

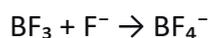
Unit- 2 Compounds of p-Block Elements

- **Double Bond Rule:** Heavier p-block elements show reluctance to form π - π bonds
- **Reason:** Poor orbital overlap due to larger atomic size
- **Example:** While C=C is common, Si=Si bonds are rare and reactive
- **Compensation:** Heavier elements use d-orbitals for π -bonding

C. Back bonding (π - $d\pi$ or π - π)

Concept: Donation of electron density from filled p-orbital of one atom to empty orbital of another atom

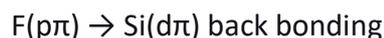
1. Boron Compounds:



- In BF_3 : Empty p-orbital on B
- In BF_4^- : Back bonding from filled F p-orbitals to empty B orbitals

2. Silicon Compounds:

- **Silicon tetrafluoride (SiF_4):**



- Si-F bond shorter than expected
- Explains high stability of SiF_4 compared to other halides

3. Phosphorus Compounds:

- In PCl_5 , axial bonds are longer due to less back bonding compared to equatorial bonds

Multicenter bonding (electron-deficient bonding)

- **Characteristics:** Bonds involving more than 2 atoms, common in Boron compounds

- **Types of Multicenter Bonds:**

1. Three-Center-Two-Electron (3c-2e) Bonds:

- Found in boranes, carboranes
- **Example: Diborane (B_2H_6)**
- **Terminal B-H bonds:** Normal 2c-2e σ bonds
- **Bridging B-H-B bonds:** 3c-2e bonds
- Four electrons shared among three atoms

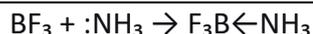
2. Three-Center-Four-Electron (3c-4e) Bonds:

- Found in interhalogens and noble gas compounds
- **Example: I_3^- ion**
- Central I uses sp^3d hybridization
- Bonding description: 3c-4e bond

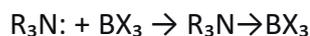
E. Coordinate (dative) bonding:

1. **Boron Compounds:** B as Lewis acid (electron acceptor)

Unit- 2 Compounds of p-Block Elements



- **Group 15 Elements:** N, P as Lewis bases (electron donors)



2. **Sulfur Compounds:**

1. In sulfoxides: S \rightarrow O coordinate bond
2. In sulfuric acid: S=O and S-OH bonds

- **Group-wise bonding characteristics**

- **Group 13: boron family**

1. **Boron (B):**

- **Small size, high ionization energy**
- **Exclusively covalent bonding**
- **Electron-deficient compounds**
- **Examples:**
 - **Boron Hydrides (Boranes):** Multicenter bonding
 - **Boron Trihalides (BX₃):** Planar, Lewis acids
 - **Boron Nitride (BN):** Isoelectronic with C₂

2. **Heavier Elements (Al, Ga, In, Tl):**

- Increasing metallic character down group
- **Inert pair effect** prominent in Tl
- Tl⁺ more stable than Tl³⁺
- More ionic character in bonding

- **GROUP 14: CARBON FAMILY**

1. **Carbon (C):**

- **Catenation:** Ability to form C-C chains
- **Multiple bonding:** pπ-pπ bonds common
- **Hybridization:** sp, sp², sp³ common
- **Allotropes:** Diamond (sp³), Graphite (sp²)

2. **Silicon (Si):**

- **Limited catenation** (max Si-Si chain length ~6)
- **Reluctance for pπ-pπ bonds**
- **pπ-dπ bonding** important

Unit- 2 Compounds of p-Block Elements

- **Example:**
- $(\text{CH}_3)_3\text{Si-O-Si}(\text{CH}_3)_3$
- Si-O-Si angle $\sim 140^\circ$ (flexible)
- $p\pi-d\pi$ back bonding from O to Si

3. Tin and Lead:

- Increasing metallic character
- Inert pair effect
- +2 oxidation state more stable down group

• **GROUP 15: NITROGEN FAMILY**

1. Nitrogen (N):

- **Strong $p\pi-p\pi$ bonds** ($\text{N}\equiv\text{N}$ triple bond)
- **Lone pair availability** (Lewis base)
- **Examples:**
 - **Ammonia (NH_3):** Pyramidal, hydrogen bonding
 - **Hydrazine (N_2H_4):** N-N single bond
 - **Nitrogen oxides:** Various π -bonding patterns

2. Phosphorus (P):

- **Poor $p\pi-p\pi$ bonding**
- **Uses d-orbitals** for π -bonding
- **Example: Phosphoric acid (H_3PO_4)**
- P=O bond: $d\pi-p\pi$ character
- P-OH bonds: Normal σ bonds

3. Heavier Elements (As, Sb, Bi):

- Increasing metallic character
- Decreasing stability of +5 oxidation state

GROUP 16: OXYGEN FAMILY

1. Oxygen (O):

- **Strong $p\pi-p\pi$ bonds**
- **Two lone pairs**
- **Hydrogen bonding capability**

Unit- 2 Compounds of p-Block Elements

- **Examples:**
 - **Water (H₂O):** Bent structure, extensive H-bonding
 - **Ozone (O₃):** Resonance hybrid with partial π -character

2. Sulfur (S):

- **Limited $p\pi$ - $p\pi$ bonding**
- **Catenation** (S-S bonds common)
- **Uses d-orbitals**
- **Example: Sulfuric acid (H₂SO₄)**
- S=O bonds: $d\pi$ - $p\pi$ character

3. Selenium and Tellurium:

- Increasing metallic character
- Semiconductor properties

GROUP 17: HALOGENS

1. Bonding Characteristics:

- **High electronegativity**
- Form both covalent and ionic bonds
- **Oxidation states:** -1 to +7 (except F, max 0)
- **Examples:**
 - **Interhalogens (ClF, BrF₃, IF₇):** Various hybridizations
 - **Polyhalides (I₃⁻):** 3c-4e bonding
 - **Hypohalous acids (HOX):** Polar O-H bond

2. Fluorine (F):

- **Highest electronegativity**
- **Small size** allows strong bonds
- **Limited oxidation states** (only 0 and -1)
- No d-orbital participation

GROUP 18: NOBLE GASES

1. Bonding (in compounds):

- **Xenon** forms maximum compounds
- **Hybridization:** sp^3d , sp^3d^2 , sp^3d^3

Unit- 2 Compounds of p-Block Elements

- **Examples:**
 - **XeF₂**: Linear (sp³d)
 - **XeF₄**: Square planar (sp³d²)
 - **XeF₆**: Distorted octahedral (sp³d³)

4. Special bonding phenomena in p-block elements

A. INERT PAIR EFFECT

Definition: Reluctance of ns² electrons to participate in bonding in heavier elements

Examples:

1. **Tl(I) vs Tl(III):** Tl⁺ more stable than Tl³⁺
2. **Pb(II) vs Pb(IV):** Pb²⁺ more stable than Pb⁴⁺
3. **Bi(III) vs Bi(V):** Bi³⁺ more stable than Bi⁵⁺

Reason:

- Poor shielding by d- and f-electrons
- Increased effective nuclear charge
- Relativistic effects in heavy elements

- **B. HYBRIDIZATION AND GEOMETRY**
- **Common Hybridizations in p-Block:**

Hybridization	Geometry	Examples
sp	Linear	CO ₂ , C ₂ H ₂ , BeCl ₂
sp²	Trigonal planar	BF ₃ , SO ₃ , NO ₃ ⁻
sp³	Tetrahedral	CH ₄ , NH ₄ ⁺ , SO ₄ ²⁻
sp³d	Trigonal bipyramidal	PCl ₅ , SF ₄
sp³d²	Octahedral	SF ₆ , PF ₆ ⁻
sp³d³	Pentagonal bipyramidal	IF ₇

- **C. RESONANCE AND DELOCALIZATION**

Unit- 2 Compounds of p-Block Elements

Important Examples:

1. Carbonate Ion (CO_3^{2-}):

- **Resonance hybrid** of three equivalent structures
- **π -electron delocalization** over three O atoms
- All C-O bonds equal length (intermediate between single and double)

2. Benzene (C_6H_6):

- **Aromatic system** with delocalized π -electrons
- **Hückel's rule:** $4n+2$ π -electrons ($n=1$)

3. Borazine ($\text{B}_3\text{N}_3\text{H}_6$):

- "Inorganic benzene"
- Delocalized but polarized π -system
- $\text{B}^+\delta\text{-N}^-\delta$ polarity reduces aromaticity

D. HYDROGEN BONDING

In p-Block Elements:

1. With N, O, F:

- Strong hydrogen bonds
- **Example:** Water, ammonia, HF

2. With other elements:

- Weaker hydrogen bonds possible
- **Example:** C-H \cdots O, N-H \cdots S bonds

Practical applications of bonding concepts

Predicting Properties from Bonding

1. Melting/Boiling Points:

- Covalent network solids: Very high (diamond, SiC)
- Molecular covalent: Low to moderate
- Ionic compounds: High

2. Electrical Conductivity:

- Metals: Good conductors
- Covalent network: Insulators/semiconductors