •N••• •O•••• •F•••••

Kössel's Observations

1. **Periodic Trends**: Highly electronegative halogens and electropositive alkali metals separated by noble gases
2. **Ion Formation**: Atoms gain/lose electrons to achieve noble gas configuration
3. **Stability**: Noble gases have stable outer shell configuration (octet)
4. **Electrostatic Attraction**: Positive and negative ions attract each other

Ionic Bond Formation

Example: NaCl Formation

```
Na → Na⁺ + e⁻     [Ne]3s¹ → [Ne]
Cl + e⁻ → Cl⁻     [Ne]3s²3p⁵ → [Ne]3s²3p⁶ or [Ar]
Na⁺ + Cl⁻ → NaCl
```

Example: CaF_2 Formation

```
Ca → Ca²⁺ + 2e⁻   [Ar]4s² → [Ar]
F + e⁻ → F⁻       [He]2s²2p⁵ → [He]2s²2p⁶ or [Ne]
Ca²⁺ + 2F⁻ → CaF₂
```

Electrovalent Bond

- **Definition**: Bond formed by electrostatic attraction between positive and negative ions
- **Electrovalence**: Number of unit charges on the ion
- **Examples**: Ca^{2+} (electrovalence = +2), Cl^- (electrovalence = -1)

4.1.1 Octet Rule

Statement

"Atoms can combine by transfer or sharing of valence electrons to have eight electrons in their valence shells."

Key Points

- **Electron Transfer**: Forms ionic bonds (Na^+Cl^-)
- **Electron Sharing**: Forms covalent bonds (Cl_2)
- **Goal**: Achieve noble gas configuration
- **Exception**: Hydrogen achieves duplet (2 electrons)

4.1.2 Covalent Bond

Langmuir's Contribution (1919)

- Refined Lewis postulations
- Introduced term "covalent bond"
- Emphasized electron pair sharing

Formation of Cl_2 Molecule

- **Electronic Configuration**: $[Ne]3s^2 3p^5$
- **Sharing**: One electron from each Cl atom
- **Result**: Both atoms achieve [Ar] configuration

Lewis Dot Structures

Important Conditions:

1. Each bond = shared electron pair
2. Each atom contributes at least one electron
3. Atoms achieve noble gas configurations

Examples:

- **Single Bond**: Cl-Cl (one shared pair)
- **Double Bond**: O=O (two shared pairs)
- **Triple Bond**: N≡N (three shared pairs)

Multiple Bonds

1. **Double Bond**: Two electron pairs shared (C=O in CO_2, C=C in C_2H_4)
2. **Triple Bond**: Three electron pairs shared (N≡N in N_2, C≡C in C_2H_2)

4.1.3 Lewis Representation of Simple Molecules

Steps to Draw Lewis Structures

1. **Count Total Valence Electrons**
   - Add valence electrons of all atoms
   - For anions: Add electrons equal to negative charge
   - For cations: Subtract electrons equal to positive charge
2. **Determine Skeletal Structure**
   - Least electronegative atom in center
   - Most electronegative atoms at periphery
3. **Distribute Electrons**

- Form single bonds first
- Complete octets with lone pairs
- Form multiple bonds if needed

Examples:

- **CH_4**: 4 + 4(1) = 8 valence electrons
- **CO_3^{2-}**: 4 + 3(6) + 2 = 24 valence electrons
- **NH_4^+**: 5 + 4(1) - 1 = 8 valence electrons

4.1.4 Formal Charge

Definition

Difference between valence electrons in free atom and electrons assigned to atom in Lewis structure.

Formula

```
Formal Charge = (Valence electrons) - (Lone pair electrons) - ½(Bonding electrons)
```

Example: Ozone (O_3)

Structure: O_1-O_2=O_3

- **Central O (atom 1)**: 6 - 2 - ½(6) = +1
- **End O (atom 2)**: 6 - 4 - ½(4) = 0
- **End O (atom 3)**: 6 - 6 - ½(2) = -1

Applications

- Select most stable structure (lowest formal charges)
- Track valence electrons
- Understand charge distribution

4.1.5 Limitations of Octet Rule

1. Incomplete Octet

Examples: LiCl, BeH_2, BCl_3, $AlCl_3$, BF_3

- Elements with less than 4 valence electrons
- Central atom has less than 8 electrons

2. Odd-Electron Molecules

Examples: NO, NO_2

- Total number of electrons is odd
- Cannot satisfy octet for all atoms

3. Expanded Octet

Examples: PF_5, SF_6, H_2SO_4

- Elements in period 3 and beyond
- Central atom has more than 8 electrons
- Utilizes d-orbitals for bonding

4. Other Limitations

- Noble gases can form compounds (XeF_2, KrF_2)

- Doesn't explain molecular shapes
- Silent about relative stability
- No explanation for bond energies

4.2 Ionic or Electrovalent Bond

Factors Favoring Ionic Bond Formation

1. Ionization Enthalpy

- **Low ionization enthalpy**: Favors cation formation
- **Process**: $M(g) \rightarrow M^+(g) + e^-$

2. Electron Gain Enthalpy

- **High negative electron gain enthalpy**: Favors anion formation
- **Process**: $X(g) + e^- \rightarrow X^-(g)$

3. Lattice Enthalpy

- **High lattice enthalpy**: Stabilizes ionic compound
- **Definition**: Energy required to separate ionic solid into gaseous ions

Crystal Structure

- **Three-dimensional arrangement**: Cations and anions in ordered lattice
- **Coulombic interactions**: Electrostatic attractions and repulsions
- **Example**: NaCl (rock salt structure)

Energy Considerations

Example: NaCl Formation

- **Ionization enthalpy** (Na): +495.8 kJ/mol
- **Electron gain enthalpy** (Cl): -348.7 kJ/mol
- **Net energy**: +147.1 kJ/mol
- **Lattice enthalpy**: -788 kJ/mol
- **Overall process**: Exothermic (-640.9 kJ/mol)

4.2.1 Lattice Enthalpy

Definition

Energy required to completely separate one mole of ionic solid into gaseous constituent ions.

Example: $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; $\Delta H = +788$ kJ/mol

Factors Affecting Lattice Enthalpy

1. **Charge on ions**: Higher charges → higher lattice enthalpy
2. **Size of ions**: Smaller ions → higher lattice enthalpy
3. **Crystal structure**: Coordination number affects stability

Applications

- Predicting stability of ionic compounds
- Understanding solubility trends
- Calculating other thermodynamic quantities

4.3 Bond Parameters

4.3.1 Bond Length

Definition: Equilibrium distance between nuclei of bonded atoms

Covalent Radius

- **Definition**: Half the distance between identical atoms in covalent bond
- **Measurement**: Spectroscopic and diffraction techniques

Van der Waals Radius

- **Definition**: Half the distance between non-bonded atoms in different molecules
- **Comparison**: Van der Waals radius > Covalent radius

Typical Bond Lengths:

- **Single bonds**: C-C (154 pm), C-H (107 pm)
- **Double bonds**: C=C (133 pm), C=O (121 pm)
- **Triple bonds**: C≡C (120 pm), C≡N (116 pm)

4.3.2 Bond Angle

Definition: Angle between orbitals containing bonding electron pairs around central atom

Examples:

- **H_2O**: H-O-H angle = 104.5°
- **NH_3**: H-N-H angle = 107°
- **CH_4**: H-C-H angle = 109.5°

4.3.3 Bond Enthalpy

Definition: Energy required to break one mole of bonds in gaseous state

Examples:

- **H_2**: H-H bond enthalpy = 435.8 kJ/mol
- **O_2**: O=O bond enthalpy = 498 kJ/mol
- **N_2**: N≡N bond enthalpy = 946.0 kJ/mol

Average Bond Enthalpy

For polyatomic molecules, different bonds of same type may have different energies.

Example: H_2O

- **First O-H bond**: 502 kJ/mol
- **Second O-H bond**: 427 kJ/mol
- **Average**: (502 + 427)/2 = 464.5 kJ/mol

4.3.4 Bond Order

Definition: Number of bonds between two atoms

Examples:

- **H_2**: Bond order = 1 (single bond)
- **O_2**: Bond order = 2 (double bond)
- **N_2**: Bond order = 3 (triple bond)
- **CO**: Bond order = 3 (triple bond)

Relationship with Bond Properties

- **Higher bond order → Shorter bond length → Higher bond enthalpy**

4.3.5 Resonance Structures

Definition: Multiple Lewis structures with similar energies representing the same molecule

Characteristics

- **Same atomic positions**
- **Different electron arrangements**
- **Similar energies**
- **Actual structure is hybrid of all forms**

Examples:

1. **Ozone (O_3)**:
   - Two resonance structures
   - Equal O-O bond lengths (128 pm)
   - Intermediate between single (148 pm) and double (121 pm) bonds
2. **Carbonate Ion (CO_3^{2-})**:
   - Three resonance structures
   - All C-O bonds equivalent
3. **Carbon Dioxide (CO_2)**:
   - Three resonance structures
   - Bond length (115 pm) between C=O (121 pm) and C≡O (110 pm)

Important Points about Resonance

- **Resonance stabilizes** molecules (lower energy than any single structure)
- **Canonical forms have no real existence**
- **No equilibrium** between forms

- **Resonance averages** bond characteristics

4.3.6 Polarity of Bonds

Nonpolar Covalent Bonds

- **Formation**: Between identical atoms (H_2, Cl_2, N_2)
- **Electron sharing**: Equal sharing
- **Dipole moment**: Zero

Polar Covalent Bonds

- **Formation**: Between different atoms (HF, HCl)
- **Electron sharing**: Unequal sharing
- **Dipole moment**: Non-zero

Dipole Moment

Definition: Product of charge and distance of separation

Formula: $\mu = Q \times r$ **Units**: Debye (D), 1 D = 3.33564×10^{-30} C·m

Molecular Dipole Moments

Vector sum of individual bond dipoles

Examples:

- **H_2O**: μ = 1.85 D (bent structure)
- **BeF_2**: μ = 0 D (linear structure, bond dipoles cancel)
- **BF_3**: μ = 0 D (trigonal planar, bond dipoles cancel)
- **NH_3**: μ = 1.47 D (pyramidal structure)

- **NF_3**: μ = 0.23 D (orbital dipole opposes bond dipoles)

Fajan's Rules (Partial Covalent Character in Ionic Bonds)

1. **Small cation, large anion**: Greater covalent character
2. **High charge on cation**: Greater covalent character
3. **Transition metal cations**: More polarizing than s-block cations

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4.4 VSEPR Theory

Postulates

1. **Electron pair repulsion**: Valence shell electron pairs repel each other
2. **Geometry determination**: Electron pairs occupy positions to minimize repulsion
3. **Maximum separation**: Electron pairs stay as far apart as possible
4. **Spherical distribution**: Electron pairs localize on spherical surface
5. **Multiple bonds**: Treated as single electron pair
6. **Resonance structures**: VSEPR applicable to any resonance form

Repulsion Order

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair

Molecular Geometries

No Lone Pairs on Central Atom

Formula	Electron Pairs	Geometry	Bond Angle	Examples
AB_2	2	Linear	180°	$BeCl_2$, CO_2
AB_3	3	Trigonal planar	120°	BF_3, SO_3
AB_4	4	Tetrahedral	109.5°	CH_4, $SiCl_4$
AB_5	5	Trigonal bipyramidal	90°, 120°	PCl_5, PF_5
AB_6	6	Octahedral	90°	SF_6

With Lone Pairs on Central Atom

Formula	Bonding Pairs	Lone Pairs	Geometry	Bond Angle	Examples
AB_2E	2	1	Bent	$<120°$	SO_2, O_3
AB_3E	3	1	Trigonal pyramidal	$<109.5°$	NH_3, PH_3
AB_2E_2	2	2	Bent	$<109.5°$	H_2O, H_2S
AB_4E	4	1	See-saw	$<90°$, $<120°$	SF_4
AB_3E_2	3	2	T-shaped	$<90°$	ClF_3
AB_2E_3	2	3	Linear	180°	XeF_2

Limitations

- **Theoretical basis unclear**
- **Limited to simple molecules**
- **No explanation for bond energies**
- **Approximations in complex cases**

4.5 Valence Bond Theory

Historical Development

- **Heitler and London (1927)**: Introduced VB theory
- **Pauling**: Further developed the theory

Basic Concept

Chemical bonds form by overlap of atomic orbitals containing unpaired electrons with opposite spins.

Orbital Overlap Concept

- **Bond formation**: Partial interpenetration of atomic orbitals
- **Electron pairing**: Electrons with opposite spins pair up
- **Bond strength**: Greater overlap → stronger bond

H_2 Molecule Formation

1. **Approaching atoms**: Attractive and repulsive forces develop
2. **Energy minimum**: Optimal bond distance (74 pm)
3. **Bond enthalpy**: Energy released = 435.8 kJ/mol

Types of Overlap

1. **Positive overlap**: Same phase orbitals, bond formation
2. **Negative overlap**: Opposite phase orbitals, no bond
3. **Zero overlap**: No interaction

4.5.1 Directional Properties

VB theory explains molecular shapes through orbital overlap geometry.

4.5.2 Types of Covalent Bonds

Sigma (σ) Bonds

- **Formation**: End-to-end (head-on) overlap
- **Orbital overlap**: Along internuclear axis
- **Types**:
  - s-s overlap
  - s-p overlap
  - p-p overlap (head-on)
- **Strength**: Stronger due to greater overlap

Pi (π) Bonds

- **Formation**: Sidewise overlap
- **Orbital orientation**: Parallel axes, perpendicular to internuclear axis
- **Shape**: Two saucer-shaped regions above and below bond axis
- **Strength**: Weaker due to lesser overlap

Multiple Bonds

- **Double bond**: One σ + One π
- **Triple bond**: One σ + Two π

4.6 Hybridization

Definition

Process of intermixing atomic orbitals of slightly different energies to form new equivalent hybrid orbitals.

Salient Features

1. **Number conservation**: Number of hybrid orbitals = Number of atomic orbitals
2. **Equivalent energy**: All hybrid orbitals have same energy and shape
3. **Better bonding**: More effective than pure atomic orbitals
4. **Directional**: Oriented to minimize electron pair repulsion

Conditions for Hybridization

1. **Valence shell orbitals**: Only outer shell orbitals participate
2. **Similar energies**: Orbitals should have comparable energies
3. **Electron promotion**: Not always necessary
4. **Filled orbitals**: Can participate in hybridization

4.6.1 Types of Hybridization

sp Hybridization

- **Orbitals involved**: One s + one p
- **Hybrid orbitals**: 2 equivalent sp hybrids
- **Geometry**: Linear
- **Bond angle**: 180°
- **Character**: 50% s, 50% p
- **Examples**: $BeCl_2$, C_2H_2 (terminal carbons)

sp^2 Hybridization

- **Orbitals involved**: One s + two p

- **Hybrid orbitals**: 3 equivalent sp^2 hybrids
- **Geometry**: Trigonal planar
- **Bond angle**: 120°
- **Character**: 33.33% s, 66.67% p
- **Examples**: BCl_3, C_2H_4 (both carbons)

sp^3 Hybridization

- **Orbitals involved**: One s + three p
- **Hybrid orbitals**: 4 equivalent sp^3 hybrids
- **Geometry**: Tetrahedral
- **Bond angle**: 109.5°
- **Character**: 25% s, 75% p
- **Examples**: CH_4, NH_3, H_2O

Molecular Examples

CH_4 (Methane)

- **C configuration**: $[He]2s^12p^3$ (excited state)
- **Hybridization**: sp^3
- **Bonds**: 4 C-H σ bonds
- **Geometry**: Tetrahedral
- **Bond angles**: 109.5°

NH_3 (Ammonia)

- **N configuration**: $[He]2s^22p^3$

- **Hybridization**: sp^3
- **Electron pairs**: 3 bonding + 1 lone pair
- **Geometry**: Trigonal pyramidal
- **Bond angles**: 107° (reduced due to lone pair repulsion)

H_2O (Water)

- **O configuration**: $[He]2s^22p^4$
- **Hybridization**: sp^3
- **Electron pairs**: 2 bonding + 2 lone pairs
- **Geometry**: Bent/Angular
- **Bond angles**: 104.5° (reduced due to lone pair repulsions)

4.6.2 Examples in Organic Molecules

C_2H_6 (Ethane)

- **Both C atoms**: sp^3 hybridized
- **C-C bond**: sp^3-sp^3 σ overlap
- **C-H bonds**: sp^3-s σ overlap
- **Bond lengths**: C-C (154 pm), C-H (109 pm)

C_2H_4 (Ethene)

- **Both C atoms**: sp^2 hybridized
- **C-C bond**: One σ (sp^2-sp^2) + One π (p-p)
- **C-H bonds**: sp^2-s σ overlap
- **Bond length**: C=C (134 pm)

- **Bond angles**: H-C-H (117.6°), H-C-C (121°)

C_2H_2 (Ethyne)

- **Both C atoms**: sp hybridized
- **C-C bond**: One σ (sp-sp) + Two π (p-p)
- **C-H bonds**: sp-s σ overlap
- **Bond length**: C≡C (120 pm)
- **Geometry**: Linear

4.6.3 Hybridization Involving d-Orbitals

sp^3d Hybridization

- **Orbitals**: s + 3p + 1d
- **Geometry**: Trigonal bipyramidal
- **Bond angles**: 90°, 120°
- **Example**: PCl_5

PCl_5 Structure:

- **Equatorial bonds**: 3 bonds in plane (120° angles)
- **Axial bonds**: 2 bonds perpendicular to plane (90° to equatorial)
- **Axial bonds**: Slightly longer and weaker due to more repulsion

sp^3d^2 Hybridization

- **Orbitals**: s + 3p + 2d
- **Geometry**: Octahedral
- **Bond angles**: 90°

- **Examples**: SF_6, $[CrF_6]^{3-}$

Other d-orbital Hybridizations

Type	Geometry	Examples
dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
sp^3d^2	Square pyramidal	BrF_5
d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$

4.7 Molecular Orbital Theory

Historical Development

F. Hund and R.S. Mulliken (1932): Developed MO theory

Key Features

1. **Molecular orbitals**: Electrons occupy molecular orbitals, not atomic orbitals
2. **Polycentric**: MO influenced by multiple nuclei
3. **Orbital combination**: Atomic orbitals combine to form molecular orbitals
4. **Number conservation**: Number of MOs = Number of AOs
5. **Energy levels**: Bonding MOs (lower energy) and antibonding MOs (higher energy)
6. **Electron filling**: Follows aufbau principle, Pauli exclusion, Hund's rule

4.7.1 Linear Combination of Atomic Orbitals (LCAO)

Mathematical Approach

Bonding MO: $\psi_1 = \psi_a + \psi_\beta$ **Antibonding MO**: $\psi_2 = \psi_a - \psi_\beta$

Constructive vs Destructive Interference

- **Bonding MO**: Constructive interference, electron density between nuclei
- **Antibonding MO**: Destructive interference, nodal plane between nuclei

4.7.2 Conditions for AO Combination

1. **Similar energies**: AOs must have comparable energies
2. **Same symmetry**: Same symmetry about molecular axis
3. **Maximum overlap**: Greater overlap → better combination
4. **Proper orientation**: Correct spatial orientation

4.7.3 Types of Molecular Orbitals

σ (Sigma) Molecular Orbitals

- **Symmetry**: Cylindrically symmetric around bond axis
- **Formation**: s-s, s-pz, pz-pz combinations
- **Examples**: σ1s, σ*1s, σ2pz, σ*2pz

π (Pi) Molecular Orbitals

- **Symmetry**: Not symmetric around bond axis
- **Formation**: px-px, py-py combinations
- **Examples**: π2px, π*2px, π2py, π*2py

4.7.4 Energy Level Diagrams

For O_2 and F_2:

σ1s < σ*1s < σ2s < σ*2s < σ2pz < (π2px = π2py) < (π*2px = π*2py) < σ*2pz

For B_2, C_2, N_2:

σ1s < σ*1s* < *σ2s* < *σ*2s < (π2px = π2py) < σ2pz < (π*2px* = *π*2py) < σ*2pz

4.7.5 Molecular Properties from MO Theory

Bond Order

Formula: Bond Order = ½(Nb - Na)

- **Nb**: Number of electrons in bonding MOs
- **Na**: Number of electrons in antibonding MOs

Stability

- **Stable**: Bond order > 0
- **Unstable**: Bond order ≤ 0

Magnetic Properties

- **Diamagnetic**: All electrons paired
- **Paramagnetic**: Unpaired electrons present

4.8 Bonding in Homonuclear Diatomic Molecules

H_2 Molecule

- **Electronic configuration**: $(\sigma 1s)^2$
- **Bond order**: ½(2-0) = 1
- **Bond energy**: 438 kJ/mol
- **Bond length**: 74 pm

- **Magnetic nature**: Diamagnetic

He_2 Molecule

- **Electronic configuration**: $(\sigma 1s)^2(\sigma^*1s)^2$
- **Bond order**: ½(2-2) = 0
- **Stability**: Does not exist

Li_2 Molecule

- **Electronic configuration**: $KK(\sigma 2s)^2$
- **Bond order**: ½(4-2) = 1
- **Magnetic nature**: Diamagnetic
- **Exists**: In vapor phase

C_2 Molecule

- **Electronic configuration**: $KK(\sigma 2s)^2(\sigma^*2s)^2(\pi 2px)^2(\pi 2py)^2$
- **Bond order**: ½(8-4) = 2
- **Bond type**: Two π bonds (unique case)
- **Magnetic nature**: Diamagnetic

N_2 Molecule

- **Electronic configuration**: $KK(\sigma 2s)^2(\sigma^*2s)^2(\pi 2px)^2(\pi 2py)^2(\sigma 2pz)^2$
- **Bond order**: ½(10-4) = 3
- **Bond strength**: Very strong (946 kJ/mol)
- **Magnetic nature**: Diamagnetic

O_2 Molecule

- **Electronic configuration**: $KK(\sigma 2s)^2(\sigma 2s)^2(\sigma 2pz)^2(\pi 2px)^2(\pi 2py)^2(\pi 2px)^1(\pi^* 2py)^1$
- **Bond order**: ½(10-6) = 2
- **Magnetic nature**: Paramagnetic (2 unpaired electrons)
- **Significance**: MO theory correctly predicts paramagnetism

F_2 Molecule

- **Electronic configuration**: $KK(\sigma 2s)^2(\sigma 2s)^2(\sigma 2pz)^2(\pi 2px)^2(\pi 2py)^2(\pi 2px)^2(\pi^* 2py)^2$
- **Bond order**: ½(10-8) = 1
- **Bond strength**: Relatively weak (155 kJ/mol)
- **Magnetic nature**: Diamagnetic

4.9 Hydrogen Bonding

Definition

Attractive force between hydrogen atom (bonded to highly electronegative atom) and another electronegative atom.

Requirements for H-bonding

1. **Hydrogen**: Must be bonded to F, O, or N
2. **Electronegativity**: Large electronegativity difference
3. **Lone pairs**: Acceptor atom must have lone pairs

4.9.1 Cause of Formation

1. **Polar bond**: H-X bond is highly polar ($\delta^+H\text{-}X\delta^-$)

2. **Electrostatic attraction**: δ^+H attracts lone pairs on other atoms
3. **Bridge formation**: H acts as bridge between two electronegative atoms

4.9.2 Types of H-bonds

Intermolecular H-bonding

- **Between different molecules**
- **Examples**: HF, H_2O, alcohols, carboxylic acids
- **Effects**: Higher boiling points, viscosity, surface tension

H_2O Structure:

- Each water molecule can form 4 H-bonds
- Tetrahedral arrangement around each O
- Ice has open hexagonal structure

Intramolecular H-bonding

- **Within same molecule**
- **Examples**: o-nitrophenol, salicylic acid
- **Effects**: Lower boiling points, reduced solubility

Effects of H-bonding

Physical Properties

1. **Boiling points**: H_2O (100°C) vs H_2S (-60°C)
2. **Solubility**: Alcohols soluble in water
3. **Viscosity**: Higher in H-bonded liquids
4. **Density anomaly**: Ice less dense than water

Biological Significance

1. **Protein structure**: Secondary and tertiary structure stabilization
2. **DNA double helix**: Base pairing (A-T, G-C)
3. **Enzyme activity**: Active site geometry
4. **Cell membranes**: Lipid bilayer stability

Additional Important Concepts

Coordinate (Dative) Bonds

Definition: Bond formed when one atom provides both electrons for sharing

Characteristics:

- Donor atom has lone pair
- Acceptor atom has empty orbital
- Once formed, indistinguishable from normal covalent bond

Examples:

- NH_4^+ ion: N donates lone pair to H^+
- $BF_3 + NH_3 \rightarrow BF_3\text{-}NH_3$ adduct
- CO molecule: C donates lone pair to form coordinate bond

Metallic Bonding

Features:

- Sea of delocalized electrons

- Positive metal ions in electron cloud
- Non-directional bonding
- Explains metallic properties (conductivity, malleability, luster)

Network Covalent Solids

Examples: Diamond, graphite, SiO_2, SiC

Properties:

- High melting points
- Hard and brittle (except graphite)
- Poor electrical conductors (except graphite)
- Extended 3D network of covalent bonds

Born-Haber Cycle

Application: Calculate lattice enthalpy using thermodynamic cycle

Steps for NaCl:

1. Na(s) → Na(g) [Sublimation enthalpy]
2. ½Cl_2(g) → Cl(g) [Bond dissociation enthalpy]
3. Na(g) → Na^+(g) + e^- [Ionization enthalpy]
4. Cl(g) + e^- → Cl^-(g) [Electron gain enthalpy]
5. Na^+(g) + Cl^-(g) → NaCl(s) [Lattice enthalpy]

Polarization Effects

Fajan's Rules Applications:

- LiCl more covalent than NaCl (smaller Li^+)

- AgCl more covalent than NaCl (polarizable Ag^+)
- MgO more ionic than BeO (despite smaller Be^{2+}, due to size of O^{2-})

NEET-Specific Important Points

High-Yield Topics

1. **Lewis structures**: Drawing and formal charge calculations
2. **VSEPR theory**: Predicting molecular geometries
3. **Hybridization**: Types and molecular shapes
4. **Bond parameters**: Length, strength, polarity
5. **Resonance**: Canonical forms and stability
6. **MO theory**: Bond order and magnetic properties
7. **Hydrogen bonding**: Types and effects

Common NEET Question Patterns

1. **Numerical Problems**:
   - Formal charge calculations
   - Bond order from MO theory
   - Dipole moment calculations
2. **Conceptual Questions**:
   - Hybridization identification
   - Molecular geometry prediction
   - Resonance structure drawing
   - H-bonding effects

3. **Comparative Analysis**:
    - Bond strength comparisons
    - Geometry variations
    - Polarity trends

Memory Aids and Mnemonics

Hybridization Memory Aid

- **sp**: "2 orbitals, Linear, 180°"
- **sp^2**: "3 orbitals, Trigonal planar, 120°"
- **sp^3**: "4 orbitals, Tetrahedral, 109.5°"
- **sp^3d**: "5 orbitals, Trigonal bipyramidal"
- **sp^3d^2**: "6 orbitals, Octahedral"

VSEPR Geometry Mnemonic

"Linear Trigonal Tetrahedral Trigonal Octahedral"

- 2 pairs → Linear
- 3 pairs → Trigonal planar
- 4 pairs → Tetrahedral
- 5 pairs → Trigonal bipyramidal
- 6 pairs → Octahedral

Bond Order Memory

- **Single bond**: Bond order = 1

- **Double bond**: Bond order = 2
- **Triple bond**: Bond order = 3
- **Higher bond order** = Shorter length + Higher energy

MO Energy Order

For B_2, C_2, N_2: "σ1s σ*1s σ2s σ*2s π2p σ2pz π*2p σ*2pz" **For O_2, F_2**: "σ1s σ*1s σ2s σ*2s σ2pz π2p π*2p σ*2pz"

Practice Questions for NEET

Multiple Choice Questions

1. **The number of σ and π bonds in ethyne (C_2H_2) are:** a) 3σ, 2π b) 2σ, 3π c) 4σ, 1π d) 5σ, 0π
2. **Which molecule has zero dipole moment?** a) NH_3 b) H_2O c) BF_3 d) HF
3. **The hybridization of carbon in diamond is:** a) sp b) sp^2 c) sp^3 d) sp^3d
4. **Bond order of O_2^- ion is:** a) 1.5 b) 2.5 c) 2 d) 1
5. **Which has maximum covalent character?** a) NaCl b) MgO c) AlF_3 d) CaF_2

Short Answer Questions

1. **Draw Lewis structure of SO_3 showing all resonance forms.**
2. **Explain why BeF_2 has zero dipole moment but H_2O has non-zero dipole moment.**
3. **Compare the bond lengths in CO, CO^+, and CO^- using MO theory.**
4. **Why is O_2 paramagnetic while N_2 is diamagnetic?**
5. **What is the effect of hydrogen bonding on the boiling point of water?**

Long Answer Questions

1. **Discuss the limitations of octet rule with suitable examples.**
2. **Explain the formation of NH_3 molecule using valence bond theory. Why is its geometry pyramidal and not trigonal planar?**
3. **Compare and contrast valence bond theory and molecular orbital theory.**
4. **Describe the different types of hybridization with examples and their geometries.**
5. **Explain hydrogen bonding. Distinguish between intermolecular and intramolecular hydrogen bonding with examples.**

Detailed Solutions to Practice Questions

MCQ Solutions

1. **Answer: a) 3σ, 2π**
   - C_2H_2 structure: H-C≡C-H
   - σ bonds: 2 C-H + 1 C-C = 3
   - π bonds: 2 (from triple bond)
2. **Answer: c) BF_3**
   - Trigonal planar geometry
   - Three B-F dipoles cancel out
   - Net dipole moment = 0
3. **Answer: c) sp^3**
   - Each carbon in diamond bonded to 4 other carbons
   - Tetrahedral arrangement requires sp^3 hybridization
4. **Answer: a) 1.5**

- O_2^-: Electronic configuration adds one electron to π* orbital
- Bond order = ½(10-7) = 1.5

5. **Answer: c) AlF_3**
   - Al^{3+} has highest charge density
   - Small, highly charged cation polarizes anion more
   - Higher covalent character

Numerical Problems

1. **Calculate the formal charges in SO_4^{2-} ion with all single bonds vs with two double bonds.**

Solution:

- All single bonds: S = +2, each O = -1
- Two double bonds: S = 0, two O = -1, two O = 0
- Structure with double bonds is more stable

2. **Determine bond order and magnetic nature of CN^- ion.**

Solution:

- Total electrons = 6(C) + 7(N) + 1(charge) = 14
- Configuration: $(\sigma 1s)^2(\sigma 1s)^2(\sigma 2s)^2(\sigma 2s)^2(\pi 2p)^4(\sigma 2p)^2$
- Bond order = ½(10-4) = 3
- Magnetic nature: Diamagnetic (all paired)

3. **Calculate the percentage ionic character in HCl given dipole moment = 1.07 D and bond length = 127 pm.**

Solution:

- Theoretical dipole (100% ionic) = charge × distance
- $= (1.6 \times 10^{-19}\ C) \times (127 \times 10^{-12}\ m)$
- $= 2.032 \times 10^{-29}\ C \cdot m = 6.09\ D$
- % ionic character = (1.07/6.09) × 100 = 17.6%

Summary Tables

Comparison of Bonding Theories

Aspect	Lewis Theory	VSEPR Theory	VB Theory	MO Theory
Focus	Electron sharing/transfer	Molecular geometry	Orbital overlap	Molecular orbitals
Bond Formation	Electron pairs	Electron pair repulsion	AO overlap	AO combination
Shapes Explained	No	Yes	Yes	Limited
Bond Energy	No	No	Qualitative	Quantitative
Magnetic Properties	No	No	No	Yes
Delocalization	Resonance	No	No	Yes

Molecular Geometry Summary

Electron Pairs	Lone Pairs	Geometry	Bond Angle	Examples
2	0	Linear	180°	$BeCl_2$, CO_2
3	0	Trigonal planar	120°	BF_3, SO_3
3	1	Bent	<120°	SO_2, O_3
4	0	Tetrahedral	109.5°	CH_4, $SiCl_4$

Electron Pairs	Lone Pairs	Geometry	Bond Angle	Examples
4	1	Trigonal pyramidal	<109.5°	NH_3, PH_3
4	2	Bent	<109.5°	H_2O, H_2S
5	0	Trigonal bipyramidal	90°, 120°	PCl_5, PF_5
5	1	See-saw	<90°, <120°	SF_4
5	2	T-shaped	<90°	ClF_3
6	0	Octahedral	90°	SF_6
6	1	Square pyramidal	<90°	BrF_5

Hybridization and Geometry

Hybridization	Geometry	Bond Angle	Examples
sp	Linear	180°	$BeCl_2$, C_2H_2
sp^2	Trigonal planar	120°	BF_3, C_2H_4
sp^3	Tetrahedral	109.5°	CH_4, NH_3, H_2O
sp^3d	Trigonal bipyramidal	90°, 120°	PCl_5
sp^3d^2	Octahedral	90°	SF_6
dsp^2	Square planar	90°	$[PtCl_4]^{2-}$

Bond Parameters Comparison

Bond Type	Length (pm)	Energy (kJ/mol)	Examples
Single	Longer	Lower	C-C (154), C-H (107)
Double	Shorter	Higher	C=C (133), C=O (121)
Triple	Shortest	Highest	C≡C (120), C≡N (116)

Intermolecular Forces Strength

Hydrogen bonding > Dipole-dipole > London forces

- **Hydrogen bonding**: 10-40 kJ/mol
- **Dipole-dipole**: 2-5 kJ/mol
- **London forces**: 0.1-2 kJ/mol

Common Molecules and Their Properties

Molecule	Hybridization	Geometry	Bond Angle	Dipole Moment
CH_4	sp^3	Tetrahedral	109.5°	0
NH_3	sp^3	Trigonal pyramidal	107°	1.47 D
H_2O	sp^3	Bent	104.5°	1.85 D
BF_3	sp^2	Trigonal planar	120°	0
CO_2	sp	Linear	180°	0
PCl_5	sp^3d	Trigonal bipyramidal	90°, 120°	0
SF_6	sp^3d^2	Octahedral	90°	0

Advanced Concepts for Competitive Exams

Heteronuclear Diatomic Molecules

HF Molecule:

- Energy levels: H(1s) higher than F(2p)
- More electron density on F in bonding MO
- Polar covalent bond character

CO Molecule:

- Isoelectronic with N_2
- Bond order = 3
- Strong σ-donation and π-backbonding

Exceptions and Special Cases

Chromium and Copper Electronic Configurations

- **Cr**: [Ar] $4s^1$ $3d^5$ (not $4s^2$ $3d^4$)
- **Cu**: [Ar] $4s^1$ $3d^{10}$ (not $4s^2$ $3d^9$)
- **Reason**: Extra stability of half-filled and fully-filled d-subshells

Expanded Octet Examples

- **PCl_5**: 10 electrons around P
- **SF_6**: 12 electrons around S
- **IF_7**: 14 electrons around I

Important Physical Properties Affected by Bonding

Boiling Points of Hydrides

Group 15: NH_3 (−33°C) > PH_3 (−88°C) > AsH_3 (−62°C) **Group 16**: H_2O (100°C) > H_2S (−60°C) > H_2Se (−41°C) **Group 17**: HF (20°C) > HCl (−85°C) > HBr (−67°C)

Explanation: Hydrogen bonding in NH_3, H_2O, and HF

Key Success Strategy

For NEET Preparation

1. **Master Lewis structures**: Practice drawing complex molecules and ions
2. **Understand hybridization**: Connect with molecular geometry
3. **MO theory applications**: Focus on bond order and magnetic properties
4. **VSEPR predictions**: Practice with various electron pair arrangements
5. **Hydrogen bonding effects**: Understand physical property changes

Important Formulas to Remember

- **Formal Charge**: FC = V - L - ½B
- **Bond Order**: BO = ½(Nb - Na)
- **Dipole Moment**: $\mu = Q \times r$
- **Hybridization Index**: ½(V + M ± charge)

Common Mistakes to Avoid

1. **Confusing formal charge with oxidation state**
2. **Forgetting lone pairs in VSEPR calculations**
3. **Mixing up σ and π bond counting**
4. **Incorrect MO energy order for different molecules**
5. **Not considering resonance in stability**

Exam Tips

1. **Practice drawing Lewis structures daily**
2. **Memorize common molecular geometries**

3. **Understand the logic behind hybridization**
4. **Connect molecular structure with properties**
5. **Solve numerical problems regularly**

EXAM SPRINT: Focus on conceptual understanding rather than rote memorization. Practice numerical problems involving bond order, formal charge, and dipole moments. Master the relationship between molecular structure and properties for NEET success.

Source: NCERT Chemistry Class 11, Unit 4 - Comprehensive coverage for NEET preparation