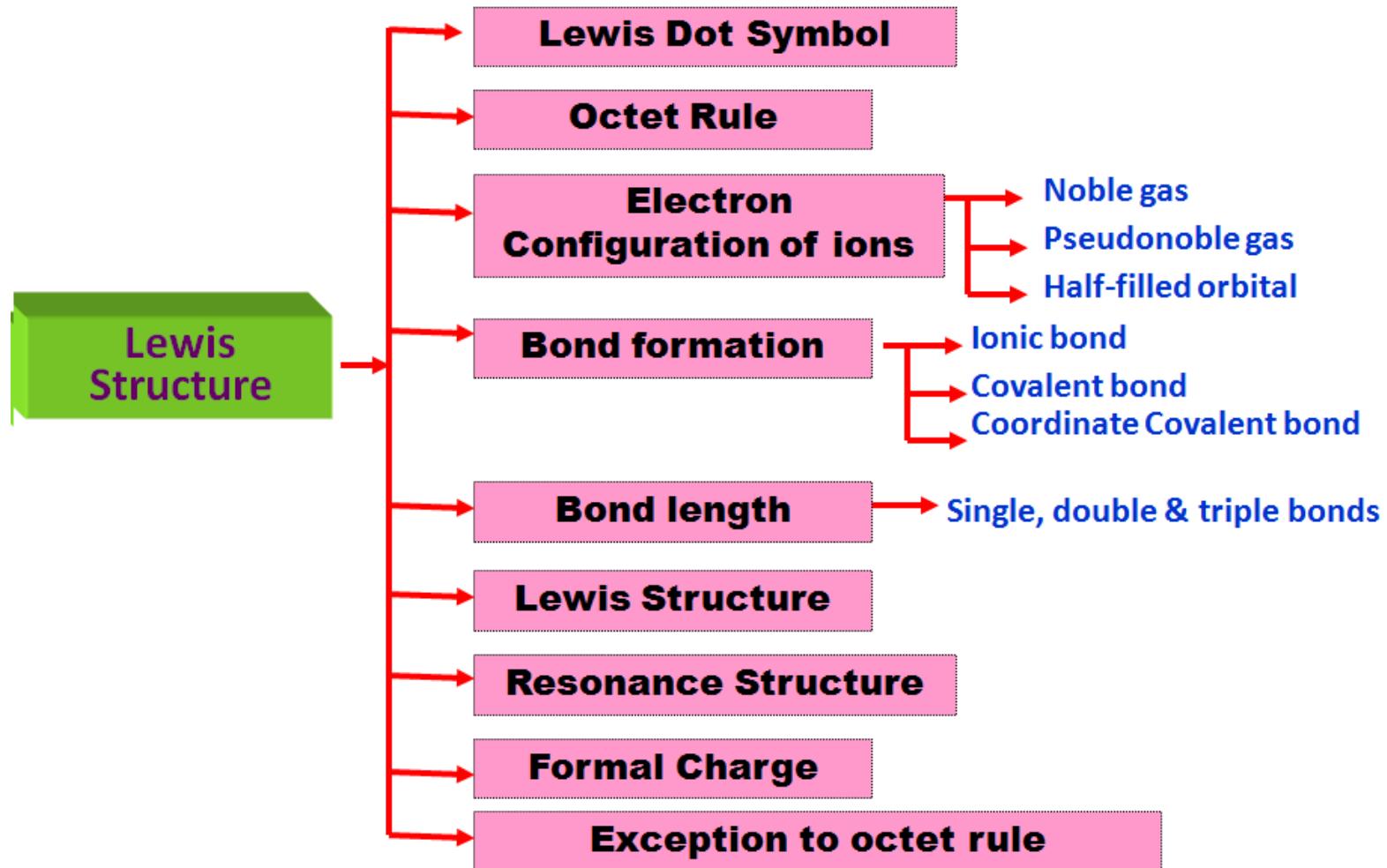


# 4.0 CHEMICAL BONDING

## 4.1 LEWIS STRUCTURE



# GILBERT N> LEWIS



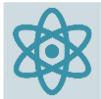
American physical chemist

known for:

- the discovery of the **covalent bond** and his concept of electron pairs
- **Lewis structures**
- other contributions to valence bond theory have shaped modern theories of chemical bonding

(October 23, 1875 – March 23, 1946)

# OCTET RULE

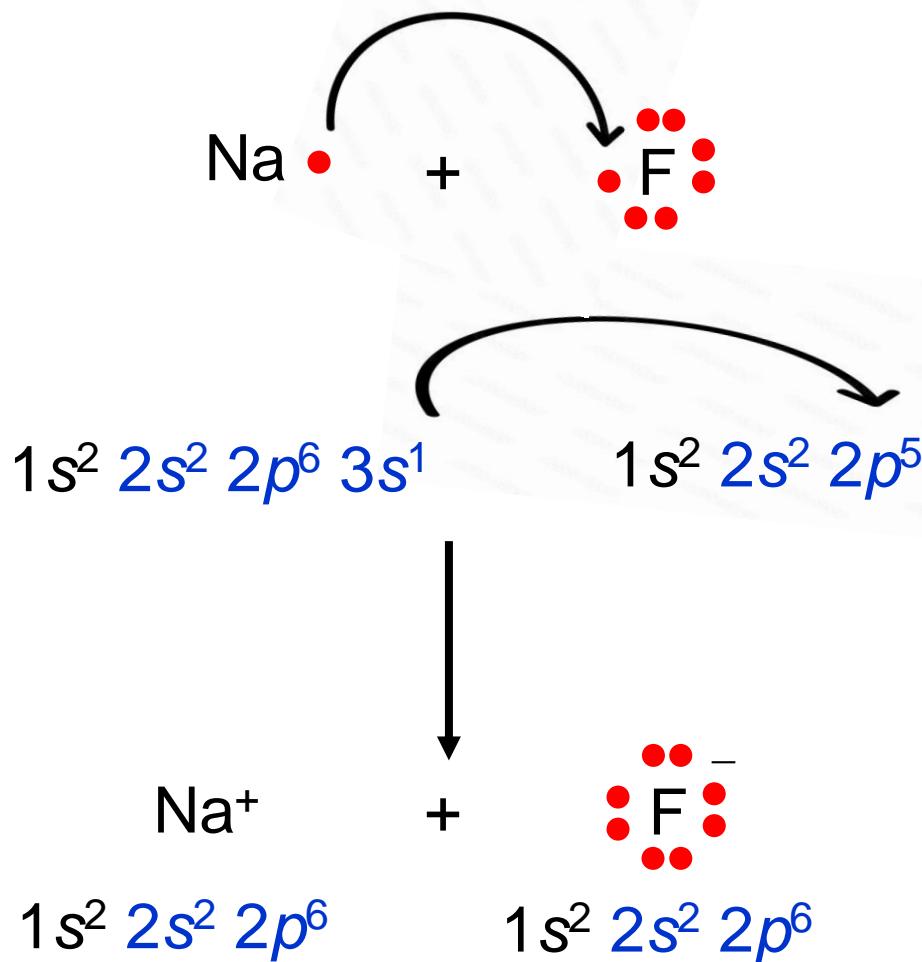


When atoms bond, they lose, gain or share electron to attain a filled outer level of eight or two electrons.

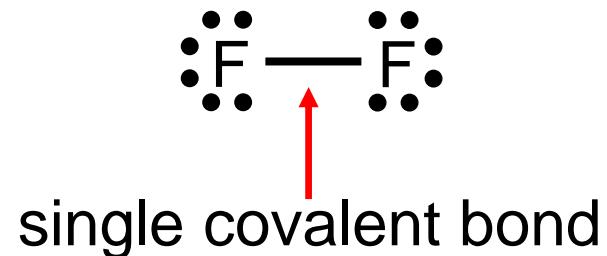
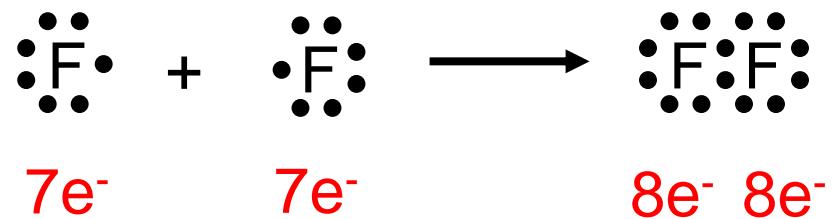


The rule works mainly for elements in Period 2.

# Achieving octet by transferring of electrons

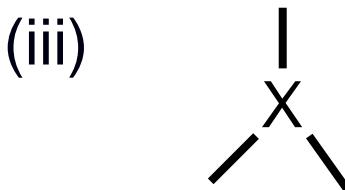
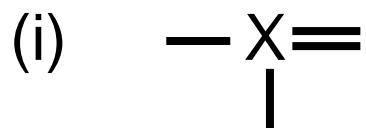


# Achieving octet by sharing of electrons

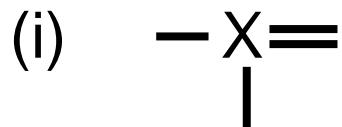


## EXERCISE

Which of the following bonding patterns does obey the octet rule?



## ANSWER



☞ X surrounded by 8 electrons

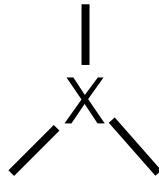
☞ **Obey octet rule**



☞ X surrounded by 8 electrons

☞ **Obey octet rule**

(iii)



👉 X surrounded by 6 electrons

👉 **Does not obey octet rule**

(iv)



👉 X surrounded by 8 electrons

👉 **Obey octet rule**

# TYPE OF STABILITY OF IONS

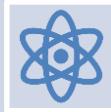
---



Noble gas configuration



Pseudo-noble gas configuration



Half-filled orbitals configuration

# NOBLE GAS CONFIGURATION

- The term given to the electronic configuration of noble gases.
- Atoms may **lose** or **gain** enough  $e^-$  so as to form a stable ion with **octet** (or **duplet**) configuration  $\rightarrow ns^2 np^6$

$$1s^2 2s^2 2p^6 = [\text{Ne}]$$

2 He Helium	10 Ne Neon	18 Ar Argon
36 Kr Krypton	54 Xe Xenon	86 Rn Radon

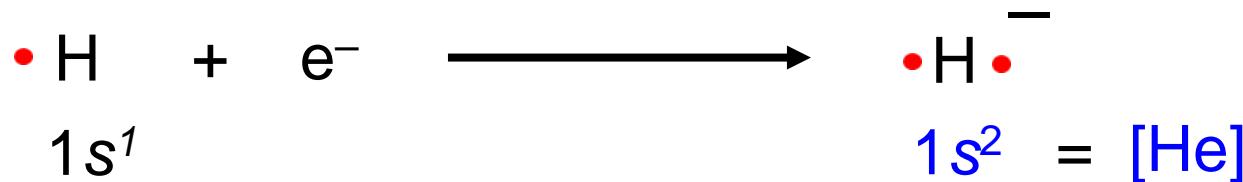
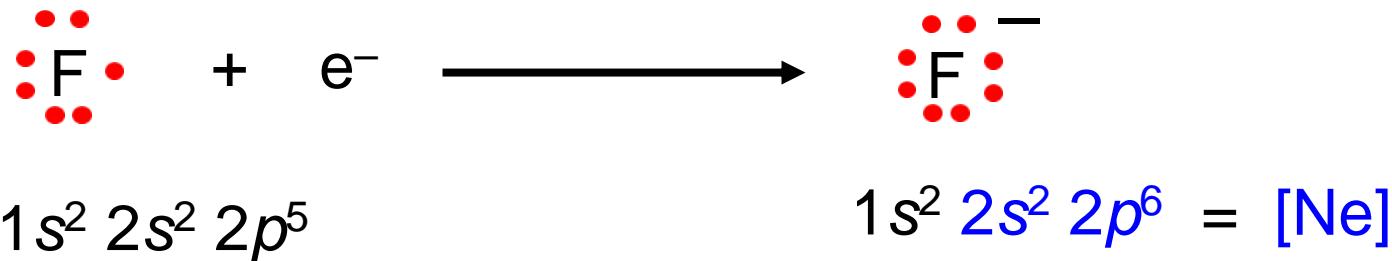
## EXAMPLE

### Cations with noble gas configurations



## EXAMPLE

### Anions with noble gas configurations

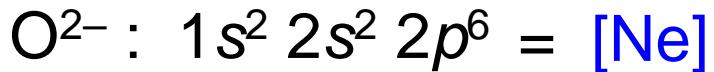
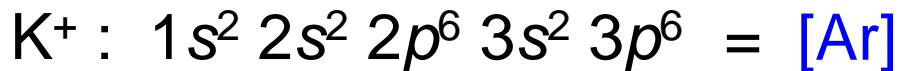
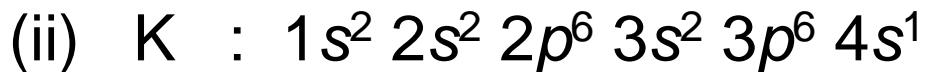
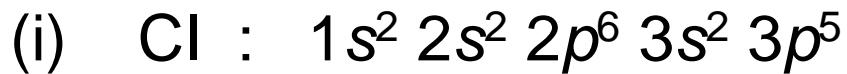


## EXAMPLE

Write the ionic symbol and ground-state electron configuration of the monoatomic ion most likely to be formed by each:

- i. Cl
- ii. K
- iii. Mg
- iv. O

## ANSWER



**Remember!**

**Elements in Groups 1,2, 16 and 17 attain noble gas configuration.**

Their ions are said to be **isoelectronic** with the nearest noble gas (Group 18)

	1 $ns^1$	2 $ns^2$	16 $ns^2np^4$	17 $ns^2np^5$	18 $ns^2np^6$
period 2	Li	Be	O	F	He
3	Na	Mg	S	Cl	Ne
4	K	Cs	Se	Br	Ar
5	Rb	Sr	Te	I	Kr
6	Cs	Ba			Xe
					Rn

**- electron**      **+ electron**

# PSEUDO-NOBLE GAS CONFIGURATION

---

- Ions with stable electronic configurations in which all their orbitals are filled with electrons.
- A noble gas core with outer  $d^{10}$  configuration:  $ns^2np^6nd^{10}$
- But electronic configuration is not that of any noble gas ↗  
***pseudo-noble gas configuration***

KNOW THE  
WORD ?

Pseudo- [soo-doh] means false, pretended, unreal or deceptive resemblance of something

## EXAMPLE

### Cation with pseudo-noble gas configuration

Gallium, Ga is an element from Group 13:



Electronic configuration of **Ga**:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$

Electronic configuration of **Ga<sup>3+</sup>**:  $1s^2 2s^2 2p^6 3s^2 3p^6 \textcolor{red}{3d}^{10}$

$$= [\text{Ar}] \textcolor{blue}{3d}^{10}$$

# HALF-FILLED ORBITALS CONFIGURATION

---

- When a **cation** is formed from an atom of a **transition metal**, electrons are always removed first from the **ns** orbital, then followed by the **( $n - 1$ )d** orbitals
  
- Some **transition metal** atoms form **cations** that have electron configuration associated with **half-filled d** orbital ( $d^5$ ).  
Example:  $3d^5$

CONSIDER  
THIS

Electronic configuration of Mn:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

**What is the electronic configuration of  $Mn^{2+}$ ?**

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$



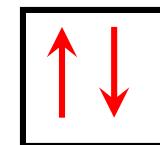
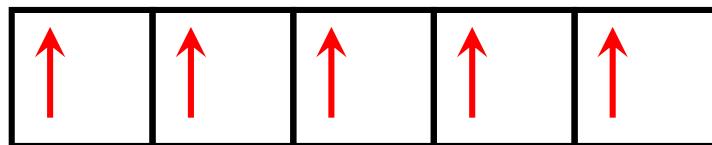
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$



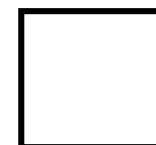
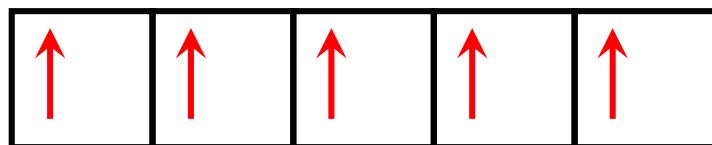
For the case of transition metal ions:

$e^-$  are removed from the 4s orbital in forming  $Mn^{2+}$  because the 3d orbital is more stable than the 4s orbital

( $n-1$ ) $d^5$  configuration achieved the stability of the half-filled orbital.



[Ar] **3d<sup>5</sup> 4s<sup>2</sup>**



[Ar] **3d<sup>5</sup>**

[Ar] = 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup>

## **EXAMPLE**

Ferric oxide is the inorganic compound with the formula  $\text{Fe}_2\text{O}_3$ . Ferric refers to iron-containing materials or compounds. In chemistry the term is reserved for iron with an oxidation number of +3, also denoted iron(III) or  $\text{Fe}^{3+}$ .

What type of stability of the electron configuration of ion  $\text{Fe}^{3+}$  ?

**Note:** Fe ( $Z = 26$ )

## ANSWER

**Fe (Z = 26)**

Electron configuration of Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$   
= [Ar]  $3d^6 4s^2$

$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$

---

Electron configuration of  $\text{Fe}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$   
= [Ar]  $3d^5$

Type of stability: **half-filled d orbital**

# IONIC BOND

---

- Ionic bond is electrostatic force of attraction between positive ion (cation) and negative ion (anion) in an ionic compound.
  
- Also known as **electrovalent bond**.

# Substances formed by ionic bonding

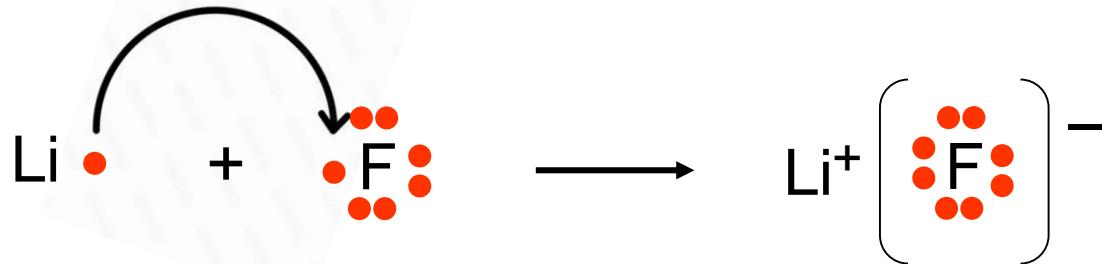
Anion Cation	$\text{Cl}^-$	$\text{OH}^-$	$\text{O}^{2-}$	$\text{SO}_4^{2-}$
$\text{Na}^+$	NaCl	NaOH	$\text{Na}_2\text{O}$	$\text{Na}_2\text{SO}_4$
$\text{Ca}^{2+}$	$\text{CaCl}_2$	$\text{Ca(OH)}_2$	CaO	$\text{CaSO}_4$
$\text{Al}^{3+}$	$\text{AlCl}_3$	$\text{Al(OH)}_3$	$\text{Al}_2\text{O}_3$	$\text{Al}_2(\text{SO}_4)_3$



*How do ionic bonds form ?*

- By **transferring of electron** from metals to non-metals.
- Total number of **electron lost** by metal atoms  
= Total number of **e<sup>-</sup> gained** by the non-metal atoms.

- Formation of ionic bond using Lewis symbol:
- Example:



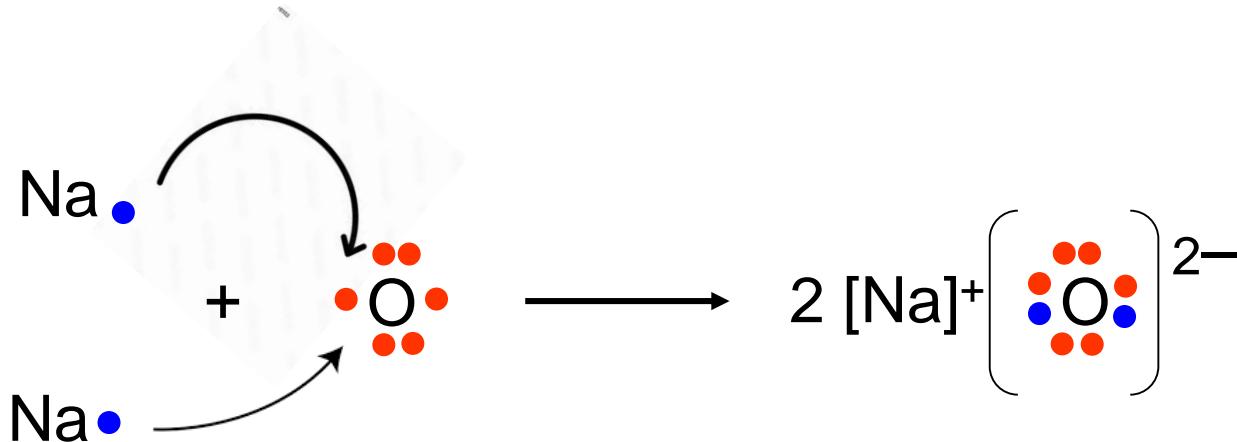
**KEEP IN MIND:**



indicates the transfer of electron

## EXAMPLE

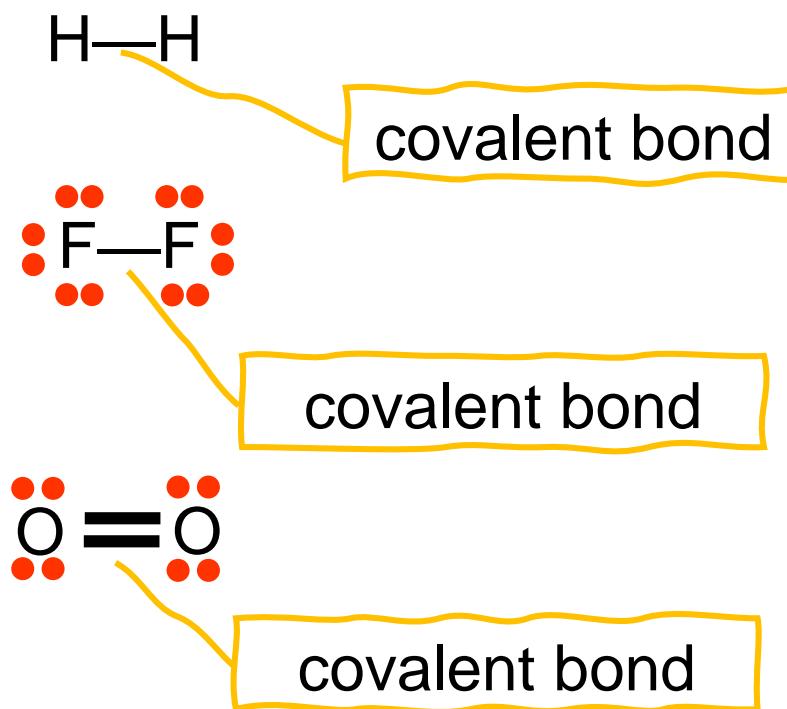
Use Lewis symbols to describe the formation of  $\text{Na}_2\text{O}$ .



- Each Na atom **loses an electron** forming  $\text{Na}^+$  ion.
- O atom **gains two electrons** forming  $\text{O}^{2-}$  ion.
- Electrostatic attraction between  $\text{Na}^+$  ion and  $\text{O}^{2-}$  ion forming **ionic bond**.
- Formula of the compound formed is  **$\text{Na}_2\text{O}$** .

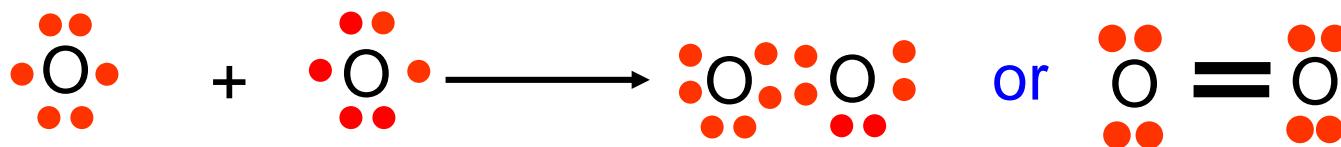
# COVALENT BOND

A chemical bond that involves the sharing of electron pairs between nonmetal atoms.

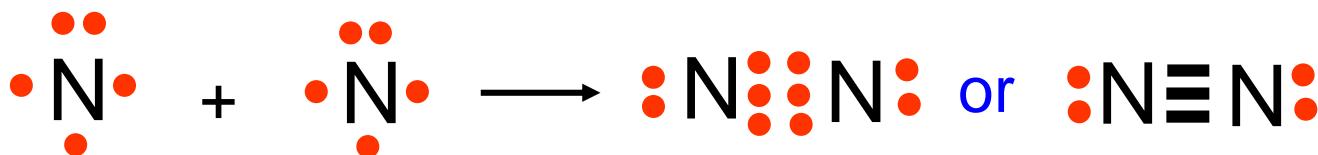




When two atoms share a pair of electrons, so the covalent bond formed is called **single bond**.

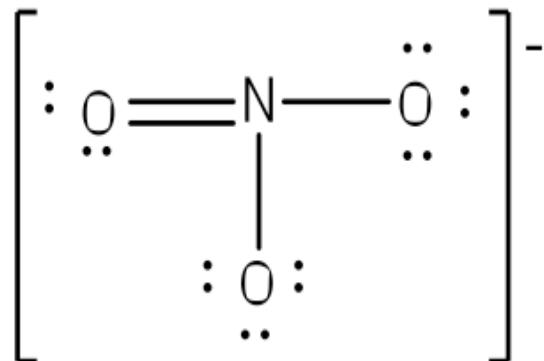
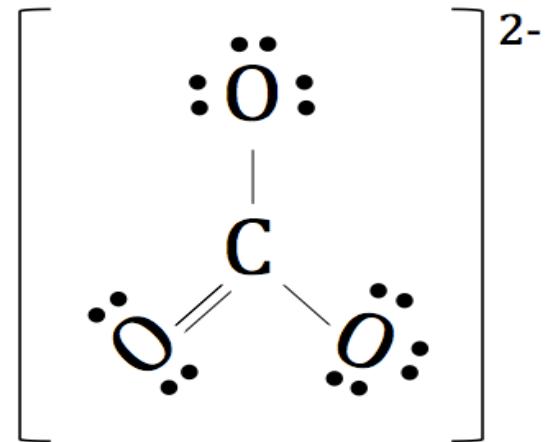
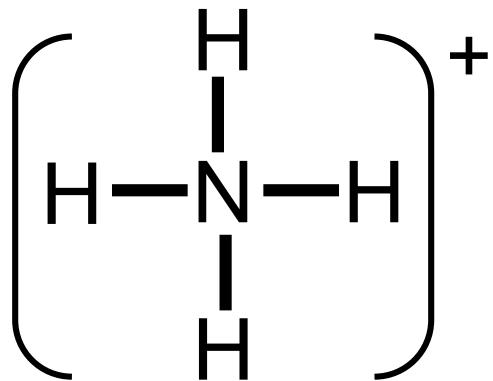


When two atoms share two pairs of electrons, so the covalent bond formed is called **double bond**.



When two atoms share three pairs of electrons, so the covalent bond formed is called **triple bond**.

# Example of Covalent Bond In Anions



# DATIVE BOND

---



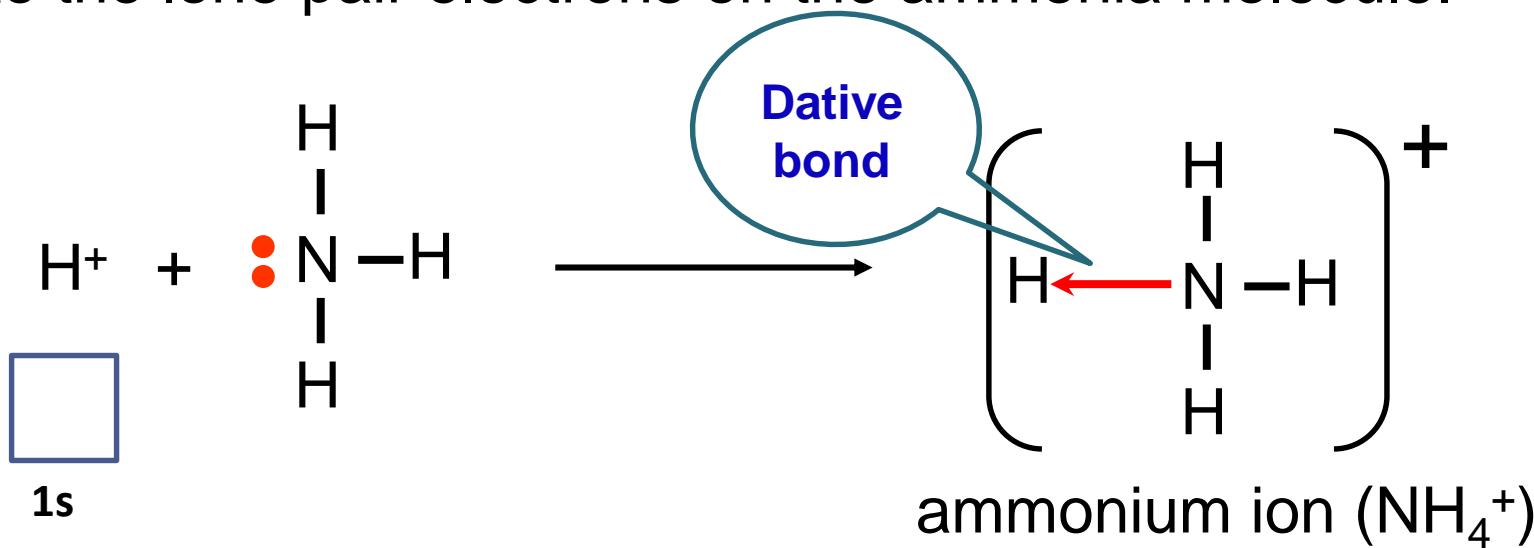
A covalent bond in which both electrons come from the same atom.



Also called as **coordinate bond**.

## EXAMPLE

Ammonium ions,  $\text{NH}_4^+$  are formed by the transfer of a hydrogen ion to the lone pair electrons on the ammonia molecule.

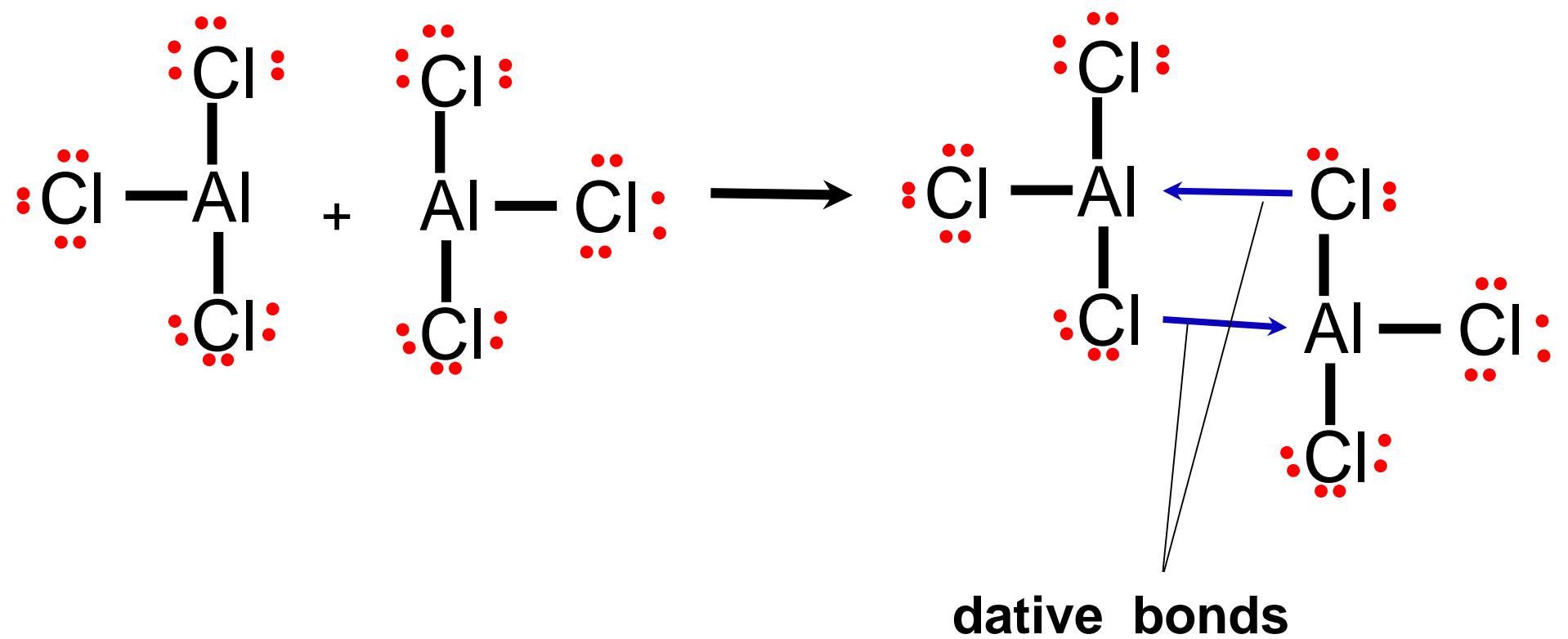


- $\text{H}^+$  has **empty 1s orbital**
- N atom has a **lone pair electron**
- $\text{H}^+$  **accepts an electron** pair from N to form **dative bond**.

- Aluminum chloride sublimes (convert from a solid to a gas phase) at about 180°C.
- This indicates that it is a covalent compound.
- $\text{AlCl}_3$  adopts three different structures, depending on the temperature and the state (solid, liquid, vapour).
- In liquid and vapour state, aluminium trichloride exists as the **dimer  $\text{Al}_2\text{Cl}_6$**  (two molecules of  $\text{AlCl}_3$  joined together).

## EXAMPLE

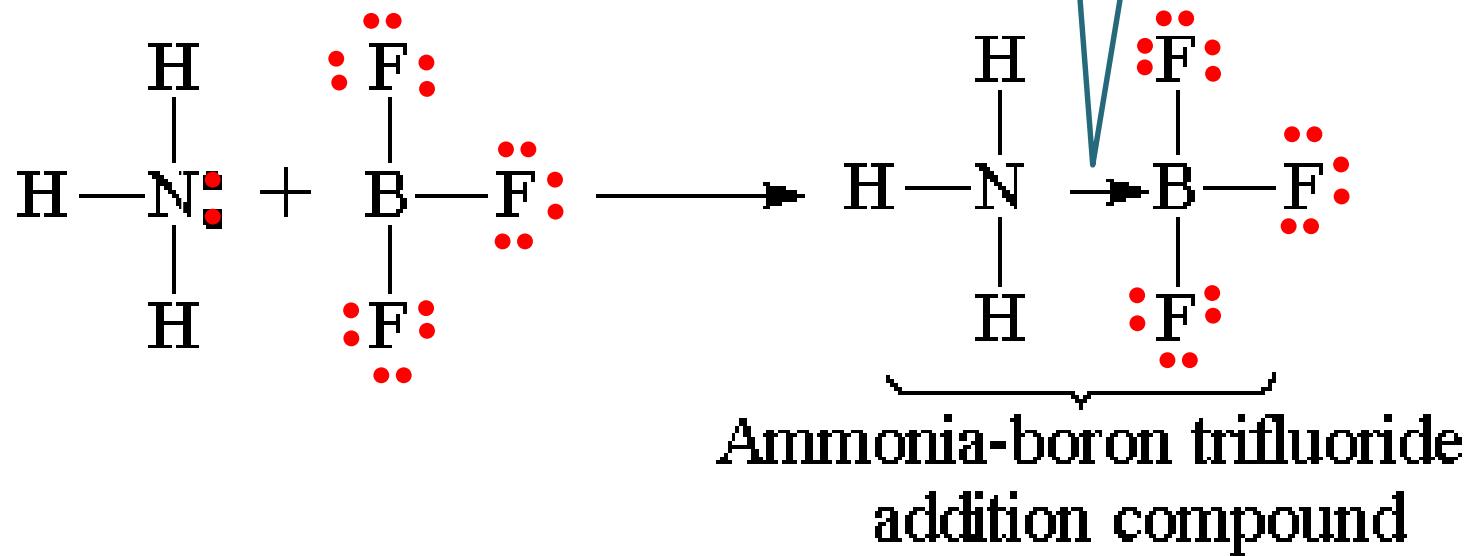
In the  $\text{Al}_2\text{Cl}_6$  dimer, two molecules of  $\text{AlCl}_3$  are linked together through two dative bonds.



## EXERCISE

Boron trifluoride ( $\text{BF}_3$ ) accepts an electron pair from ammonia ( $\text{NH}_3$ ) to form  $\text{BF}_3\text{-NH}_3$ . **Show which of the bond is the coordinate bond?**

# ANSWER



# LEWIS STRUCTURE

Lewis structure is a diagram that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule.



*Problem 1: How to draw the Lewis structure of a covalent molecule?*

## EXAMPLE: $\text{NF}_3$

**Step 1:** Count all valence electrons

<b>Atom</b>	<b>Number of valence e<sup>-</sup></b>
$\text{N} \times 1$	$5\text{e}^- \times 1 = 5\text{e}^-$
$\text{F} \times 3$	$7\text{e}^- \times 3 = 21\text{e}^-$
<b>Total = 26e<sup>-</sup></b>	

**Step 2:** Draw the skeletal structure: Nitrogen atom, **N** is less electronegative than fluorine, **F**. Thus,

F as terminal atom (*also known as surrounding atom*)

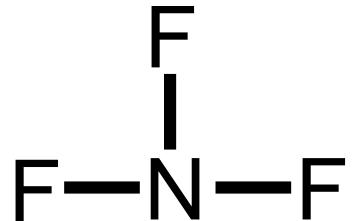
N as central atom

*The skeletal structure;*

F

F N F

**Step 3:** Draw single covalent bond between **N** and each **F**.

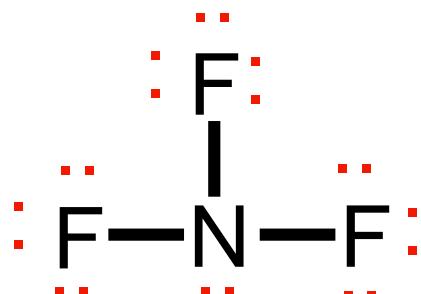


$$\begin{aligned}\text{Number of valence electrons} &= 26e^- \\ &\quad - \underline{6e^- \text{(bonding electrons)}} \\ \text{Remaining electrons} &= 20e^-\end{aligned}$$

## Step 4:

- Complete the octets for the terminal atom, F with the remaining electrons ( $20\text{ e}^-$ ).
- Add the remaining electrons (if any) to the central atom, N.

\* *The electrons that aren't involved as bond are presented as lone pairs.*



OK!

## Step 5: Check

$$8\text{e}^- \times 3 = 24\text{e}^-$$

$$+ 2\text{e}^-$$

---

$$\text{Total} = 26\text{e}^-$$

?



*Problem 2: How to draw the Lewis structure of a polyatomic ion ?*

**EXAMPLE:**  $\text{NH}_4^+$

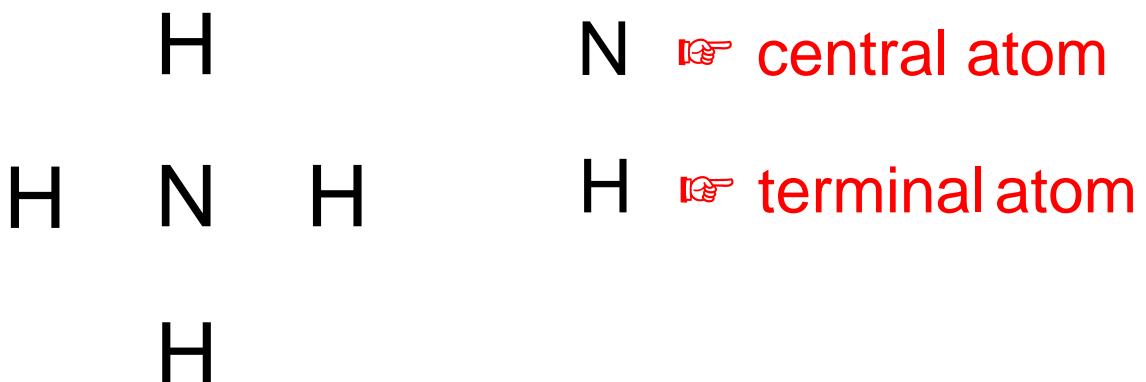
**Step 1:** Count all valence electrons

Atom	Number of valence e <sup>-</sup>
N x 1	$5\text{e}^- \times 1 = 5\text{e}^-$
H x 4	$1\text{e}^- \times 4 = 4\text{e}^-$
+1 charge	Total = 8e <sup>-</sup>

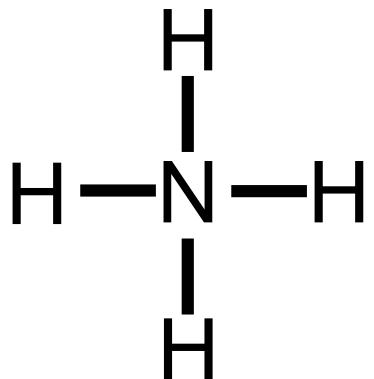
Add electrons if -ve charge  
Minus electrons if +ve charge

= 1e<sup>-</sup>

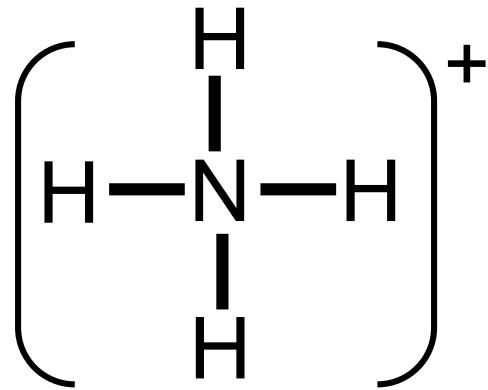
## Step 2: H atom is always as the terminal atom



## Step 3: Draw single covalent bond between N and each H



**Step 4:** Draw a bracket and write 1+ charge



**Step 5: Check**

$$2e^- \times 4 = 8e^-$$

---

$$\text{Total} = 8e^-$$

OK!

## EXAMPLE 2: $\text{CO}_3^{2-}$

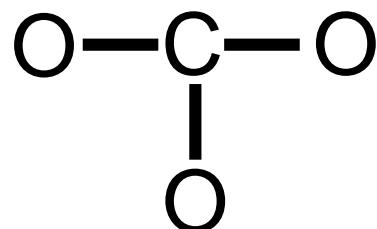
**Step 1:** Count all valence electrons

Atom	Number of valence e <sup>-</sup>
C x 1	$4\text{e}^- \times 1 = 4\text{e}^-$
O x 3	$6\text{e}^- \times 3 = 18\text{e}^-$
-2 charge	$= + 2\text{e}^-$
	<b>Total = 24e<sup>-</sup></b>

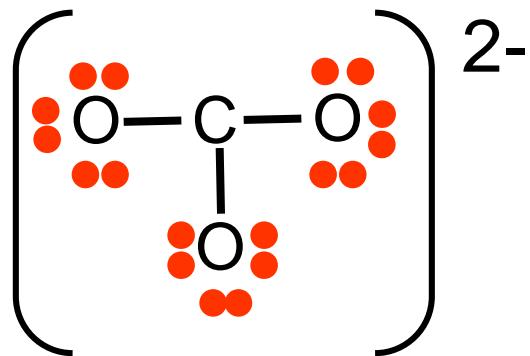
**Step 2:** Draw the skeletal structure



**Step 3:** Draw single covalent bond between C and each O



**Step 4:** Draw a bracket and write 2- charge

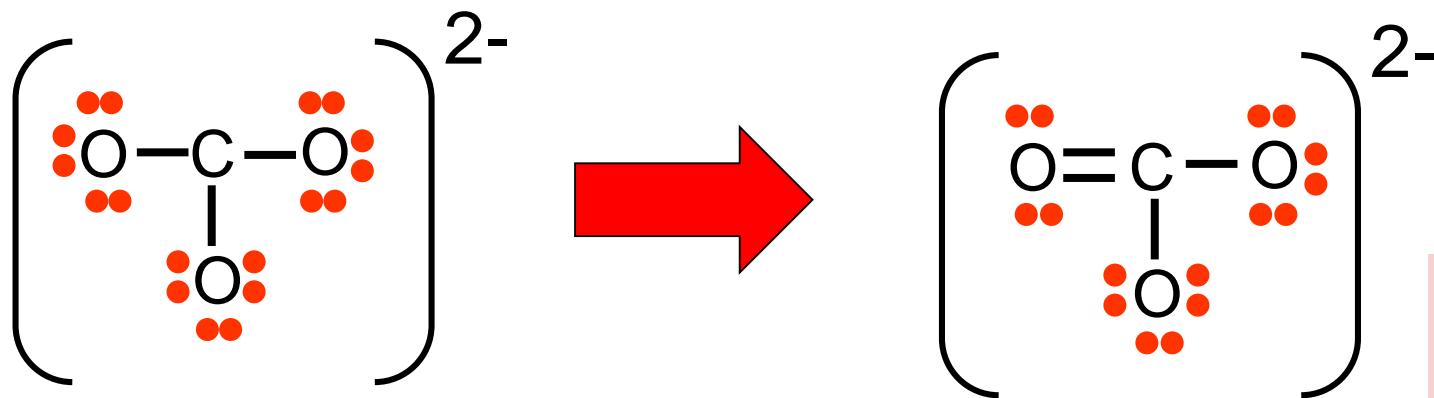


*What you should do if  
the central atom is not octet?*



## Step 4:

If the central atom is not octet yet, make a multiple bond (double or triple) by using a lone pair from the terminal atoms.



OK!

Check:

$$8e^- \times 3 = 24e^-$$

---

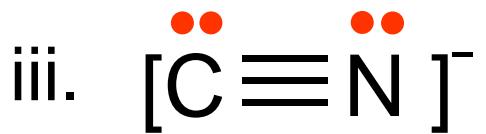
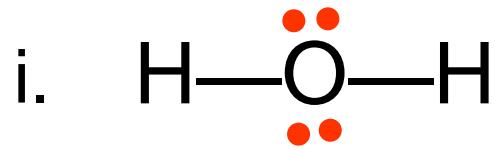
$$\text{Total} = 24e^-$$

## EXERCISE

Draw the Lewis structure for each of the following:



## ANSWER

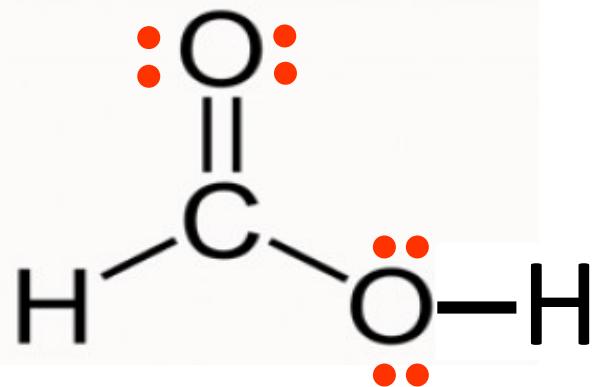


## **EXERCISE**

Formic acid (also called methanoic acid) is the simplest carboxylic acid. Its chemical formula is HCOOH. It is an important intermediate in chemical synthesis and occurs naturally, most notably in ant venom.

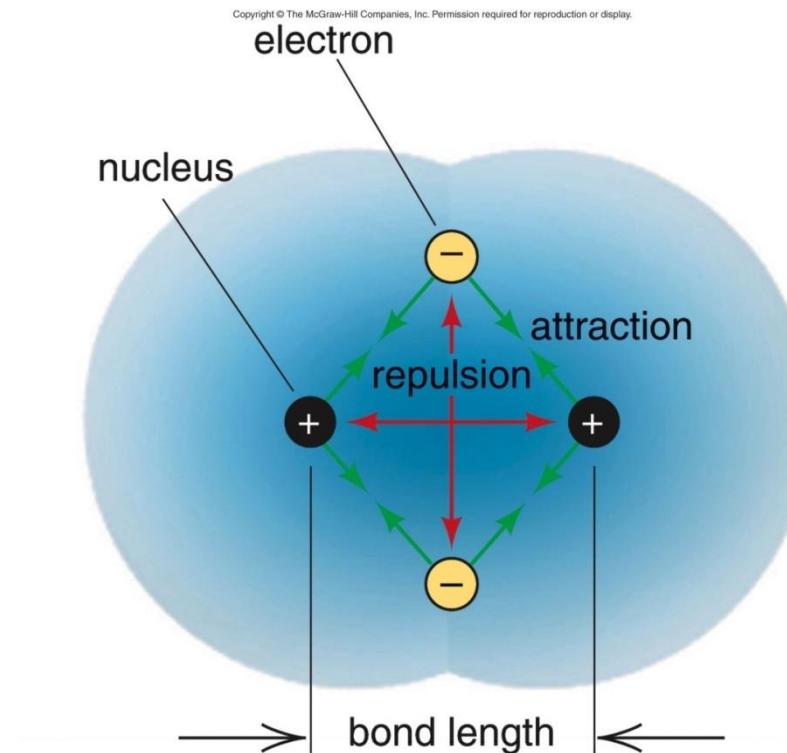
**Draw the Lewis structure of formic acid.**

# ANSWER



# BOND LENGTH

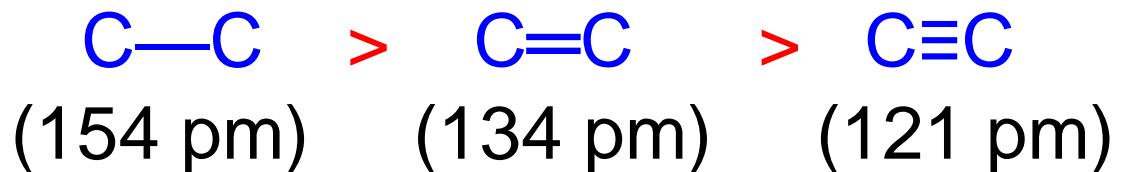
- The distance between nuclei of two covalently bonded atoms in a molecule.



□ For a given pair of atoms:

**Bond length: single > double > triple**

Average bond length:



$$1 \text{ pm} = 1.0 \times 10^{-12} \text{ m}$$

$$1 \text{ Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \text{ Å} = 0.1 \text{ nm} = 100 \text{ pm}$$

## **EXERCISE**

Arrange the bonds in each set-in order of decreasing bond length:

- i. C=O, C–O, C≡O
- ii. N=N, N–N, N≡N

## ANSWER

(i)  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$ ,  $\text{C}\equiv\text{O}$

Bond length:  $\text{C}-\text{O} > \text{C}=\text{O} > \text{C}\equiv\text{O}$

(ii)  $\text{N}=\text{N}$ ,  $\text{N}-\text{N}$ ,  $\text{N}\equiv\text{N}$

Bond length:  $\text{N}-\text{N} > \text{N}=\text{N} > \text{N}\equiv\text{N}$

# THE MOST PLAUSIBLE LEWIS STRUCTURE

---

- Certain molecules are possible to have more than one Lewis structure.
- However, the most stable structure is used to represent the molecule, which is referred to as **the most plausible Lewis structure**.
- One way to determine the most plausible Lewis structure is based on the concept of **formal charge**.

# FORMAL CHARGE

- The difference between the valence electron in an isolated atom and the number of electron assigned to that atom in a Lewis structure.
- Formal charge of an atom in a Lewis structure.

Formal  
charge =

Total number  
of valence  $e^-$   
in the free  
atom

- Total number  
of non-bonding  
electrons

$\frac{1}{2}$  [Total number  
of bonding  
electrons]

@

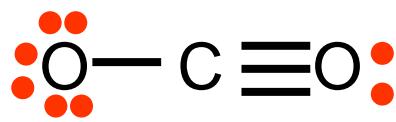
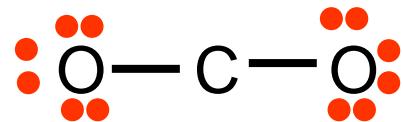
Formal charge =

Number of  
valence  
electron

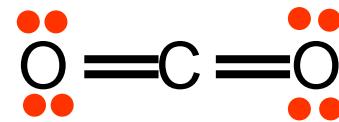
-

Number of  
lone pair  
electron

+  $\frac{1}{2}$  of bonding  
electron

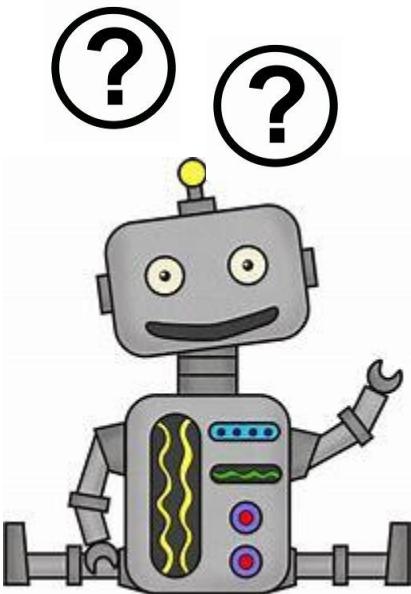


or



**Structure I**

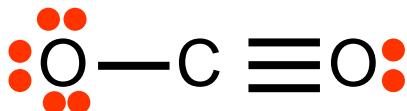
**Structure II**



*Which one is the  
Lewis structure of  $\text{CO}_2$ ?*

## Structure I :

(-1) (0) (+1)



Net charge:

$$\begin{aligned} &= -1 + 1 + 0 \\ &= 0 \end{aligned}$$

## Formal Charge:

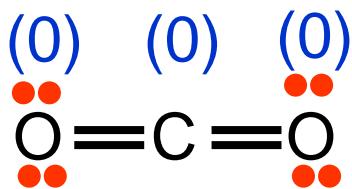


$$\text{NO}_2 \quad \text{☞ } 6 - [6 + \frac{1}{2}(2)] = -1$$

$$\equiv\text{O}\ddot{\text{O}} \quad \text{☞ } 6 - [2 + \frac{1}{2}(6)] = +1$$

$$-\text{C}\equiv \quad \text{☞ } 4 - [0 + \frac{1}{2}(8)] = 0$$

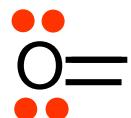
## Structure II :



Net charge:

$$\begin{aligned} &= 0 + 0 + 0 \\ &= 0 \end{aligned}$$

Formal Charge:



$$\text{O} = \quad \text{→} \quad 6 - [4 + \frac{1}{2}(4)] = 0$$

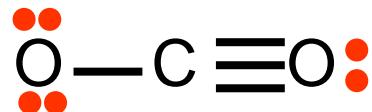


$$=\text{C}= \quad \text{→} \quad 4 - [0 + \frac{1}{2}(8)] = 0$$



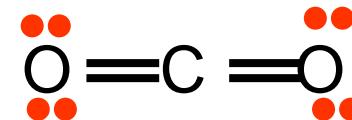
Which one is the most plausible Lewis structure of CO<sub>2</sub>?

(-1) (0) (+1)



Structure I

(0) (0) (0)



Structure II

The most plausible Lewis structure is Structure II because all atoms have zero formal charge.



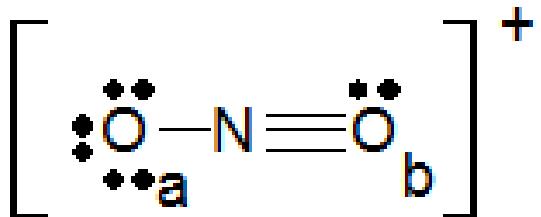
## In general;

- a) The sum of the formal charges of the atoms in a Lewis structure is equal to zero for a neutral molecule and equal to the ionic charge for an ion.
- b) For positive ions, the sum of the formal charges of the atoms is equal to the positive charge of the ion.
- c) For negative ions, the sum of the formal charges of the atoms is equal to the negative charge of the ion.

If several Lewis structures are possible for a molecule or polyatomic ion, the most plausible Lewis structure is the one which:

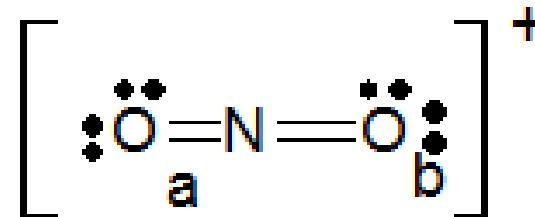
- Zero formal charge on all atoms (for neutral molecules)
- The smallest formal charge (closest to zero)
- Negative formal charges are placed on the more electronegative atoms (for polyatomic ions)

# EXAMPLE: $\text{NO}_2^+$



**Structure I**

$$O_a = 6 - [(6 + \frac{1}{2} \cdot 2)] = -1$$



**Structure II**

$$O_a = 6 - [(4 + \frac{1}{2} \cdot 4)] = 0$$

$$N = 5 - [(0 + \frac{1}{2} \cdot 8)] = +1$$

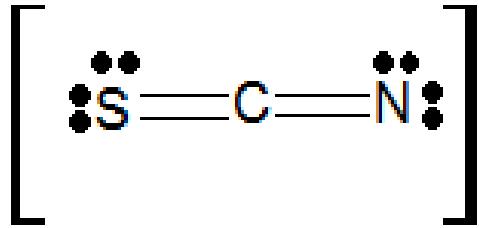
$$N = 5 - [(0 + \frac{1}{2} \cdot 8)] = +1$$

$$O_b = 6 - [(2 + \frac{1}{2} \cdot 6)] = +1$$

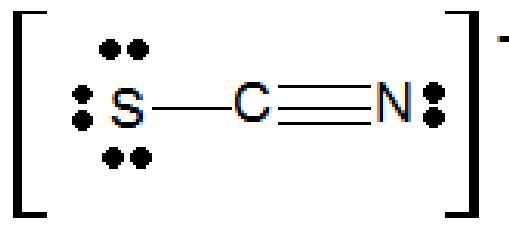
$$O_b = 6 - [(4 + \frac{1}{2} \cdot 4)] = 0$$

The most plausible Lewis structure is **Structure II** because it has the lowest (smallest) formal charge.

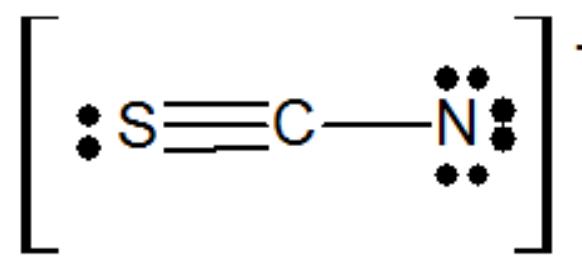
## EXAMPLE: $\text{SCN}^-$



**Structure I**



**Structure II**



**Structure III**

$$S = 6 - [(4 + \frac{1}{2} \cdot 4)] = 0$$

$$S = 6 - [(6 + \frac{1}{2} \cdot 2)] = -1$$

$$S = 6 - [(2 + \frac{1}{2} \cdot 6)] = +1$$

$$C = 4 - [(0 + \frac{1}{2} \cdot 8)] = 0$$

$$C = 4 - [(0 + \frac{1}{2} \cdot 8)] = 0$$

$$C = 4 - [(0 + \frac{1}{2} \cdot 8)] = 0$$

$$N = 5 - [(4 + \frac{1}{2} \cdot 4)] = -1$$

$$N = 5 - [(2 + \frac{1}{2} \cdot 6)] = 0$$

$$N = 5 - [(6 + \frac{1}{2} \cdot 2)] = -2$$

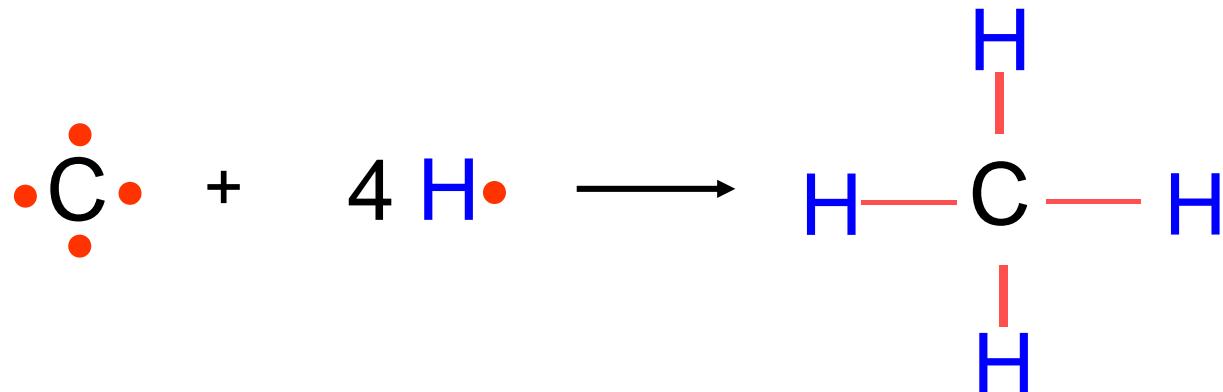
The most plausible Lewis structure is **Structure I** because it has the lowest formal charge and the negative formal charge is placed on the more electronegative atom which is nitrogen atom

# EXCEPTION TO THE OCTET RULE

---

There are three categories which characterized by:

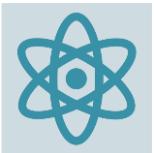
- ✓ Incomplete octet
- ✓ Expanded octet
- ✓ Odd number electrons



- C atom has four valence electrons.
- To achieve noble gas configuration (octet), C atom must acquire four more electron through sharing of electron.
- In the formation of methane,  $\text{CH}_4$ , C atom forms four single covalent bonds with four H atoms.

However, there are some molecules or ions that **DO NOT** follow the octet rule!!!

# INCOMPLETE OCTET



Occurs when the central atom has fewer than eight electrons in its valence shell.



Elements in group 2 and 13 in period 2 with low metallic properties, do not donate but share the electrons.

4

# Be

9.012182  
Beryllium

Boron

5

**B**

10.811

aluminium

13

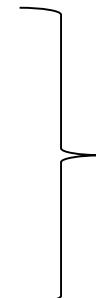
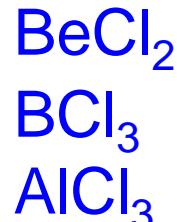
**Al**

26.982

- Metals: **Be** and **Al**, and metalloid **B**, exhibit **covalent character** when they combine with non-metals.

- Be**, **B** and **Al** cannot achieve octet configuration even after sharing electrons with other atoms.

- Example:**



Electron deficient  
covalent  
compounds

## **EXAMPLE**

Beryllium hydride (systematically named beryllium dihydride) is an inorganic compound with the chemical formula  $\text{BeH}_2$ . It is a colourless solid that is insoluble in solvents that do not decompose it. Unlike the ionically bonded hydrides of the heavier Group 2 elements, beryllium hydride is covalently bonded.

- ✓ Draw the Lewis structure of  $\text{BeH}_2$ .
- ✓ State the type of exception to the octet rule.

# ANSWER

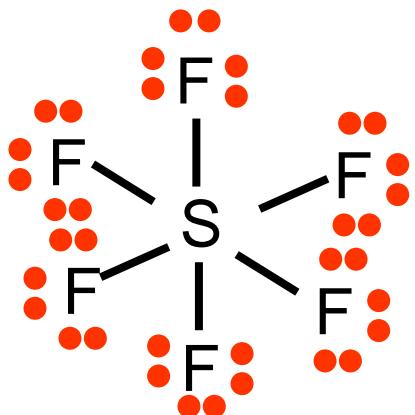


**Incomplete octet**

Atom	Number of valence e <sup>-</sup>
Be	2e <sup>-</sup>
2H	2 x 1e <sup>-</sup>
	4e <sup>-</sup>

# EXPANDED OCTET

- Occurs when the central atom has more than eight electron in its valence shell.
- Usually involves non-metal atoms of **3<sup>rd</sup> period and beyond** which have empty 3d subshell.
- Example:



Atom	Number of valence e <sup>-</sup>
S	= 5e <sup>-</sup>
6F	= 6 x 7e <sup>-</sup>
	<b>48e<sup>-</sup></b>

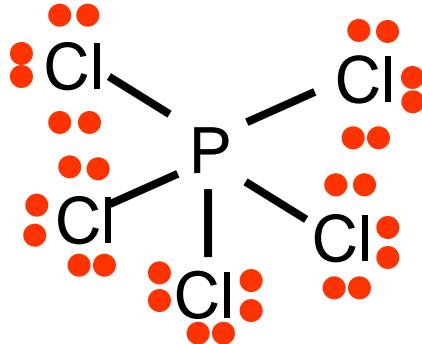
## EXAMPLE

Phosphorus pentachloride is the chemical compound with the formula  $\text{PCl}_5$ . It is one of the most important phosphorus chlorides, others being  $\text{PCl}_3$  and  $\text{POCl}_3$ .  $\text{PCl}_5$  finds use as a chlorinating reagent. It is a colorless, water - and moisture - sensitive solid, although commercial samples can be yellowish and contaminated with hydrogen chloride.

- ✓ Draw the Lewis structure of  $\text{PCl}_5$ .
- ✓ State the type of exception to the octet rule.



# ANSWER



expanded octet

Atom	Number of valence e <sup>-</sup>
------	----------------------------------

---

$$\text{P} = 5\text{e}^-$$

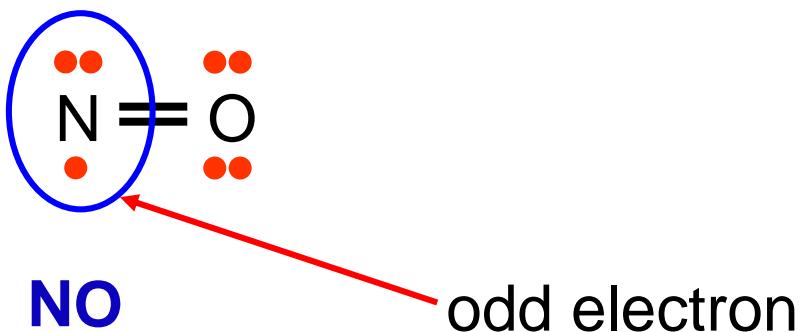
$$5\text{Cl} = 5 \times 7\text{e}^-$$

---

$$40\text{e}^-$$

# ODD NUMBER ELECTRONS

- Some molecules have an odd number of valence electron.
- Example

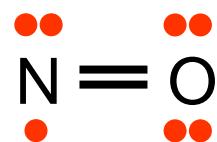


Atom	Number of valence $e^-$
N	$5e^-$
O	$6e^-$
	$11e^-$

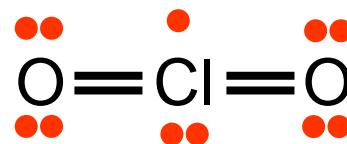
# **REMEMBER**



Most odd-electron molecule have a central atom from an odd-numbered group, such as N (Group 15) and Cl (Group 17)



Nitric oxide



Chlorine dioxide

## **EXAMPLE**

Nitrogen dioxide is the chemical compound with the formula  $\text{NO}_2$ . It is one of several nitrogen oxides.  $\text{NO}_2$  is an intermediate in the industrial synthesis of nitric acid, millions of tons of which are produced each year. This reddish- brown toxic gas has a characteristic sharp, biting odor and is a prominent air pollutant.

**Draw the Lewis structure for nitrogen dioxide.**

# ANSWER



Atom	Number of valence e <sup>-</sup>
N	5e <sup>-</sup>
O x 2	12e <sup>-</sup>
<hr/>	
	17e <sup>-</sup>

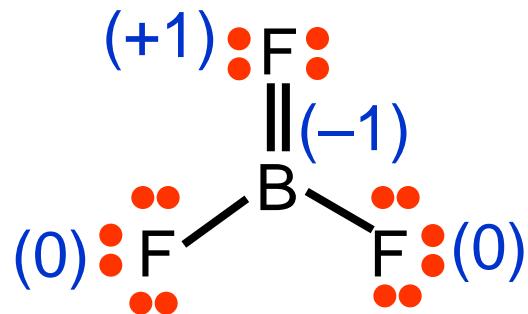
## **EXERCISE**

Boron trifluoride is the inorganic compound with the formula  $\text{BF}_3$ . This pungent colourless toxic gas forms white fumes in moist air. It is a useful Lewis acid and a versatile building block for other boron compounds.

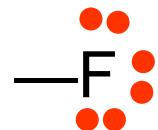
- ✓ Draw the Lewis structure of  $\text{BF}_3$  that obey the octet rule.
- ✓ Calculate the formal charge of each atom.
- ✓ Compare with the incomplete octet Lewis structure of  $\text{BF}_3$ .

# ANSWER

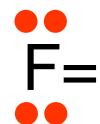
If octet rule is obeyed:



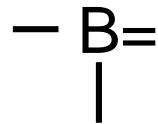
Formal Charge:



$$\Rightarrow [7 - (6 + \frac{1}{2}(2))] = 0$$

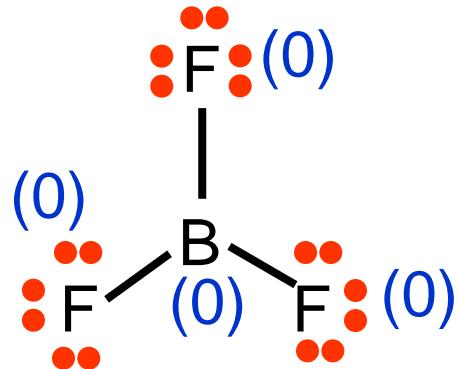


$$\Rightarrow [7 - (4 + \frac{1}{2}(4))] = +1$$

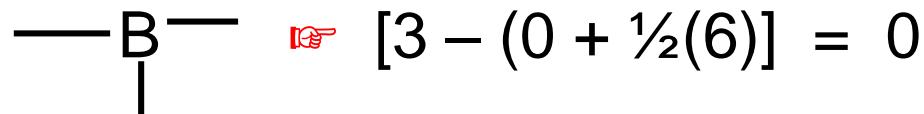
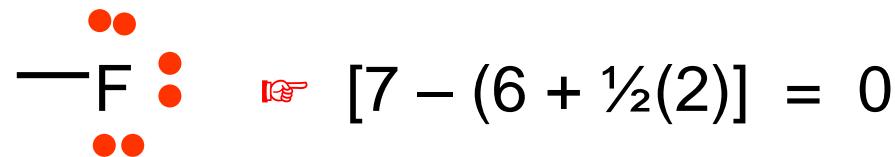


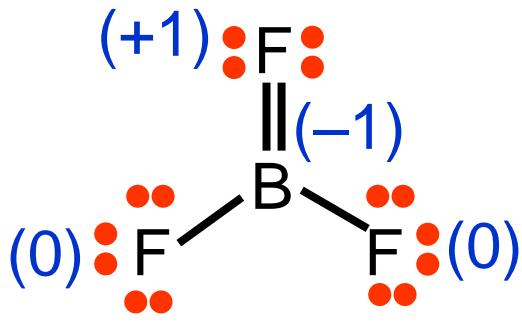
$$\Rightarrow [3 - (0 + \frac{1}{2}(4))] = -1$$

If the structure is **incomplete octet**:

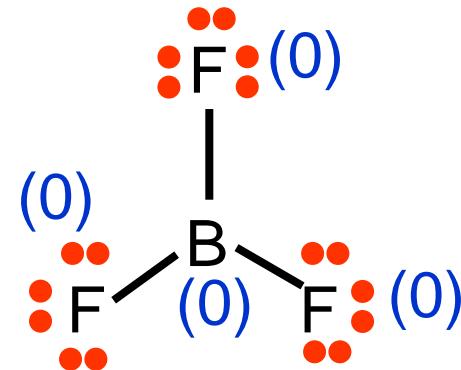


Formal Charge:





octet



incomplete octet

Structure with **incomplete octet** is **more stable** because it has **zero formal charges on all atoms**.

# RESONANCE STRUCTURE



Two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.

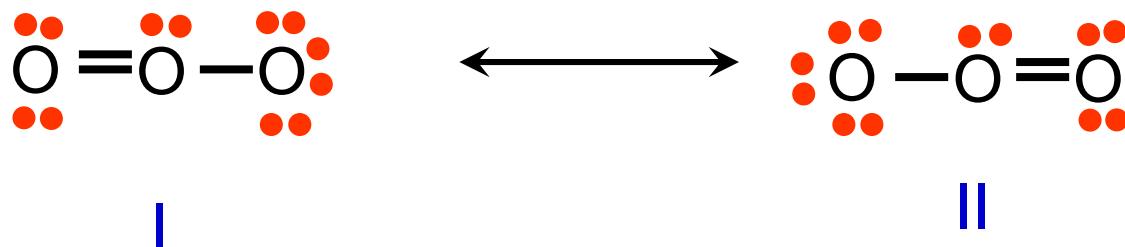


The same relative placement of atoms but different locations of bonding and lone pairs of electrons.

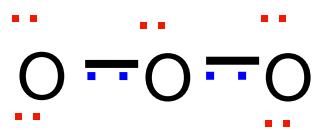


**Example:** Ozone ( $O_3$ ).

# Resonance structures of ozone:



- The Lewis **structures I** and **II** for ozone cannot accurately represent the ozone molecule
- Ozone molecule has a true Lewis structure which is neither I nor II but a resonance hybrid of the two



Resonance hybrid  
structure of ozone

Dotted line indicates that some of the  $e^-$  are delocalised over the entire molecule

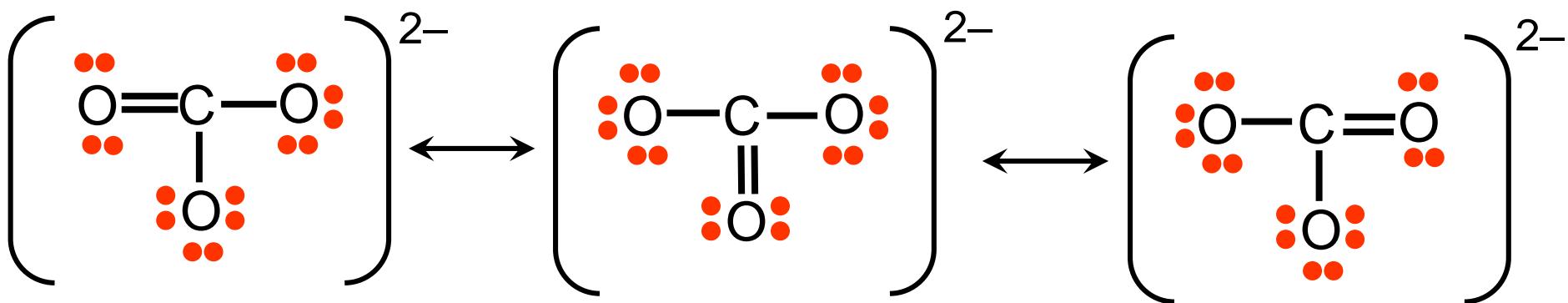
- ❑ The arrow ( $\leftrightarrow$ ) does not mean that the molecule shifts quickly back and forth from one resonance structure to the other.
- ❑ The molecule actually has the same structure all the time.

## **EXAMPLE**

Calcium carbonate is a chemical compound with the formula  $\text{CaCO}_3$ . It is formed by three main elements: carbon, oxygen and calcium. It is a common substance found in rocks in all parts of the world and is the main component of shells of marine organisms, snails, coal balls, pearls, and eggshells. Calcium carbonate is the active ingredient in agricultural lime and is created when calcium ions in hard water react with carbonate ions creating limescale.

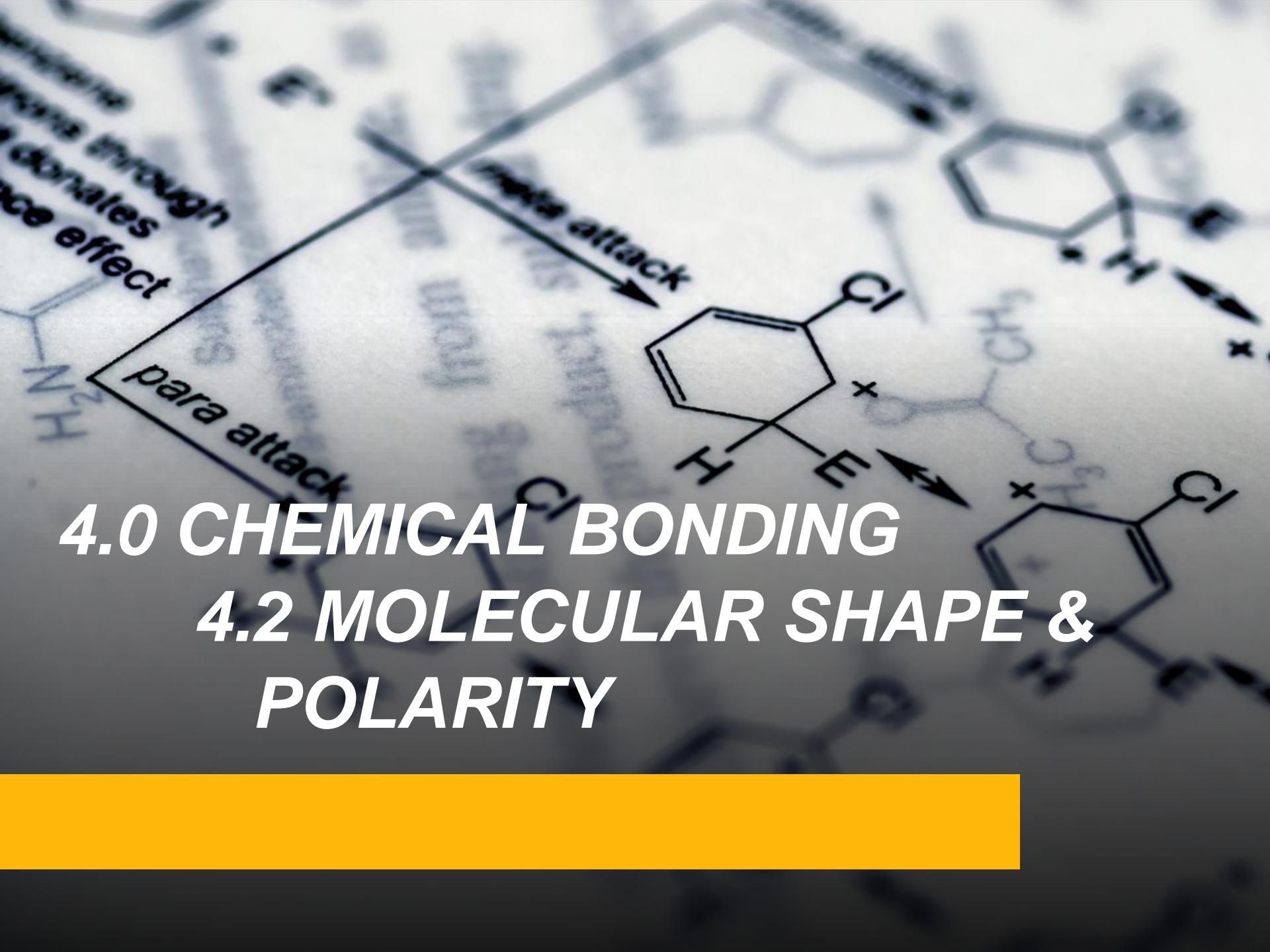
**What are the resonance structures of the carbonate ion,  $\text{CO}_3^{2-}$ ?**

# ANSWER

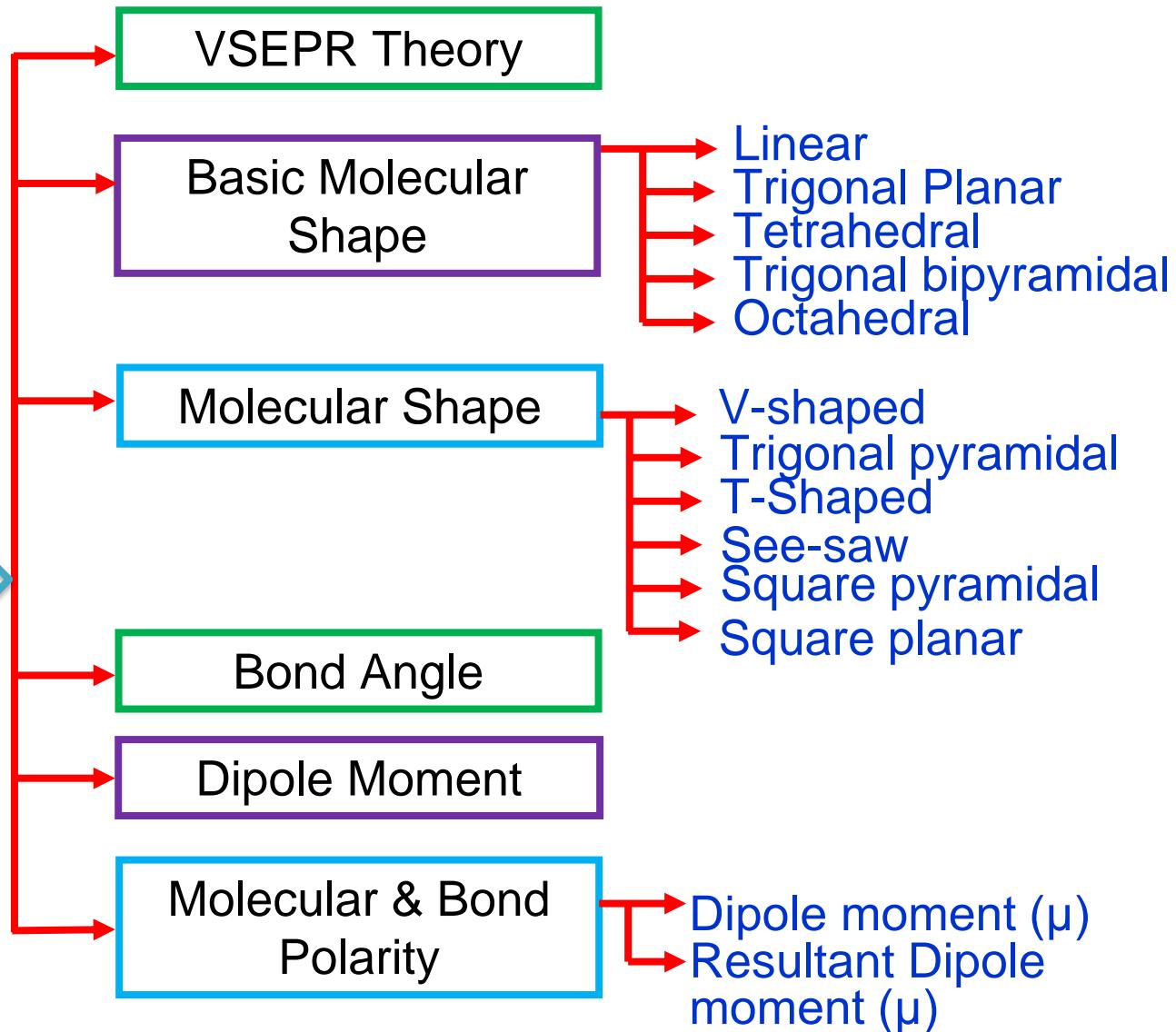


# 4.0 CHEMICAL BONDING

## 4.2 MOLECULAR SHAPE & POLARITY



## 4.2 Molecular Shape & Polarity



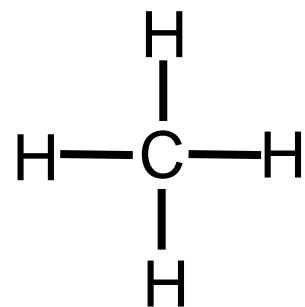
# VSEPR THEORY

---

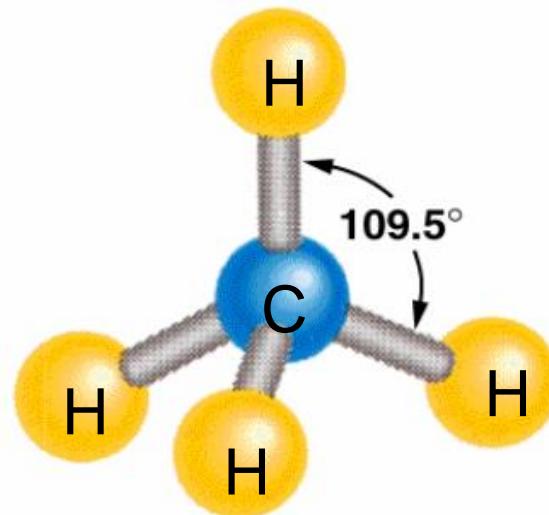
- ❑ Valence–Shell Electron–Pair Repulsion Theory
- ❑ Electron pairs around a **central atom** will repel one another and **arrange themselves as far as possible** from each other in order to **minimize repulsion.**

- To predict the molecular shape from the Lewis structure.
- **Example:**

## Lewis Structure



## Molecular Shape



# The followings are counted as one electron pair

<p>1 Bonding pair - a single bond - a double bond - a triple bond</p>	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	No. of electron pairs around the central atom = 4
	$\begin{array}{c} \bullet\bullet \\ \text{O}=\text{C}=\text{O} \\ \bullet\bullet \end{array}$	No. of electron pairs around the central atom = 2
<p>2 lone pair</p>	$\begin{array}{c} \bullet\bullet \\ \text{H}-\text{O}-\text{H} \\ \bullet\bullet \end{array}$	No. of electron pairs around the central atom = 4
	$\begin{array}{c} \bullet\bullet \quad \bullet\bullet \\ \quad \quad   \\ \bullet\bullet \quad \bullet\bullet \\ \text{I}-\text{N}-\text{I} \\ \bullet\bullet \quad \bullet\bullet \end{array}$	No. of electron pairs around the central atom = 4

# Electron Pair Repulsion

□ Order:

**lone-pair electron  
vs.  
lone-pair electron  
repulsion**

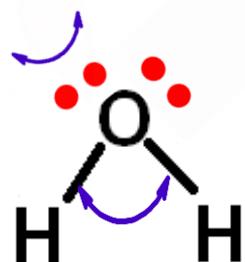


**lone-pair electron  
vs.  
bonding-pair electron  
repulsion**

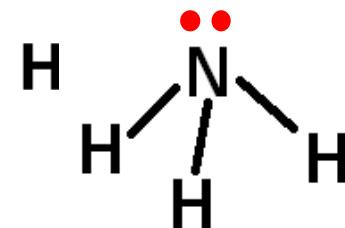


**bonding-pair electron  
vs.  
bonding-pair electron  
repulsion**

$104.5^\circ$



H  $107.5^\circ$



# BASIC MOLECULAR SHAPE

1 Linear

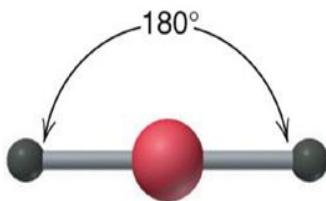
2 Trigonal planar

3 Tetrahedral

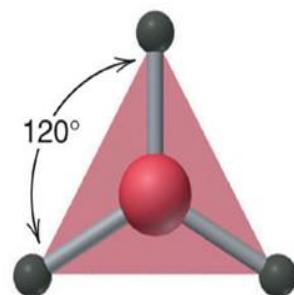
4 Trigonal bipyramidal

5 Octahedral

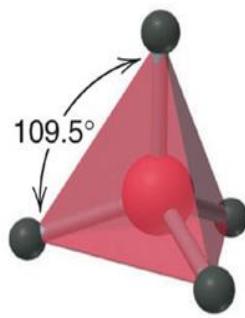
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



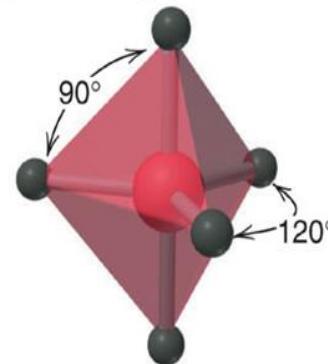
Linear



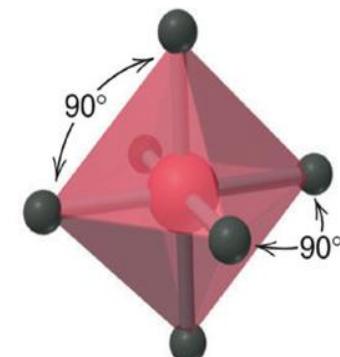
Trigonal planar



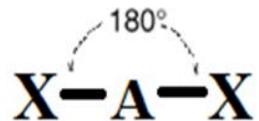
Tetrahedral



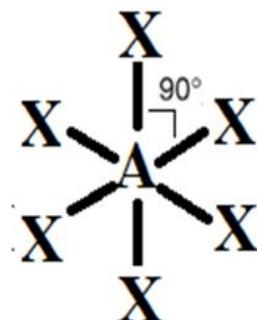
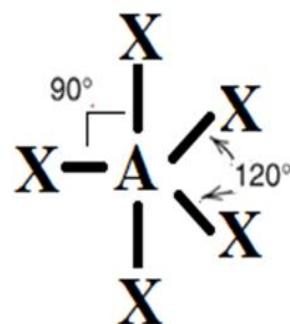
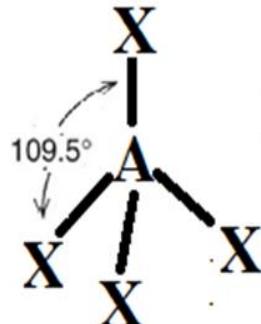
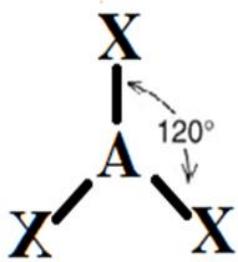
Trigonal bipyramidal

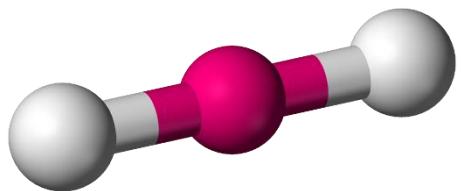


Octahedral

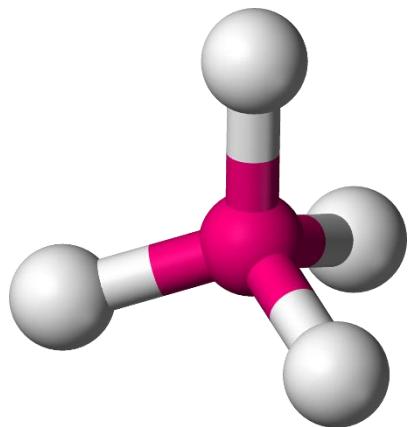


GEN FORMULA:

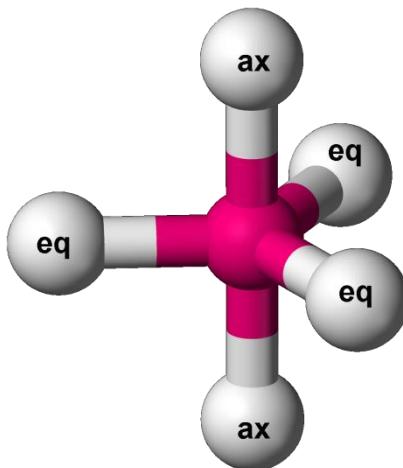




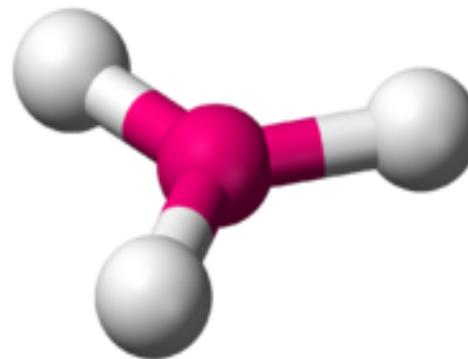
**Linear**



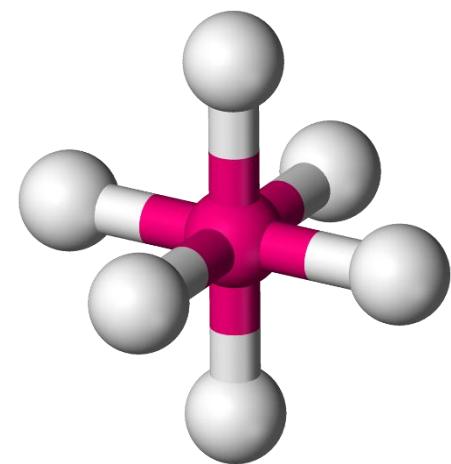
**Tetrahedral**



**Trigonal  
bipyramidal**



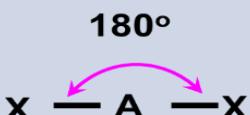
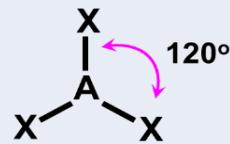
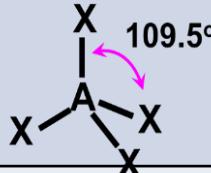
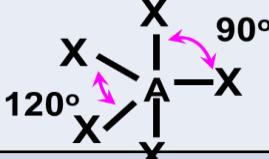
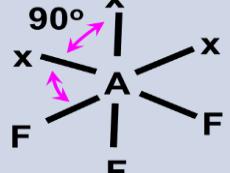
**Trigonal planar**



**Octahedral**

# PREDICT AND EXPLAIN THE SHAPE OF MOLECULES & BOND ANGLE

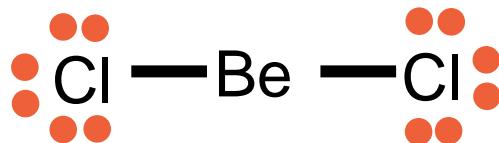
Electron Pair Arrangement is determined by the number of electron pairs around the central atom.

Geometry	No. of e <sup>-</sup> pairs	Electron Pair Arrangement
 180° $x - A - x$	2	Linear
 120°	3	Trigonal planar
 109.5°	4	Tetrahedral
 90° 120°	5	Trigonal bipyramidal
 90°	6	Octahedral

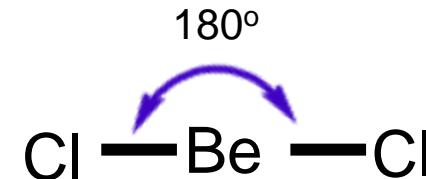
# TWO ELECTRON PAIRS

EXAMPLE:  $\text{BeCl}_2$  (gaseous beryllium chloride)

## Lewis Structure



## Molecular Shape



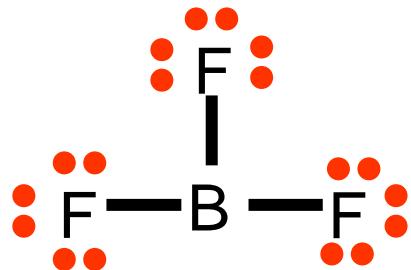
Bond angle:  $180^\circ$

- There are **2 electron pairs** around the central atom Beryllium (Be) which **all bonding pair electrons**. ( $\text{AX}_2$ )
- The electron pair arrangement is **linear**.
- According to the VSEPR theory, repulsion of all **bonding pair - bonding pair electrons** are equal.
- The molecular shape is **linear** with the bond angle of  **$180^\circ$** .

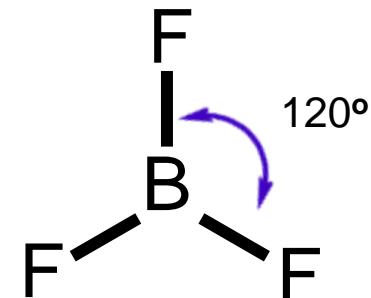
# THREE ELECTRON PAIRS

EXAMPLE:  $\text{BF}_3$  (Boron trifluoride)

## Lewis Structure



## Molecular Shape



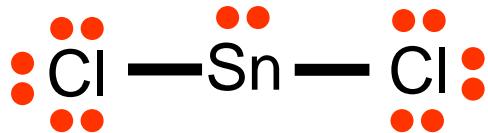
Bond angle:  $120^\circ$

- There are **3 electron pairs around** the central atom Boron (B) which **all bonding pair electrons**. ( $\text{AX}_3$ )
- The electron pair arrangement is **trigonal planar**.
- According to the VSEPR Theory, repulsion of all **bonding pair - bonding pair electrons** are equal.
- The molecular shape is **trigonal planar** with the bond angle of  **$120^\circ$** .

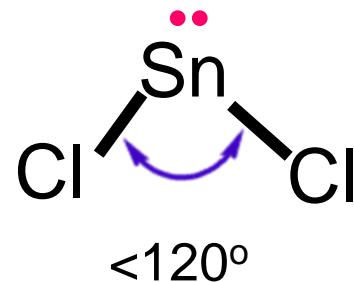
# THREE ELECTRON PAIRS

EXAMPLE:  $\text{SnCl}_2$  (tin (II) chloride)

## Lewis Structure



## Molecular Shape



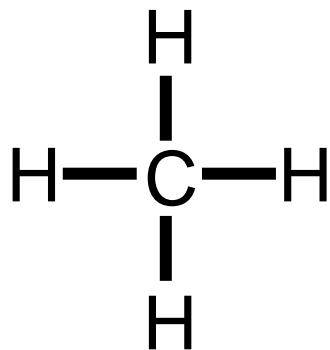
Bond angle:  $< 120^\circ$

- There are **3 electron pairs** around the central atom, Tin (Sn) which are **2 bonding pairs** and **1 lone pair electrons ( $\text{AX}_2\text{E}_1$ )**
- The electron pairs arrangement is **trigonal planar**.
- According to the VSEPR theory, repulsion between **lone pair-bonding pair electrons** are stronger than **bonding pair - bonding pair electrons** and thus push the bonding pairs closer to each other.
- The molecular shape is **V-shaped @ bent** with the bond angle  **$<120^\circ$** .

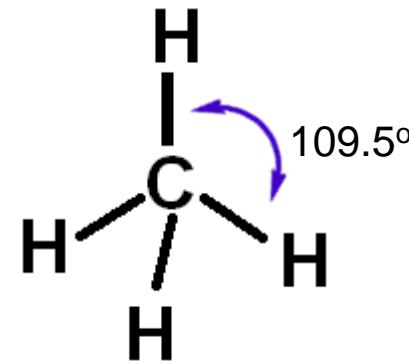
# FOUR ELECTRON PAIRS

EXAMPLE:  $\text{CH}_4$  (methane)

## Lewis Structure



## Molecular Shape



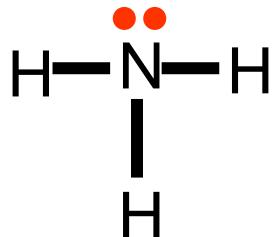
Bond angle: **109.5°**

- There are **4 electron pairs** around the central atom Carbon (C) which are **all bonding pair electrons**. ( $\text{AX}_4$ )
- The electron pairs arrangement is **tetrahedral**.
- According to the VSEPR theory, repulsion of all **bonding pair - bonding pair electrons** are equal.
- The molecular shape is **tetrahedral** with the bond angle of **109.5°**.

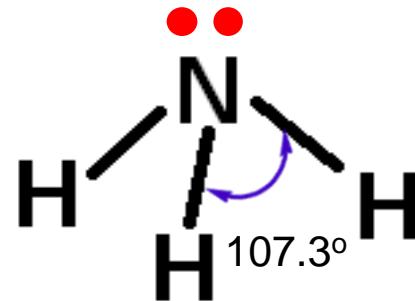
# FOUR ELECTRON PAIRS

EXAMPLE:  $\text{NH}_3$  (ammonia)

## Lewis structure



## Molecular Shape



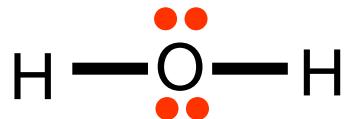
Bond angle:  $< 109.5^\circ$  ( $107.3^\circ$ )

- There are **4 electron pairs** around the central atom, Nitrogen (N) which are **3 bonding pairs** and **1 lone pair electrons**. ( $\text{AX}_3\text{E}_1$ ).
- The electron pairs arrangement is **tetrahedral**.
- According to the VSEPR theory, repulsion between **lone pair-bonding pair electrons** greater than **bonding pair - bonding pair electrons** and thus push the bonding pairs closer to each other.
- The molecular shape is **trigonal pyramidal** with the bond angle of  **$<109.5^\circ$  ( $107.3^\circ$ )**.

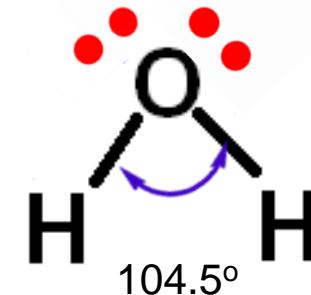
# FOUR ELECTRON PAIRS

EXAMPLE:  $\text{H}_2\text{O}$  (water)

## Lewis Structure



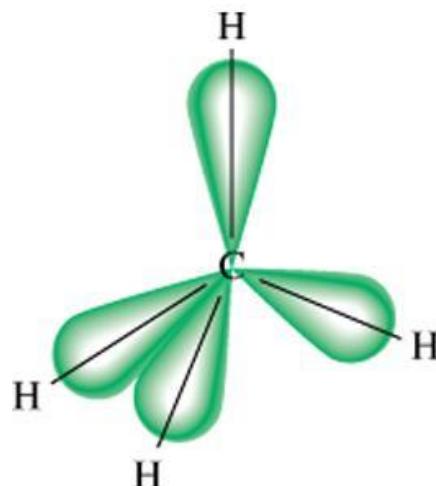
## Molecular Shape



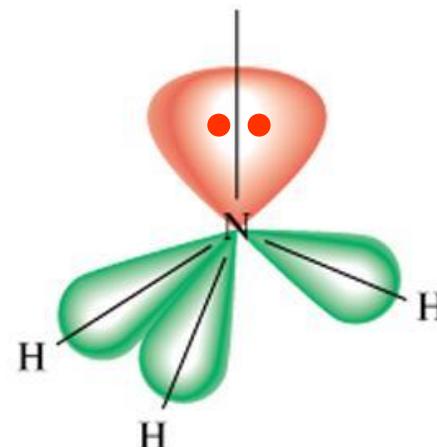
Bond angle: << 109.5° (104.5°)

- There are **4 electron pairs** around the central atom Oxygen (O) which are **2 bonding pairs** and **2 lone pair electrons**. ( $\text{AX}_2\text{E}_2$ )
- The electron pairs arrangement is **tetrahedral**.
- According to the VSEPR theory, repulsion between **lone pair-lone pair** > **lone pair-bonding pair** > **bonding pair-bonding pair electrons**.
- The molecular shape is **V-shape @ bent** with the bond angle of <<109.5° (**104.5°**).

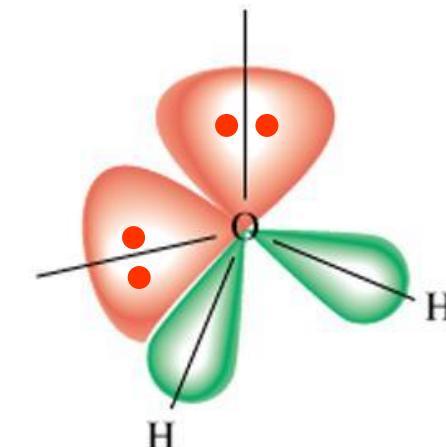
# TETRAHEDRAL ELECTRON PAIR ARRANGEMENT



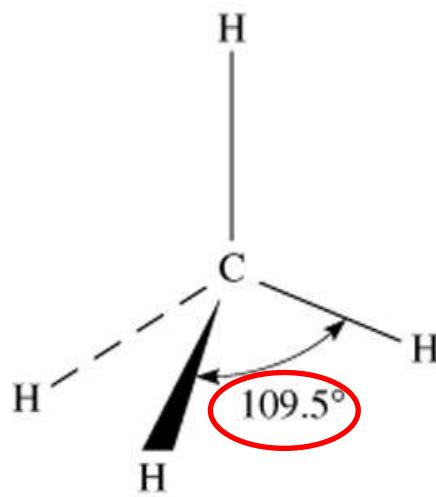
tetrahedral



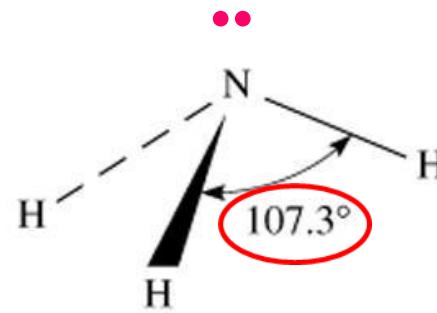
trigonal pyramidal



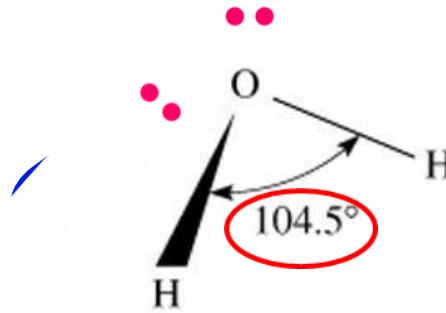
V-shaped



bonding-pair vs. bonding  
pair electrons repulsion



< lone-pair vs. bonding  
electrons pair repulsion <

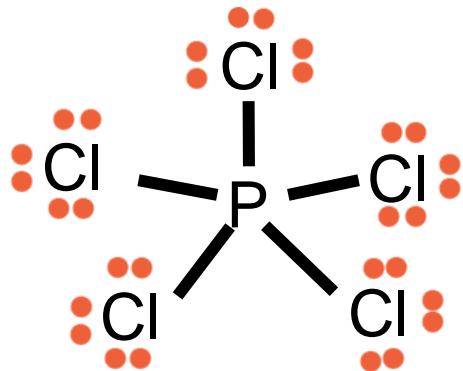


lone-pair vs. lone pair  
electrons repulsion

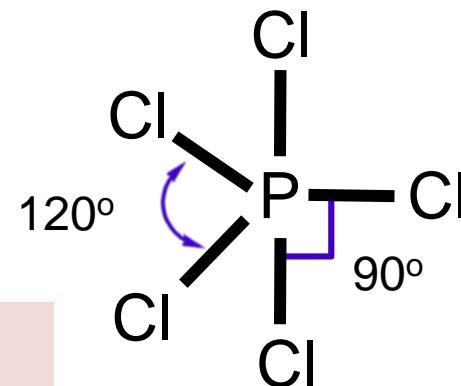
# FIVE ELECTRON PAIRS

EXAMPLE:  $\text{PCl}_5$  (phosphorus pentachloride)

## Lewis Structure



## Molecular Shape



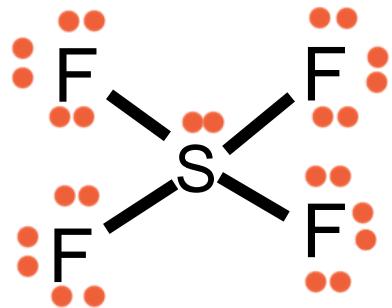
**Bond angle:**  
**Equatorial angle: 120°**  
**Axial angle: 90°**

- There are **5 electron pairs** around the central atom, Phosphorous (P) which **all bonding pairs**. ( $\text{AX}_5$ )
- Electron pairs arrangement is **trigonal bipyramidal**.
- According to the VSEPR theory, repulsion of all **bonding pair-bonding pair electrons** are equal.
- Molecular shape is **trigonal bipyramidal** with the bond angle of **120 ° and 90 °**.

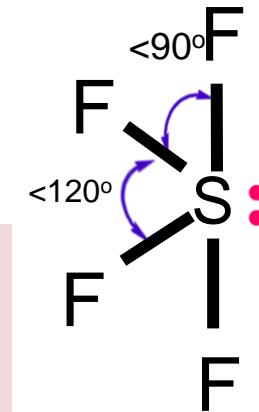
# FIVE ELECTRON PAIRS

EXAMPLE:  $\text{SF}_4$  (Sulphur tetrafluoride)

## Lewis Structure



## Molecular Shape



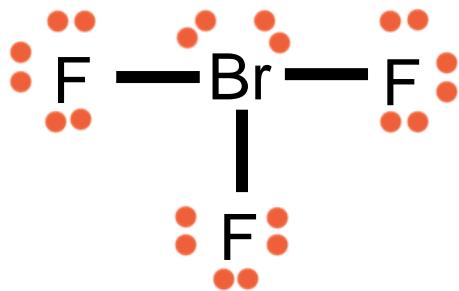
**Bond angle:**  
Equatorial angle  $< 120^\circ$   
Axial angle  $< 90^\circ$

- There are **5 electron pairs** around the central atom, Sulphur (S) which are **4 bonding pairs** and **1 lone pair electrons**. ( $\text{AX}_4\text{E}_1$ )
- The electron pairs arrangement is **trigonal bipyramidal**
- According to the VSEPR theory, repulsion between **lone pair-bonding pair electrons** are stronger than **bonding pair-bonding pair electrons** and thus push the bonding pairs closer to each other.
- The molecular shape is **see-saw @ distorted tetrahedral @ disphenoidal** with the bond angle of  $<120^\circ$  and  $<90^\circ$ .

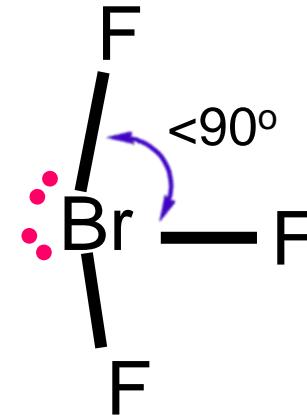
# FIVE ELECTRON PAIRS

EXAMPLE:  $\text{BrF}_3$  (Bromine trifluoride)

## Lewis Structure



## Molecular Shape



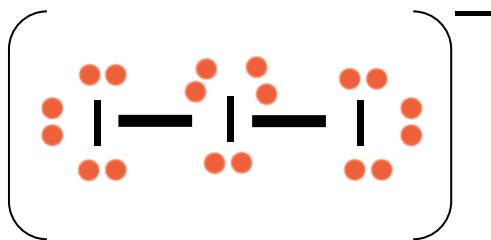
Bond angle:  $< 90^\circ$

- There are **5 electron pairs** around the central atom Bromine (Br) which are **3 bonding pairs** and **2 lone pair electrons**. ( $\text{AX}_3\text{E}_2$ )
- The electron pairs arrangement is **trigonal bipyramidal**
- According to the VSEPR theory, repulsion between **lone pair-lone pair** > **lone pair-bonding pair** > **bonding pair-bonding pair electrons**.
- The molecular shape is **T-shaped** with the bond angle of  $< 90^\circ$ .

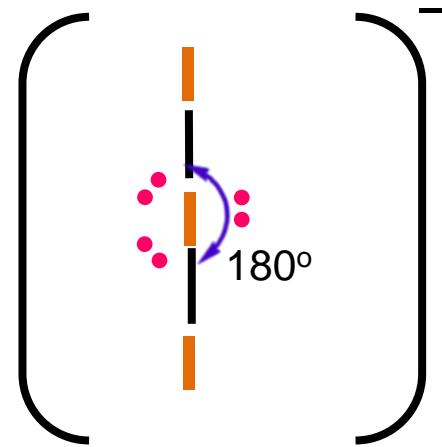
# FIVE ELECTRON PAIRS

EXAMPLE:  $I_3^-$  (triiodide ion)

## Lewis Structure



## Molecular Shape



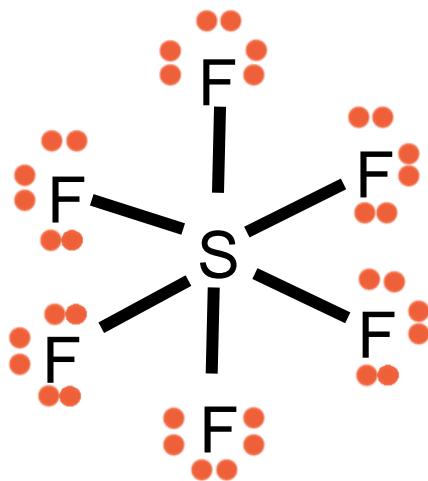
Bond angle:  $180^\circ$

- There are **5 electron pairs** around the central atom, Iodine (I) which are **2 bonding pairs** and **3 lone pair electrons**. ( $AX_2E_3$ )
- The electron pairs arrangement is **trigonal bipyramidal**
- According to the VSEPR Theory, repulsion of **lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair electrons**.
- Thus, the molecular shape is **linear** with the bond angle of  **$180^\circ$** .

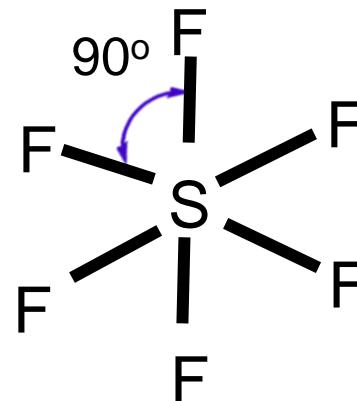
# SIX ELECTRON PAIRS

EXAMPLE:  $\text{SF}_6$  (sulfur hexafluoride)

## Lewis Structure



## Molecular Shape



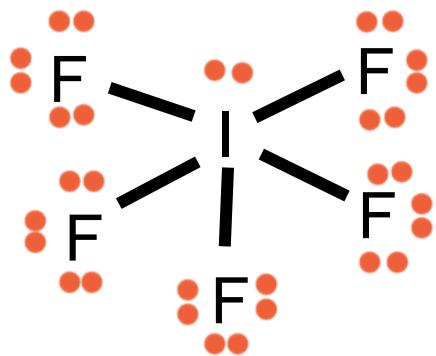
Bond angle:  $90^\circ$

- There are **6 electron pairs** around the central atom Sulphur (S) which **all bonding pairs**. ( $\text{AX}_6$ )
- The electron pairs arrangement is **octahedral**.
- According to the VSEPR theory, repulsion of all **bonding pair-bonding pair electrons** are equal.
- The molecular shape is **octahedral** with the bond angle of  **$90^\circ$** .

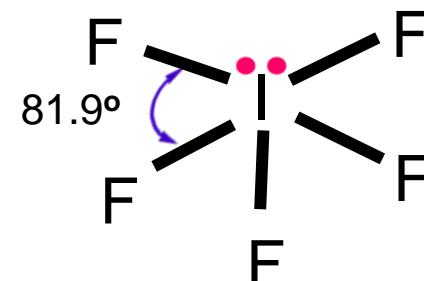
# SIX ELECTRON PAIRS

EXAMPLE:  $\text{IF}_5$  (iodine pentafluoride)

## Lewis Structure



## Molecular Shape



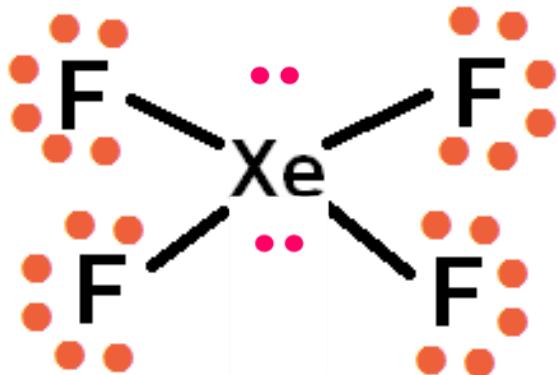
Bond angle: < 90°

- There are **6 electron pairs** around the central atom Iodine (I) which are **5 bonding pairs** and **1 lone pair electrons**. ( $\text{AX}_5\text{E}_1$ )
- The electron pairs arrangement is **octahedral**.
- According to the VSEPR theory, repulsion of **lone pair-bonding pair** are stronger than **bonding pair - bonding pair electrons** and thus push the bonding pairs closer to each other.
- The molecular shape is **square pyramidal** with the bond angle of **<90°**.

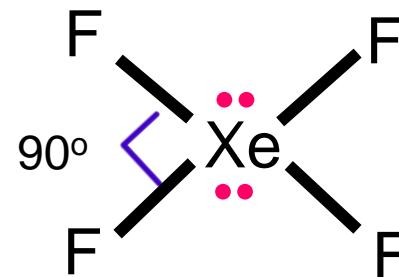
# SIX ELECTRON PAIRS

EXAMPLE:  $\text{XeF}_4$  (xenon tetrafluoride)

## Lewis Structure



## Molecular Shape



Bond angle:  $90^\circ$

- There are **6 electron pairs** around the central atom Xenon (Xe) which are **4 bonding pairs** and **2 lone pair electrons**. ( $\text{AX}_4\text{E}_2$ )
- The electron pairs arrangement is **octahedral**
- According to the VSEPR theory, repulsion of **lone pair-lone pair > lone pair-bonding pair > bonding pair - bonding pair electrons**.
- The molecular shape is **square planar** with the bond angle of  **$90^\circ$** .

# SUMMARY

No. of electron pairs	X	E	Electron pair arrangement	Molecular shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
	2	1	trigonal planar	V-shaped
4	4	0	tetrahedral	tetrahedral
	3	1	tetrahedral	trigonal pyramidal
	2	2	tetrahedral	V-shaped

Note : X - no. of bonding pair  
E - no. of lone pair

No. of electron pairs	X	E	Electron pair arrangement	Molecular shape
5	5	0	trigonal bipyramidal	trigonal bipyramidal
	4	1	trigonal bipyramidal	see saw
	3	2	trigonal bipyramidal	T-shaped
	2	3	trigonal bipyramidal	linear
6	6	0	octahedral	octahedral
	5	1	octahedral	square pyramidal
	4	2	octahedral	square planar

**Note :** X - num. of bonding pair  
E - num. of lone pair

## EXERCISE

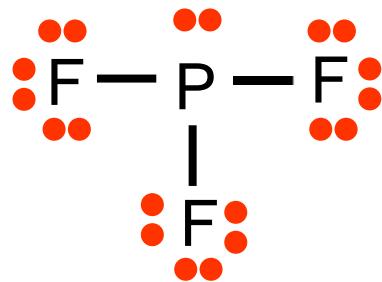
Draw the molecular shape and predict the bond angles (relative to the ideal angles). What are the electron pairs arrangements and the molecular shapes of:

- $\text{PF}_3$
- $\text{ClF}_2^-$

## ANSWER

(a)  $\text{PF}_3$

**Step 1: Draw the Lewis structure.**



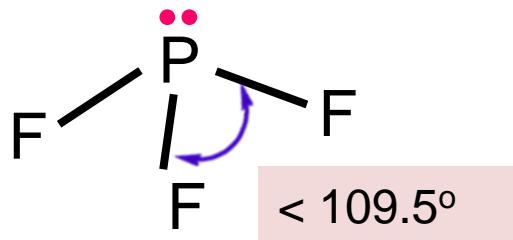
**Step 2: Determine the electron pairs arrangement.**

- There are 4 electron pairs around the central atom, Phosphorous (P) which are **3 bonding pairs** and **1 lone pair electrons**. ( $\text{AX}_3\text{E}$ ).
- The electron pairs arrangement is **tetrahedral**.

## Step 3: Predict the bond angle.

- According to VSEPR theory, repulsion of **lone pair-bonding pair** are stronger than **bonding pair-bonding pair electrons**.
- With lone pair at P, the bond angle is  $< 109.5^\circ$

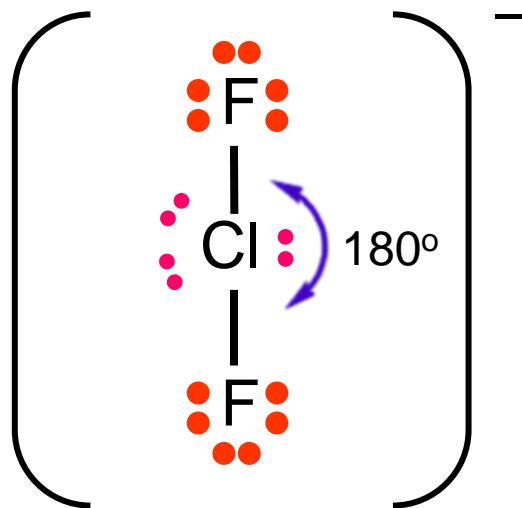
## Step 4: Draw and name the molecular shape.



- The molecular shape is **trigonal pyramidal**

## ANSWER

(b)  $\text{ClF}_2^-$



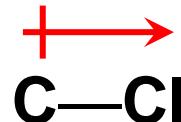
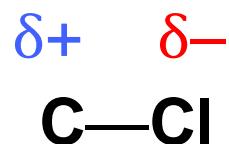
- There are 5 electron pairs around the central atom Chlorine (Cl) which are **2 bonding pairs** and **3 lone pair electrons**. ( $\text{AX}_2\text{E}_3$ )
- Electron pairs arrangement is **trigonal bipyramidal**.
- According to VSEPR theory, repulsion of **lone pair-lone pair** > **lone pair-bonding pair** > **bonding pair-bonding pair electrons**.
- The molecular shape is **linear** with the bond angle of  **$180^\circ$**

# BOND POLARITY

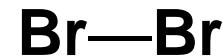
- Atoms with different electronegativities form polar bonds.
- Depicted as a **polar arrow**:



## EXAMPLE



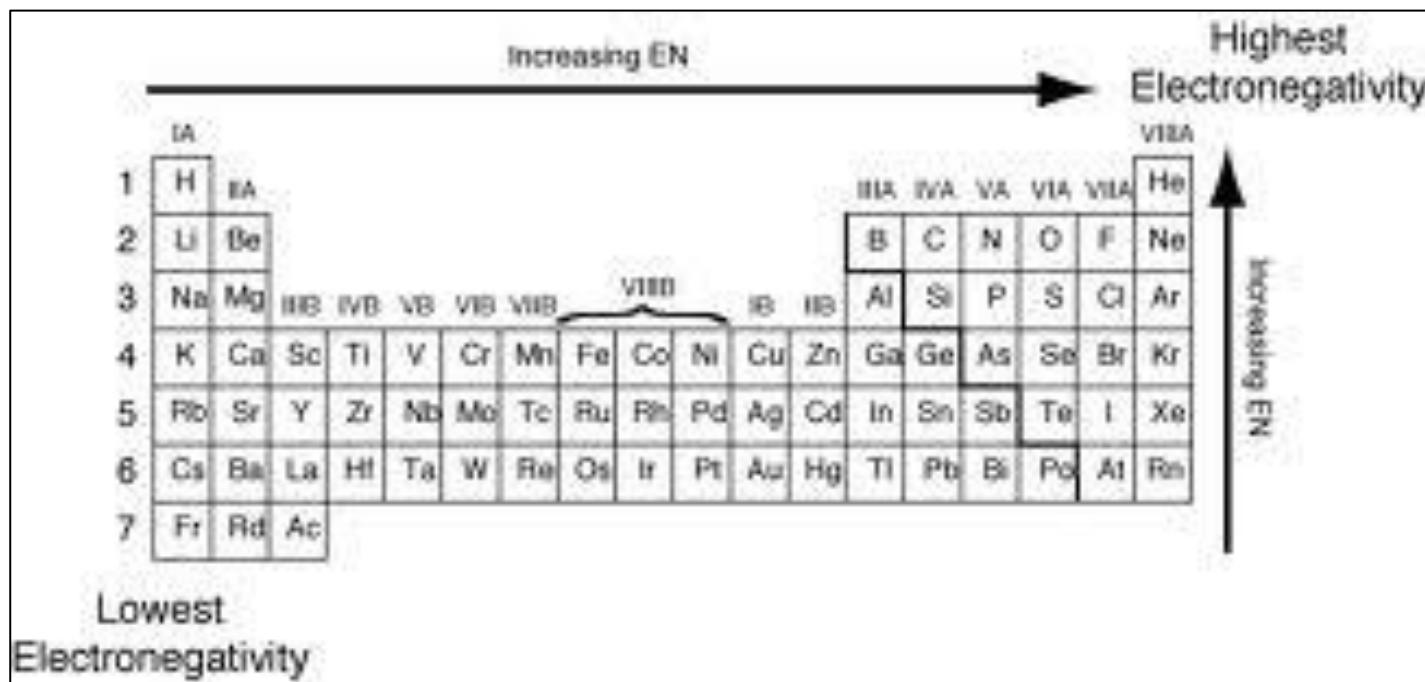
Polar bond



Nonpolar bond

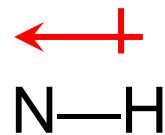
## EXERCISE

- (a) Use a polar arrow to indicate the polarity of each bond: N–H, F–N, I–Cl
- (b) Rank the following bonds in order of increasing polarity: H–N, H–O, H–C

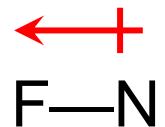


## ANSWER

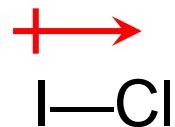
(a)



**N** is more electronegative than **H**



**F** is more electronegative than **N**



**Cl** is more electronegative than **I**

(b) Bond polarity:

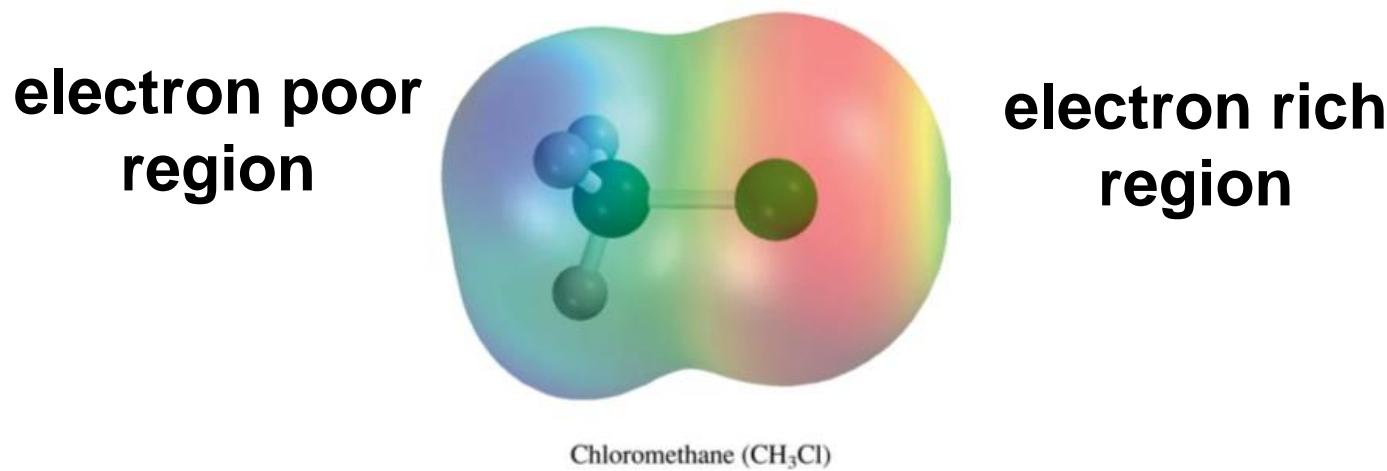


**Increasing order of bond polarity:**



# MOLECULAR POLARITY

- Net imbalanced of charge
- Electron rich regions ( $\delta^-$ ) and electron poor regions ( $\delta^+$ )



# DIPOLE MOMENT ( $\mu$ )

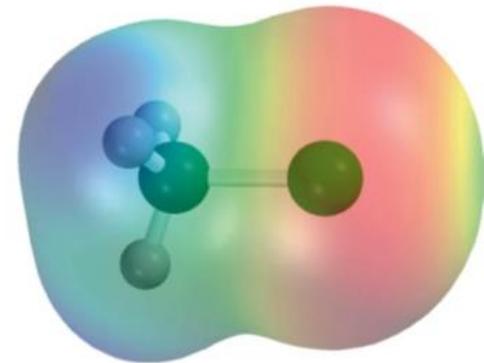
- Quantitative measure of molecular polarity

$$\mu = Q \times r$$

Q : charge

r : distance between charges

$$1 \text{ D (Debye)} = 3.36 \times 10^{-30} \text{ C m}$$



Chloromethane ( $\text{CH}_3\text{Cl}$ )

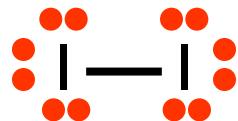
# RESULTANT DIPOLE MOMENT

---

- ❑ Determined by molecular shape and bond polarity
  - $\mu \neq 0$  ↗ polar molecules
  - $\mu = 0$  ↗ nonpolar molecules

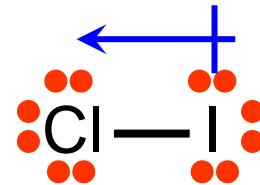
# DEDUCE THE POLARITY OF MOLECULES

## EXAMPLE



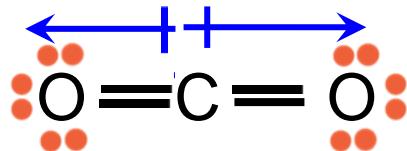
- Difference in electronegativity,  $\Delta EN = 0$
- Resultant dipole moment,  $\mu = 0$
- Therefore,  $I_2$  is a **nonpolar molecule**

## EXAMPLE



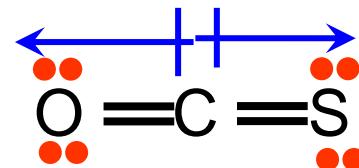
- $\Delta EN \neq 0$
- $\mu \neq 0$
- ICl is a **polar molecule**

## EXAMPLE



- Molecular shape of CO<sub>2</sub> is **linear**
- It is a symmetrical structure
- Two C=O bonds are polar since O is more electronegative than C atom.
- The two bond dipoles can cancel each other
- Resultant dipole moment,  $\mu = 0$
- CO<sub>2</sub> is a **nonpolar molecule**

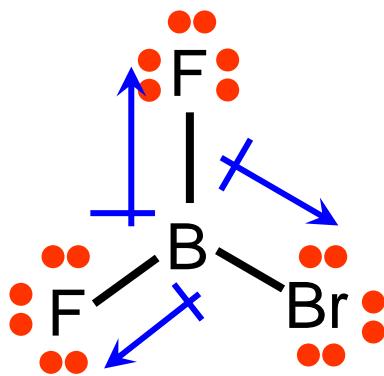
## EXAMPLE



resultant  $\mu \neq 0$

- Molecular shape of OCS is **linear**
- It is an unsymmetrical structure
- C=O and C=S bonds are polar because O and S are more electronegative than C atom
- The two-bond dipole cannot cancel each other
- Resultant dipole moment,  $\mu \neq 0$
- OCS is a **polar molecule**

## EXAMPLE

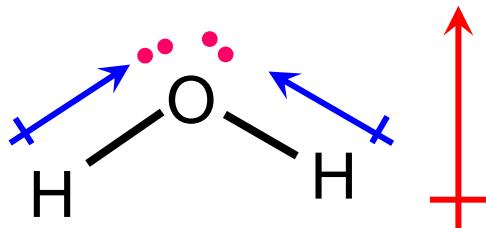


- Molecular shape of  $\text{BF}_2\text{Br}$  is **trigonal planar**
- It is an unsymmetrical structure
- 2B-F, 1B-Br bonds are polar because F and Br are more electronegative than B atom
- The bond dipoles cannot cancel each other
- Resultant dipole moment,  $\mu \neq 0$
- $\text{BF}_2\text{Br}$  is a **polar molecule**

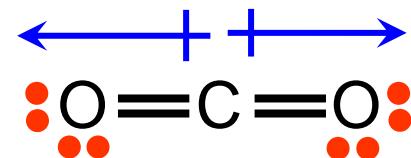
## EXERCISE

Which of the following molecules have a dipole moment (polar molecule)  $\text{H}_2\text{O}$  or  $\text{CO}_2$ ? Explain.

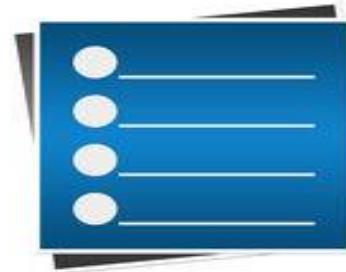
## ANSWER



- Molecular shape: **Bent** shaped
- It is an unsymmetrical structure.
- The two **O-H bonds** are polar because oxygen atom **is more electronegative** than hydrogen atom.
- The bond dipoles cannot cancel each other
- Resultant dipole moment,  $\mu \neq 0$
- Thus,  $\text{H}_2\text{O}$  is a **polar molecule**

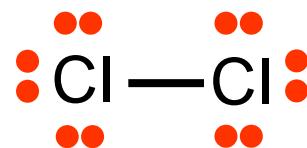


- Molecular shape: **Linear**
- It is a symmetrical structure.
- The two **C=O bonds** are polar because oxygen atom is more electronegative than carbon atom.
- The bond dipoles can cancel each other
- Resultant dipole moment,  $\mu = 0$
- Thus,  $\text{CO}_2$  is a **nonpolar molecule**



# Summary

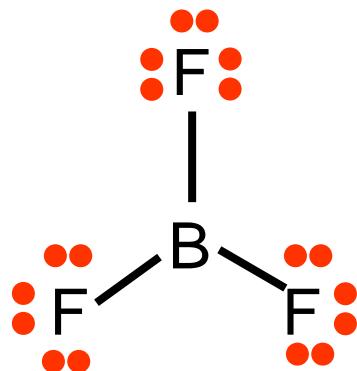
- A molecule will be **nonpolar** if the bonds are nonpolar.
- Example:**



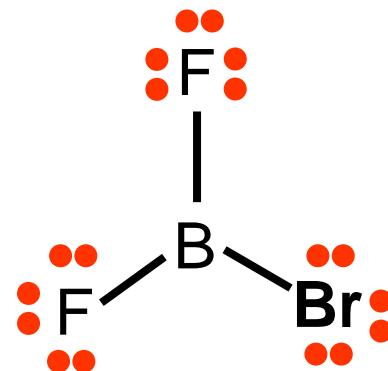
**nonpolar molecule**

- A molecule will be **nonpolar** if no lone pair in the central atom and all the surrounding atoms are the same.

**Example:**



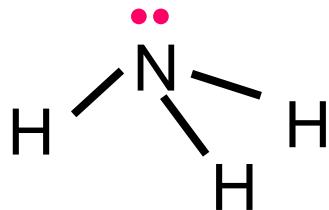
**nonpolar molecule**



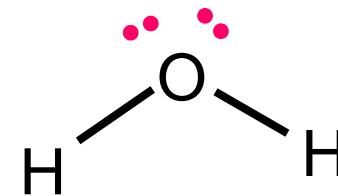
**polar molecule**

- A molecule in which the central atom has lone pair electron will usually be polar with few exceptions.

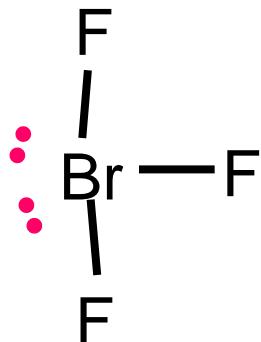
**Example:**



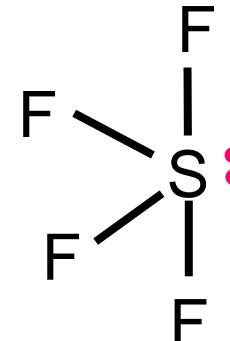
**polar molecule**



**polar molecule**

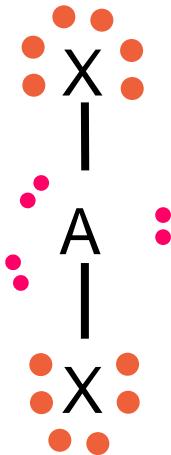


**polar molecule**

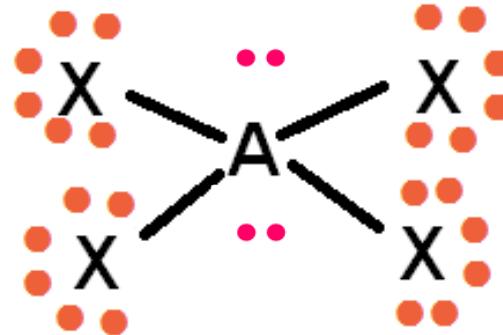


**polar molecule**

# EXCEPTION

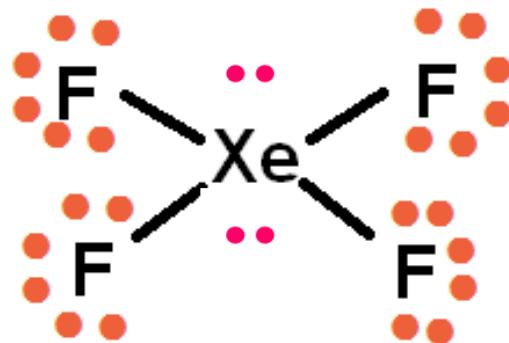


Nonpolar molecule



Nonpolar molecule

# EXAMPLE



Are there any polar bond present?

No

Are there any lone pairs on the central atom?

No

Yes

Do the bond dipoles cancel each other?

Yes

Yes

Are the electron groups arranged symmetrically?

Yes

No

No

Molecule is  
**POLAR**

Molecule is  
**NONPOLAR**

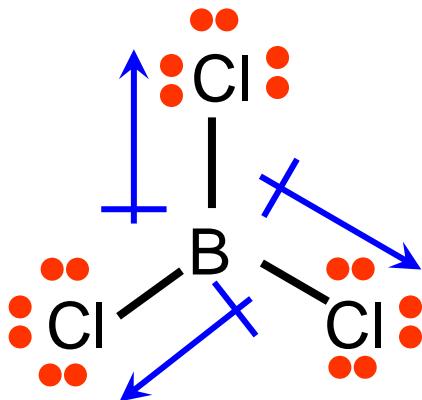
## EXERCISE

Predict whether each of the following molecules is polar and show the direction of bond polarity and net dipole moment.

- a) Boron trichloride,  $\text{BCl}_3$
- b) Hydrogen bromide,  $\text{HBr}$

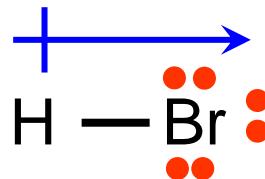
# ANSWER

(a)  $\text{BCl}_3$



- Molecular shape of  $\text{BCl}_3$  is **trigonal planar**
- It is a symmetrical structure
- Three B-Cl bonds are polar since Chlorine (Cl) is more electronegative than Boron (B).
- The bond dipoles can cancel each other
- Resultant dipole moment,  $\mu = 0$
- Thus,  $\text{BCl}_3$  is a **nonpolar molecule**

(b)  $\text{HBr}$



- H-Br bond is polar since Bromine (Br) is more electronegative than Hydrogen (H)
- Resultant dipole moment,  $\mu \neq 0$
- Thus,  $\text{HBr}$  is a **polar molecule**

# 4.0 CHEMICAL BONDING

## 4.3 ORBITAL OVERLAP & HYBRIDISATION

## 4.3 Orbital Overlap & Hybridization

Illustrate the formation of sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds from overlapping orbitals

Describe the formation of hybrid orbitals for central atom

$sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$  &  $sp^3d^2$

Illustrate the hybridization of the central atom and the overlapping of orbitals in molecules

# VALENCE BOND THEORY

---

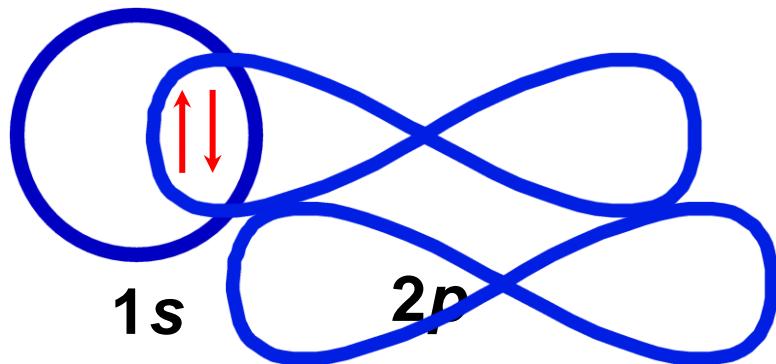
- A theoretical model that explain covalent bond.
- Important concepts in valence bond theory:
  - Covalent bonds formed by **sharing electrons** from overlapping of atomic orbitals.
  - The space formed by **overlapping** orbitals has a **maximum capacity of two electrons** that must have **opposite spins**.
  - Due to the overlapping, electrons are **localized in the bond region**.
  - The strength of the bond depends on the degree of overlapping.
  - As the **number of orbital overlap increase, bond strength increase**.

# VALENCE BOND THEORY

---

- Covalent bonds are formed by sharing electrons from **overlapping** atomic orbitals

**EXAMPLE:**



# ORBITALS OVERLAPPING

---

- Atoms in **simple** molecules or ions such as  $\text{H}_2$ ,  $\text{HF}$ ,  $\text{N}_2$ , normally use **pure** s and/or p orbitals in forming **covalent bonds**

## EXAMPLE:

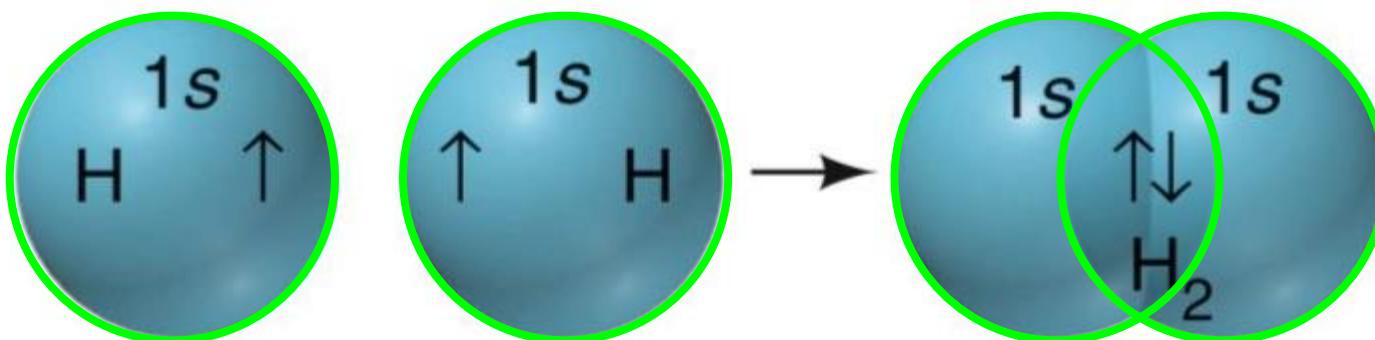
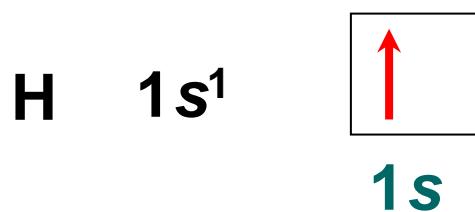
**s orbital overlaps with s orbital**

**p orbital overlaps with p orbital**

**s orbital overlaps with p orbital**

# **s orbital overlap with s orbital**

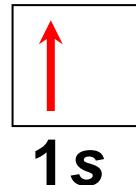
**EXAMPLE: H<sub>2</sub>**



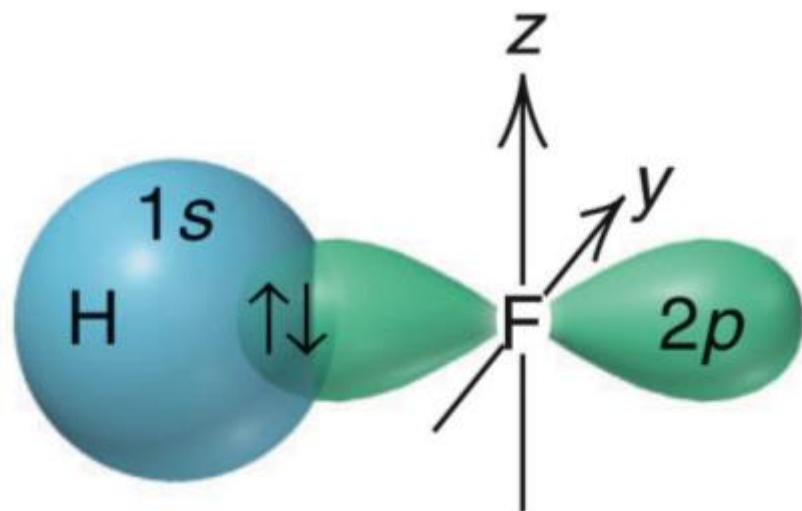
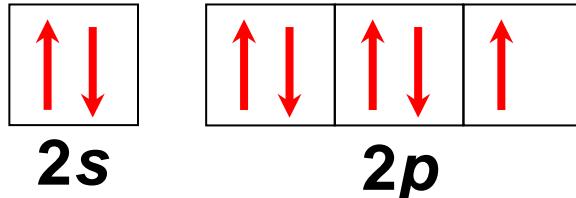
# **s orbital overlaps with p orbital**

**EXAMPLE: HF**

H :  $1s^1$



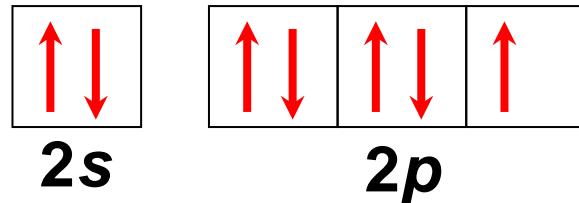
F :  $1s^2$   $2s^2$   $2p^5$



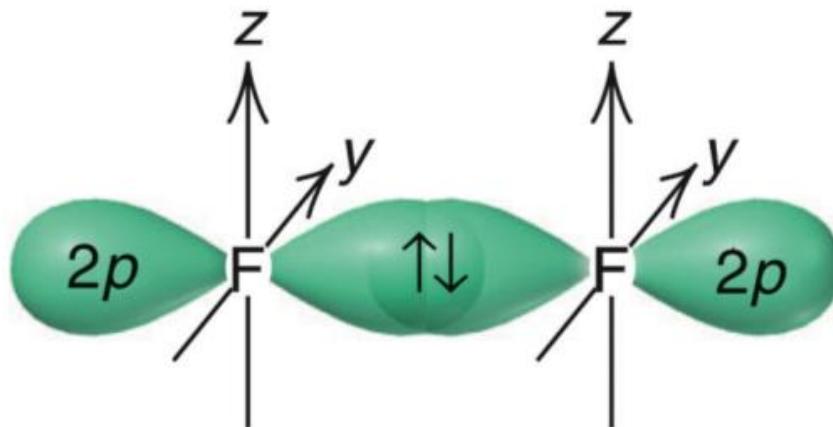
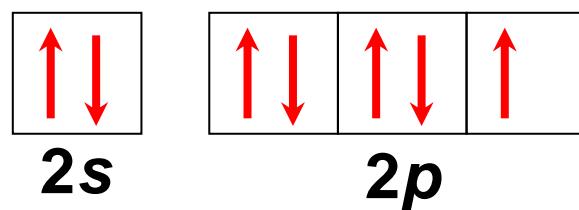
## *p* orbital overlaps with *p* orbital

**EXAMPLE: F<sub>2</sub>**

F : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>



F : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>



# MODE OF OVERLAP

Two types:

End-to-end

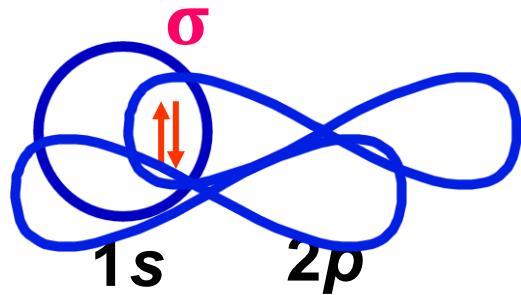


sigma ( $\sigma$ ) bond

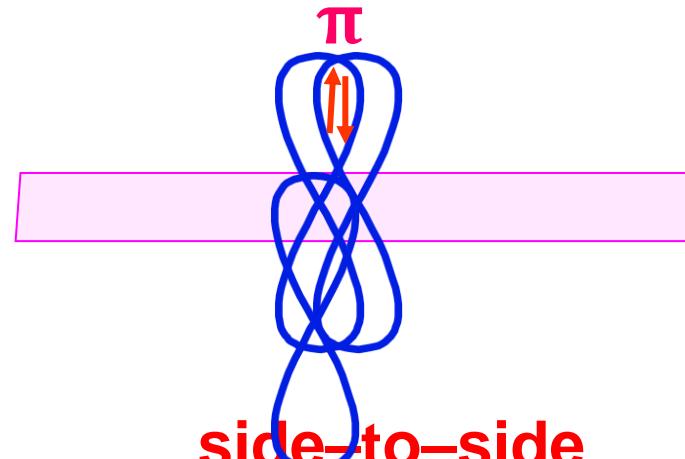
Side-to-side



pi ( $\pi$ ) bond



end-to-end  
overlap



side-to-side  
overlap

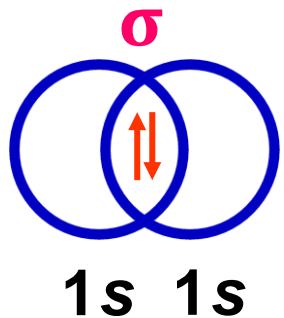
# SIGMA ( $\sigma$ ) BOND

---

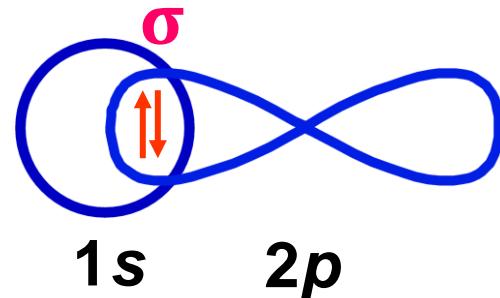
- Resulting from **end-to-end overlap**.
- Has highest electron density **along** the bond axis.
- Allow **free rotation**.
- All single bonds are  **$\sigma$  bond**.

## EXAMPLE:

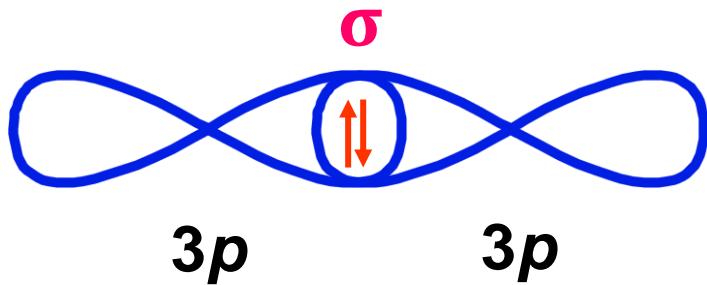
### Overlapping between original orbital



$H\overset{\sigma}{—}H$  bond



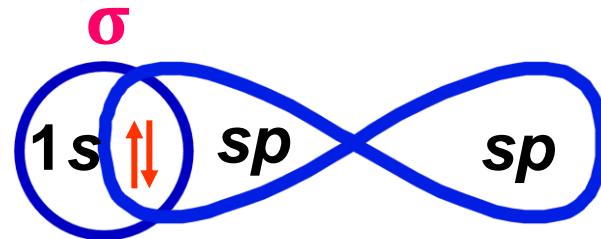
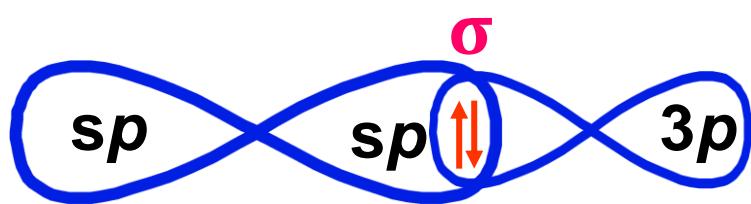
$H\overset{\sigma}{—}F$  bond



$Cl\overset{\sigma}{—}Cl$  bond

## EXAMPLE:

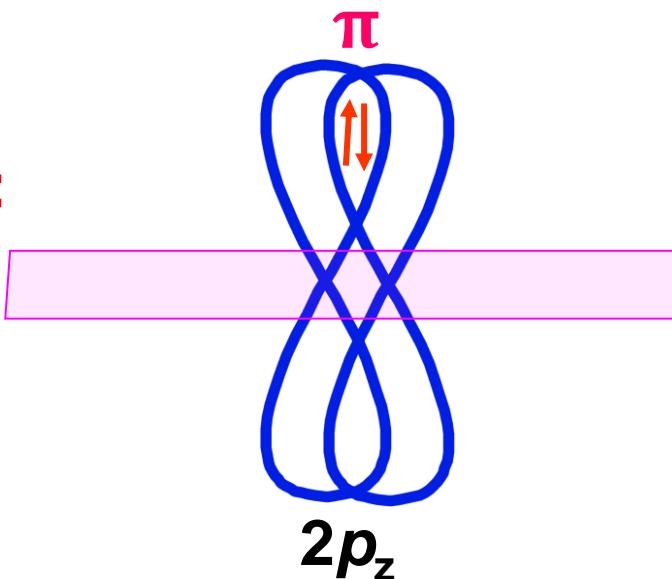
Overlapping with hybrid orbital



# PI ( $\pi$ ) BOND

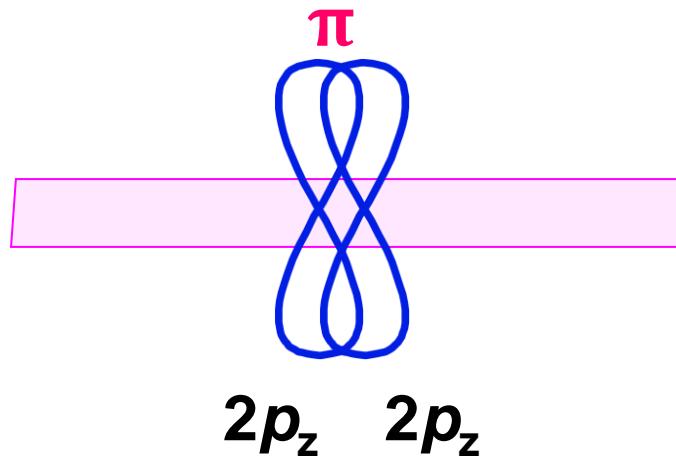
- Resulting from **side-to-side** overlap
- Has **two regions** of e<sup>-</sup> density
  - one above and one below the  **$\sigma$ -bond axis**

**EXAMPLE:**



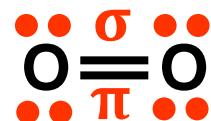
- One **π bond** hold **two e<sup>-</sup>** that move through both regions of the bond
- π bond **restricts rotation**

**EXAMPLE:**



- Double bond consists of one  $\sigma$  bond and one  $\pi$  bond

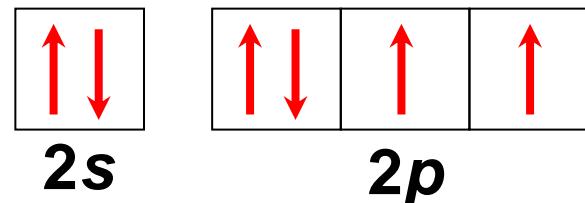
EXAMPLE:



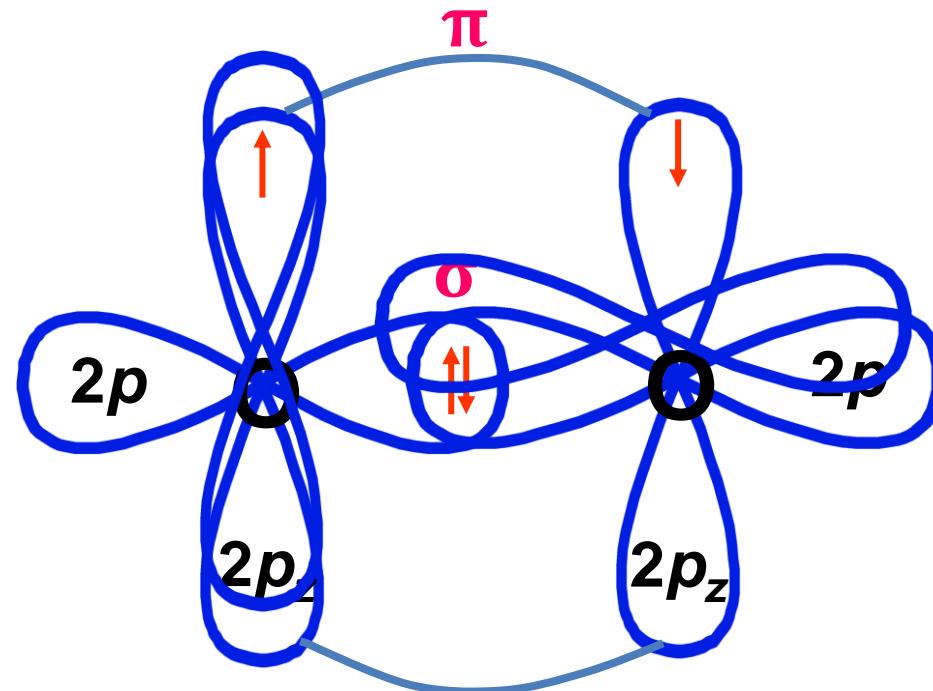
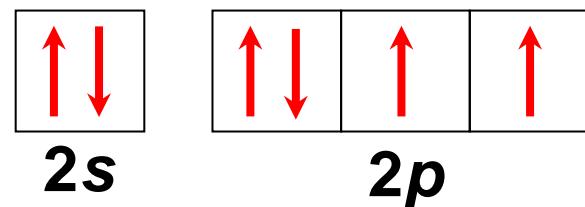
- ☞  $O_2$  has one  $\pi$  bond and one  $\sigma$  bond

## EXAMPLE: O<sub>2</sub>

O : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

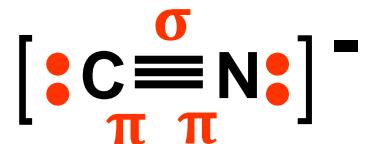


O : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>



Triple bond consists of one  $\sigma$  bond and two  $\pi$  bond

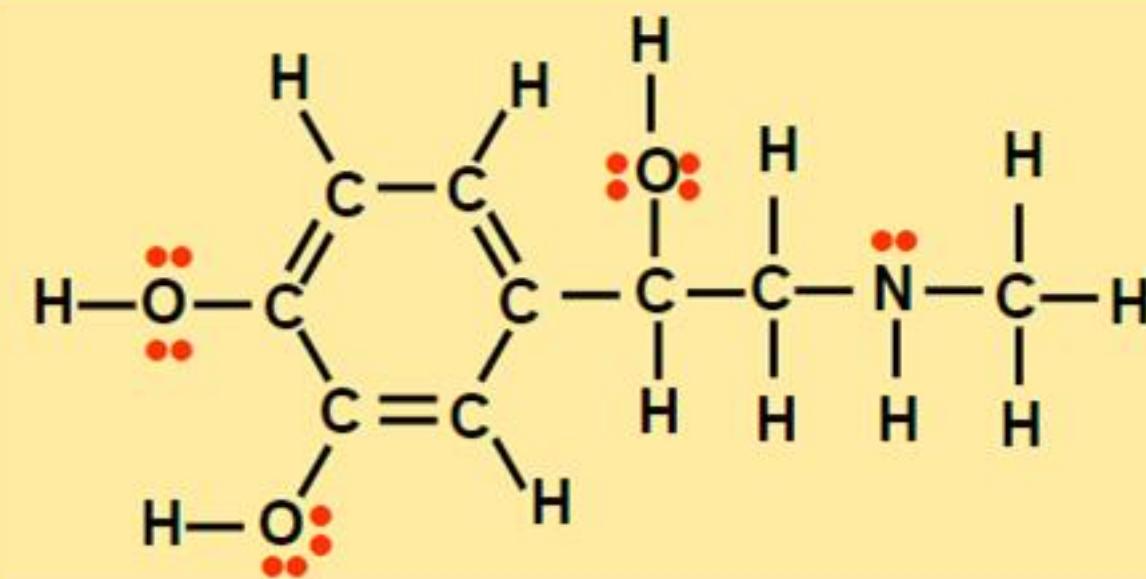
EXAMPLE:



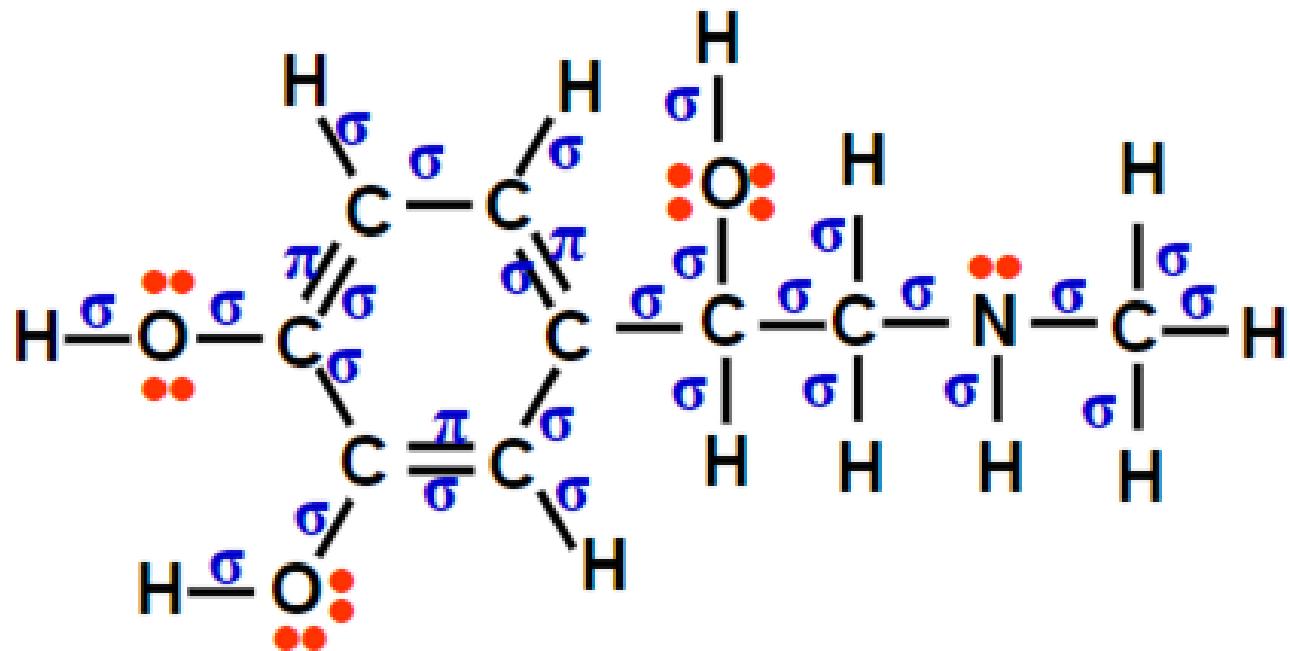
☞ CN<sup>-</sup> has two  $\pi$  bonds and one  $\sigma$  bond

# EXAMPLE :1

Adrenaline has the following Lewis structure:



How many  $\sigma$  and  $\pi$  bonds are in the molecule ?



Total: 26 σ bonds and 3 π bonds

# HYBRIDIZATION

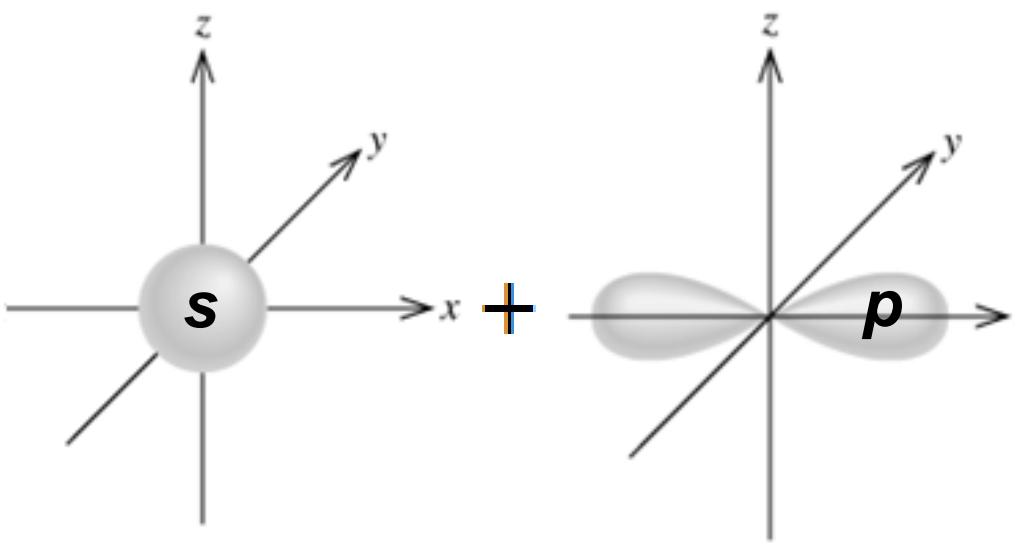
---

- **Mixing** of two or more atomic orbitals to form a **new** set of equivalent **hybrid orbitals**
- The spatial **orientation** of the new orbitals cause more **stable** bonds and are consistent with the **observed** molecular shape
- **Number** of hybrid orbitals obtained **equals** to the number of **atomic orbitals mixed**
- **Type** of hybrid orbitals obtained differ with the types of **atomic orbitals mixed**

# TYPES OF HYBRID ORBITALS

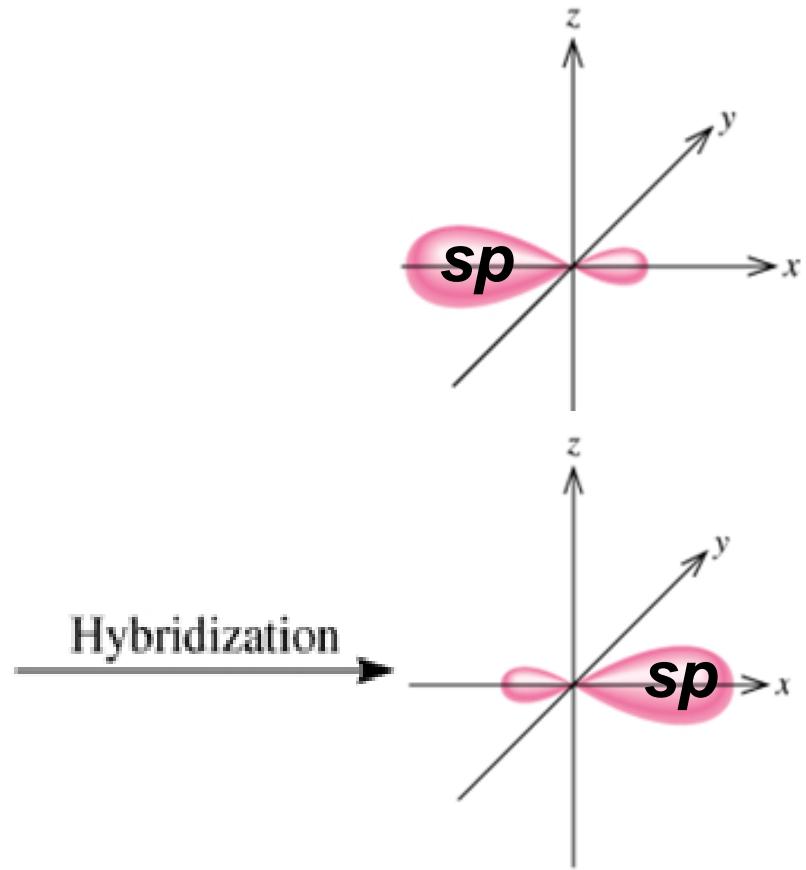
Hybridization	Type
$s + p$	$sp$
$s + p + p$	$sp^2$
$s + p + p + p$	$sp^3$
$s + p + p + p + d$	$sp^3d$
$s + p + p + p + d + d$	$sp^3d^2$

## EXAMPLE:

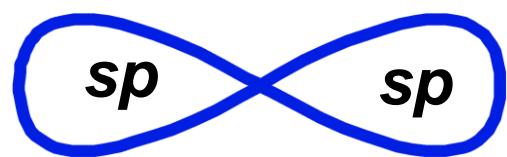


**s orbital**

**p orbital**



**sp orbitals**

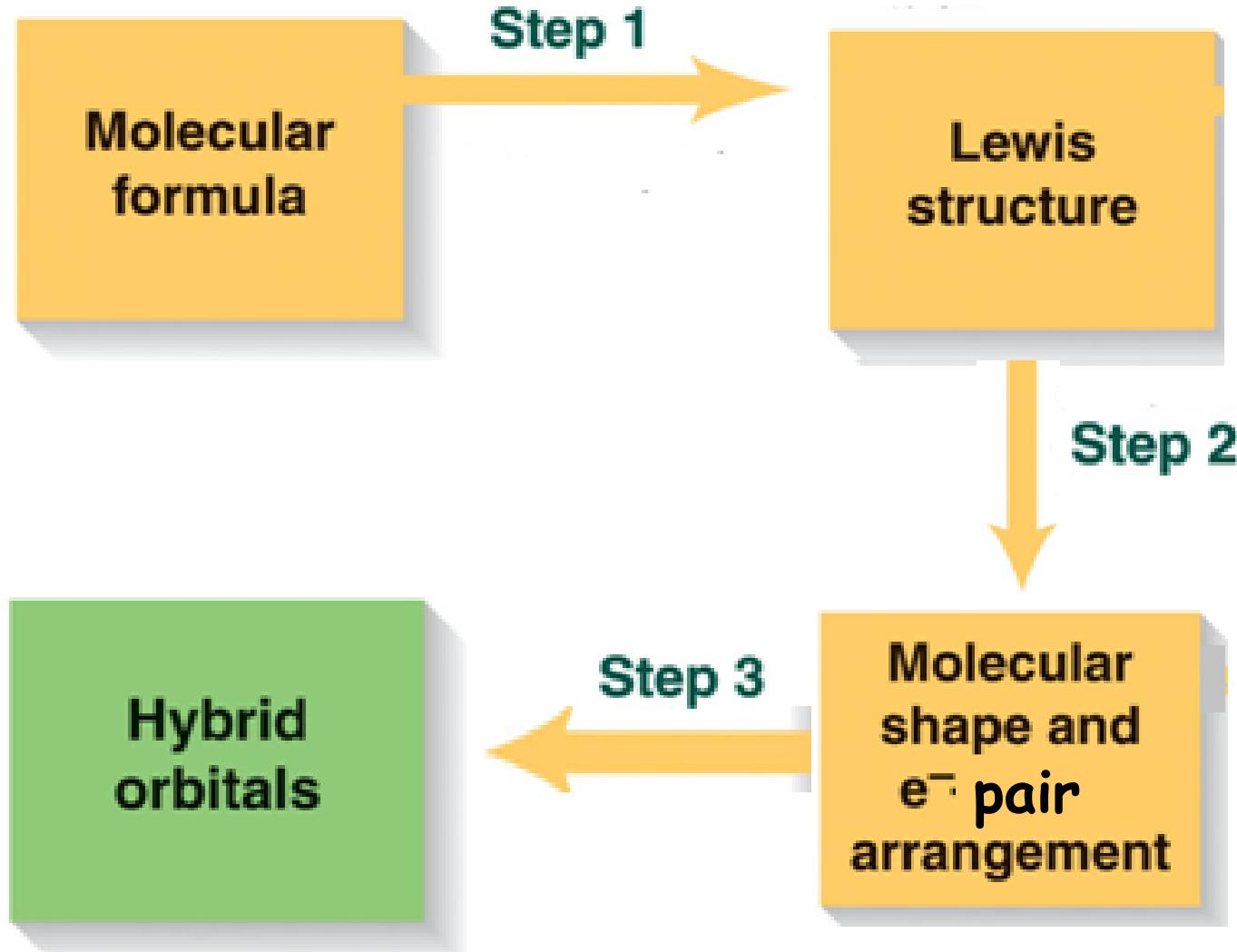


# DETERMINING TYPE OF HYBRID ORBITALS

---

- 1 Draw **Lewis structure**
- 2 Predict the **electron pair arrangement** using **VSEPR model**
- 3 Deduce the **hybridization** of the central atom by matching the **arrangement** of the e<sup>-</sup> pair with the hybrid orbitals

# Steps In Determining The Type of Hybrid Orbitals



$e^-$  pair

$e^-$  pair arrangement

Type of hybridization

2

linear

$sp$

3

trigonal planar

$sp^2$

4

tetrahedral

$sp^3$

5

trigonal bipyramidal

$sp^3d$

6

octahedral

$sp^3d^2$

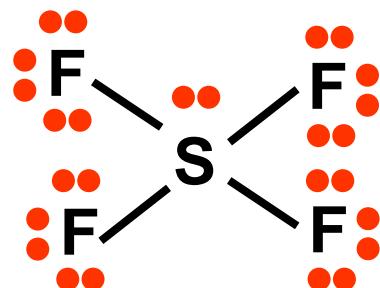
## **EXAMPLE:2**

Determine the hybridization state of the central (underlined) atom in each of the following molecules:

- (a) SF<sub>4</sub>
- (b) BeF<sub>2</sub>
- (c) (d) SiCl<sub>4</sub>
- (e) XeF<sub>4</sub>

(a) SF<sub>4</sub>

Lewis structure:



S: Electron pairs = 5

Hybridization of S = ***sp<sup>3</sup>d***

(b) BeF<sub>2</sub>

Lewis structure:

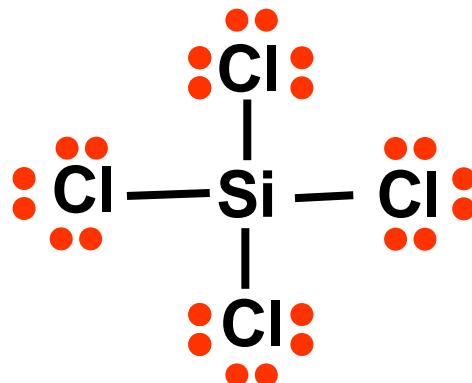


Be: Electron pairs = 2

Hybridization of Be = ***sp***

(c) SiCl<sub>4</sub>

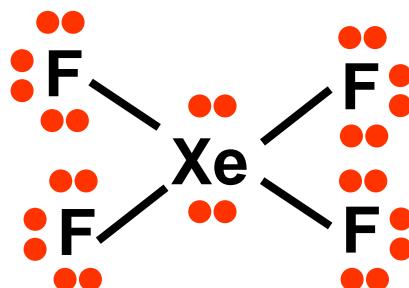
Lewis Structure:



Si: Electron pairs = 4

Hybridization of Si =  $sp^3$ (d) XeF<sub>4</sub>

Lewis Structure:



Xe: Electron pairs = 6

Hybridization of Xe =  $sp^3d^2$

# ***sp* HYBRIDIZATION**

**EXAMPLE:  $\text{BeCl}_2$**

e<sup>-</sup> configuration of Cl :  $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^5$

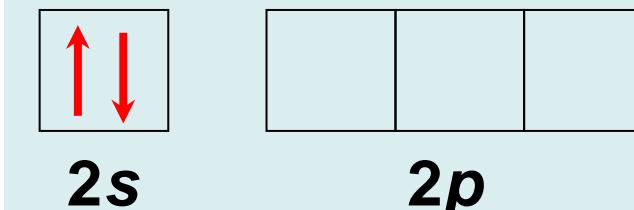
e<sup>-</sup> configuration of Be :  $1\text{s}^2 2\text{s}^2$

180°

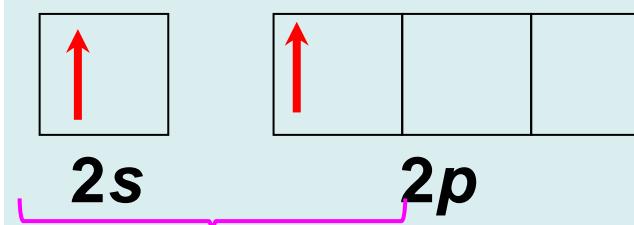


**Valence e<sup>-</sup> in Be :**

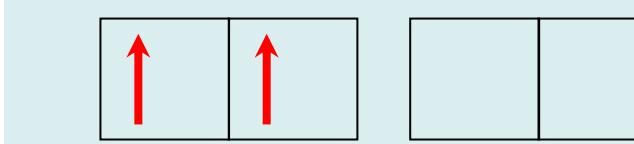
**Ground state** :



**Excited state** :



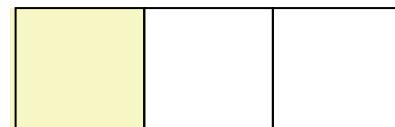
***sp* hybridization** :



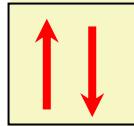
***sp* orbitals empty 2p orbitals**

## *sp* hybridization

Energy

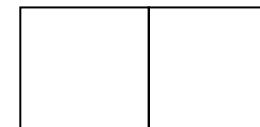
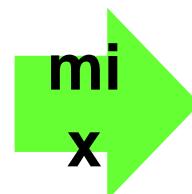


**2p**

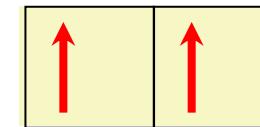


**2s**

**isolated Be atom**



**2p**

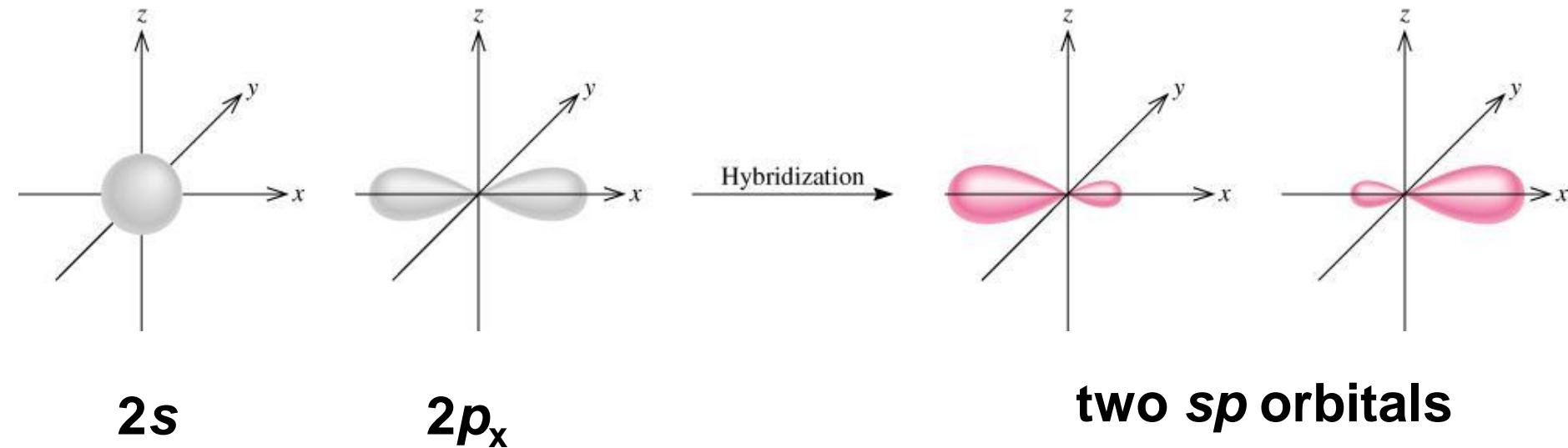


***sp***

**hybridized Be atom**

**one *s* orbital + one *p* orbital → two equivalent *sp* orbitals**

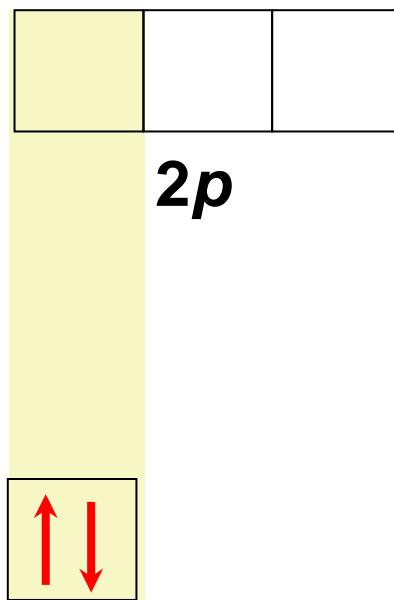
# *sp* hybridization



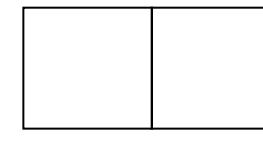
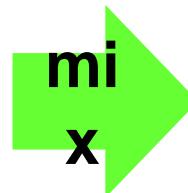
one **s** orbital + one **p** orbital → two equivalent ***sp*** orbitals

**Energy level of the hybrid orbitals is in  
between the energy level of the pure orbitals**

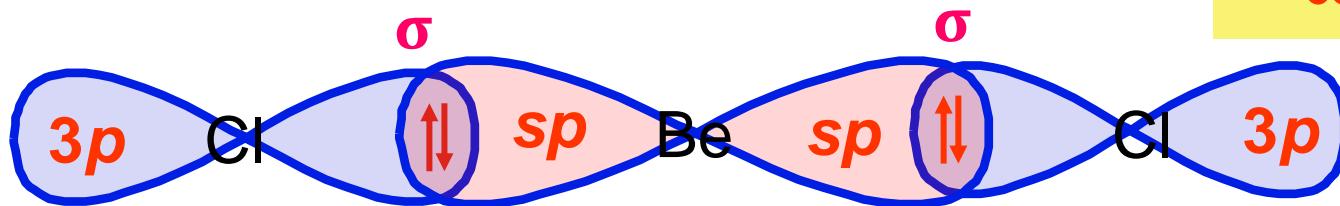
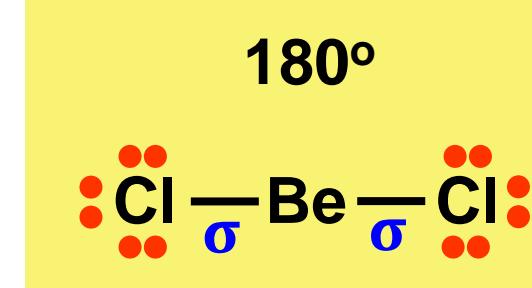
Energy



**isolated Be atom**



**hybridized Be atom**



- Each Be–Cl ( $\sigma$ ) bond formed by overlapping of **one  $sp$**  hybrid of Be atom and **one  $3p$**  orbital of Cl atom
- Two equivalent  $sp$  hybrid orbitals that lie **180°** apart
  - ☞ **two e<sup>-</sup> pairs** (from **VSEPR theory**)
- e<sup>-</sup> pair arrangement = **linear**  
Molecular shape = **linear**

# $sp^2$ HYBRIDIZATION

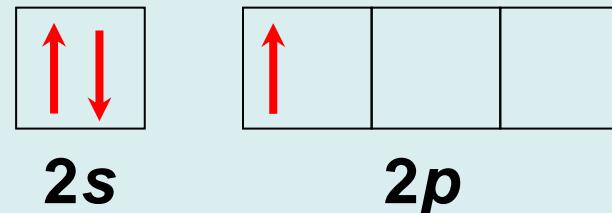
**EXAMPLE:  $\text{BF}_3$**

e<sup>-</sup> configuration of F :  $1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^5$

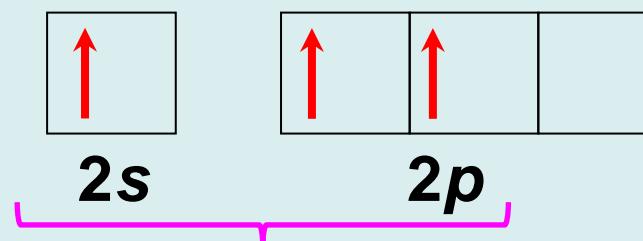
e<sup>-</sup> configuration of B :  $1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^1$

**Valence e<sup>-</sup> in B:**

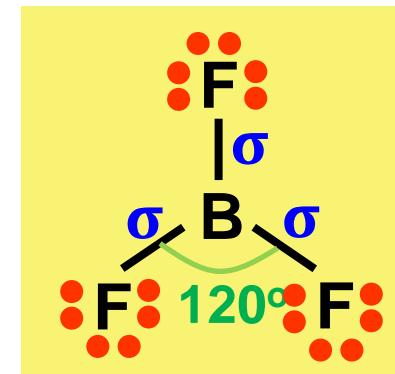
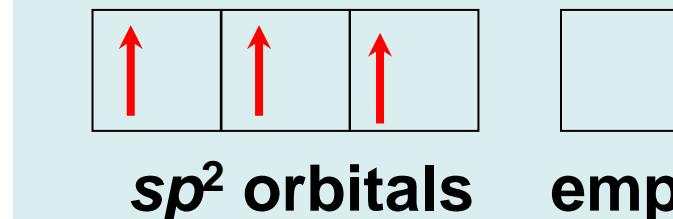
Ground state :



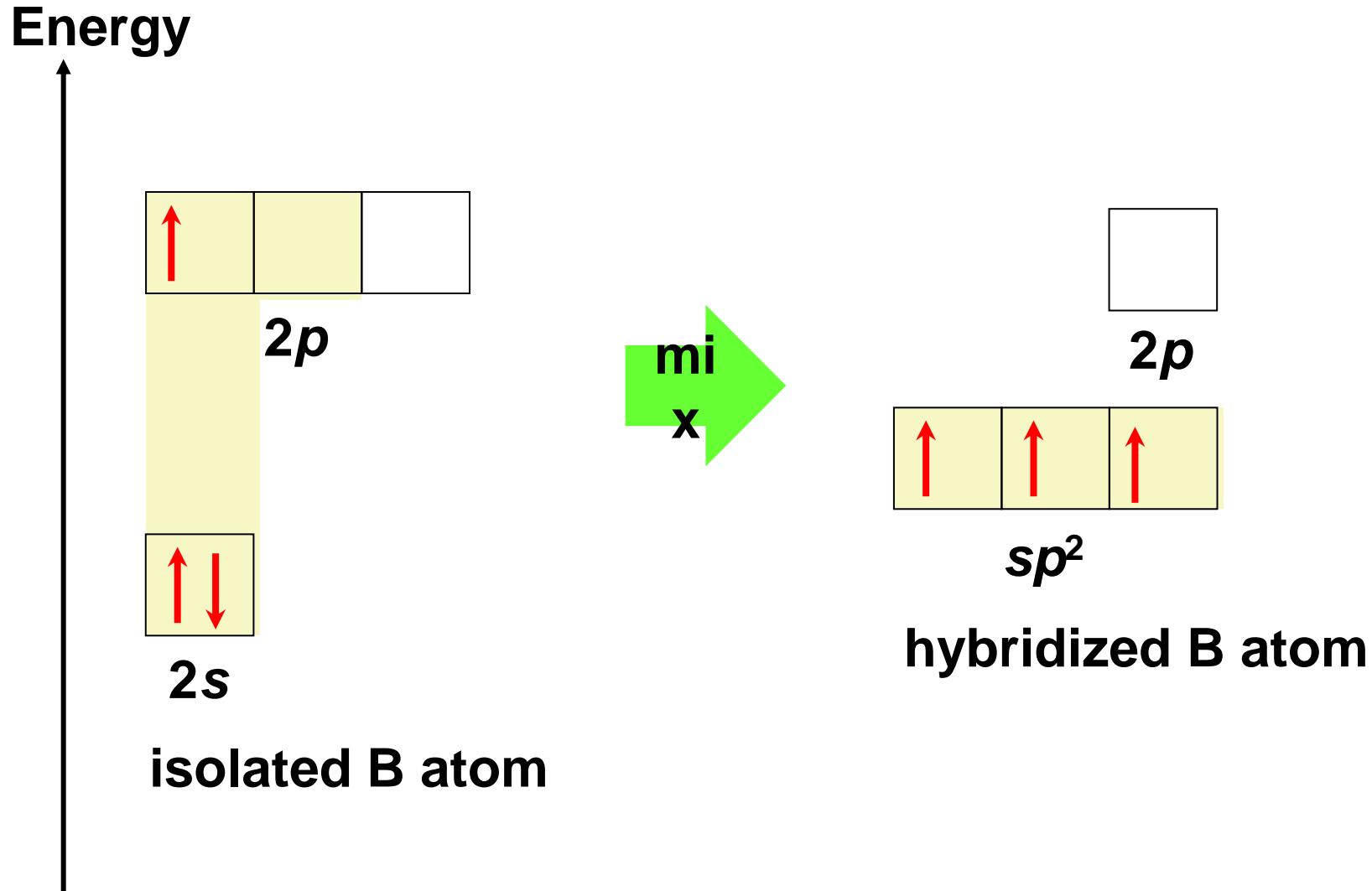
Excited state :



$sp^2$  hybridization :

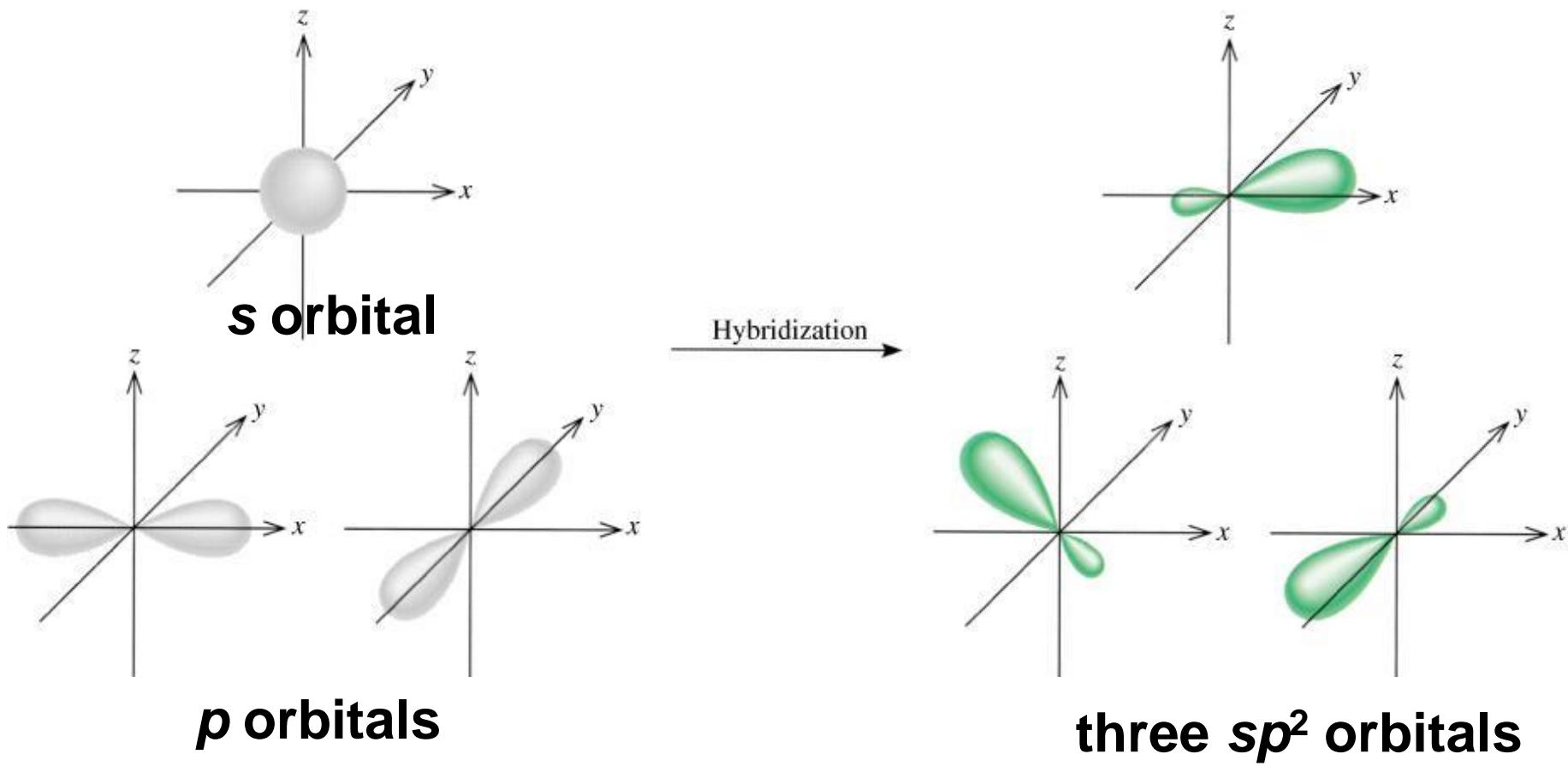


## $sp^2$ hybridization

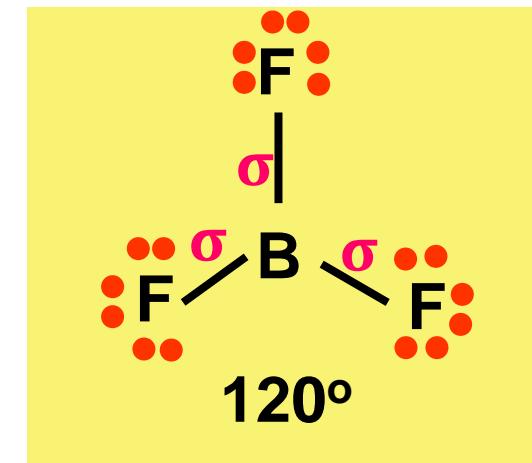
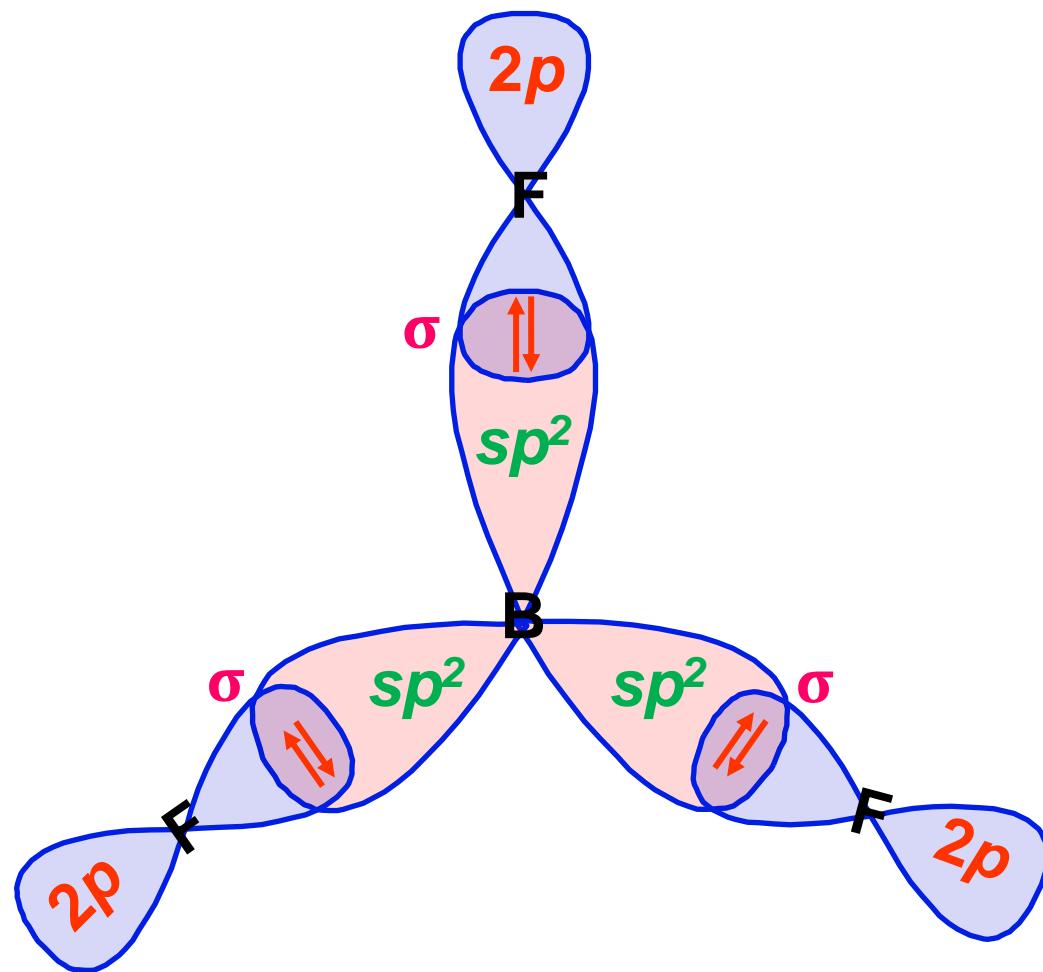


one s orbital + two p orbital → three equivalent  $sp^2$  orbitals

# $sp^2$ hybridization



**one s orbital + two p orbital → three equivalent  $sp^2$  orbitals**



Each **B–F ( $\sigma$ )** bond formed by overlapping of **one  $sp^2$**  hybrid of B atom and **one  $2p$**  orbital of F atom

- Three equivalent  $sp^2$  hybrid orbitals that lie **120°** apart
  - ☞ three e<sup>-</sup> pairs (from VSEPR theory)
- e<sup>-</sup> pair arrangement = trigonal planar  
Molecular shape = trigonal planar

# $sp^3$ HYBRIDIZATION

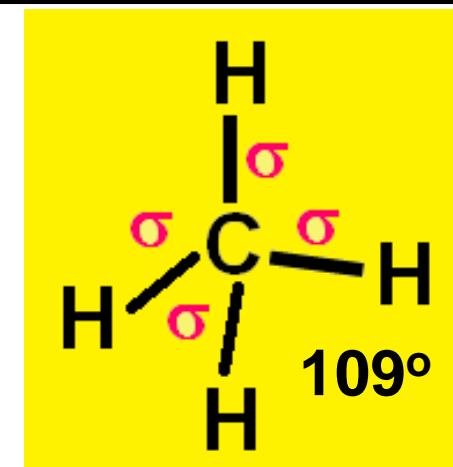
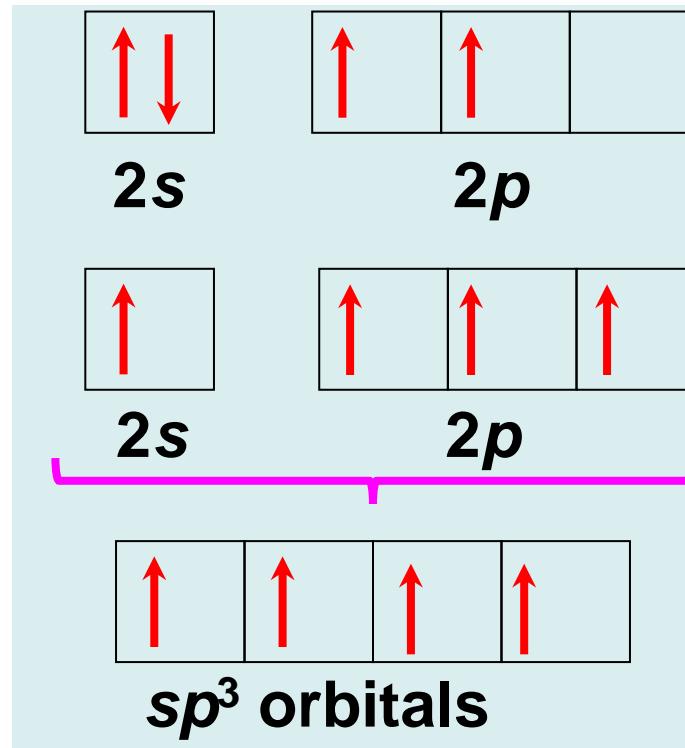
**EXAMPLE:  $\text{CH}_4$**

e<sup>-</sup> configuration of H :  $1s^1$

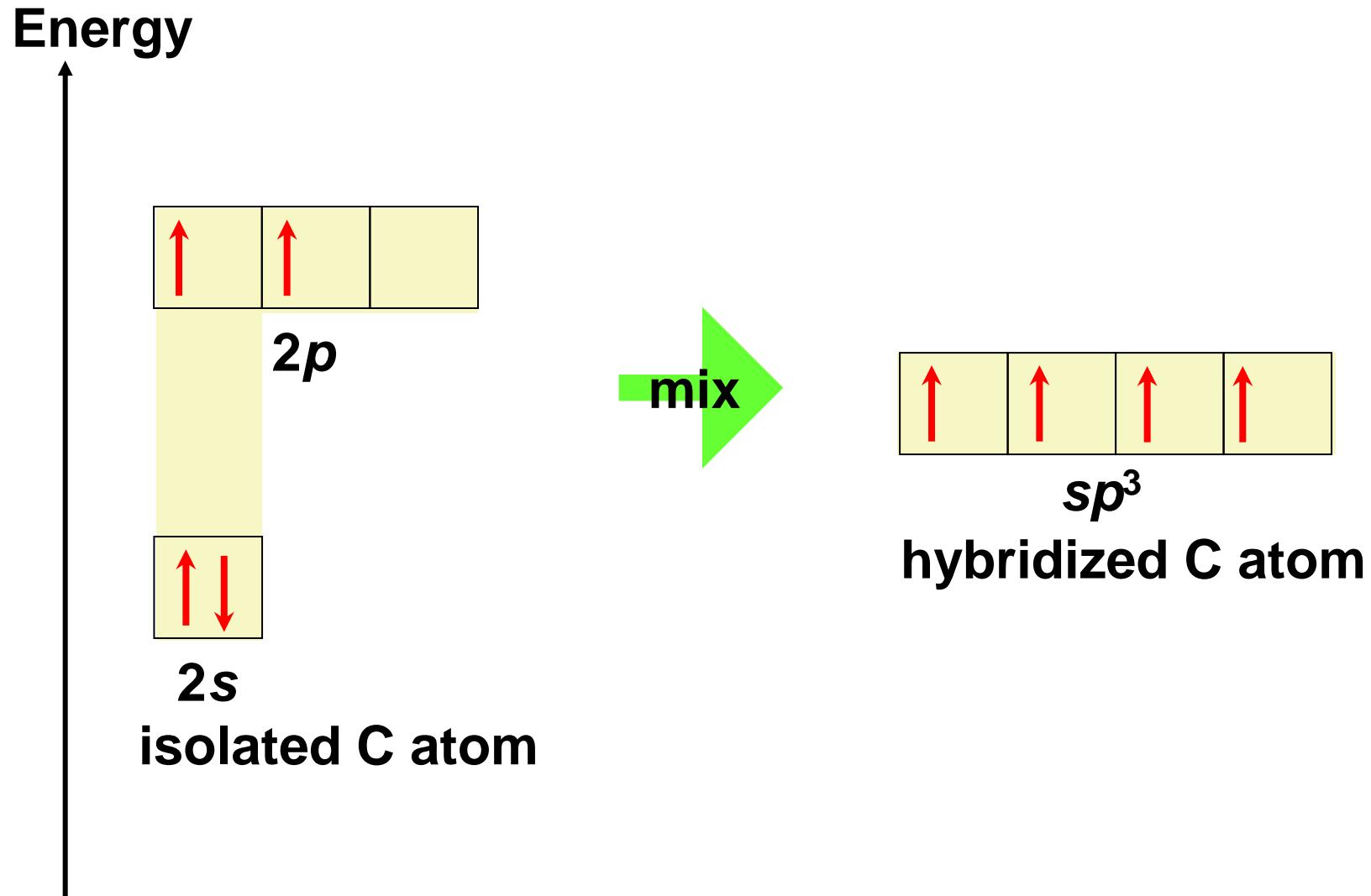
e<sup>-</sup> configuration of C :  $1s^2 2s^2 2p^2$

**Valence e<sup>-</sup> in C:**

**Ground state** :

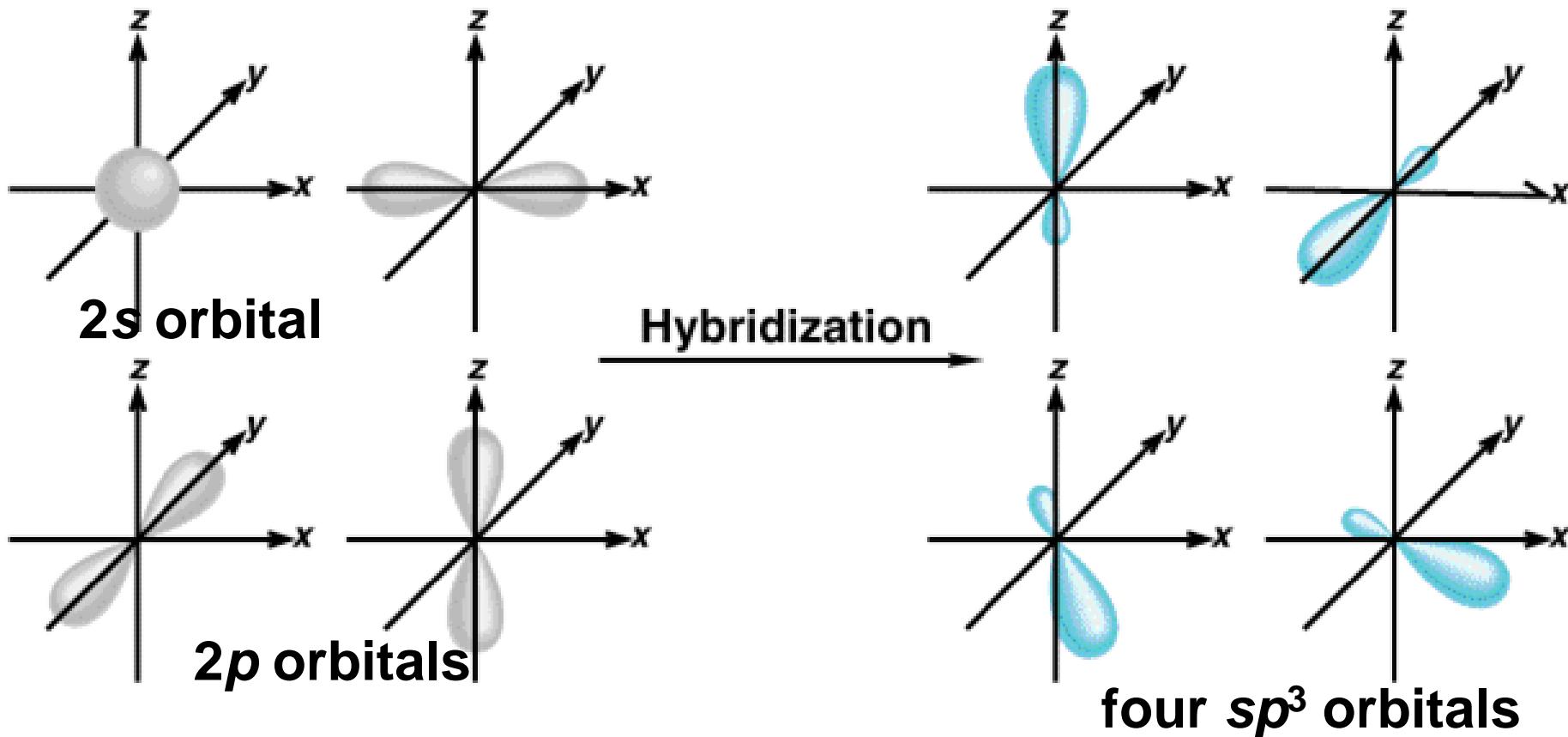


# $sp^3$ hybridization

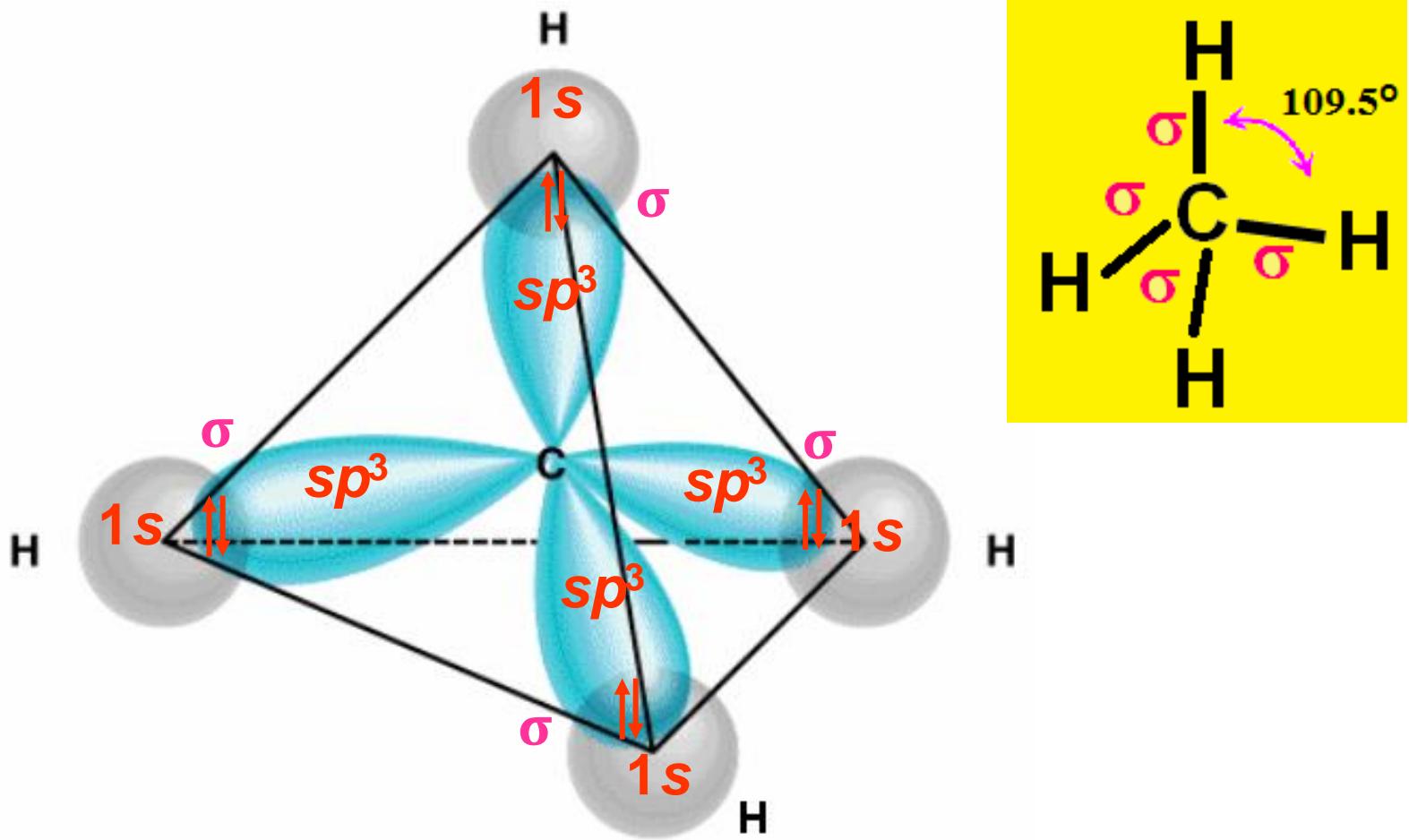


one s orbital + three p orbital → four equivalent  $sp^3$  orbitals

# $sp^3$ hybridization



one s orbital + three p orbital → four equivalent  $sp^3$  orbitals



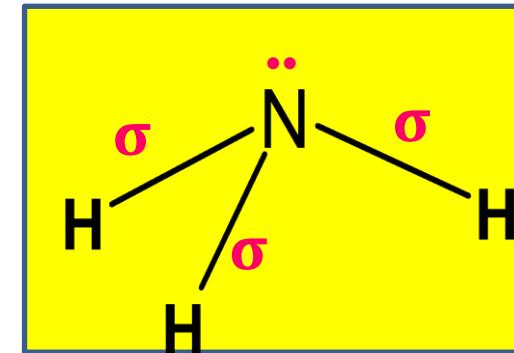
Each C–H ( $\sigma$ ) bond formed by overlapping of **one  $sp^3$**  hybrid of C atom and **one 1s** orbital of H atom

- Four equivalent *sp<sup>3</sup>* hybrid orbitals that lie 109.5° apart
  - ☞ four e<sup>-</sup> pairs (from VSEPR theory)
- e<sup>-</sup> pair arrangement = tetrahedral
- Molecular shape = tetrahedral

## EXAMPLE: $\text{NH}_3$

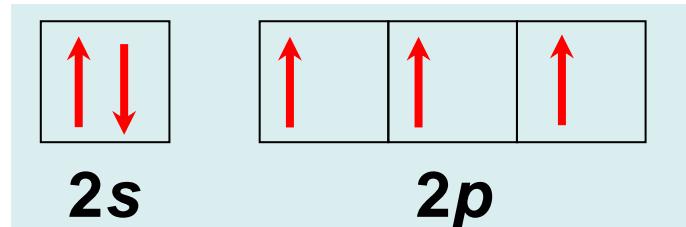
e<sup>-</sup> configuration of H :  $1s^1$

e<sup>-</sup> configuration of N :  $1s^2 2s^2 2p^3$

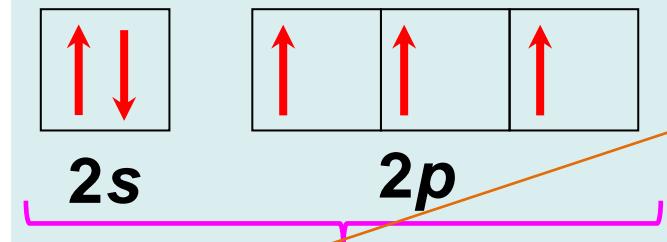


Valence e<sup>-</sup> in N:

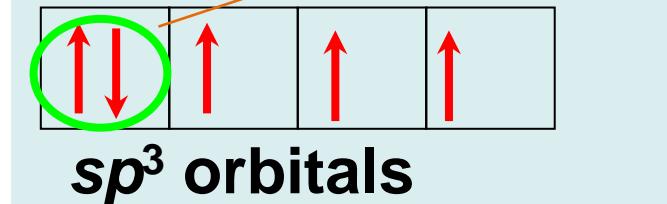
Ground state :



Excited state :

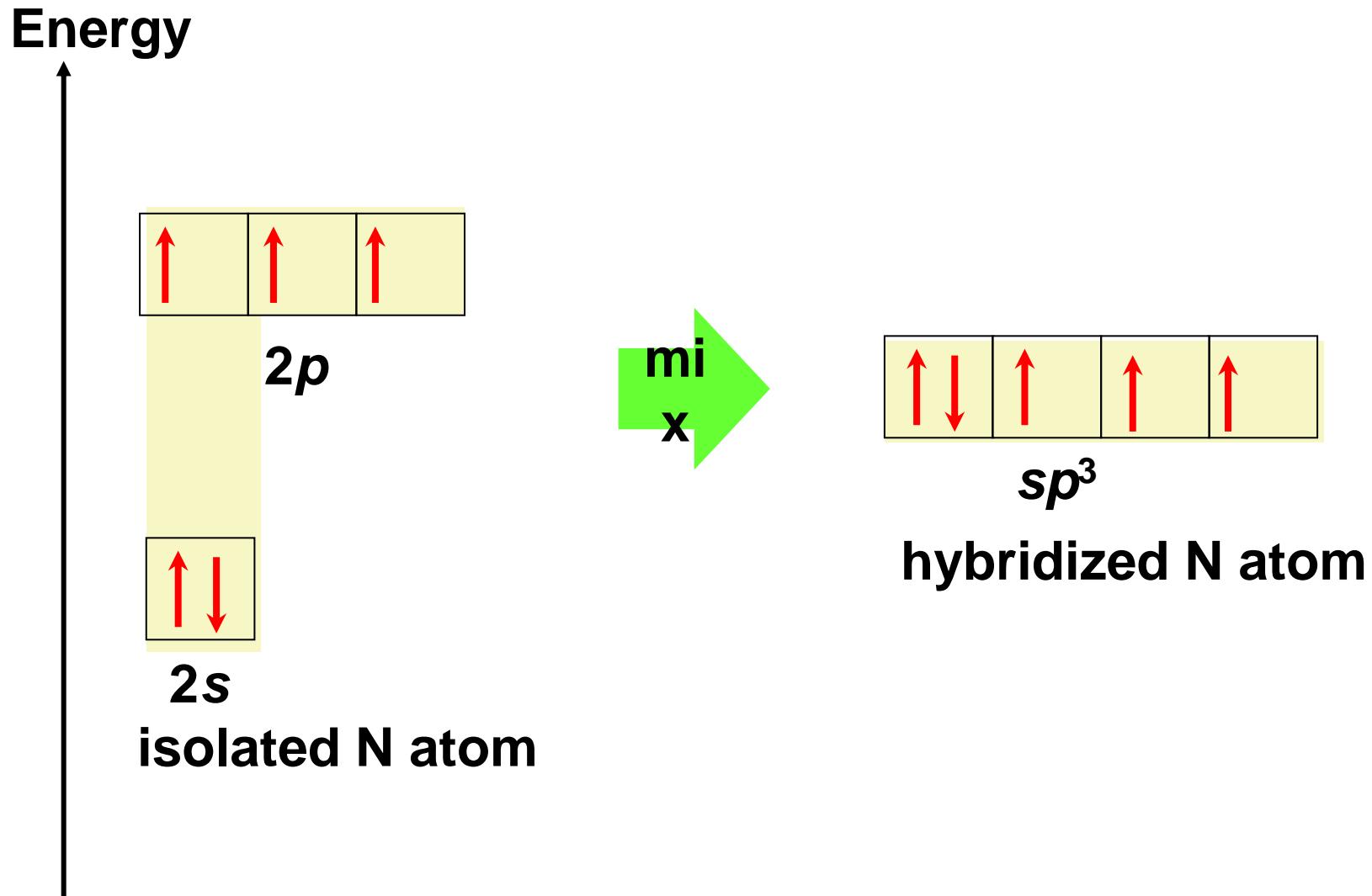


$sp^3$  hybridization :



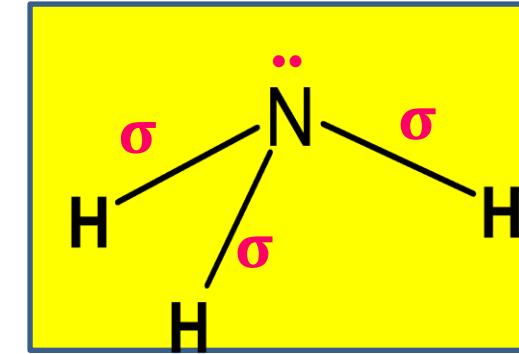
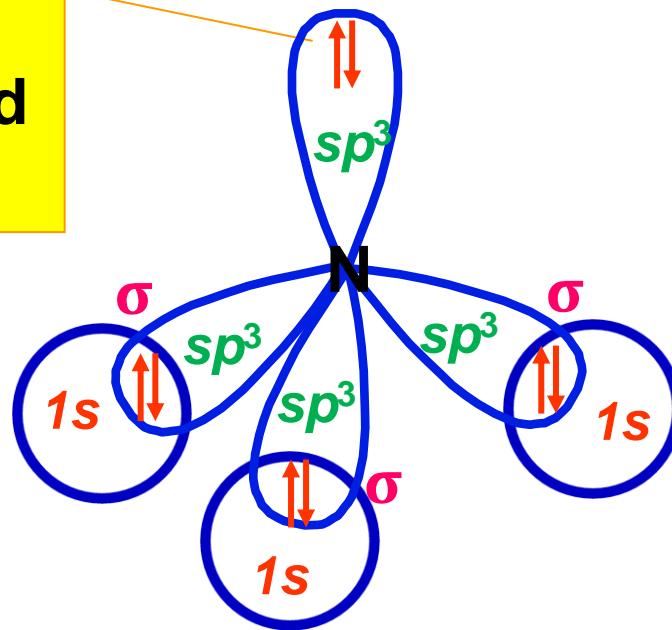
One of the  $sp^3$  hybrid occupied by lone pair e<sup>-</sup>

# $sp^3$ hybridization



one s orbital + three p orbital → four equivalent  $sp^3$  orbitals

One of the  $sp^3$  hybrid occupied by lone pair  $e^-$

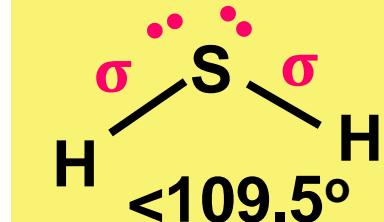


Each N–H ( $\sigma$ ) bond formed by overlapping of one  $sp^3$  hybrid of N atom and one 1s orbital of H atom

- Four equivalent  $sp^3$  hybrid orbitals that lie  $109.5^\circ$  apart:
    - ☞ four  $e^-$  pairs (from VSEPR theory)
  - One  $sp^3$  hybrid orbital occupied by lone pair electron. Repulsion of lone pair-bonding pair is greater than between bonding pairs  
Bond angle <  $109.5^\circ$
  - $e^-$  pair arrangement = tetrahedral
  - Molecular shape = trigonal pyramidal

## **EXAMPLE :3**

**Describe a hybridization scheme for the central S atom in the molecule H<sub>2</sub>S that is consistent with the molecular shape.**

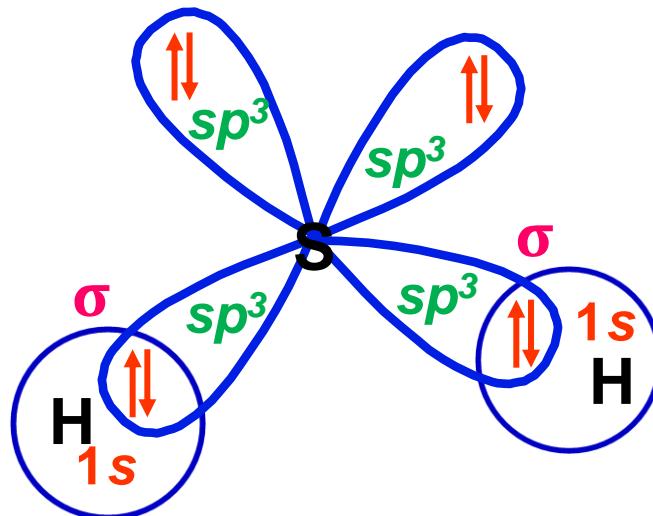


e<sup>-</sup> configuration of H : 1s<sup>1</sup>

e<sup>-</sup> configuration of S : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup>

### Valence e<sup>-</sup> in S atom:

<b>Ground state</b>	:	$\frac{\uparrow \downarrow}{3s}$	$\frac{\uparrow \downarrow}{3p}$	$\frac{\uparrow}{3p}$
<b>Excited state</b>	:	$\frac{\uparrow \downarrow}{3s}$	$\frac{\uparrow \downarrow}{3p}$	$\frac{\uparrow}{3p}$
<b>sp<sup>3</sup> hybridization</b>	:	$\frac{\uparrow \downarrow}{sp^3}$	$\frac{\uparrow \downarrow}{sp^3}$	$\frac{\uparrow}{sp^3}$



Each S–H ( $\sigma$ ) bond formed by:  
Overlap of **one  $sp^3$**  hybrid of S atom and **one  $1s$**  orbital  
of H atom

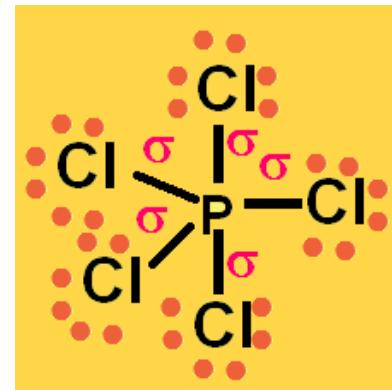
Electron pair arrangement : tetrahedral  
Molecular shape : bent (V-shaped)

# $sp^3d$ HYBRIDIZATION

**EXAMPLE:  $PCl_5$**

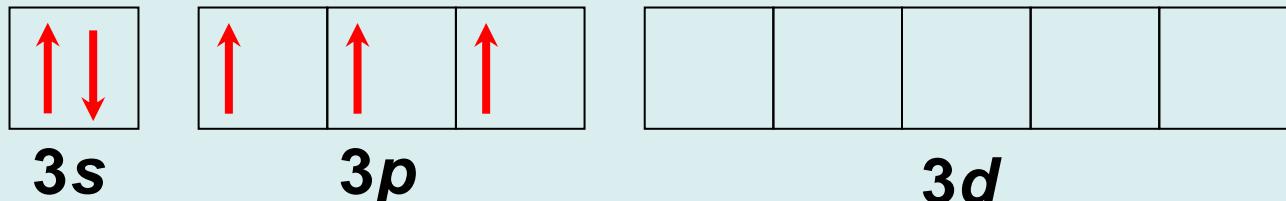
e<sup>-</sup> configuration of Cl :  $1s^2 2s^2 2p^6 3s^2 3p^5$

e<sup>-</sup> configuration of P :  $1s^2 2s^2 2p^6 3s^2 3p^3$

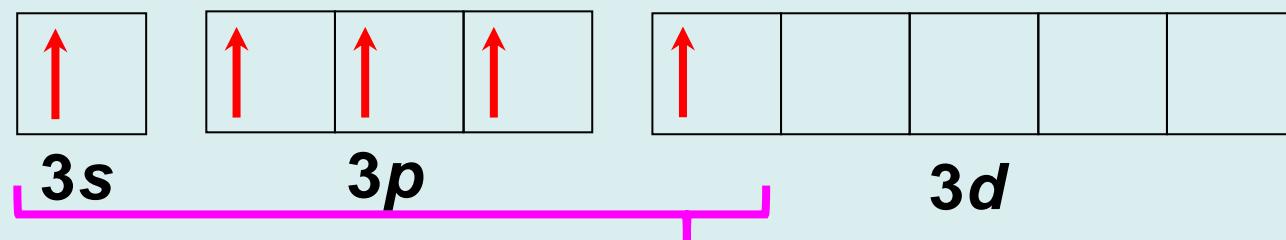


**Valence e<sup>-</sup> in P:**

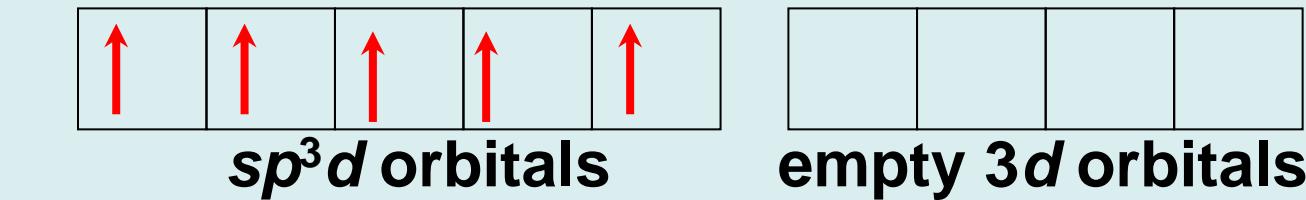
Ground state :



Excited state :

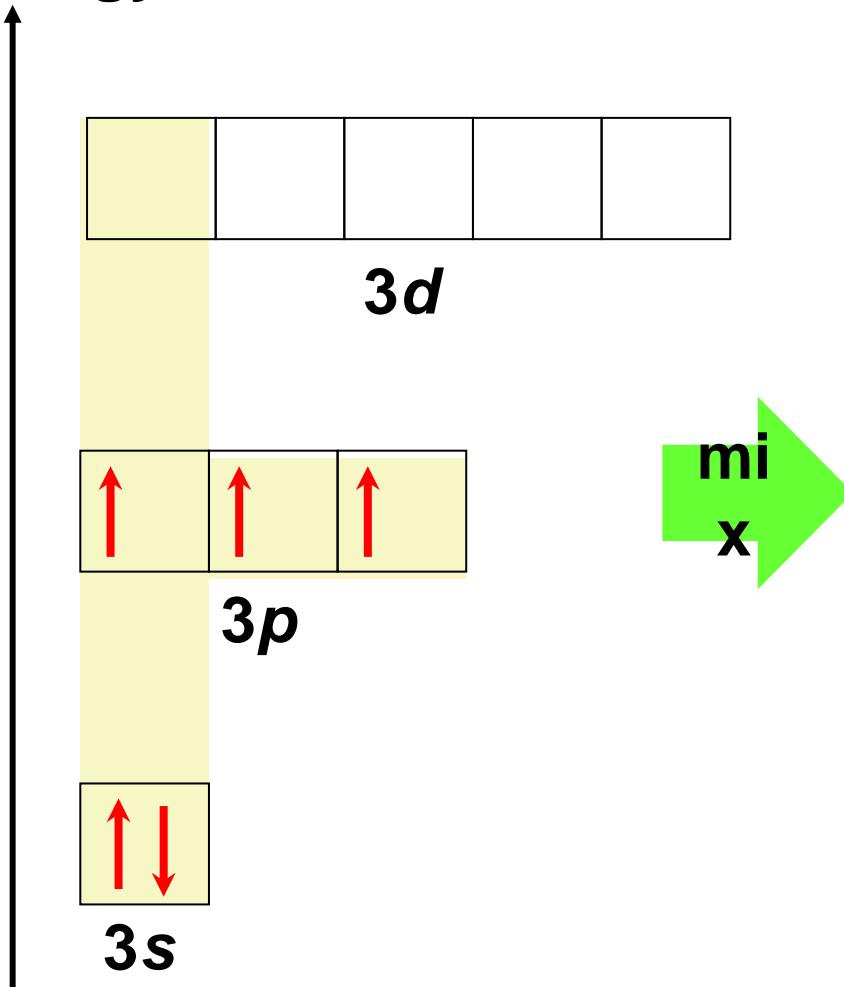


**$sp^3d$  hybridization:**



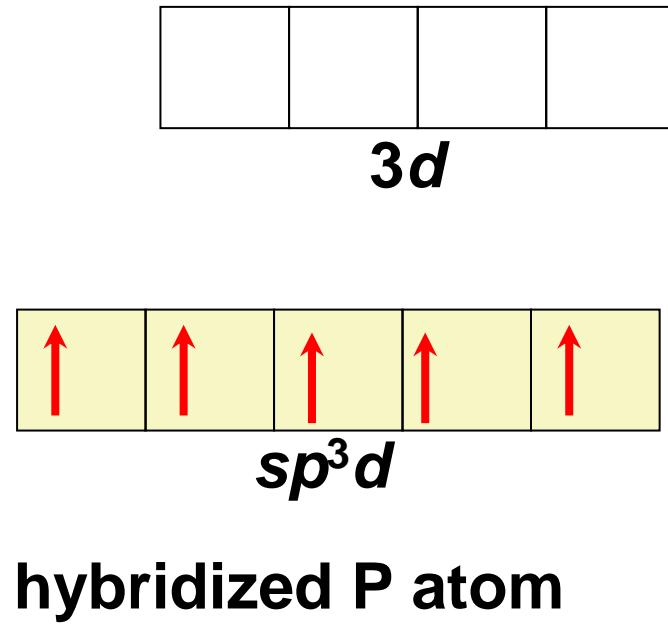
$sp^3d$  hybridization

Energy



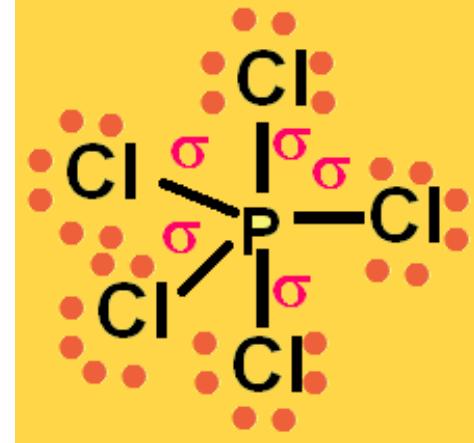
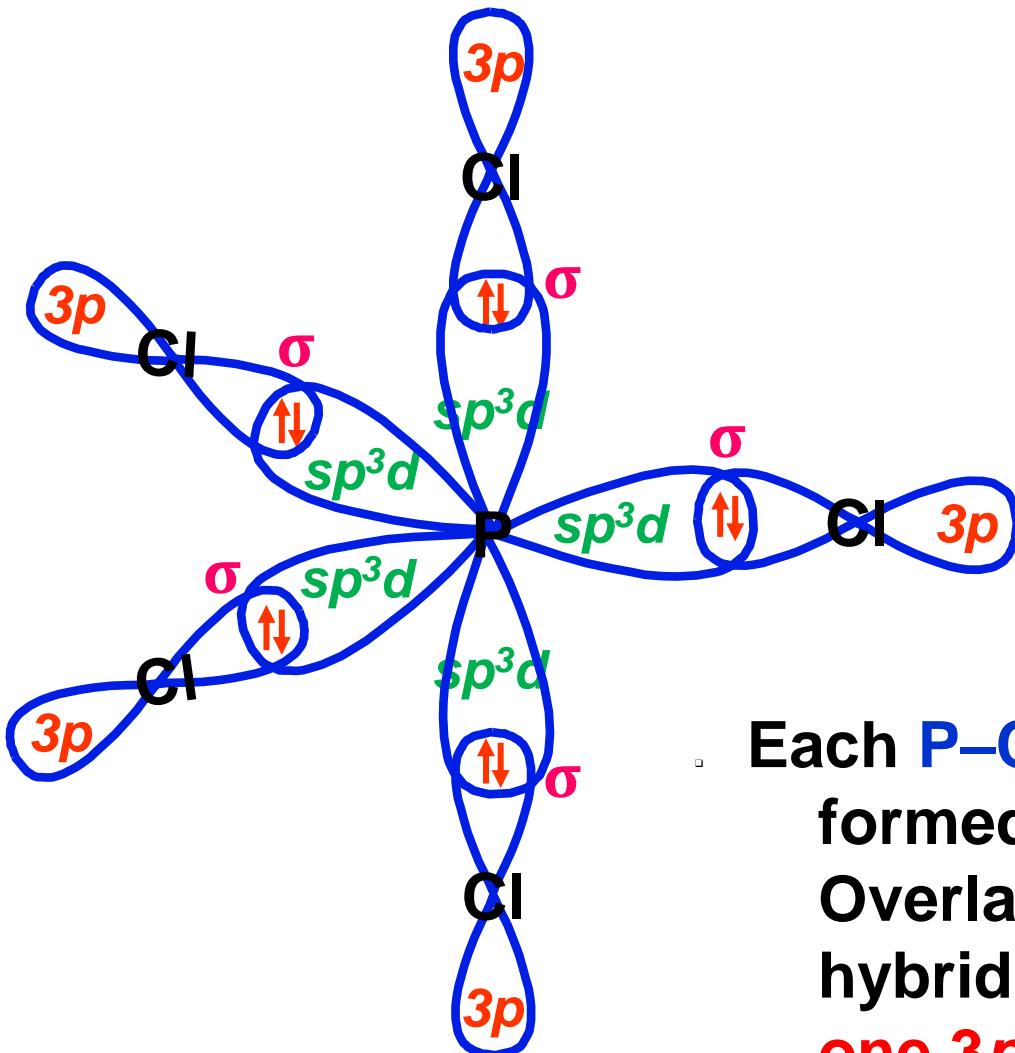
isolated P atom

mix



hybridized P atom

one s orbital + three p orbital + one d orbital → five equivalent  $sp^3d$  orbitals



- Each **P–Cl sigma bond** formed by:  
Overlap of **one  $sp^3d$**   
hybrid of P atom and  
**one  $3p$**  orbital of Cl  
atom.

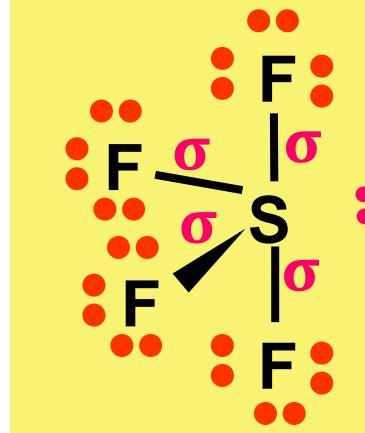
- Five equivalent  $sp^3d$  hybrid orbitals that lie  $90^\circ$  and  $120^\circ$  apart
  - ☞ five e<sup>-</sup> pairs (from VSEPR theory)
- e<sup>-</sup> pair arrangement = trigonal bipyramidal  
Molecular shape = trigonal bipyramidal

## **EXAMPLE :4**

**Describe a hybridization scheme for the central S atom in the molecule  $\text{SF}_4$  that is consistent with the molecular shape.**

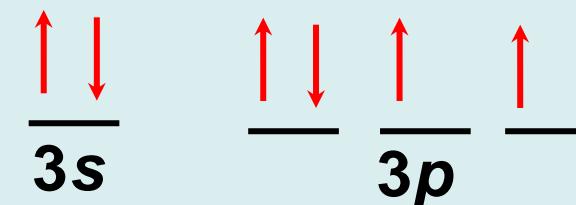
e<sup>-</sup> configuration of F : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

e<sup>-</sup> configuration of S : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup>

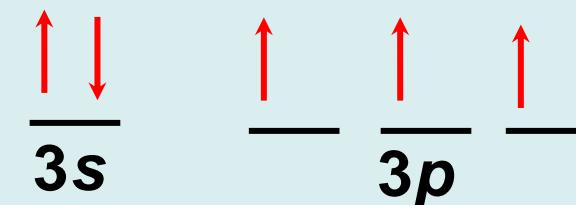


### Valence e<sup>-</sup> in S atom:

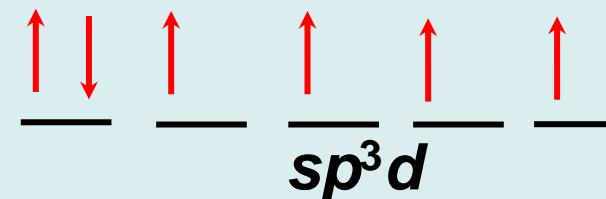
**Ground State** :



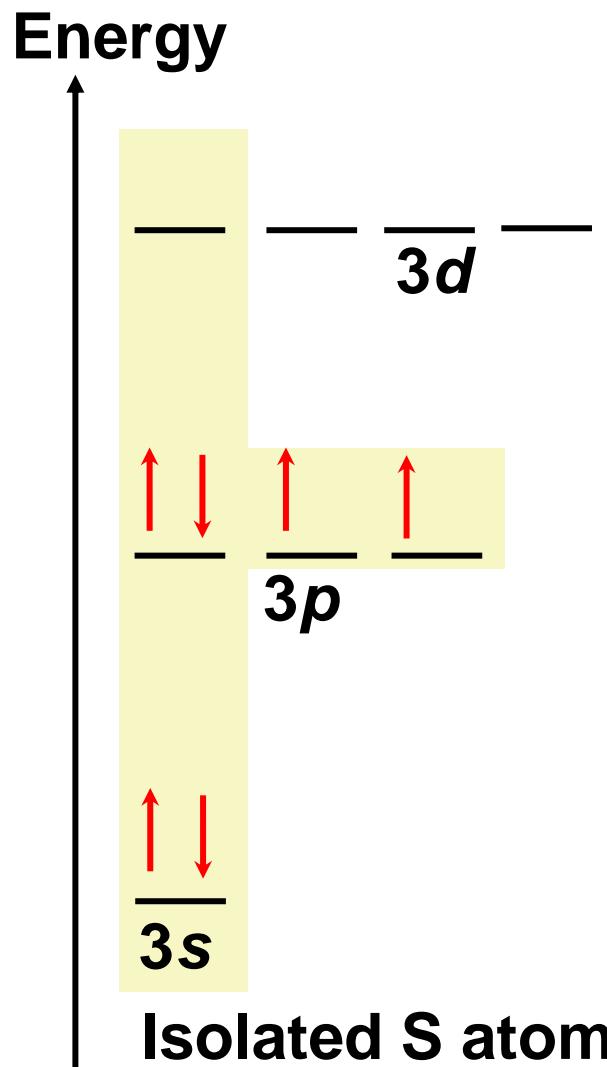
**Excited State** :



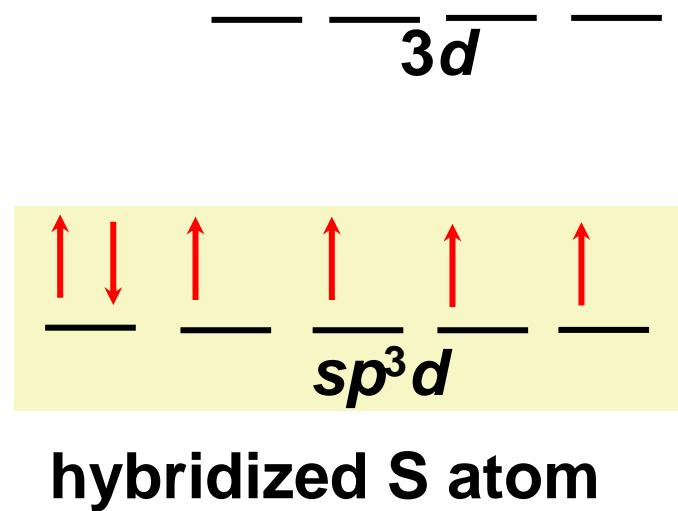
**sp<sup>3</sup>d hybridization:**

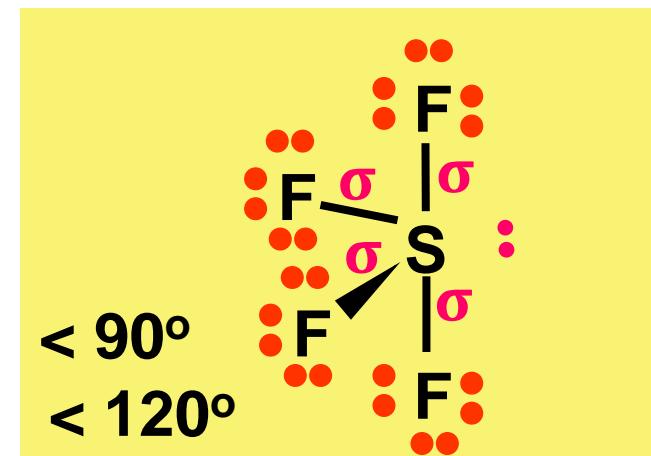
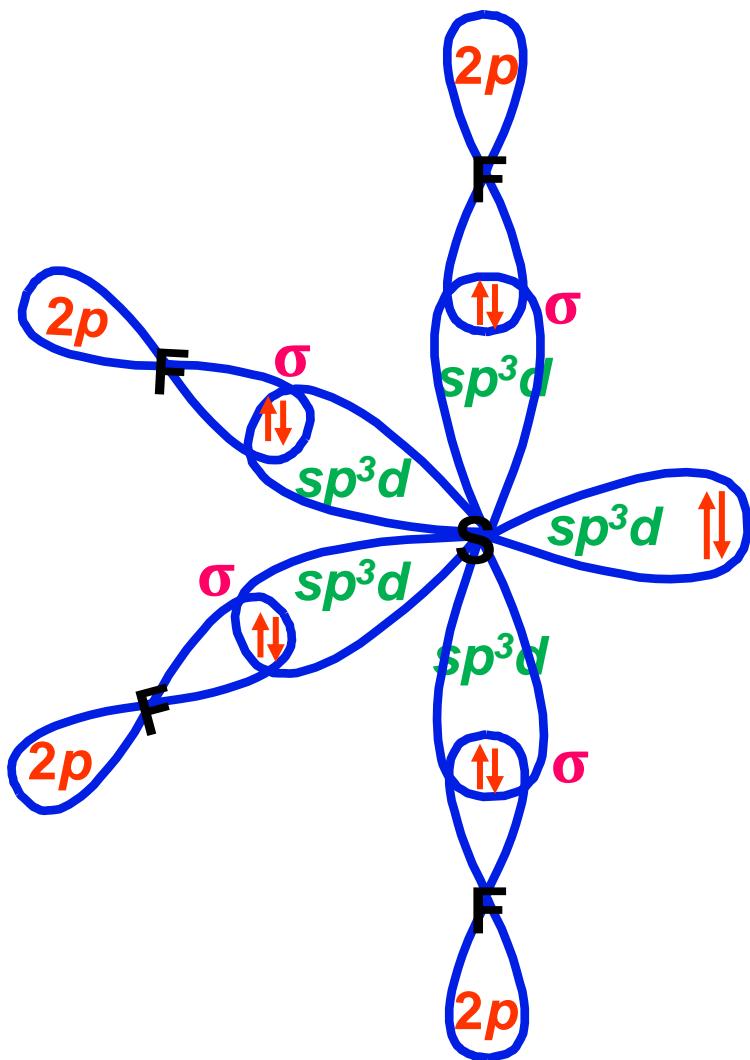


empty 3d orbitals



mi  
x →



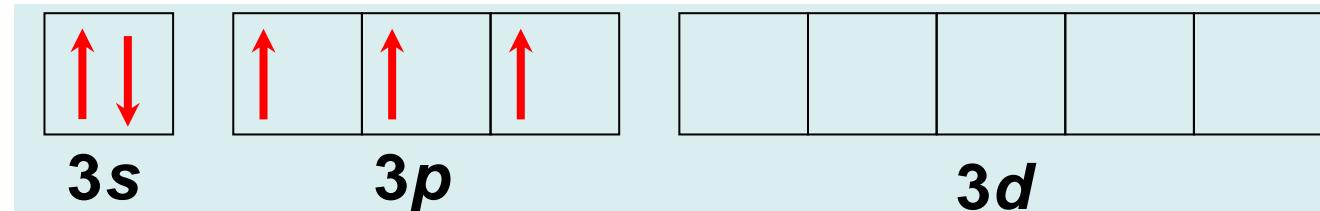


- Each **S-F sigma bond** formed by overlapping of **one  $sp^3d$  hybrid of S atom and one  $2p$  orbital of F atom.**
- Electron pair arrangement:** trigonal bipyramidal  
**Molecular shape :** seesaw

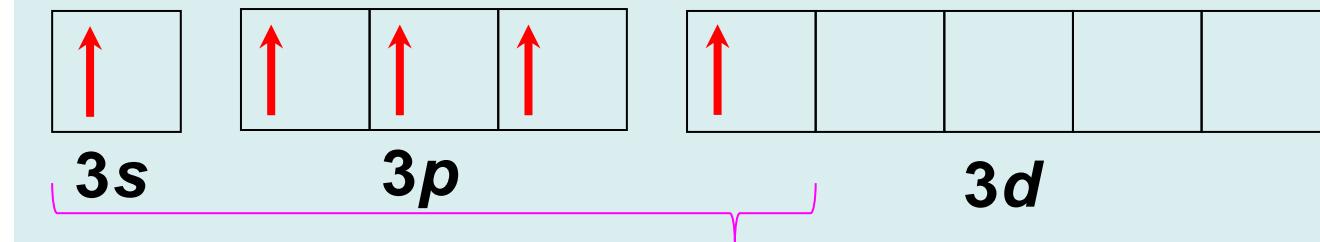
Atoms of period 3 and higher can expand because they have empty *d* orbitals

Valence e<sup>-</sup> in P:

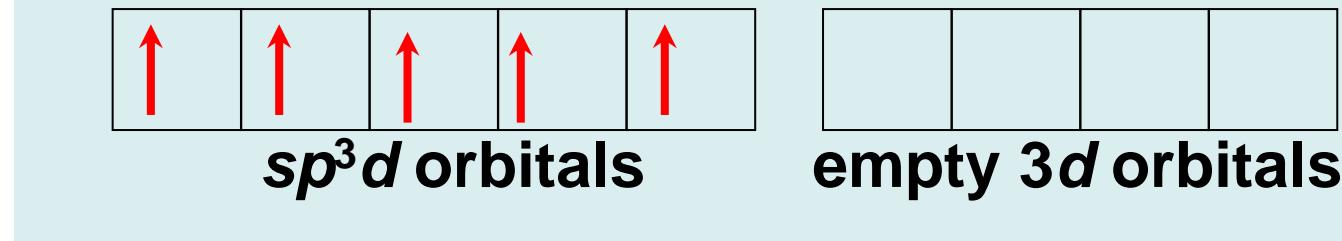
Ground state:



Excited State:



*sp*<sup>3</sup>*d*  
hybridization:

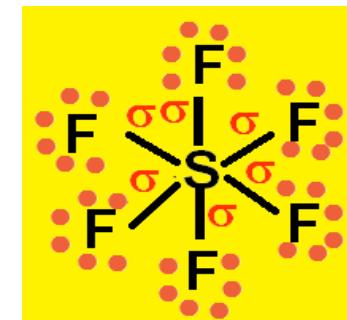


# $sp^3d^2$ HYBRIDIZATION

**EXAMPLE: SF<sub>6</sub>**

e<sup>-</sup> configuration of S : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup>

e<sup>-</sup> configuration of F : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

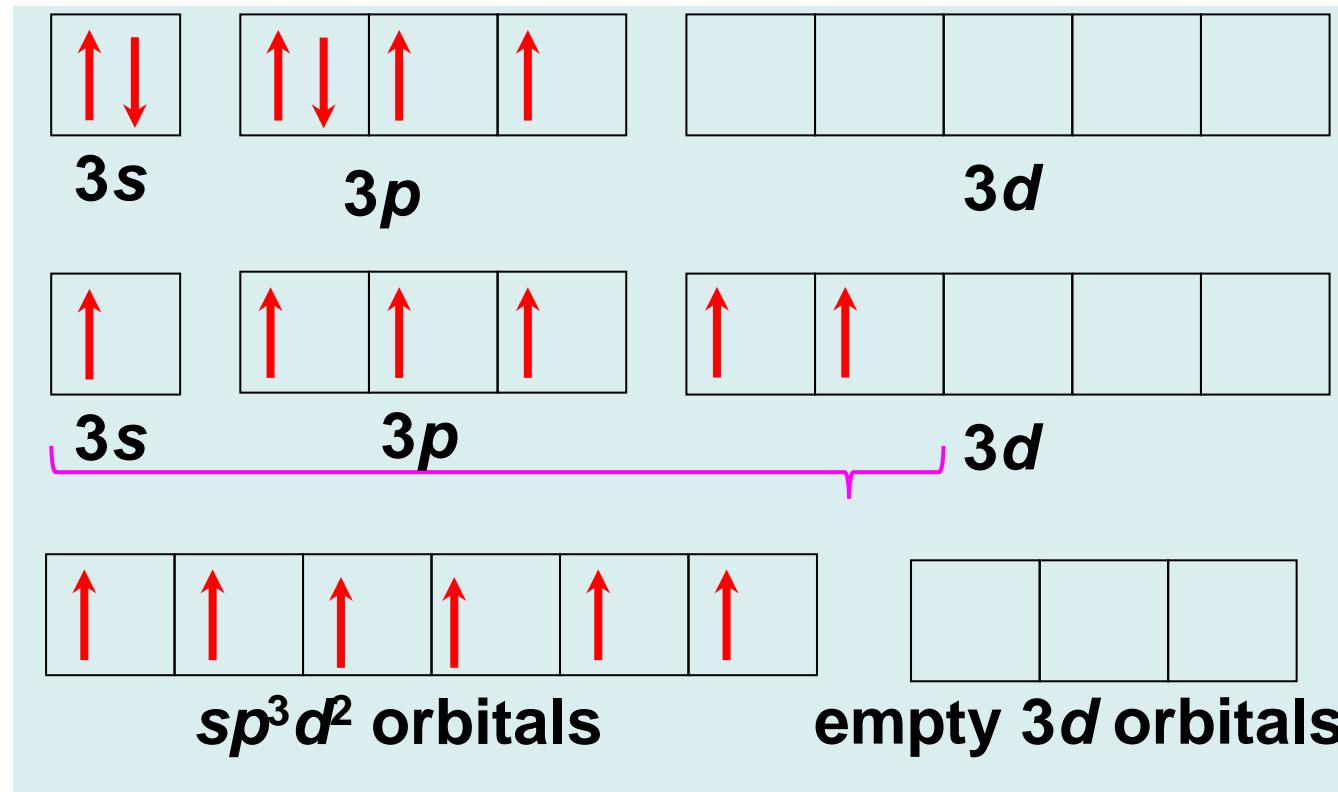


**Valence e<sup>-</sup> in S:**

**Ground state:**

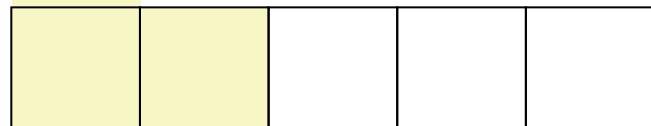
**Excited state:**

**$sp^3d^2$   
hybridization:**

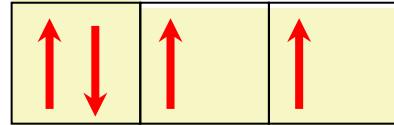


# Energy

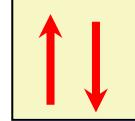
$sp^3d^2$  hybridization



**3d**

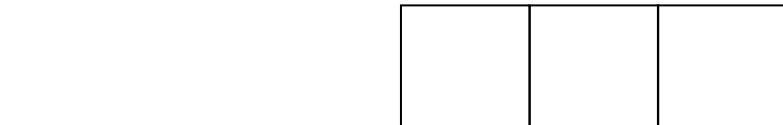
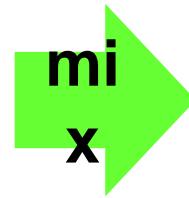


**3p**

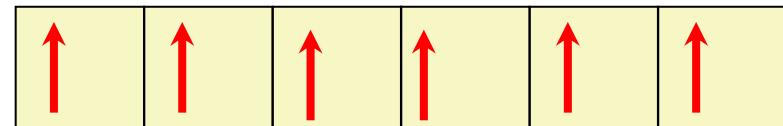


**3s**

**isolated S atom**



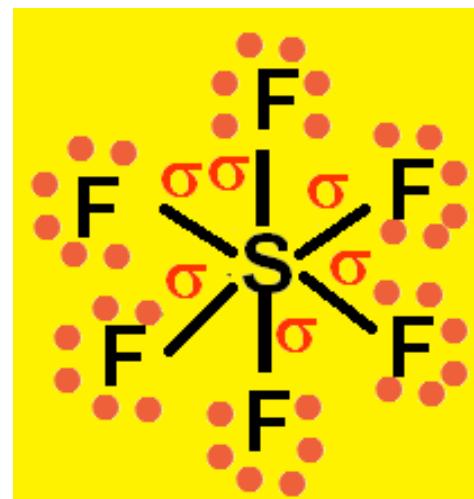
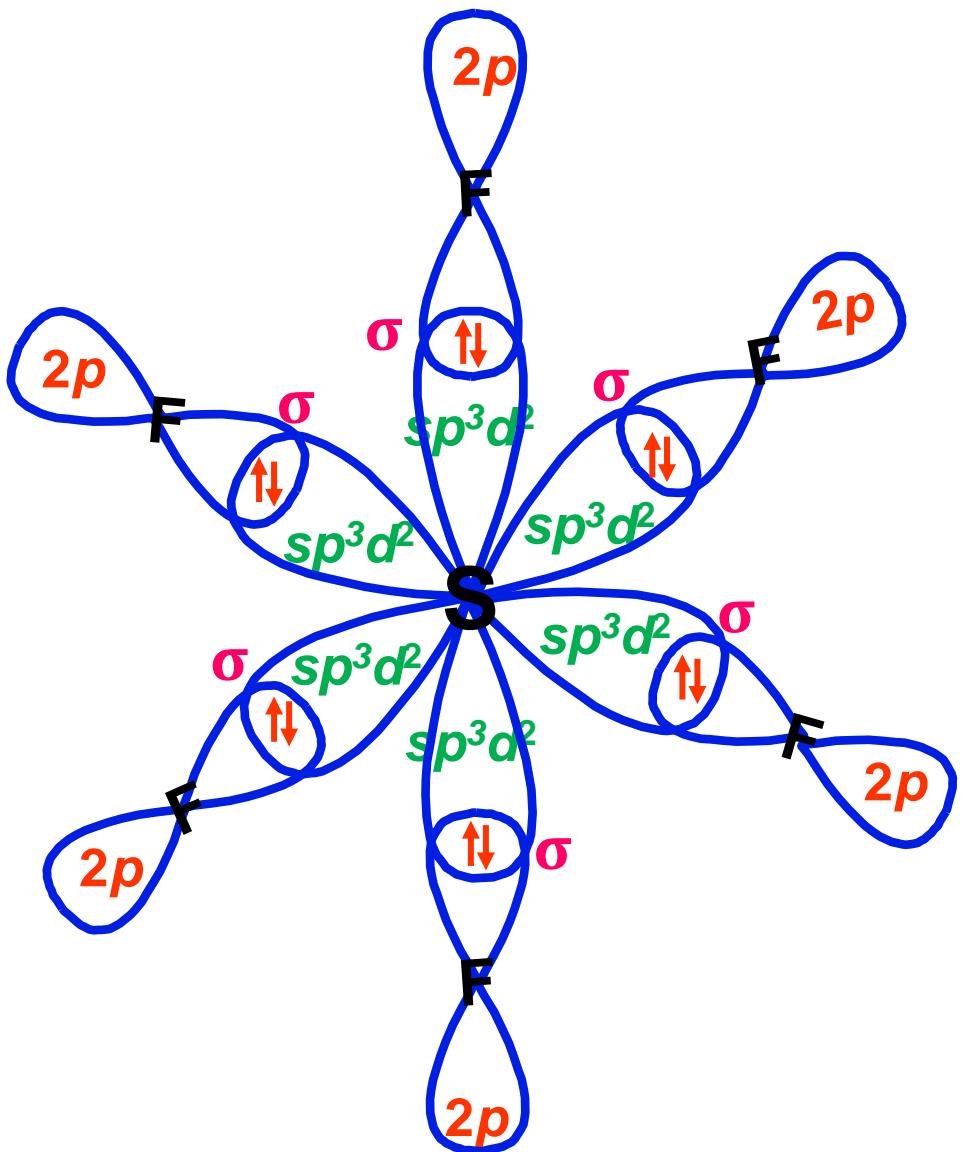
**3d**



**$sp^3d^2$**

**hybridized S atom**

one s orbital + three p orbital + two d orbitals  
→ six equivalent  $sp^3d^2$  orbitals



Each S–F sigma bond formed by:

Overlap of **one  $sp^3d^2$**  hybrid of S atom and **one  $2p$**  orbital of F atom

- Six equivalent  $sp^3d^2$  hybrid orbitals that lie **90°** apart
  - ☞ **six e<sup>-</sup> pairs (from VSEPR theory)**
- e<sup>-</sup> pair arrangement = **octahedral**  
Molecular shape = **octahedral**

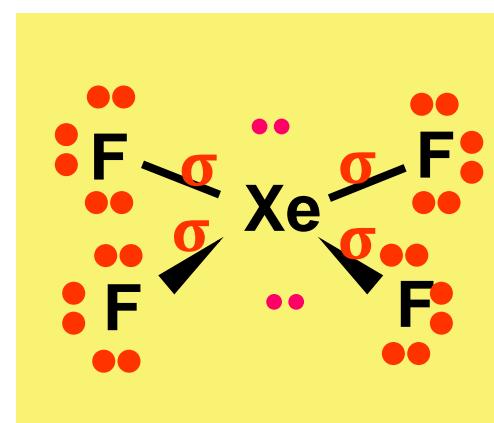
## **EXAMPLE :5**

**Describe a hybridization scheme for the central Xe atom in the molecule  $\text{XeF}_4$  that is consistent with the molecular shape.**



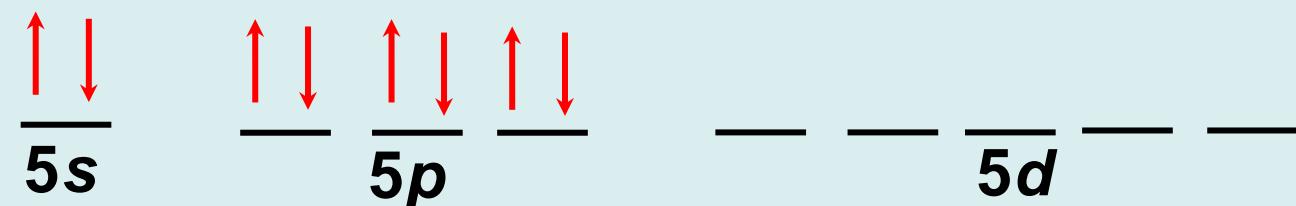
e<sup>-</sup> configuration of F : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>5</sup>

e<sup>-</sup> configuration of Xe : [Kr]4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>6</sup>

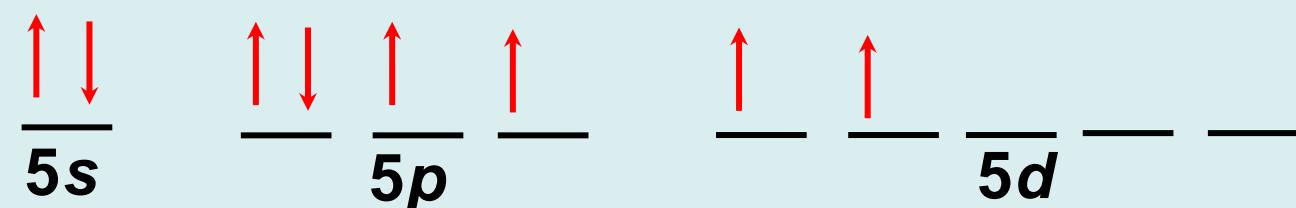


### Valence e<sup>-</sup> in Xe atom:

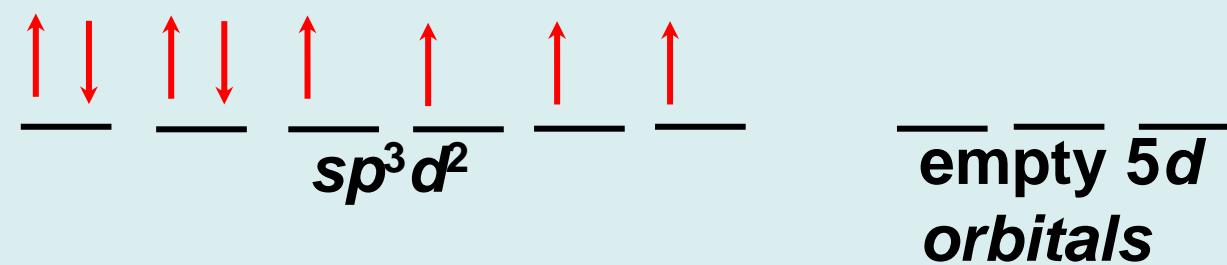
Ground state:



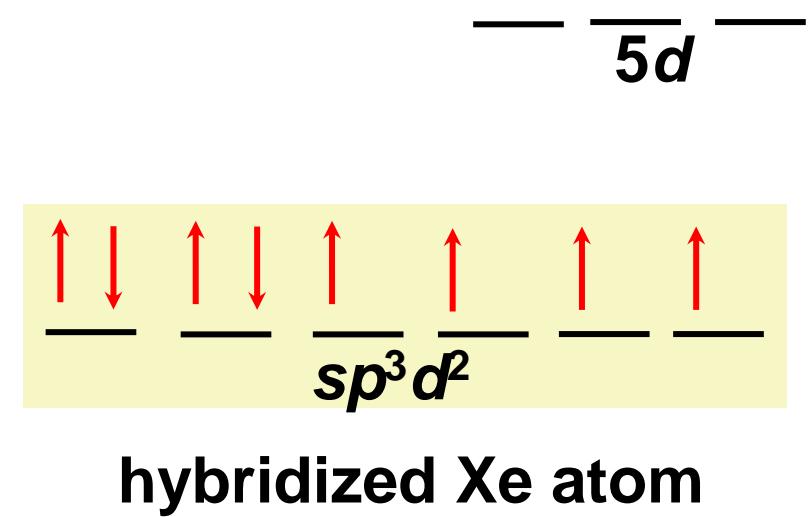
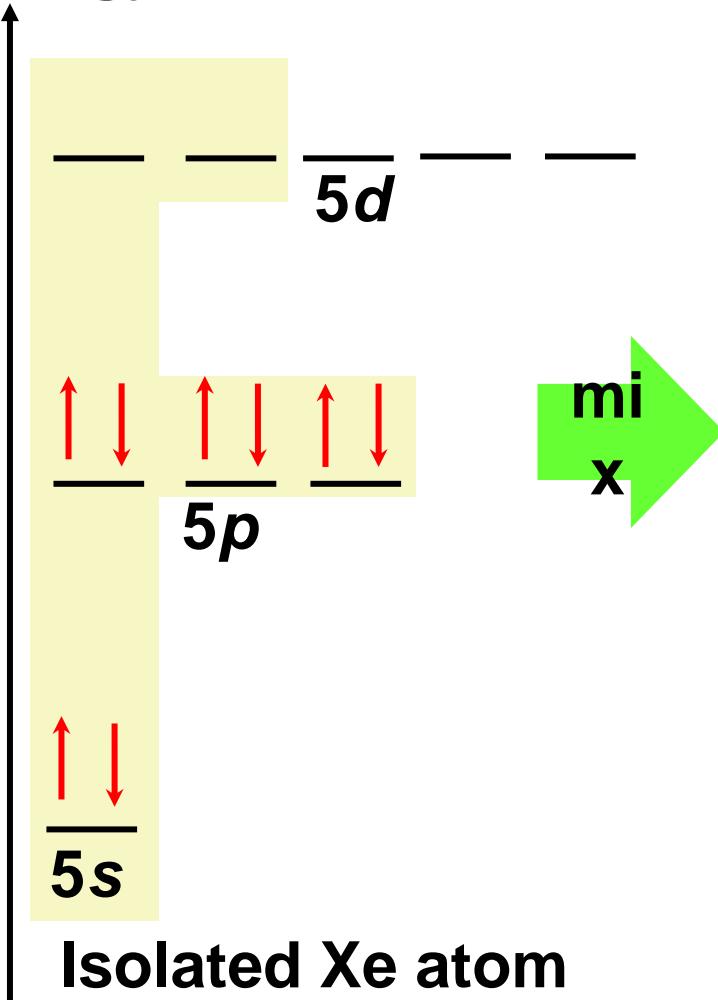
Excited state:

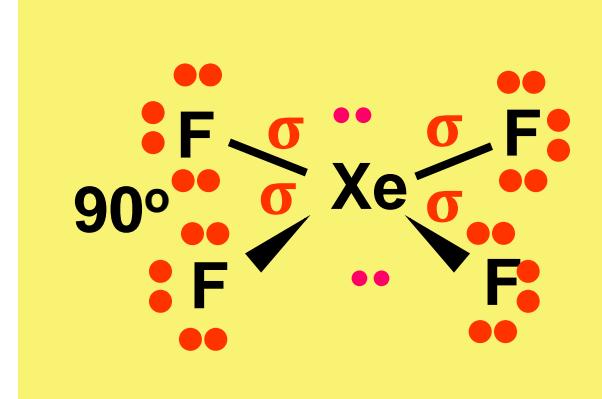
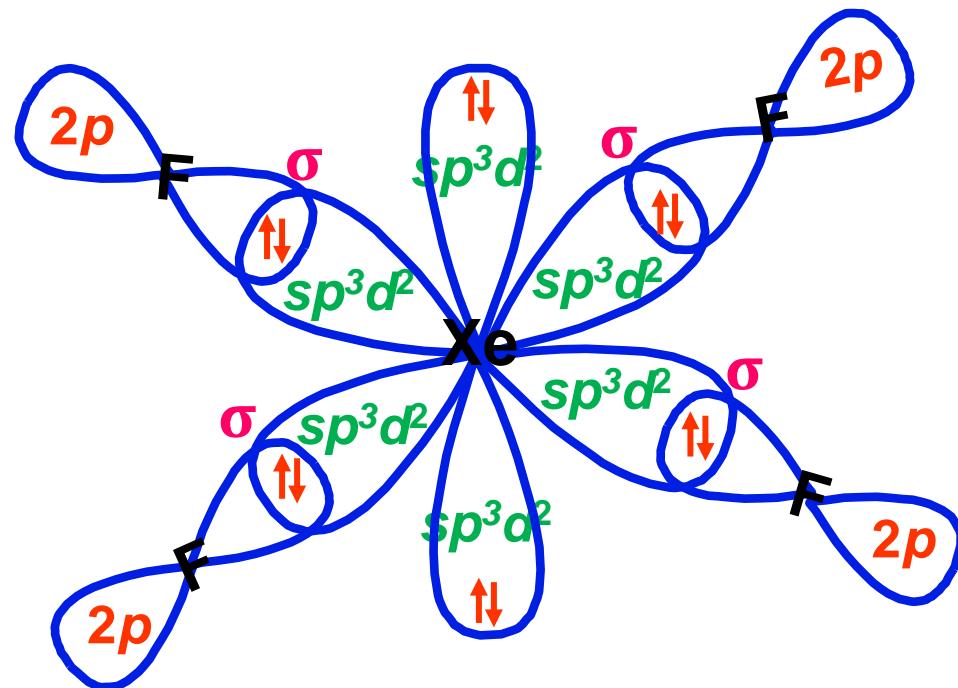


$sp^3d^2$   
hybridization:



Energy





Each Xe–F sigma bond formed by:

Overlap of **one  $sp^3d^2$**  hybrid of Xe atom and **one  $2p$**  orbital of F atom

Electron pair arrangement  
Molecular shape

: octahedral  
: square planar

# MOLECULES CONTAINING MULTIPLE BONDS

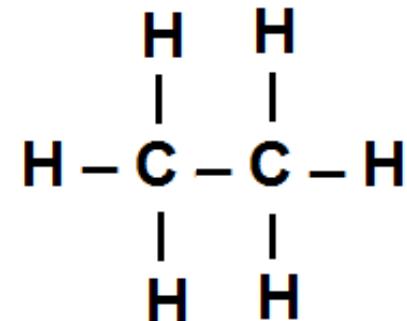


ethane

Tetrahedral

H-C-H about  $109.5^\circ$

$sp^3$

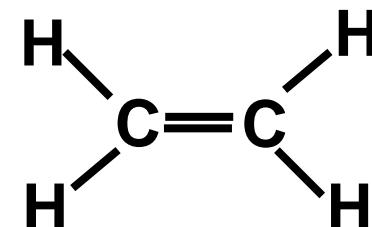


ethylene

Trigonal planar

H-C-H is  $120^\circ$

$sp^2$



acetylene

linear

H-C-H is  $180^\circ$

$sp$

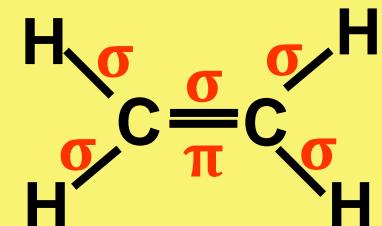


# BONDS IN C<sub>2</sub>H<sub>4</sub>

Ethylene (CH<sub>2</sub>=CH<sub>2</sub>)

e<sup>-</sup> configuration of C : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>

e<sup>-</sup> configuration of H : 1s<sup>1</sup>



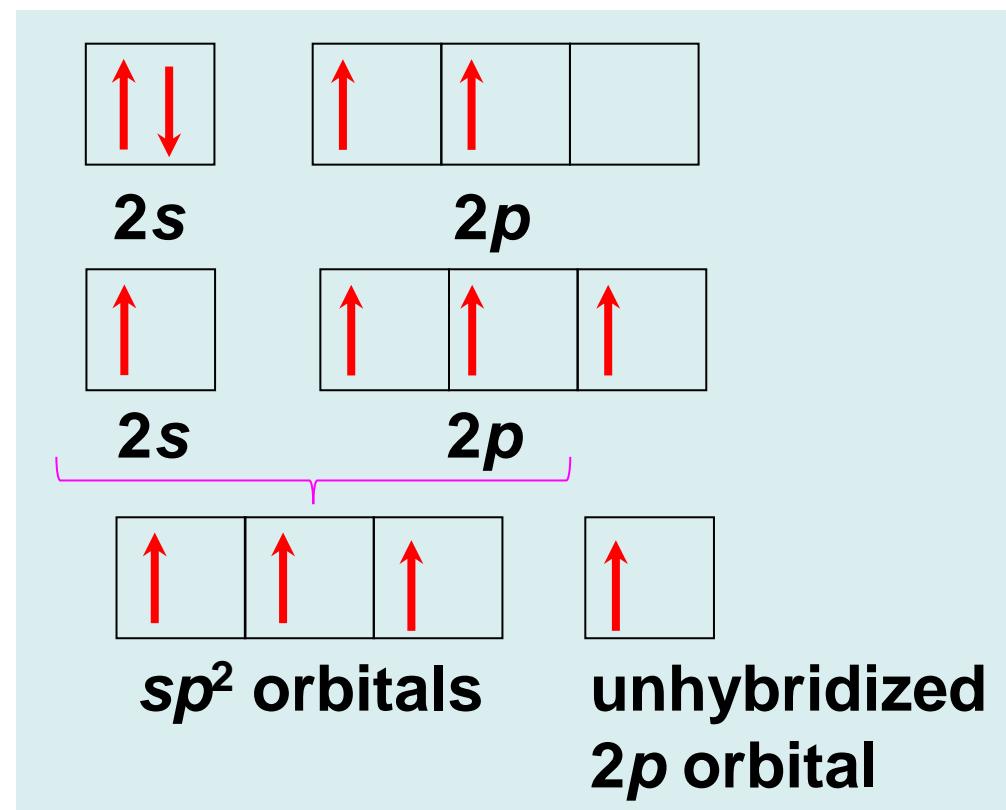
Valence e<sup>-</sup> in C:

Ground state:

Excited state:

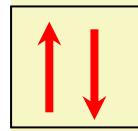
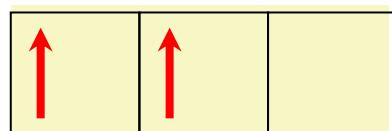
sp<sup>2</sup>

hybridization:

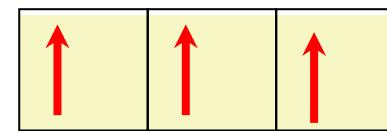
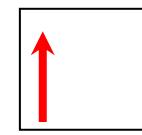
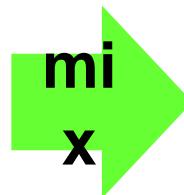


# $sp^2$ hybridization

Energy

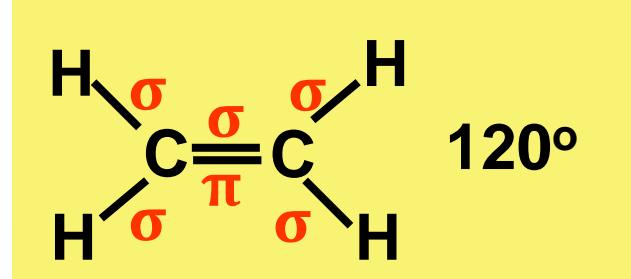
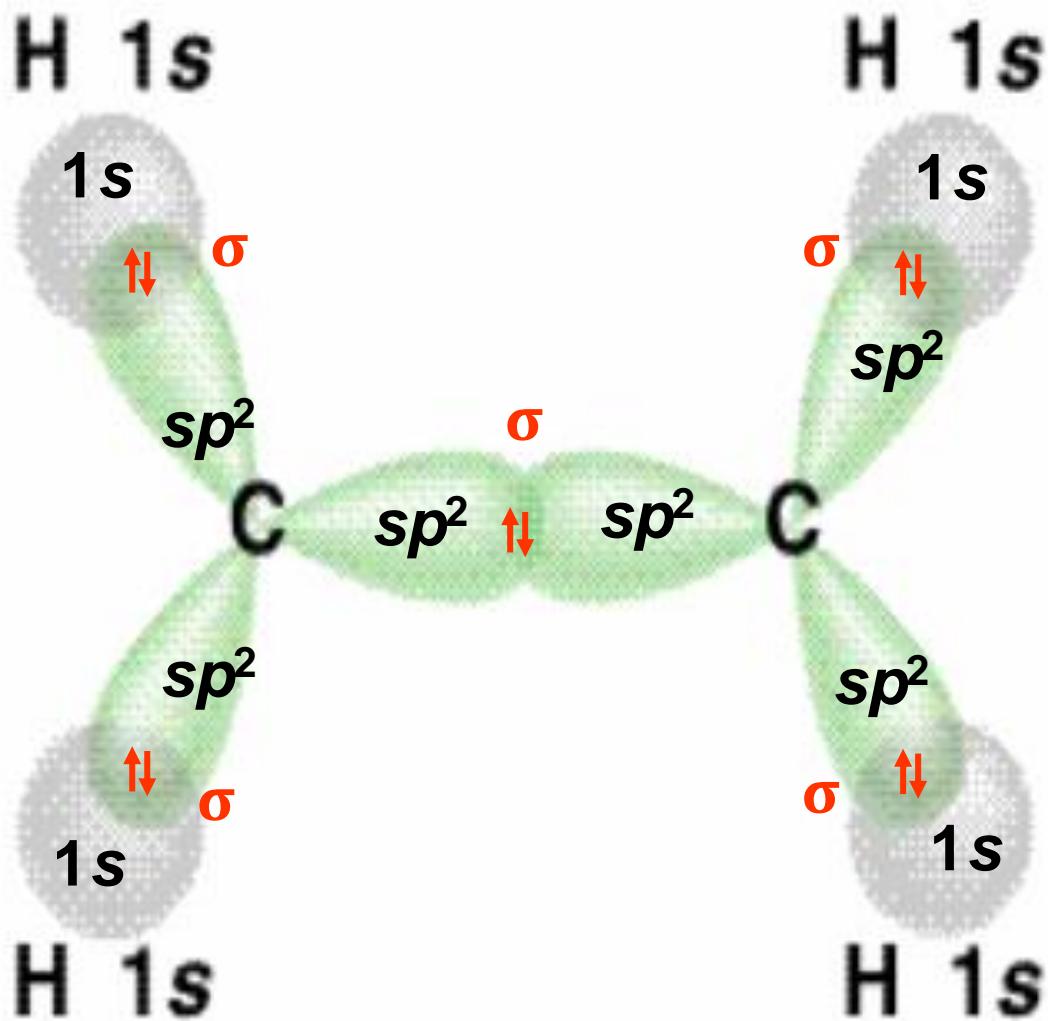


isolated C atom

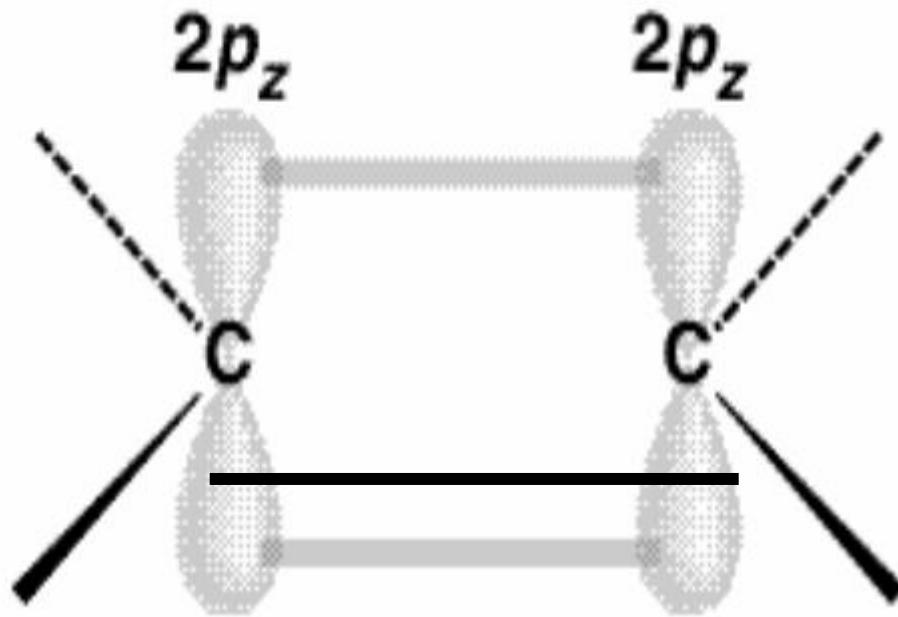


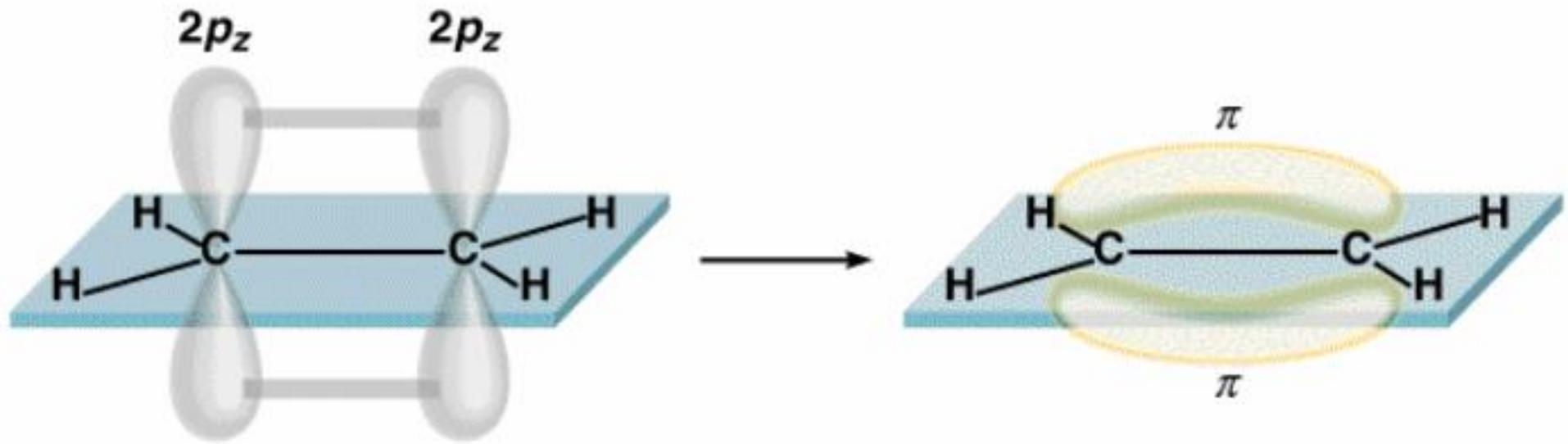
hybridized C atom

## $\sigma$ in Ethene ( $C_2H_4$ )

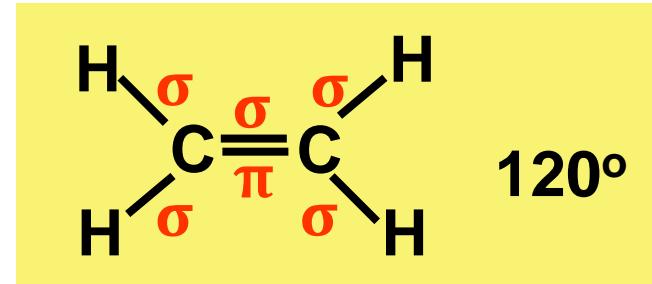
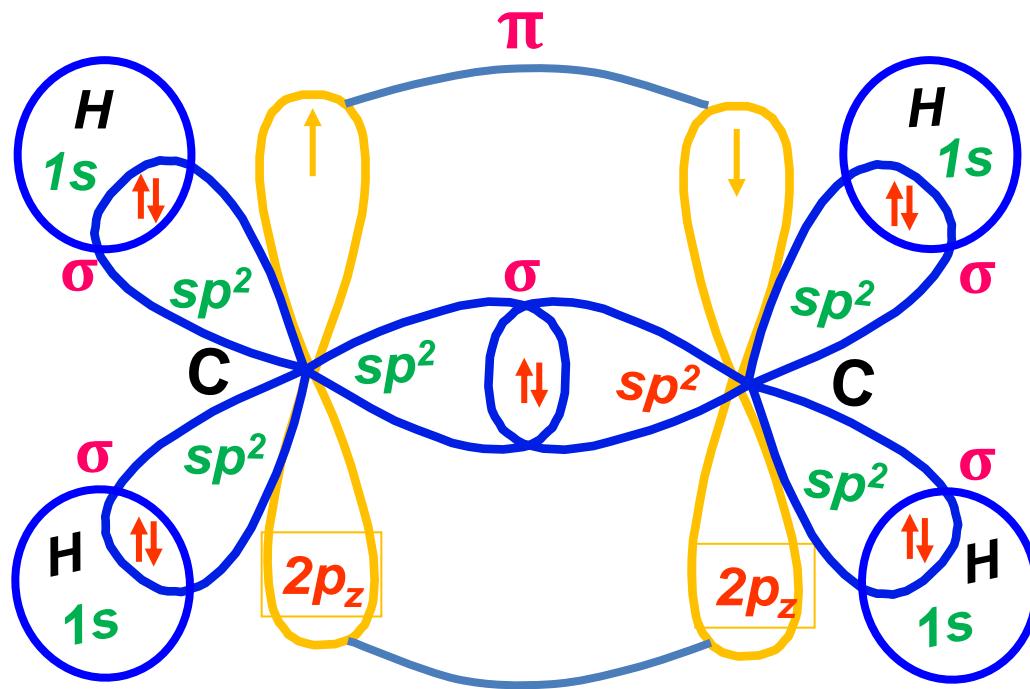


## $\pi$ in Ethene ( $C_2H_4$ )





- All 6 atoms are in the **same plane**
- Overlap of the **2p** orbitals **restricts rotation** of **C–C bond** and cause ethylene takes **planar structure**



### **σ-bond:**

C–H: overlap of  $sp^2$  of C with **1s** of H

C–C: overlap of  $sp^2$  of both C

### **π-bond in C=C bond:**

Overlap of **unhybridized  $2p_z$**  of C with another **unhybridized  $2p_z$**  of C

# BONDS IN C<sub>2</sub>H<sub>2</sub>

Acetylene (CH≡CH)

e<sup>-</sup> configuration of C : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>

e<sup>-</sup> configuration of H : 1s<sup>1</sup>

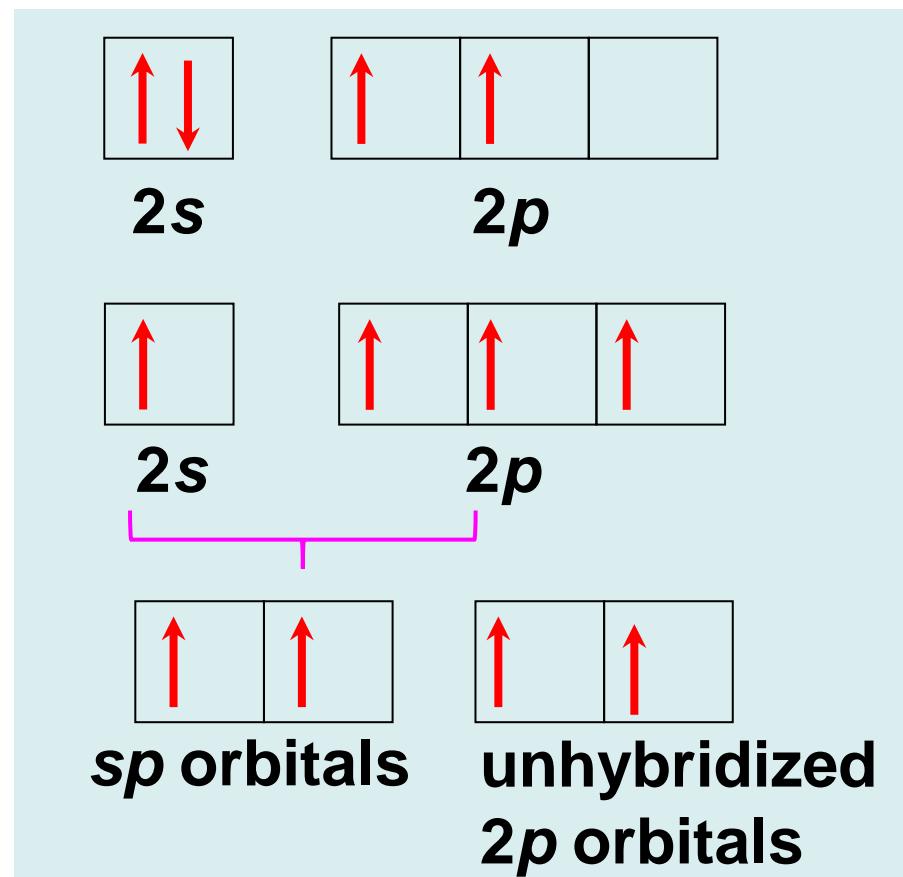


Valence e<sup>-</sup> in C:

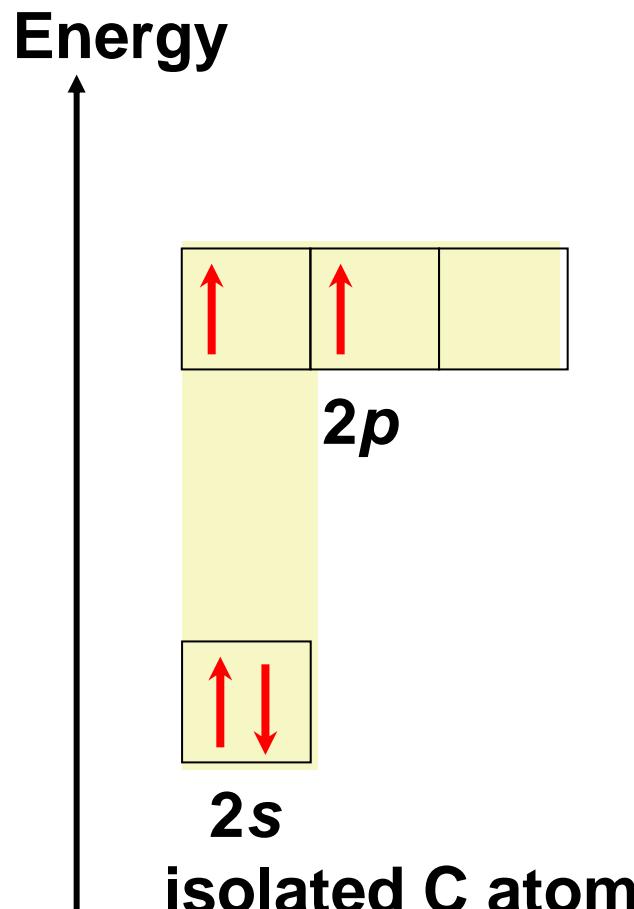
Ground state:

Excited state:

sp hybridization:

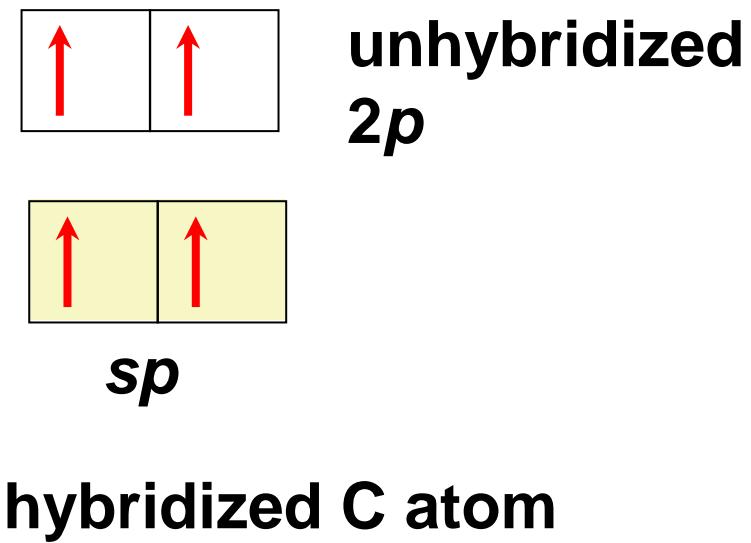


# *sp* hybridization

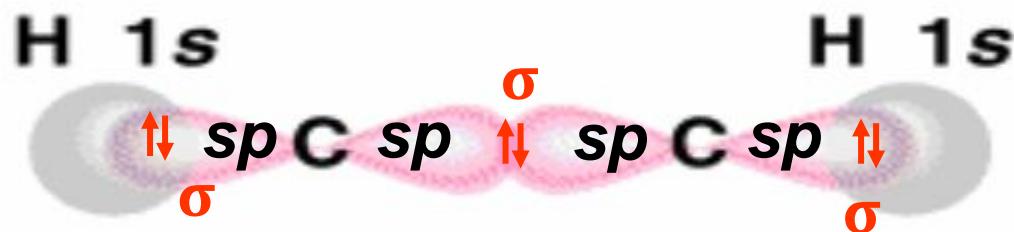
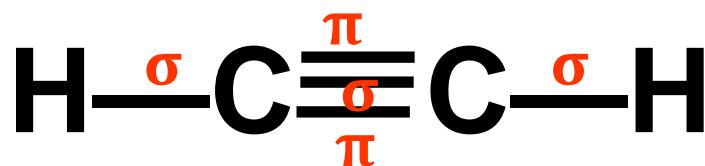


mix

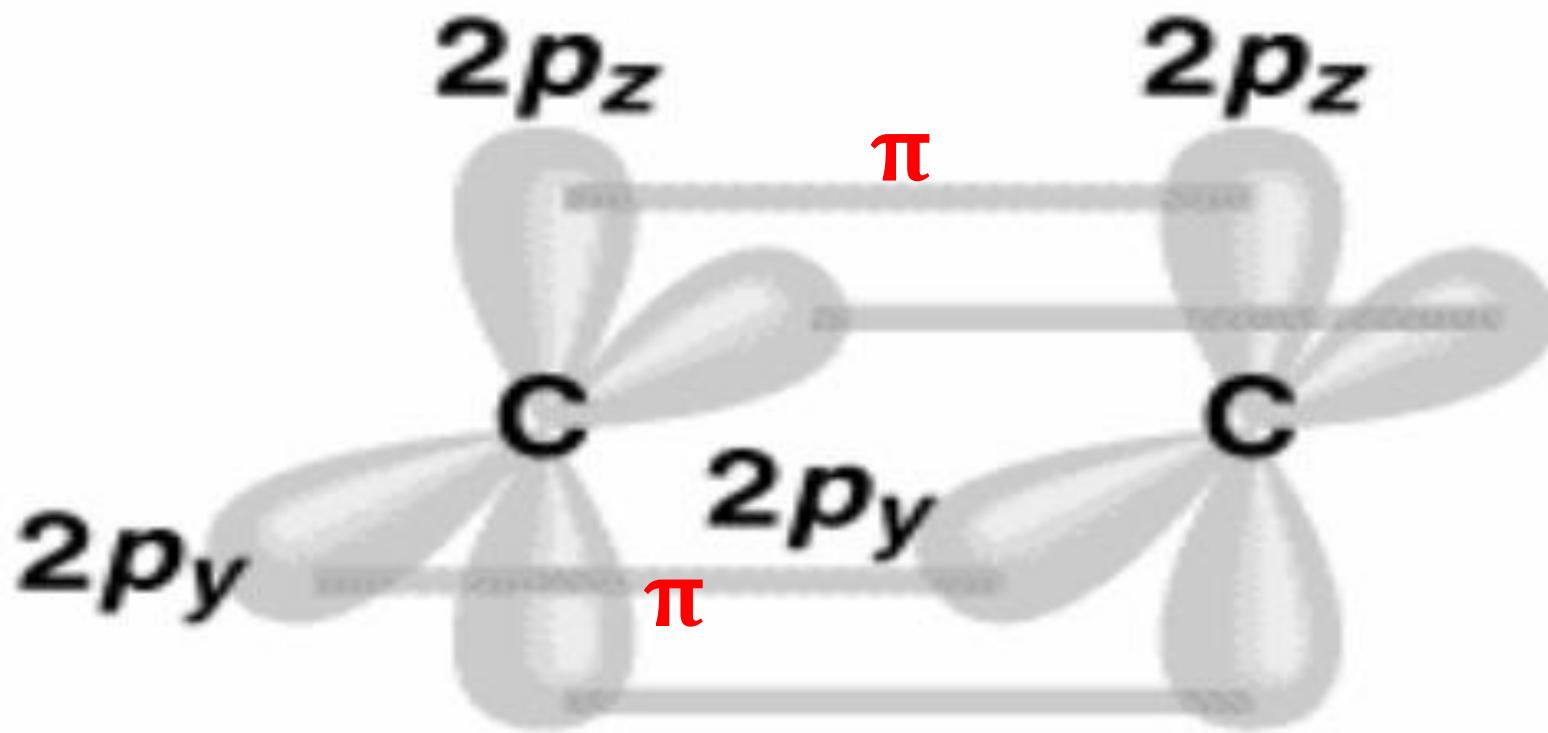
A large green arrow points from left to right, with the word 'mix' written vertically along its center.

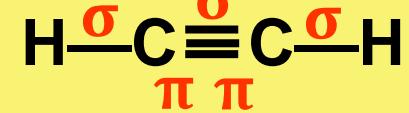
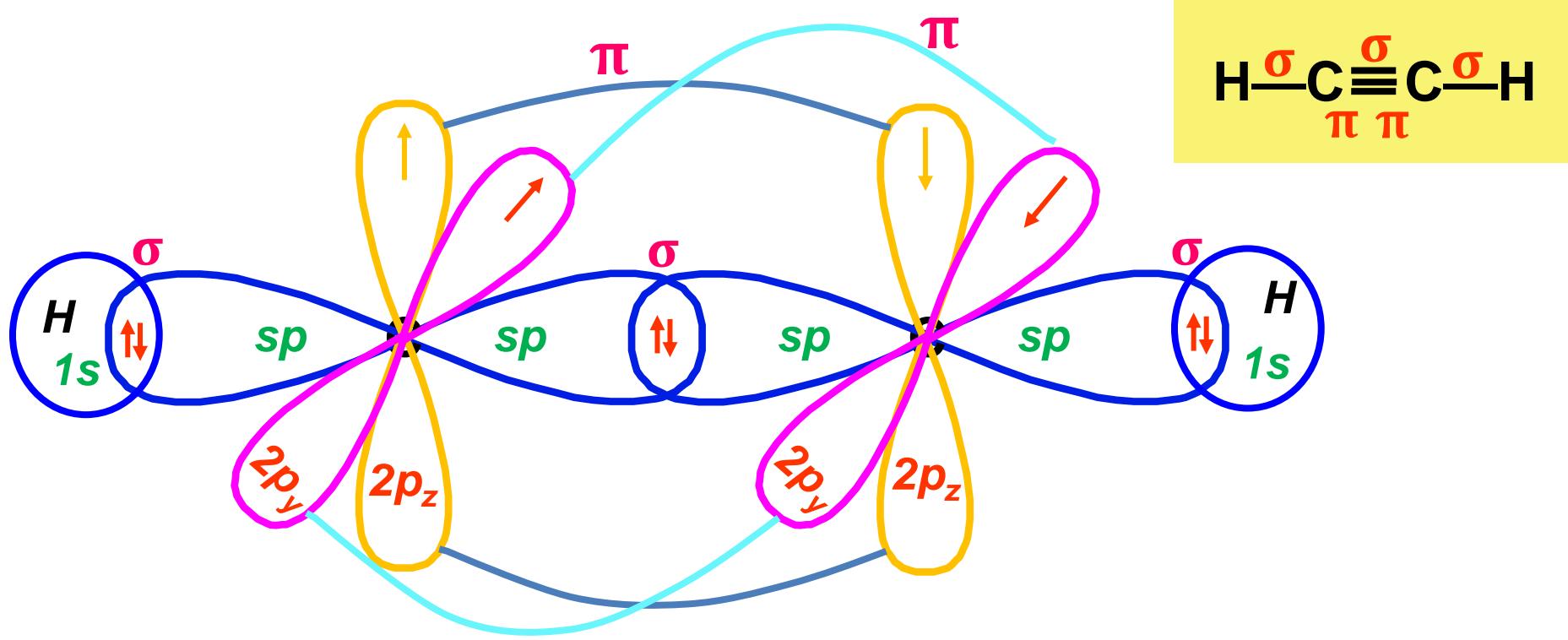


$\sigma$  in Ethyne ( $\text{C}_2\text{H}_2$ )



## $\pi$ bond in Ethyne ( $C_2H_2$ )





### **σ-bond:**

C–H: overlap of **sp** of C with **1s** of H

C–C: overlap of **sp** of both C

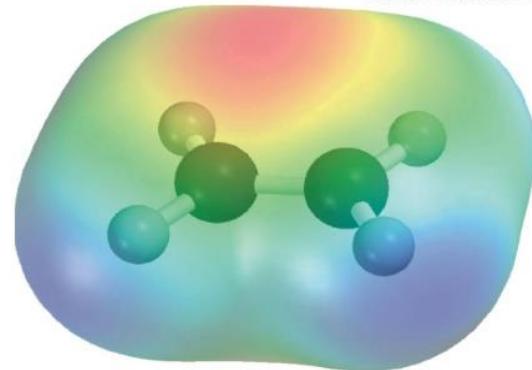
### **π-bond:**

C–C: overlap of **2p<sub>y</sub>** with **2p<sub>y</sub>** and  
overlap of **2p<sub>z</sub>** with **2p<sub>z</sub>**

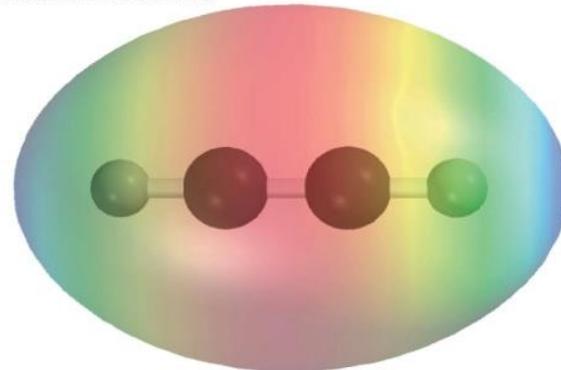
# EXAMPLE :6

**Describe the hybridization in  $\text{CO}_2$ .  
Draw the orbitals overlap of  $\sigma$  and  $\pi$  bonds.**

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.



Ethylene

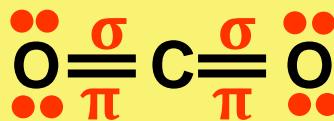


Acetylene



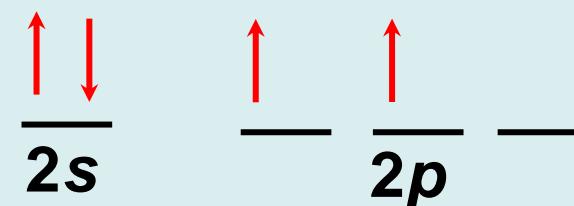
e<sup>-</sup> configuration of C : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>  
e<sup>-</sup> configuration of O : 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

Molecular shape:

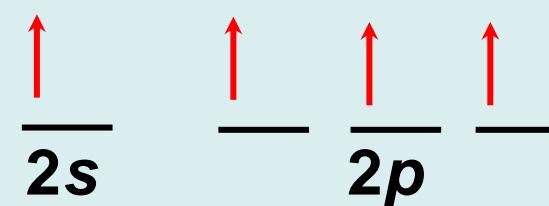


Valence e<sup>-</sup> in C atom:

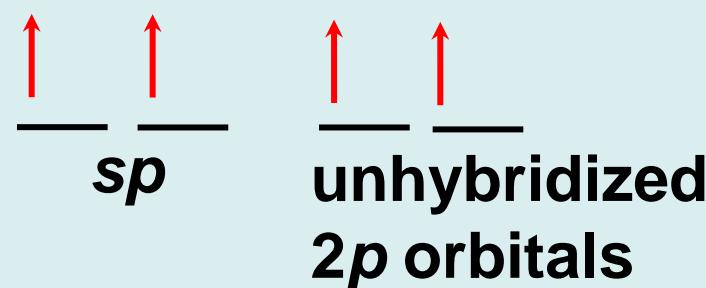
Ground state:

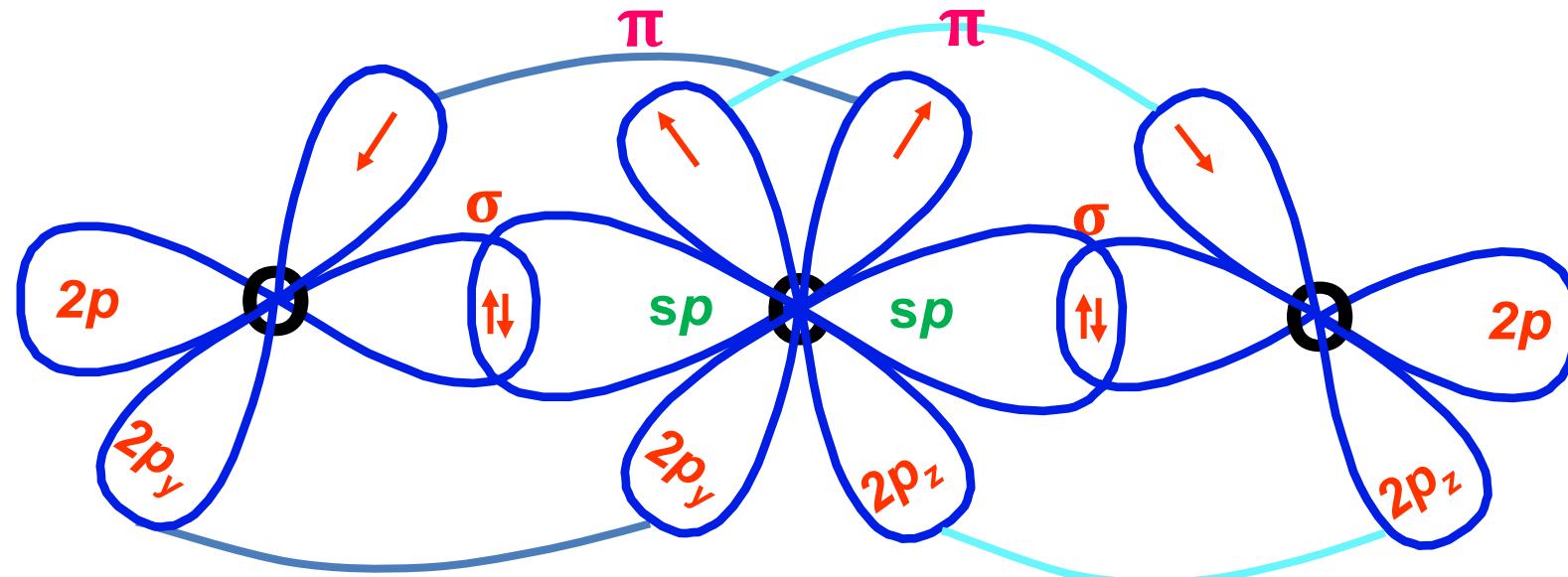
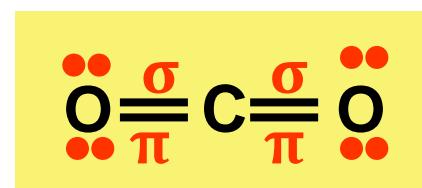


Excited state:



sp<sup>3</sup> hybridization:





### σ-bond:

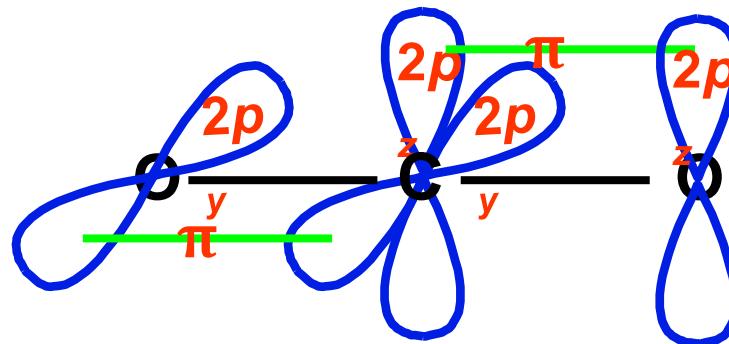
C–O: overlap of **sp** of C with **2p** of O

### π-bond:

C–O: overlap of **2p<sub>y</sub>** with **2p<sub>y</sub>** and  
overlap of **2p<sub>z</sub>** with **2p<sub>z</sub>**

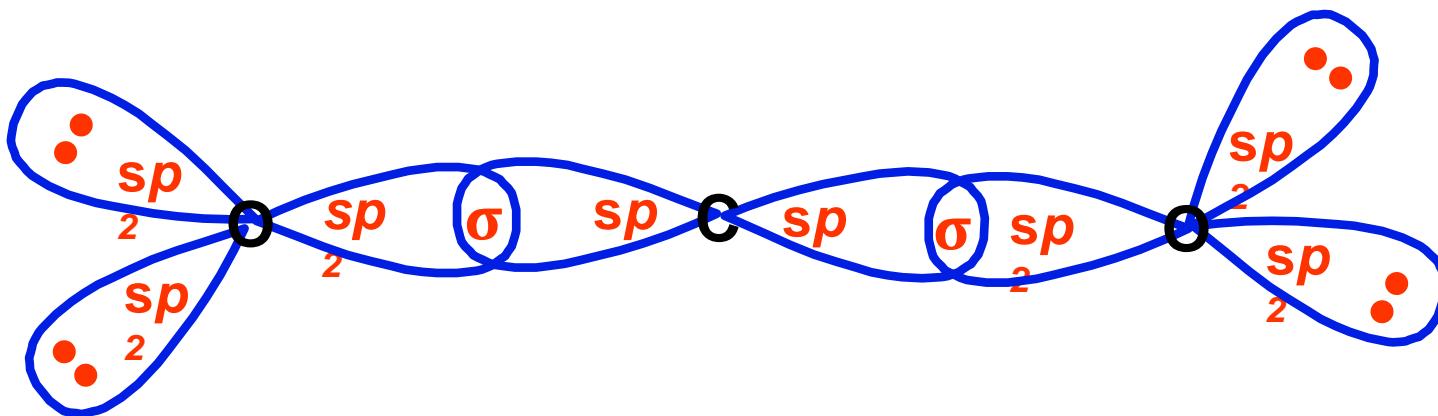
ANS:

$\pi$  bond in  $\text{CO}_2$



ANS:

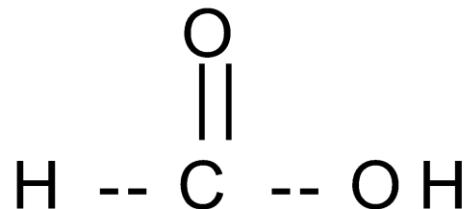
$\sigma$  Framework in  $\text{CO}_2$



# **EXERCISE:**

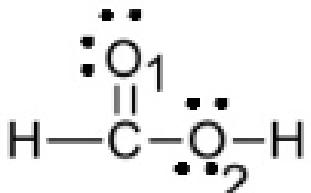
**DO IT!!!!**

**Formic acid is widely used in the preservation of biological specimens. Its chemical structure is shown below:**



**Draw and describe the formation of bonds  
by involving the overlapping of orbitals**

# Answer:



Type of hybrid:

C:  $\text{sp}^2$

$\text{O}_1$ :  $\text{sp}^2$

$\text{O}_2$ :  $\text{sp}^3$

C(ground state):

2s	2p

$\text{O}_1$ (ground state):

2s	2p

$\text{O}_2$ (ground state):

2s	2p

C(excited state):

2s	2p

$\text{O}_1$ (excited state):

2s	2p

$\text{O}_2$ (excited state):

2s	2p

C(hybrid state):

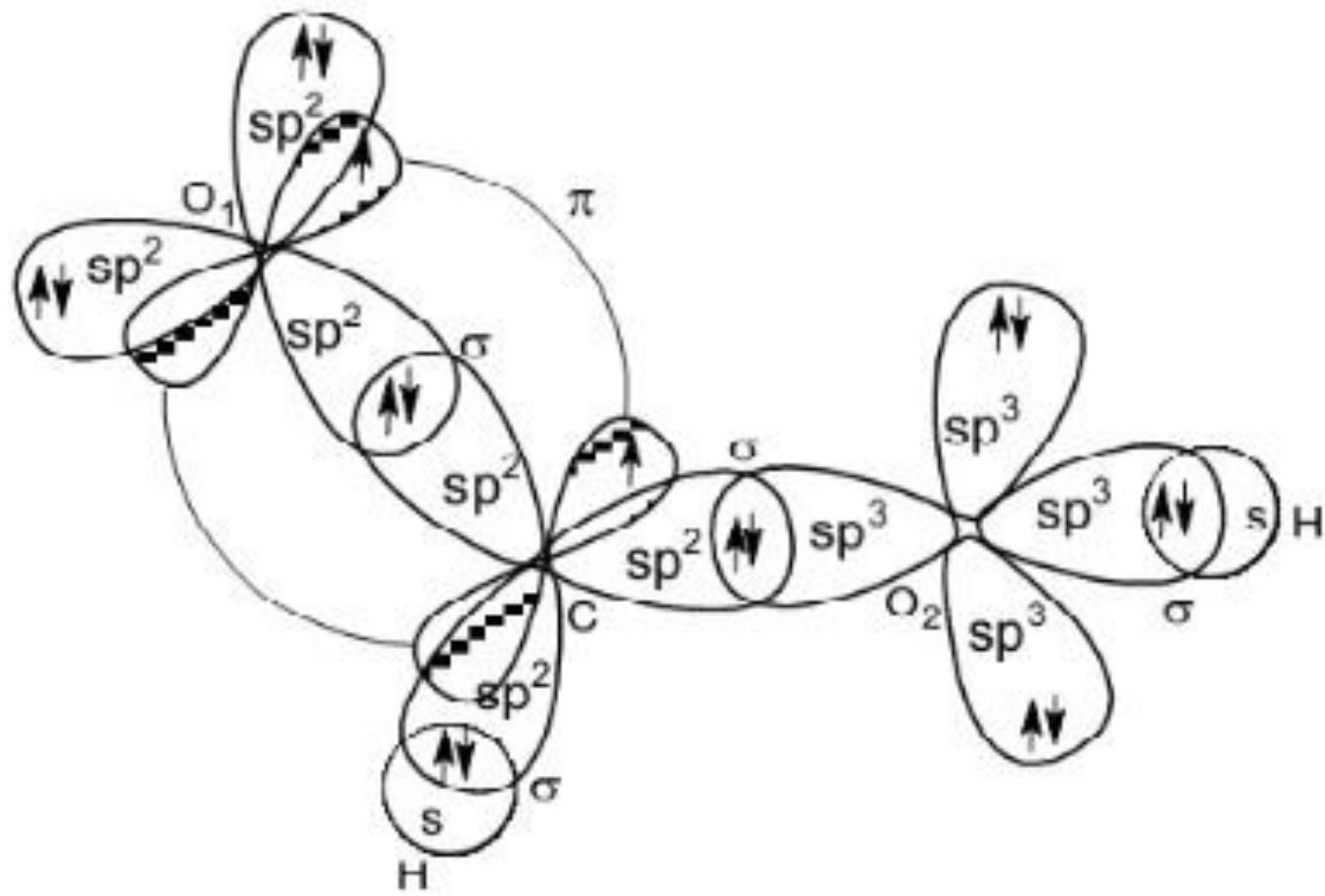
$\text{sp}^2$	p

$\text{O}_1$ (hybrid state):

$\text{sp}^2$	p

$\text{O}_2$ (hybrid state):

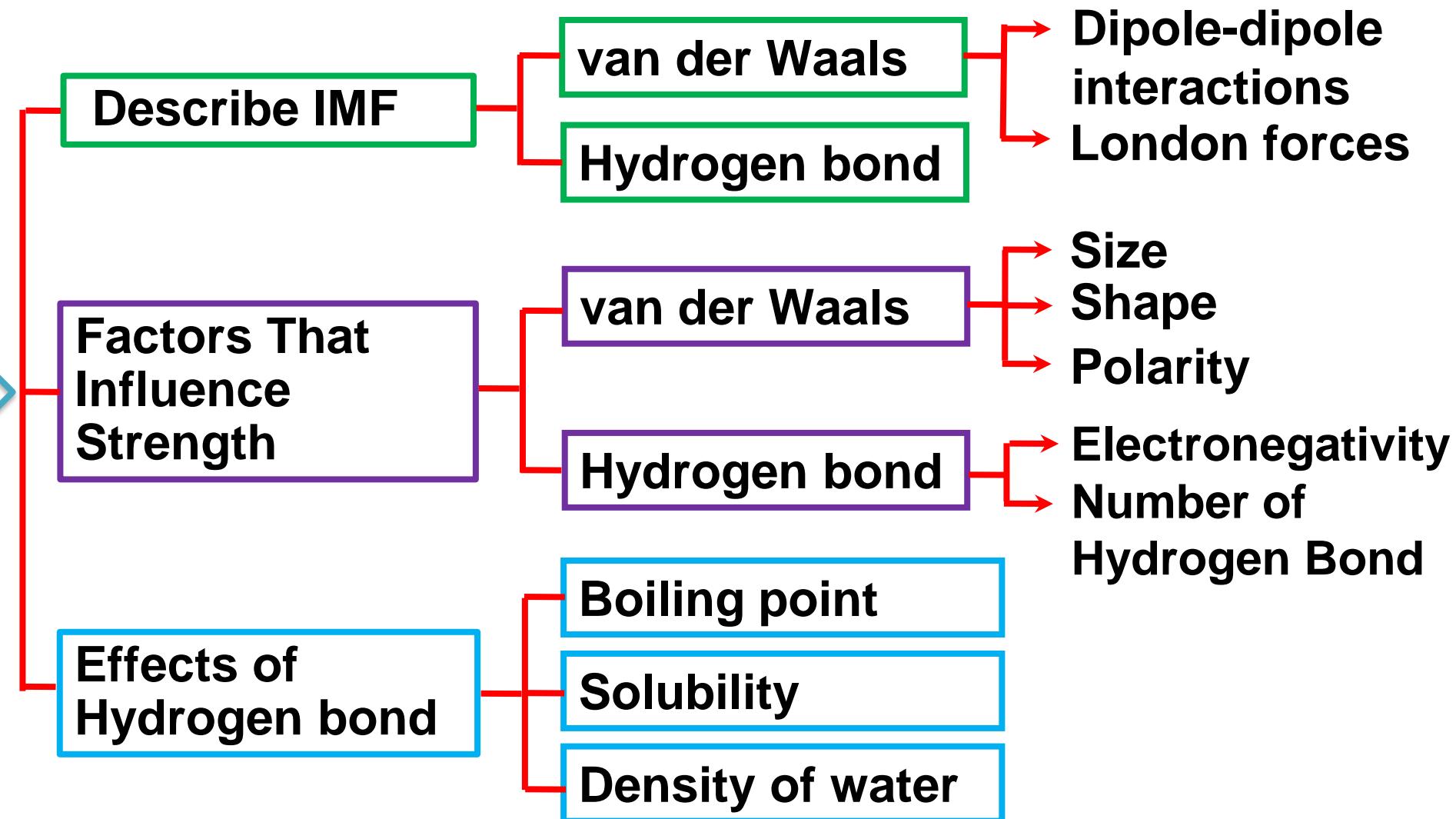
$\text{sp}^3$	p



# **4.0 CHEMICAL BONDING**

## **4.4 INTERMOLECULAR FORCES**

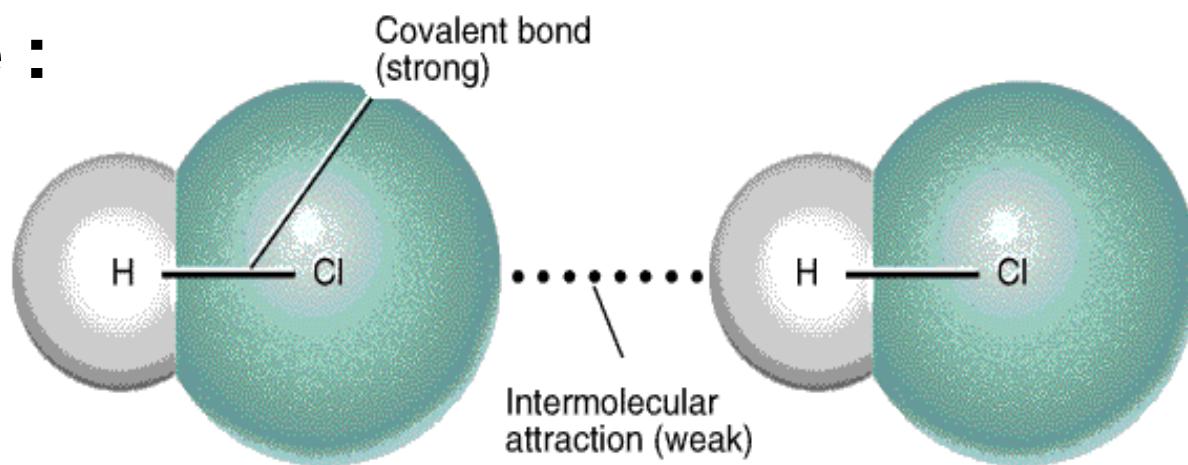
## 4.4 Intermolecular Forces (IMF)



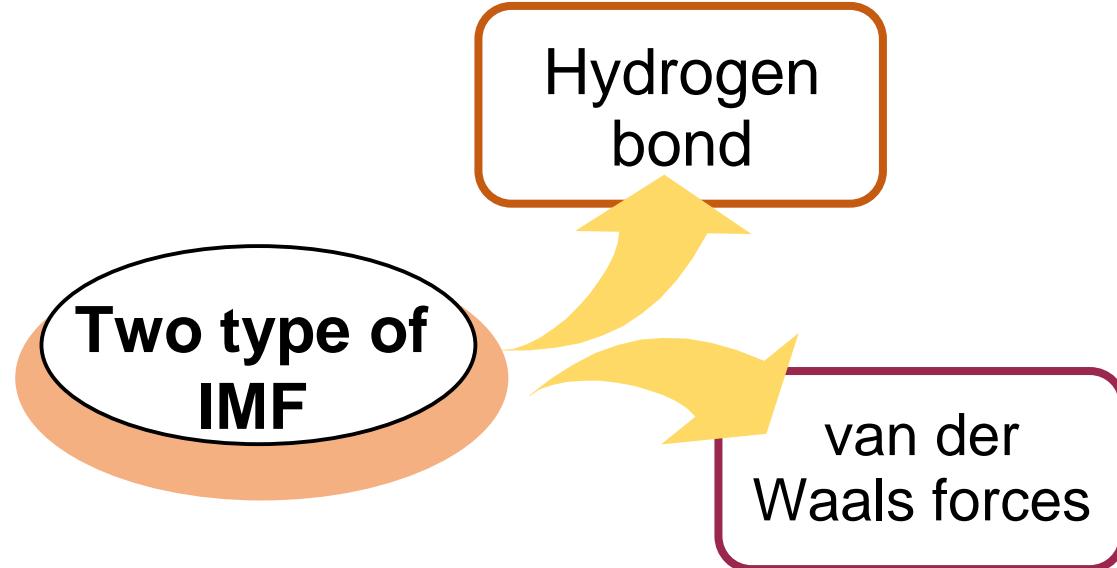
# INTERMOLECULAR FORCES

- Attractive forces between neighbouring particles (atoms, molecules or ions).
- Exist when the molecules are sufficiently close to each other.
- Relatively weaker than intramolecular forces (such as covalent bonds).

**Example :**

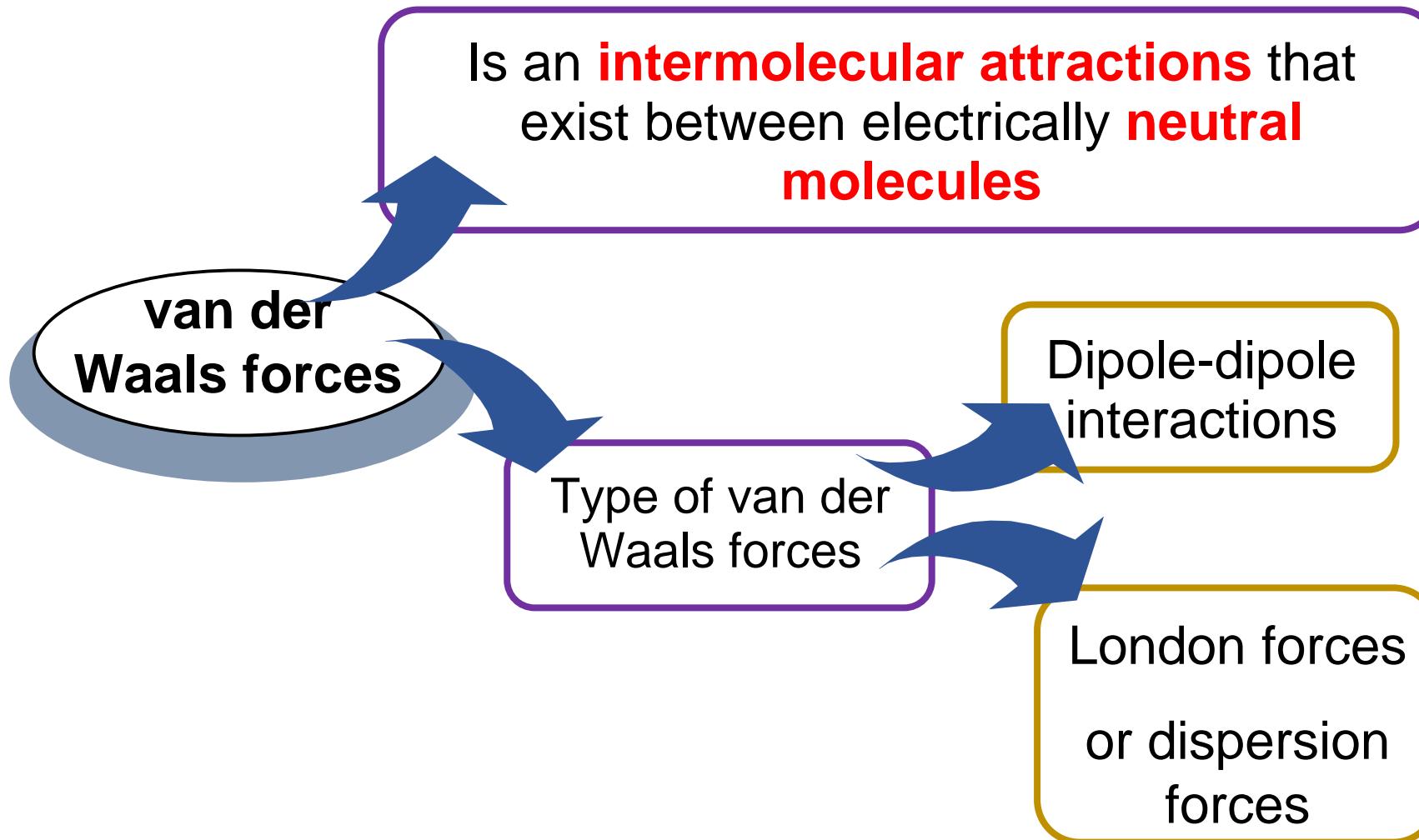


# TYPE OF INTERMOLECULAR FORCES



van der Waals forces are **WEAKER** than hydrogen bond

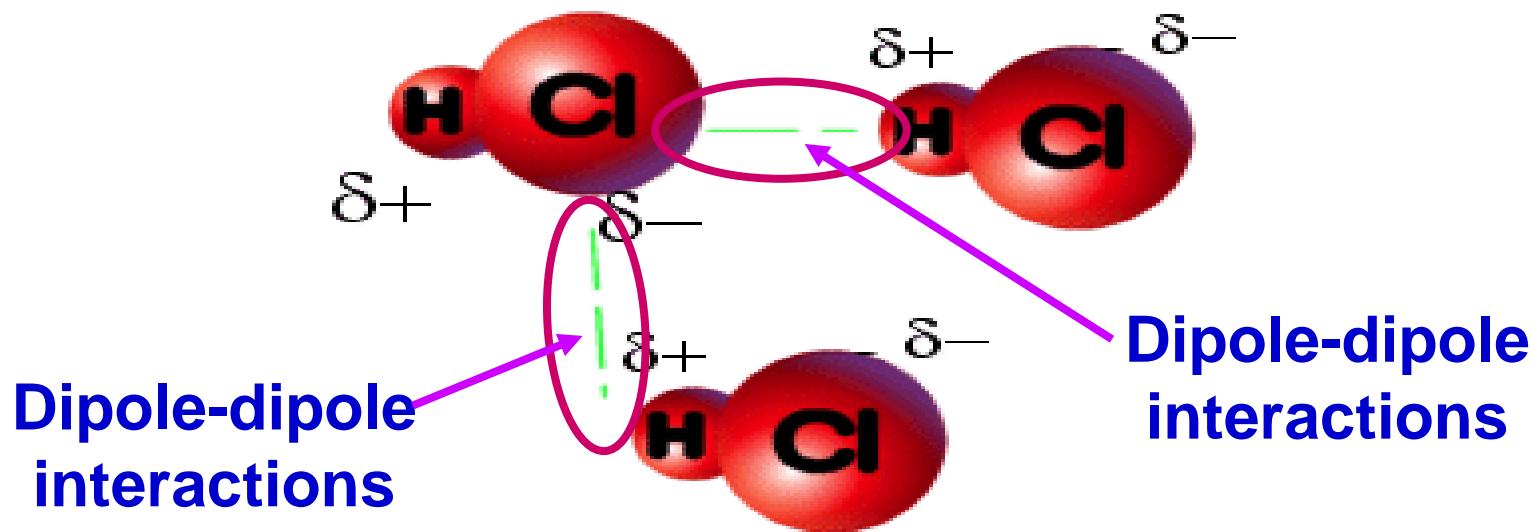
# VAN DER WAALS FORCES



# DIPOLE-DIPOLE INTERACTIONS

- The interactions arise from the attraction of the **permanently positive** and **negative end** of a neutral polar molecule.

Example :



- A **more polar** molecules (have **large dipole moment**), has a **stronger** dipole-dipole interactions.
- More energy is needed to overcome the strong dipole-dipole interactions. Thus, its **boiling point increase**.

In conclusion, the **more polar** the molecules, the **stronger** the dipole-dipole interactions, the **higher the boiling point**.

## Example :

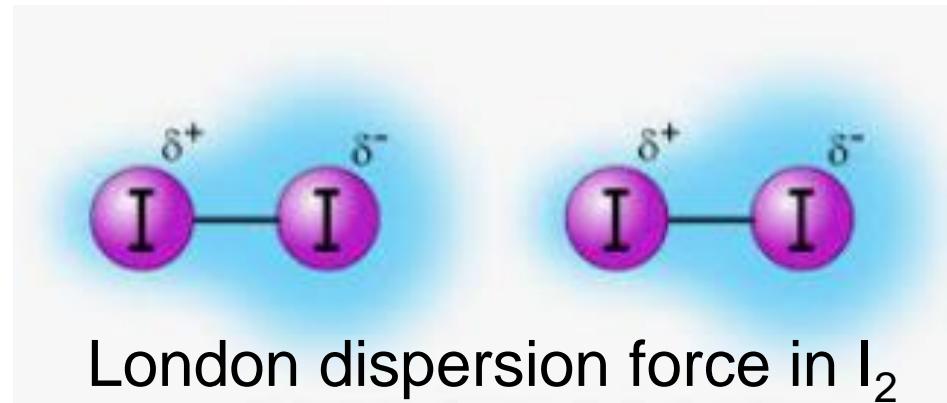
Substance	Molecular formula	$M_r$	Dipole moment (D)	Boiling point (K)
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	44	0.1	231
Acetaldehyde	$\text{CH}_3\text{COH}$	44	2.7	294

- Both propane and acetaldehyde have **same relative molecular mass**.
- However, **acetaldehyde** has **higher boiling point** than propane.
- Acetaldehyde is **polar molecule** and has **stronger dipole-dipole interactions** while propane is **non polar molecule** and has **London forces**.
- Dipole-dipole interactions is **stronger than London forces**. Therefore, the boiling point of acetaldehyde is higher than propane.

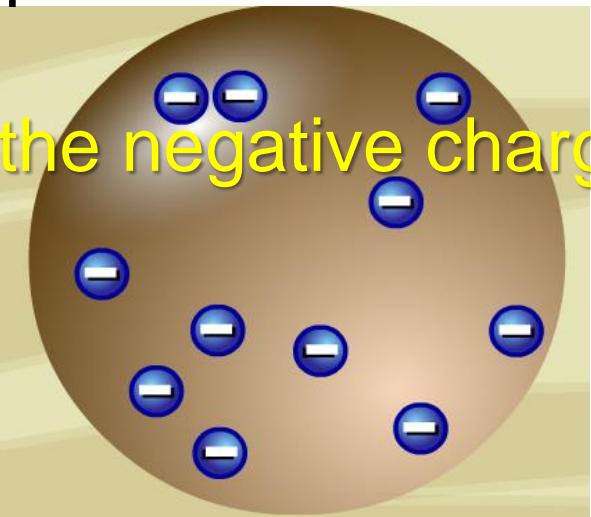
# LONDON FORCES @ DISPERSION FORCES

- Is a **weak temporary** forces of attraction that occur between **polar** and **non-polar** molecules.
- Exist in **all** atoms and molecules.
- The forces arise because electrons in atoms or molecules are in **constant motion**.
- Are weak because the **temporary dipole changes** with the motion of the electrons.

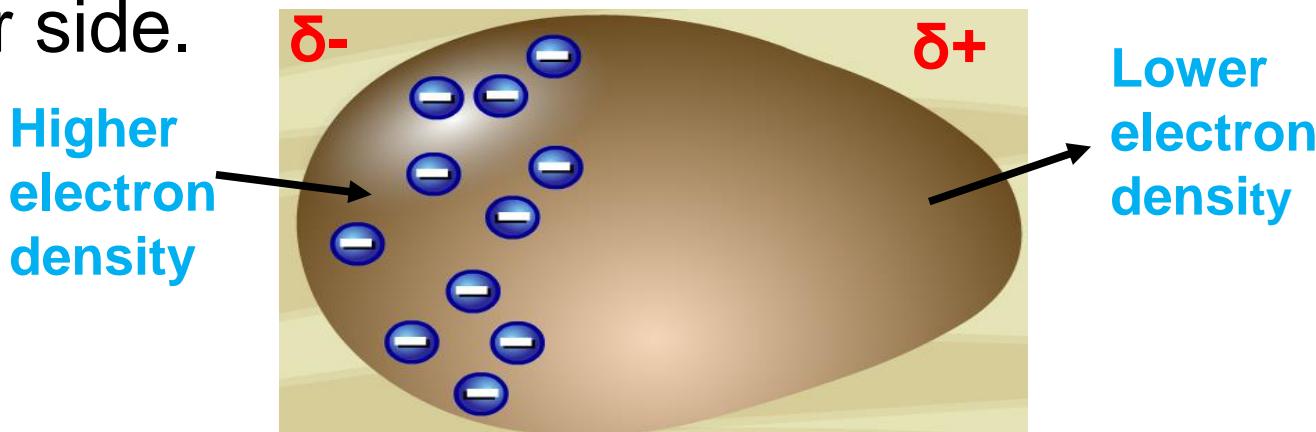
**Example :**



- An atom has protons in its nucleus and electrons surrounding the nucleus.
- On average, **the negative charge** of the atom is spread evenly around the nucleus.

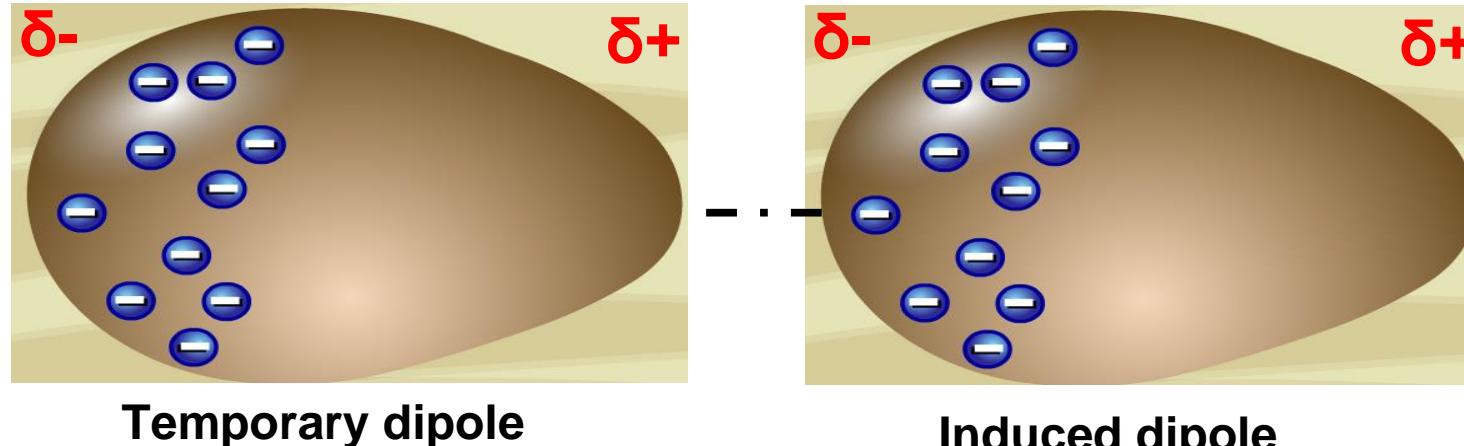


- At any instant, one side of the molecule has higher electron density than the other side.



- The atoms or molecules become a small instantaneous (temporary) dipole.

- The temporary dipole can induce a similar dipole on a neighboring atom and can be attracted to one another



- This interaction is called London Forces @ Dispersion Forces and only significant when atoms are close together.

# HYDROGEN BOND

---

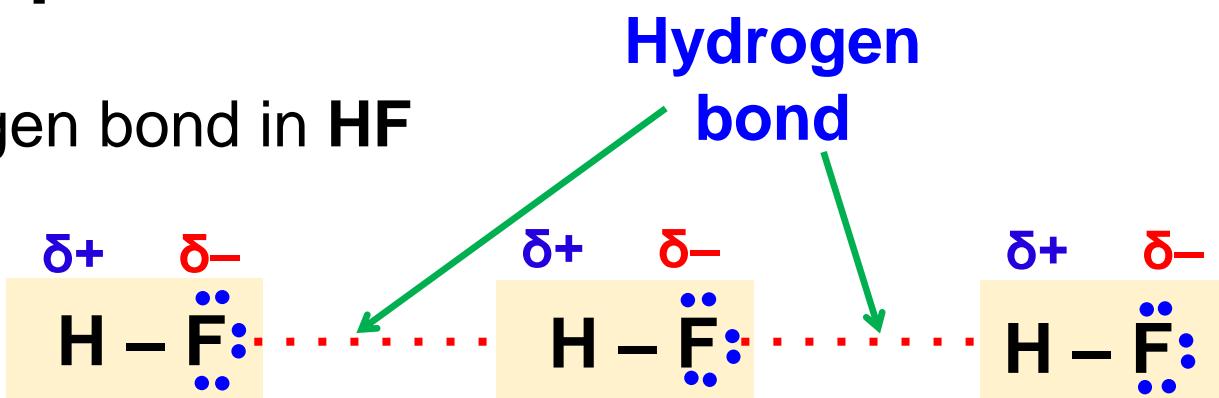
- Hydrogen bond is a type of intermolecular forces of **attraction between a hydrogen atom** that **bonded to highly electronegative atom (F, O or N)** AND **highly negative atom (F, O or N)** of another molecule.



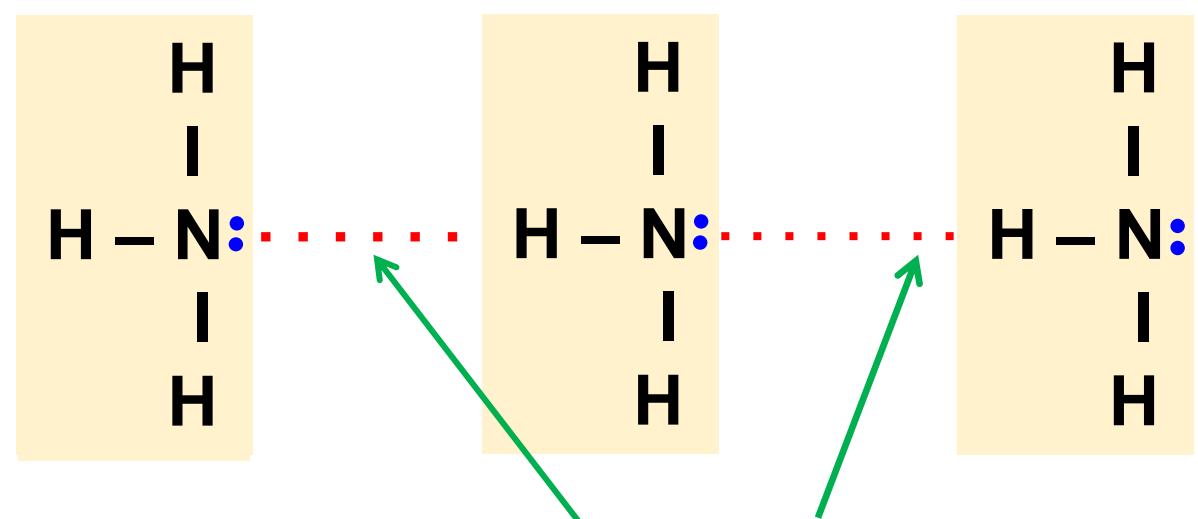
- Hydrogen bonds are **stronger** than van der Waals forces but **weaker** than covalent bonds.

## Example :

a) Hydrogen bond in  $\text{HF}$



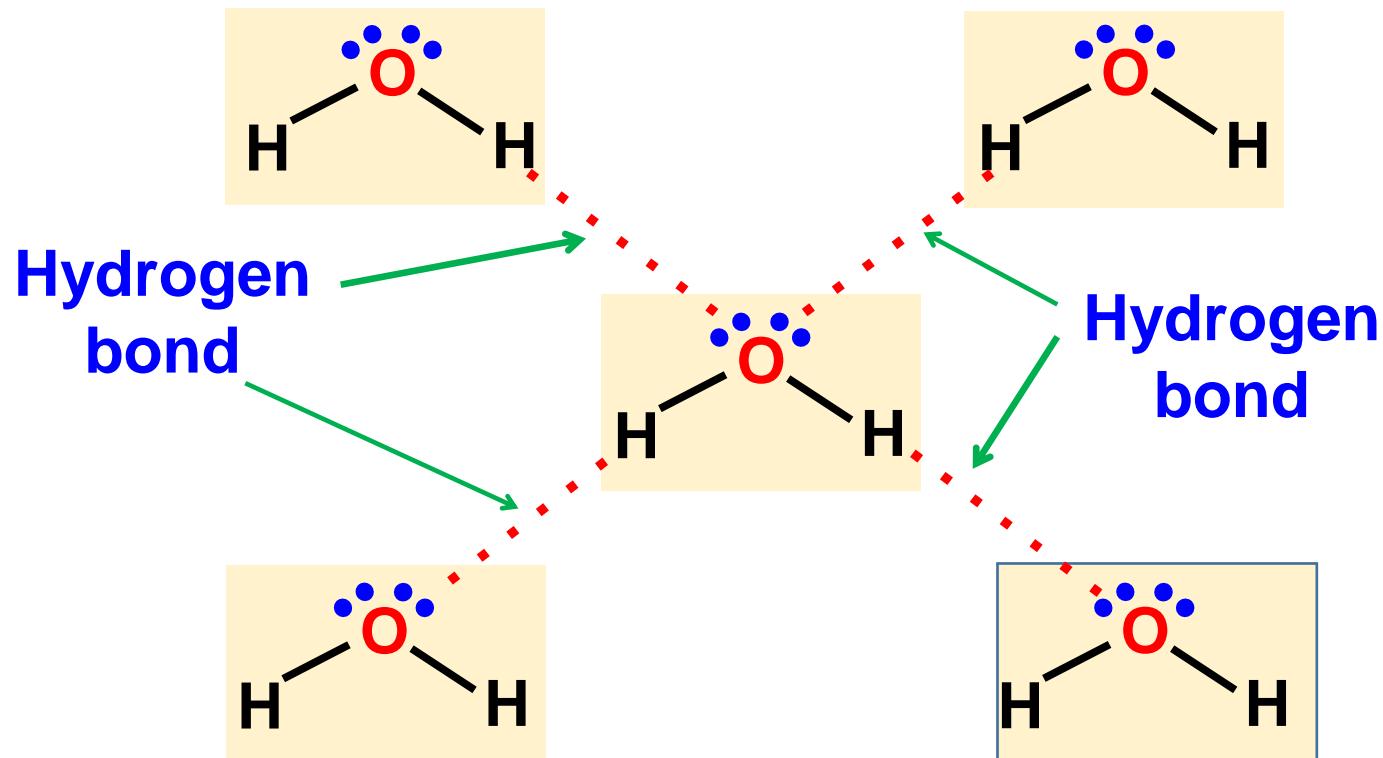
b) Hydrogen bond in  $\text{NH}_3$



**Hydrogen  
bond**

## Example :

c) Hydrogen bond in  $\text{H}_2\text{O}$



## Example :

Hydrogen bond between HF and H <sub>2</sub> O	$\delta^+$ $\delta^-$ H - F: ..... $\delta^+$ $\delta^-$ $\delta^+$ H - O - H
Hydrogen bond between NH <sub>3</sub> and H <sub>2</sub> O	H   H - N - H ..... :O - H
Hydrogen bond between NH <sub>3</sub> and HF	H - F: ..... H - N - H

# ENRICHMENT QUESTION

1. Which of the covalent compounds can form hydrogen bonds between molecules.
  - A. HCl
  - B. PH<sub>3</sub>
  - C. HBr
  - D. HF

# ENRICHMENT QUESTION

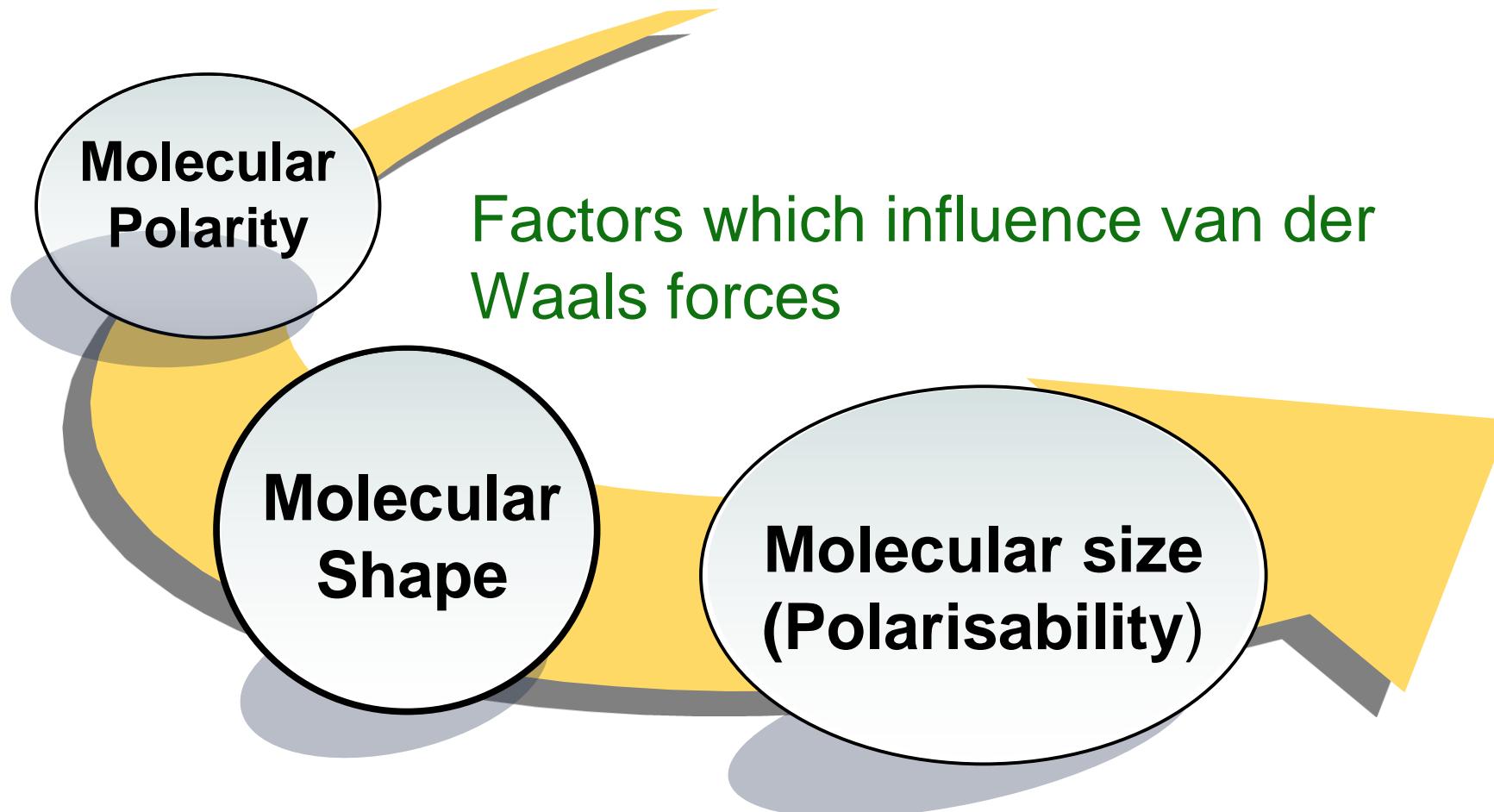
2. Which of the following compounds has van der Waals forces only?
  - A. Water
  - B. Alcohol
  - C. Tetrachloromethane
  - D. Magnesium chloride

# ENRICHMENT QUESTION

3. By referring to the following table, which of the following answers is correct?

	Types molecules	London forces @ Dispersion forces	Dipole-dipole forces	Hydrogen bond
A	$\text{CH}_3\text{OCH}_3$	/		
B	$\text{CH}_3\text{CH}_2\text{CH}_3$		/	/
C	$\text{CH}_3\text{CH}_2\text{Cl}$			/
D	$\text{CH}_3\text{NH}_2$	/	/	/

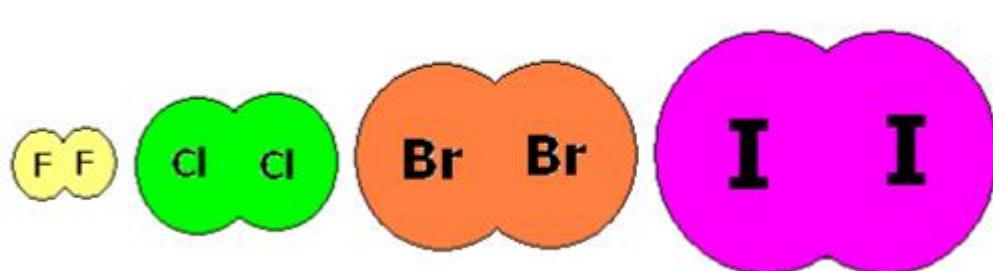
# FACTORS THAT INFLUENCE THE STRENGTH OF VAN DER WAALS FORCES



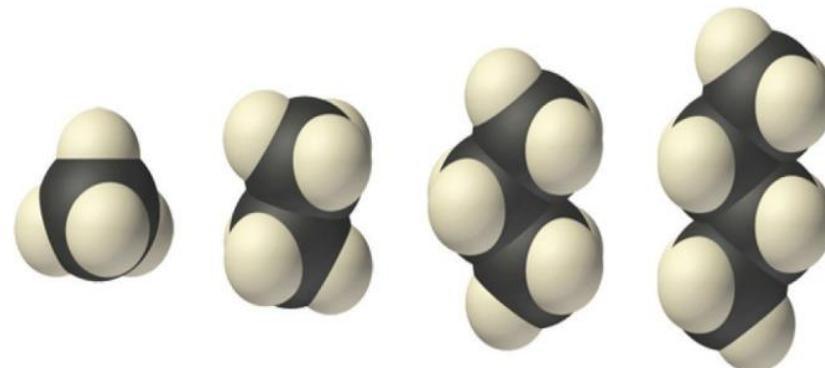
# MOLECULAR SIZE

- Depends on number of electron, which correlates closely with size/molar mass.
  - ✓ Molecules with bigger size / larger molar mass,
  - ✓ Have greater number of electrons,
  - ✓ Polarizability of molecule increases,
  - ✓ Stronger London force.

**Example :**



Diatomc molecule

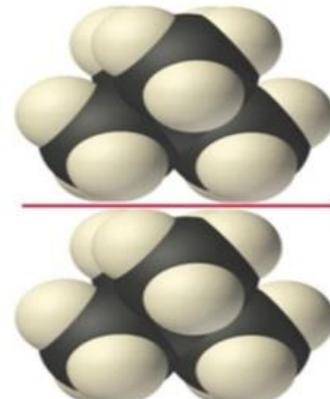


	Methane 16 g/mol –161.5°C	Ethane 30 g/mol –88.6°C	Propane 44 g/mol –42.1°C	n-Butane 58 g/mol –0.5°C
--	---------------------------------	-------------------------------	--------------------------------	--------------------------------

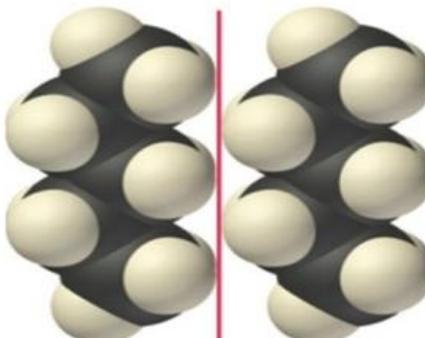
# MOLECULAR SHAPE

- For nonpolar molecules with the **same molar mass**:
  - ✓ The straight chain molecules have **larger contact surface area of molecules**.
  - ✓ Therefore it have stronger London force.

**Example :**



2,2-Dimethylpropane  
(neopentane)  
72 g/mol, 9.5°C



*n*-Pentane  
72 g/mol, 36.1°C

Comparable molecular weight, C<sub>5</sub>H<sub>12</sub>

## Example :

Compound	Molecular formula	Boiling point (°C)
Butane	$\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_3$	-0.5
2-methylpropane	$\begin{array}{c} \text{CH}_3 \text{CH} \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	-11.7

- Butane and 2-methylpropane have **same molecular weight**.
- Butane has a **higher boiling point** because it is a straight alkanes with **larger contact surface area** and thus, **stronger dispersion forces**.
- 2-methylpropane is a branched alkanes, more compact and has a smaller contact surface area. Hence, it has weaker dispersion forces.

# POLARITY OF MOLECULE

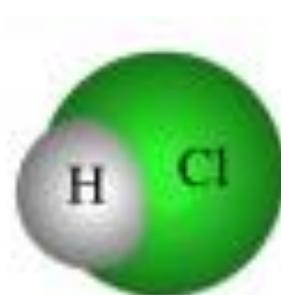
---

- The van der Waals forces between polar molecules are **stronger** compared to the forces between non-polar molecules with similar molar mass.
- Dipole-dipole interactions is stronger than London forces or dispersion forces.

**Example:**

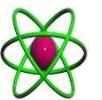
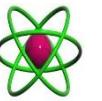


**vs**

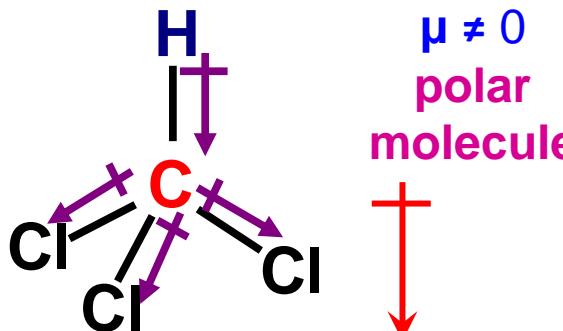
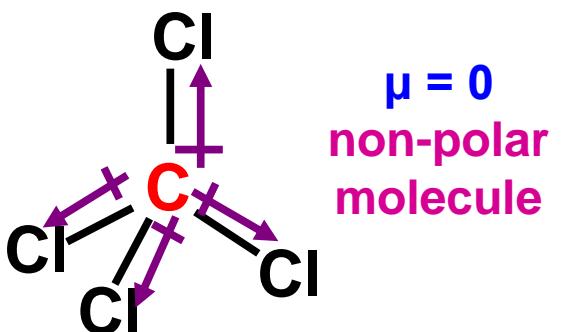


## Example :

Compound	Molecular formula	Boiling point (K)
ethane	$\text{CH}_3\text{CH}_3$	184.5
fluoromethane	$\text{CH}_3\text{F}$	194.7

-  Both molecules having almost similar molecular mass.
-  However, fluoromethane has higher boiling point than ethane because it is a **polar molecules** and has a strong **dipole-dipole interactions**.
-  Ethane is a **nonpolar molecules** and has a **weak London forces @ dispersion forces**.

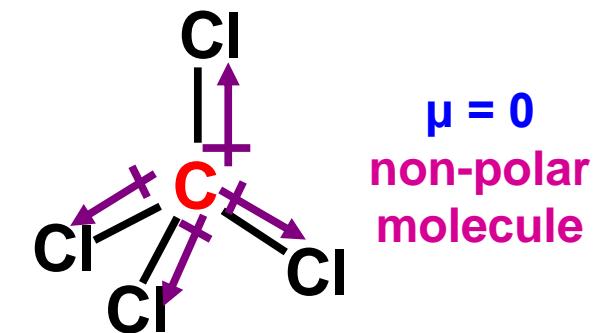
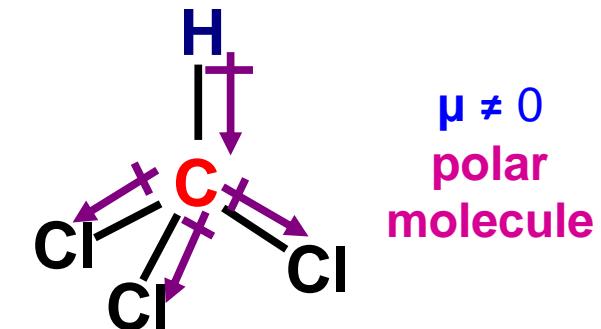
## Example :

Compound	Molecular geometry	Boiling point (°C)
Trichloromethane, $\text{CHCl}_3$		61.2
Tetrachloromethane, $\text{CCl}_4$		76.8

 CHCl<sub>3</sub> is a polar molecules and has dipole-dipole interactions while CCl<sub>4</sub> is a non-polar molecules and has London forces @ dispersion forces between its molecules.

 CCl<sub>4</sub> has higher boiling point because it is a bigger molecule with more electrons (larger molar mass).

 The increase in the dispersion forces between CCl<sub>4</sub> molecules dominates the dipole-dipole interactions between CHCl<sub>3</sub> molecules.



# FACTORS THAT INFLUENCE THE STRENGTH OF HYDROGEN BOND

---

1. Electronegativity of the element.

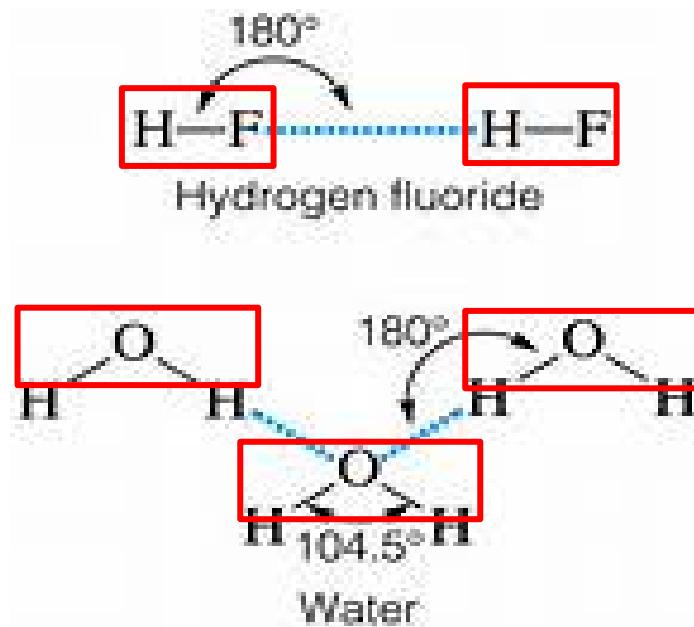
N < O < F

**Example :**

- Hydrogen bonding between H<sub>2</sub>O is **stronger** than between NH<sub>3</sub> because O is **more electronegative** than N.

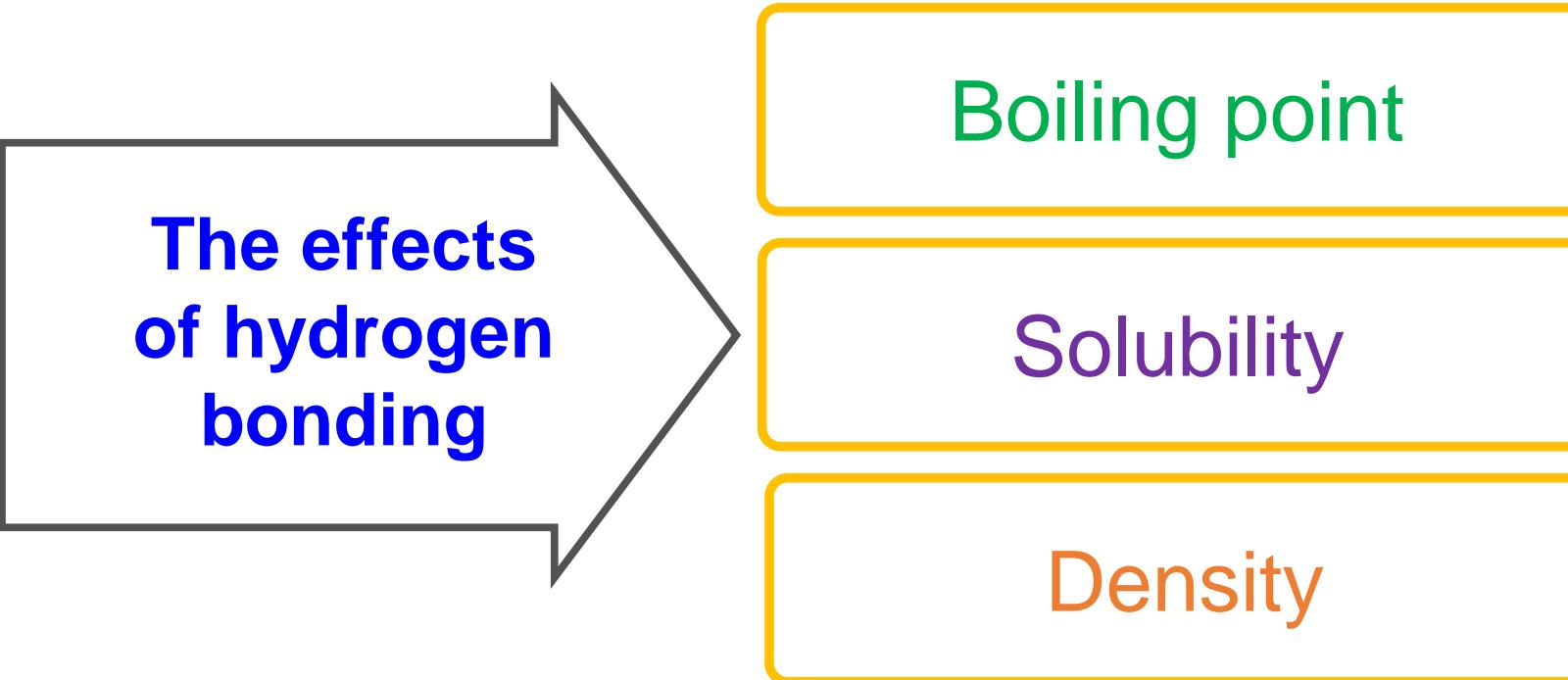
## 2. Number of hydrogen bonds

Although F is more electronegative than O, the **boiling point** of HF is **lower** than H<sub>2</sub>O because a molecule of H<sub>2</sub>O can form more **hydrogen bond per molecule** than HF.



# EFFECTS OF HYDROGEN BONDING ON PHYSICAL PROPERTIES

---

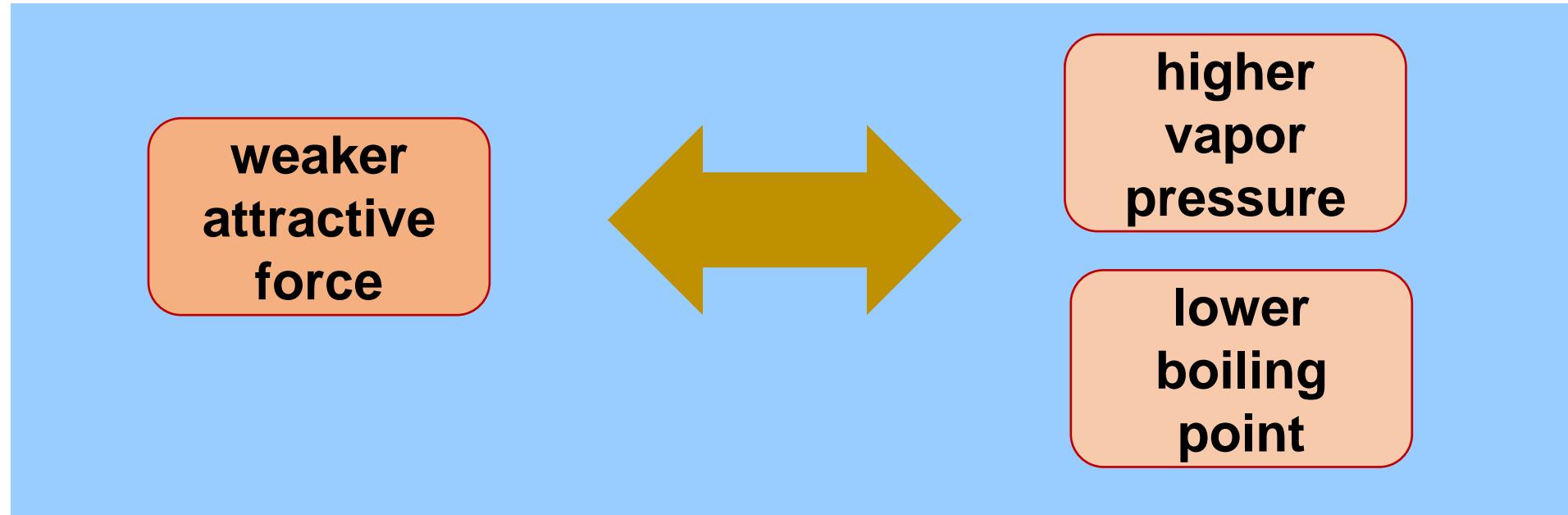


# BOILING POINT

---

- Higher molar mass will increase the **boiling point**.
- Relatively strong hydrogen bonds keep the molecules together.
- Much higher energy needed to break the hydrogen bonds before the molecules can separate and enter the gas phase.

The weaker the **intermolecular forces**, the more **volatile** the liquid (the higher its **vapor pressure**), hence lower the **boiling point**.



ATTRACTIVE FORCE  $\alpha$  ————— BOILING POINT  
VAPOR PRESSURE

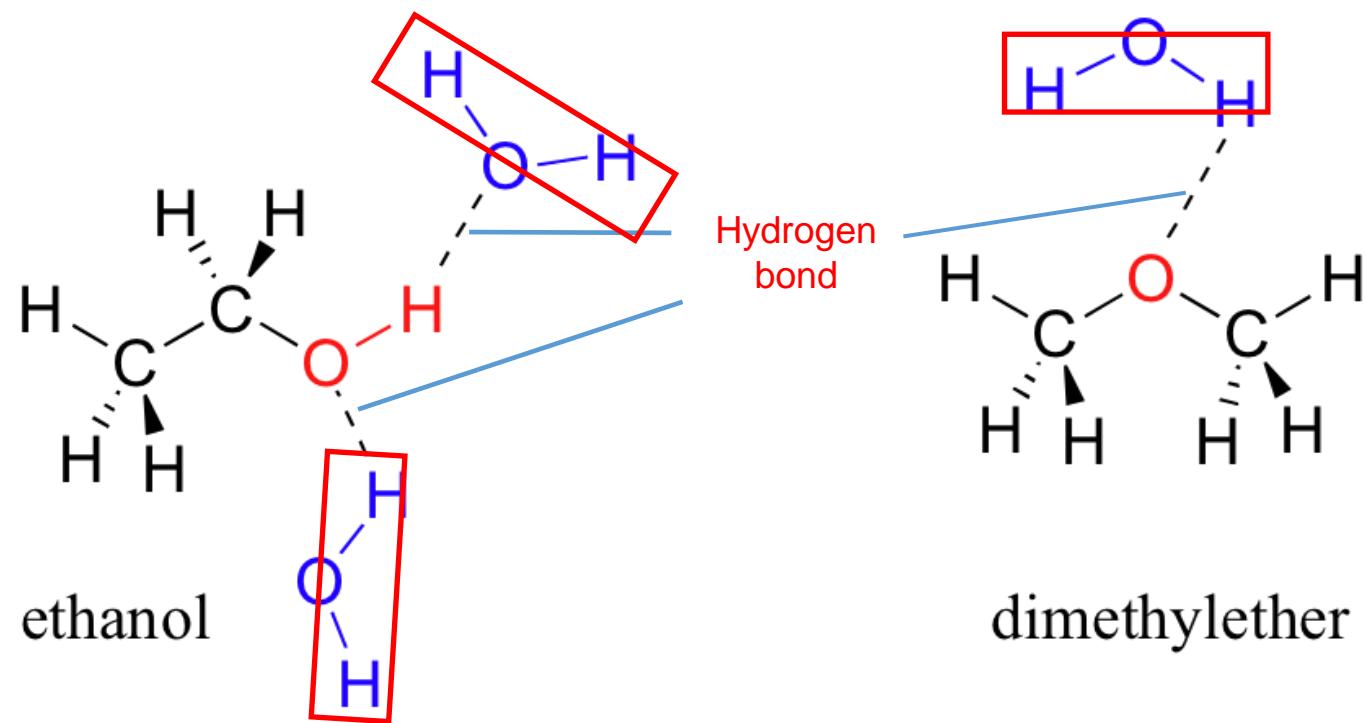
# SOLUBILITY

- Polar molecules tends to dissolve in polar solvents.
- Water is polar molecules and able to form hydrogen bonds.
- Thus polar molecules that **can form hydrogen bond with water** tends to be **soluble in water**.

As the relative **molecular mass increases**,  
the non-polar hydrocarbon portion  
(hydrophobic area) becomes larger.

Since hydrocarbons are **insoluble** in water,  
the **solubility decreases** as the **molecular mass** of the organic compound **increases**

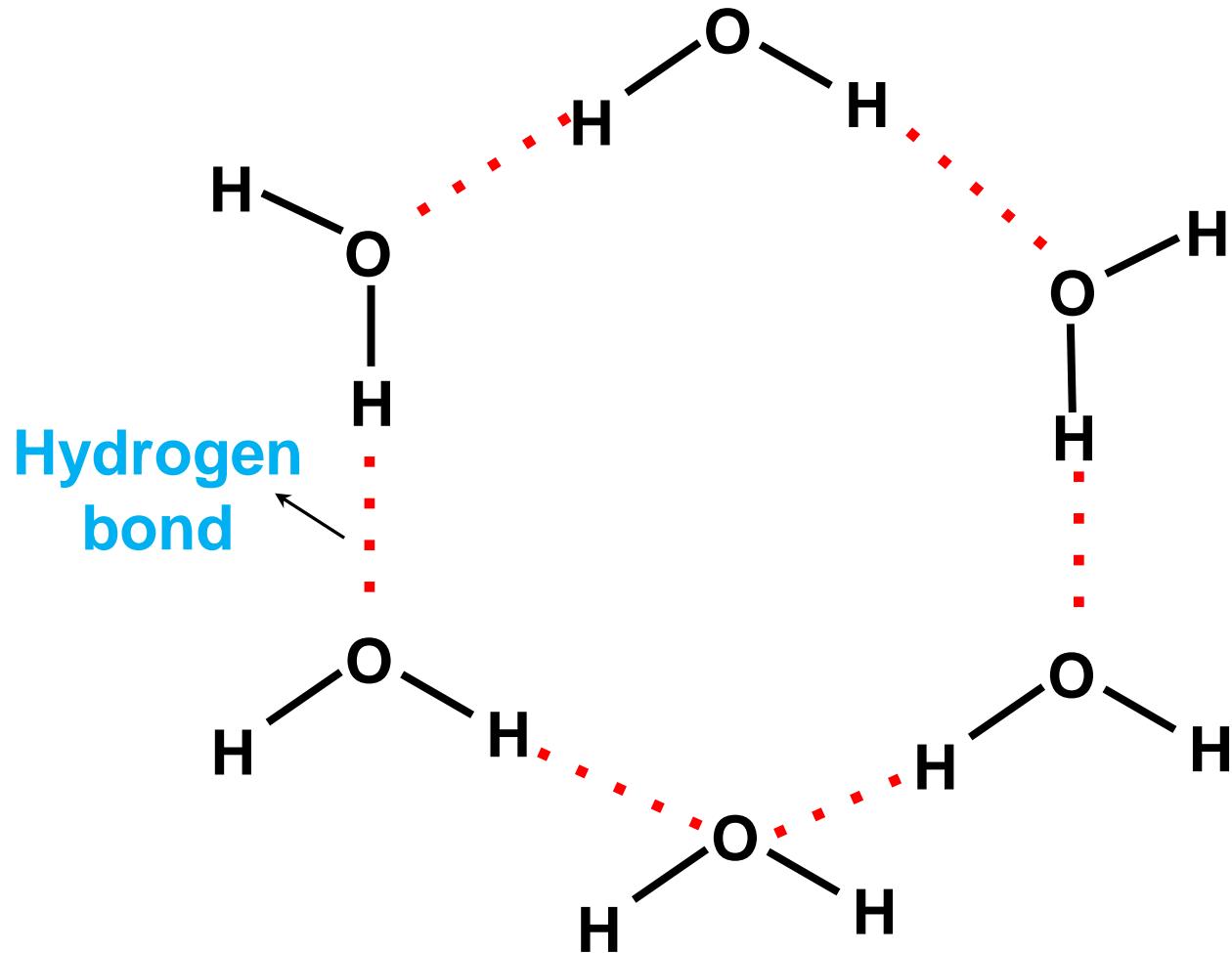
# Formation of hydrogen bonding between polar molecule and water



# DENSITY OF WATER

---

- In most substances the molecules in solid are more denser than its liquid but the **density of ice** is **less** than **water**.
- It results from the geometrical arrangement of hydrogen bond in water. **Ice** has an **open structure, hexagonally** shaped crystal structure.
- When water freeze
  - ☞ **volume** increases
  - ☞ **density** decrease
  - ☞ **ice floats** in water



- Open structure, hexagonally shaped ice ( $\text{H}_2\text{O}$ )



1

- i) Explain the van der Waals forces and give its types.
- ii) Explain how the atomic size or molecular size can influence the strength of these forces.



- i) van der Waals forces:
  - Is an **intermolecular attractions** that exist between electrically **neutral molecules**
  
- Type of van der Waals forces:
  - ❖ dipole-dipole interactions
  - ❖ London forces@ dispersion forces.
  
- ii) When size of atom is bigger, there are many electrons (bigger electron cloud), so the attractive force will increase.

EXERCISES

2

The table below shows the melting points, boiling points and solubility in water and  $\text{CCl}_4$  for compounds E and F. Predict the type of compound for E and F.

Compound	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )	Solubility in water	Solubility in $\text{CCl}_4$
E	2800	3600	High	Very low
F	-25	-10	Low	High

- Predict the type of compound for E and F.
- The boiling point of compound E is higher than that of compound F. Explain.
- Compound E has a higher solubility in water. Explain.



- a) E - ionic compound  
F - simple covalent molecules
  
- b) E - ionic compound
  - is formed by the electrostatic forces between the positive ions and negative ions that attract one another  
F - simple covalent molecules
  - Van der Waal forces
  
- c) E - can form hydrogen bond with water @ can form bond with water through its anion and cation



1. Give the factors that influence the strength of the van der Waals forces.
  
2. Oxygen and sulphur are elements in the group 16 in the Periodic Table. Compare the boiling points of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  based on the intermolecular forces.



1. Factors: size of molecules, shape of molecules and polarity of a molecules
2. The boiling point of  $\text{H}_2\text{S}$  is lower than  $\text{H}_2\text{O}$  because
  - $\text{H}_2\text{O}$  - hydrogen bond
  - each  $\text{H}_2\text{O}$  can make more hydrogen bonds between intermolecular
  - $\text{H}_2\text{S}$  - van der Waals forces



EXERCISE

4

Referring to butane, propanal and propanol, explain the type of intermolecular forces in the compounds and the relative boiling point among those compounds.



- Butane : London force
- Propanal : dipole-dipole interactions
- Propanol : hydrogen bond

Propanol > propanal > butane

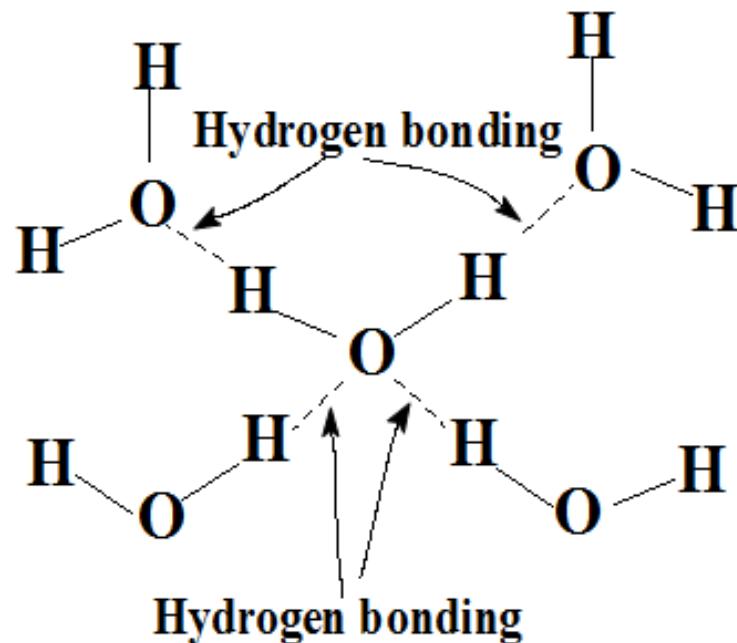
Propanol has highest boiling point and butane has lowest boiling point because hydrogen bond in propanol is stronger than van der Waals forces



EXERCISES

5

By using a suitable example, explain hydrogen bonding and its effects on two physical properties of the substance.



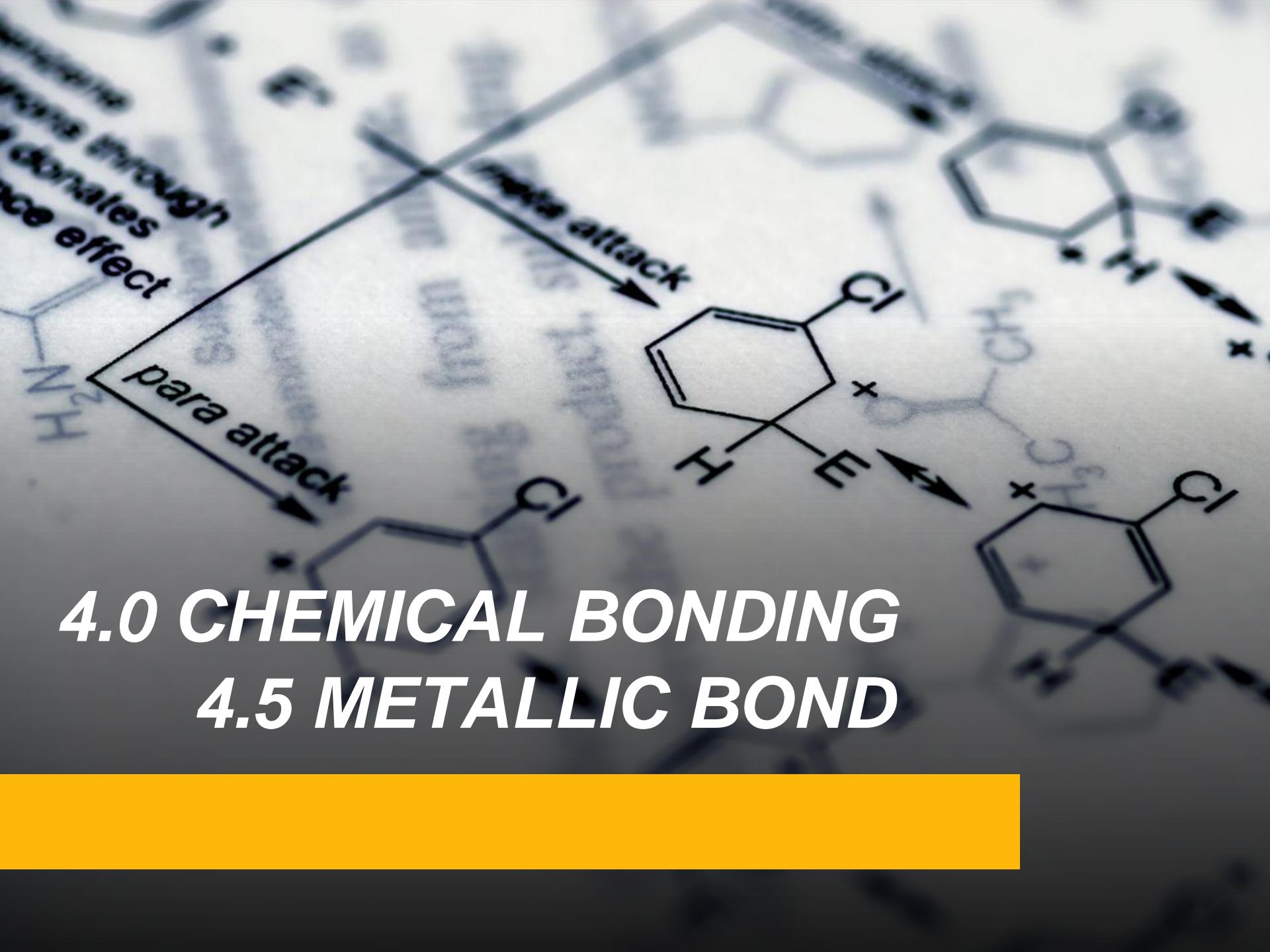
Hydrogen bonding is the force of attraction between the positively charged H atom of one molecule and the negatively charged electronegative atom such as fluorine, oxygen and nitrogen of another molecule

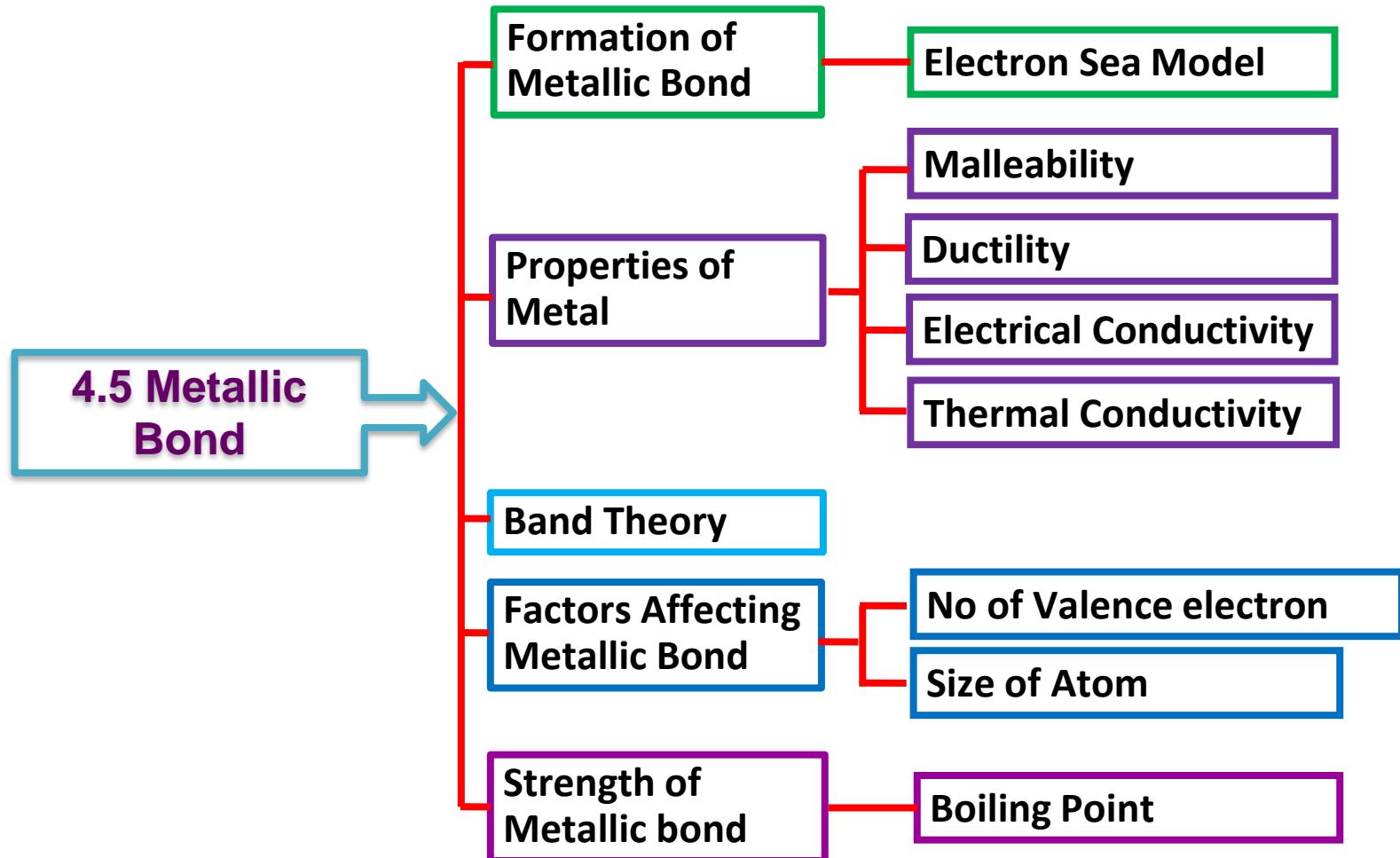
Effect of hydrogen bonding

- higher boiling point and melting point
- ice (solid) is less dense than water (liquid)

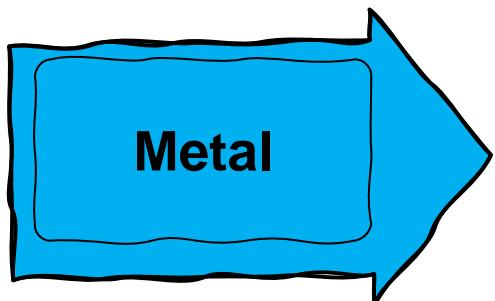
# 4.0 CHEMICAL BONDING

## 4.5 METALLIC BOND

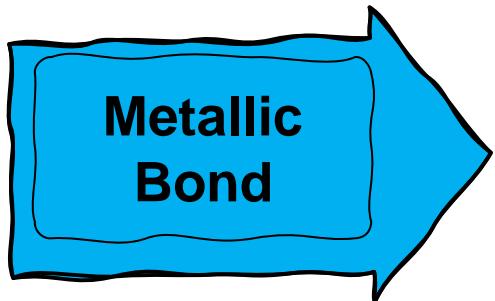




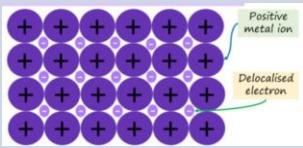
# FORMATION OF METALLIC BOND



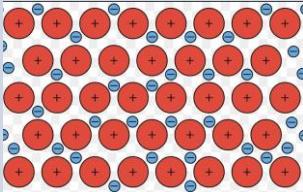
Are shiny solids at room temperature (except mercury), with characteristic high melting points and densities



**Electrostatic force** between the **positively charged** metallic ions and the 'sea' of delocalized valence electrons.



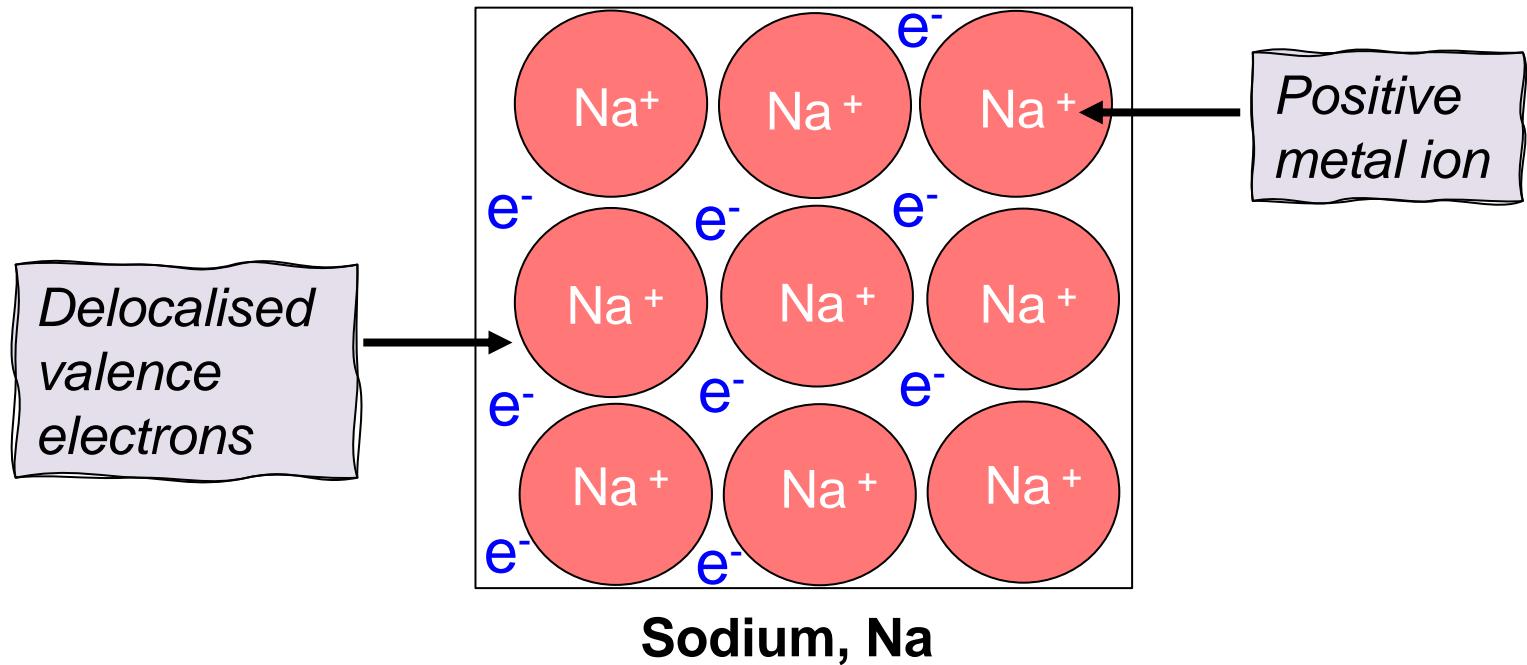
In a metallic bond, metal atoms can be imagined as an array of positive ions immersed in a sea of delocalized valence electrons.



These delocalized electrons are not bound to individual atoms, and they can therefore serve to bind large numbers of metal atoms together.

# EXAMPLE:

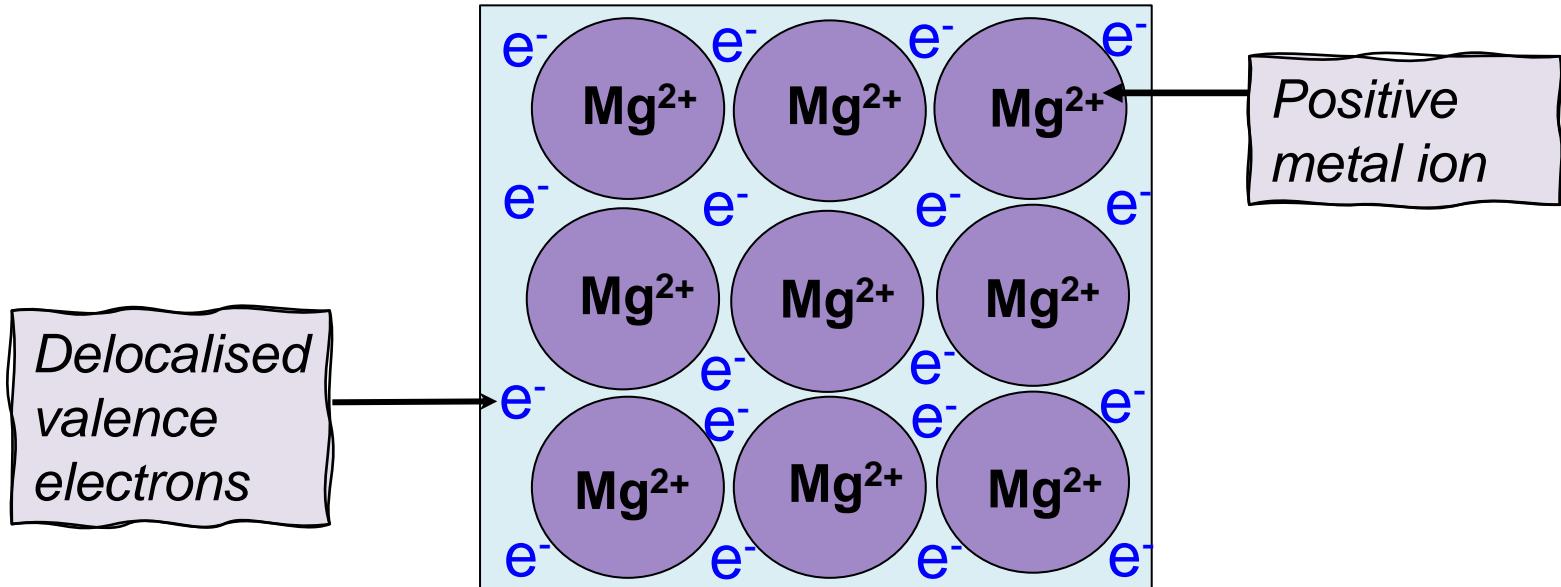
## “Electron-sea” Model



- Sodium (Na) metal is an element in group 1.
- The Na atom releases its **one valence electron** in open space which can imagined as a sea of delocalised electrons and forms  **$\text{Na}^+$  ion**.
- There is **electrostatic force** between the positively charged  $\text{Na}^+$  ions and the negative charge of the sea electrons. These attractive forces are called as metallic bond.

# EXAMPLE:

## “Electron-sea” Model



### Magnesium, Mg

- Magnesium (Mg) metal is an element in group 2.
- Mg atom releases its **two valence electrons** in open space which can imagined as a sea of delocalised electrons and forms to form  **$\text{Mg}^{2+}$  ion**.
- There is **electrostatic force** between the positively charged  $\text{Mg}^{2+}$  ion ions and the negative charge of the sea electrons. These attractive forces are called as metallic bond.

# PROPERTIES OF METALS

---

- **Lustrous** in appearance



- Most are solids with moderate to **high melting point** and much higher boiling point.
- **Bent** or **dent** rather than crack or shatter.



## **Malleability**

☞ Is the ability of a metal to be hammered shapes



## **Ductility**

☞ Is the ability of a metal to be drawn into wire.



## **Conduct heat and electricity**

☞ Well in both the solid and liquid states

Why most are solids with moderate melting point and much higher boiling point?

## EXPLANATION

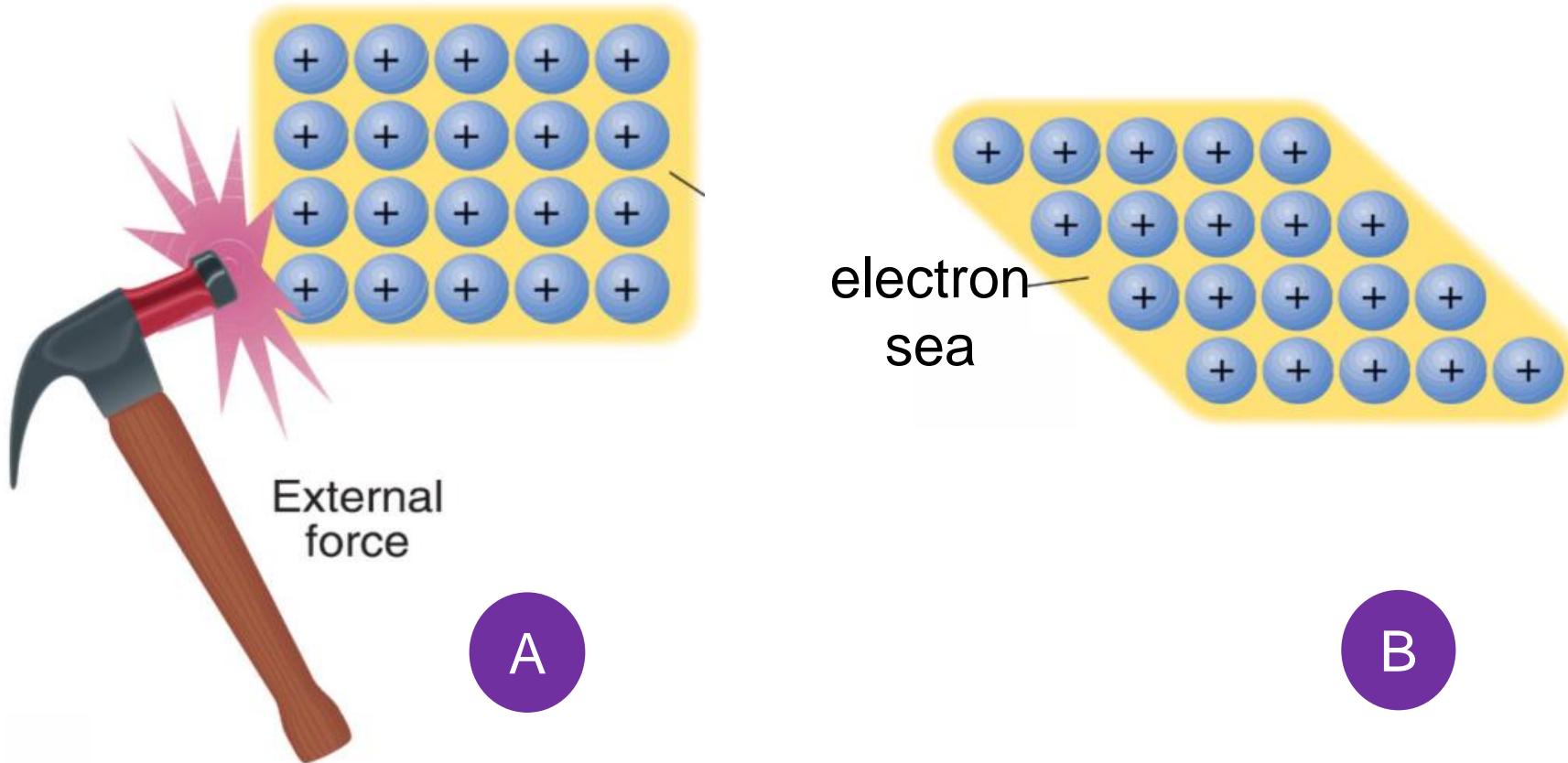
- **Melting point** is moderate because the attraction between moveable cations (nuclei) and mobile e<sup>-</sup> need not be broken during melting.
- Boiling point is higher because it requires each cation (nuclei) and the mobile e<sup>-</sup> to break away from the others.
- The metallic bond is strong enough to resist separation of the atom.

# Why metals are malleable and ductile?

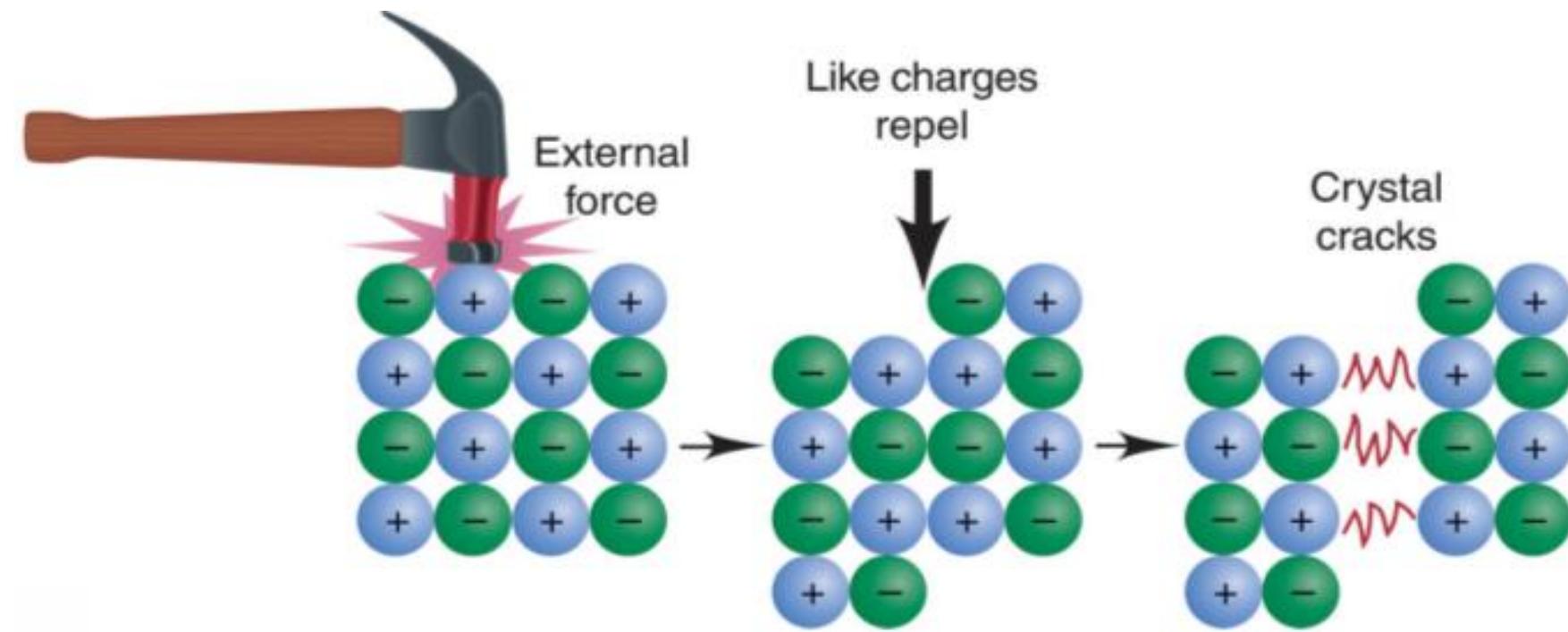
## EXPLANATION

- When a piece of metal deformed by a hammer, the **metal ions (nuclei)** slide past each other through the e<sup>-</sup> sea to new lattice positions.
  
- Thus, the metal ions (nuclei) do not repel each other.

# The Metal Ions (Nuclei) slide



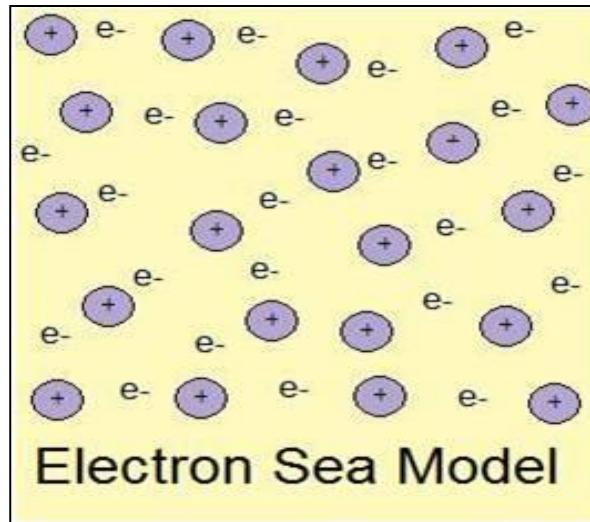
# Ionic Compounds crack due to Electrostatic Force



# Why metal conduct heat and electricity well in both the solid and liquid states ?

## EXPLANATION

- Because the valence electron at electron sea model is delocalized (not static), so it can conduct electricity.



# BAND THEORY

---

- **Band:**

An array of closely spaced molecular orbitals occupying a continuous range of energy.

- **Band gap:**

The energy gap between a fully occupied valence band and an empty conduction band.

- **Conduction band:**

A band of unoccupied molecular orbitals lying higher in energy than the occupied valence band.

- **Valence band:**

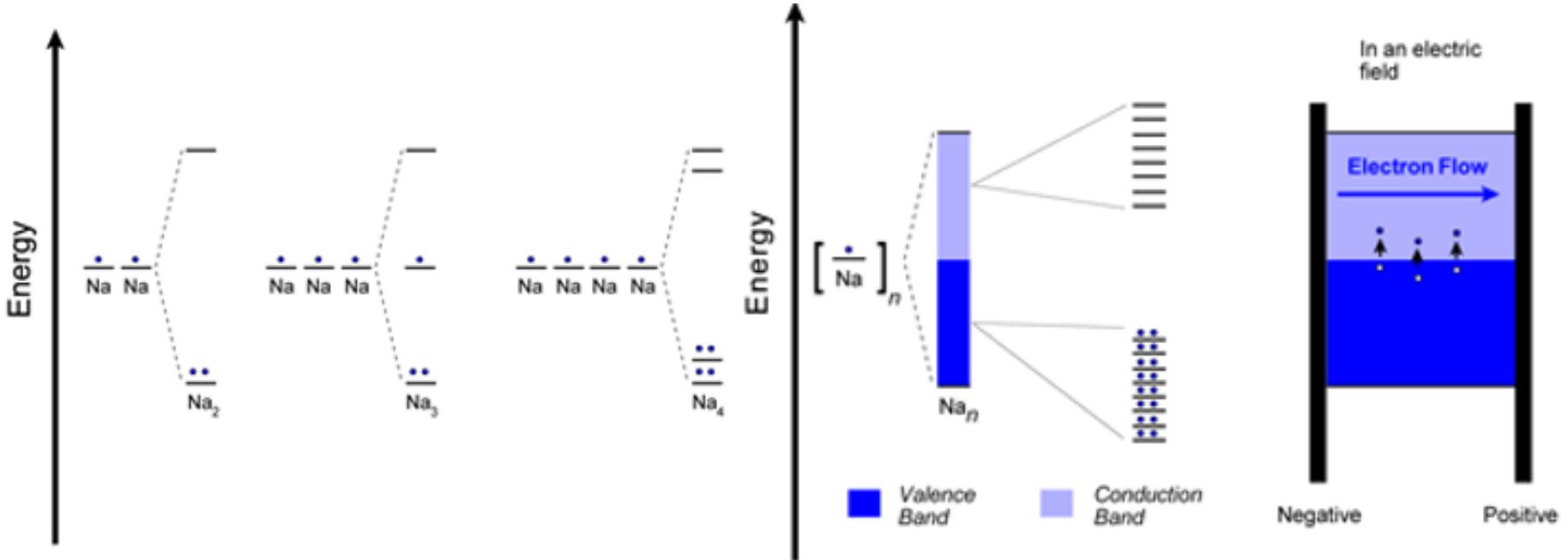
A band closely spaced bonding molecular orbitals that is essentially fully occupied by electron.

# BAND THEORY OF ELECTRICAL CONDUCTIVITY

---

## Band Theory of Solids

- The delocalized electrons move freely through “band” formed by overlapping molecular orbitals.
- The electronic structure of a bulk solid is referred to as a band structure
- When **valence band** (lower energy) and **conduction band** (higher energy) **overlapping**, allowing **electrons to flow** through the metals with minimal applied voltage.

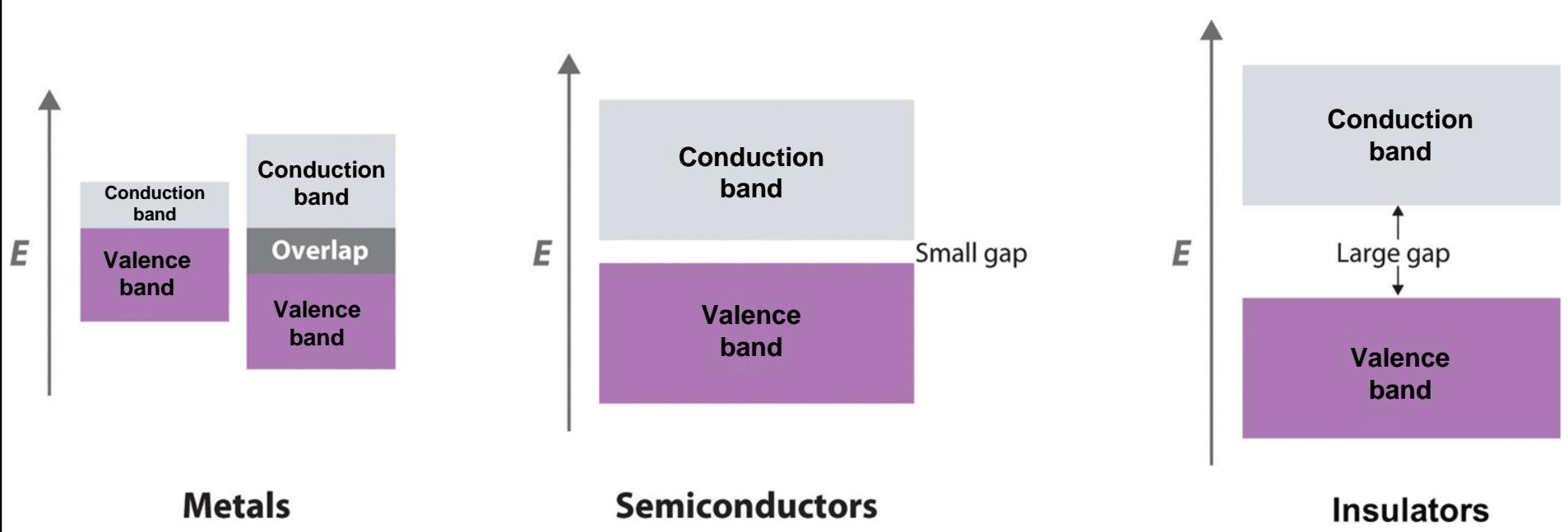


# BAND THEORY OF SOLIDS

- Electrons jump from **valence band** to **conduction band** even at ordinary temperature and if this happens then the solid conducts electricity.
- Conductivity **depends on the gap** between the valence band and conduction band.

Conductors	Semiconductors	Insulators
There is no band gap between their valence band and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.	have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.	The band gap between the valence band the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

# BAND STRUCTURE OF CONDUCTORS, SEMICONDUCTORS AND INSULATORS



# FACTORS AFFECTING THE STRENGTH OF METALLIC BOND

1

Number of valence electron

- The more number of valence electron, the stronger the metallic bond.

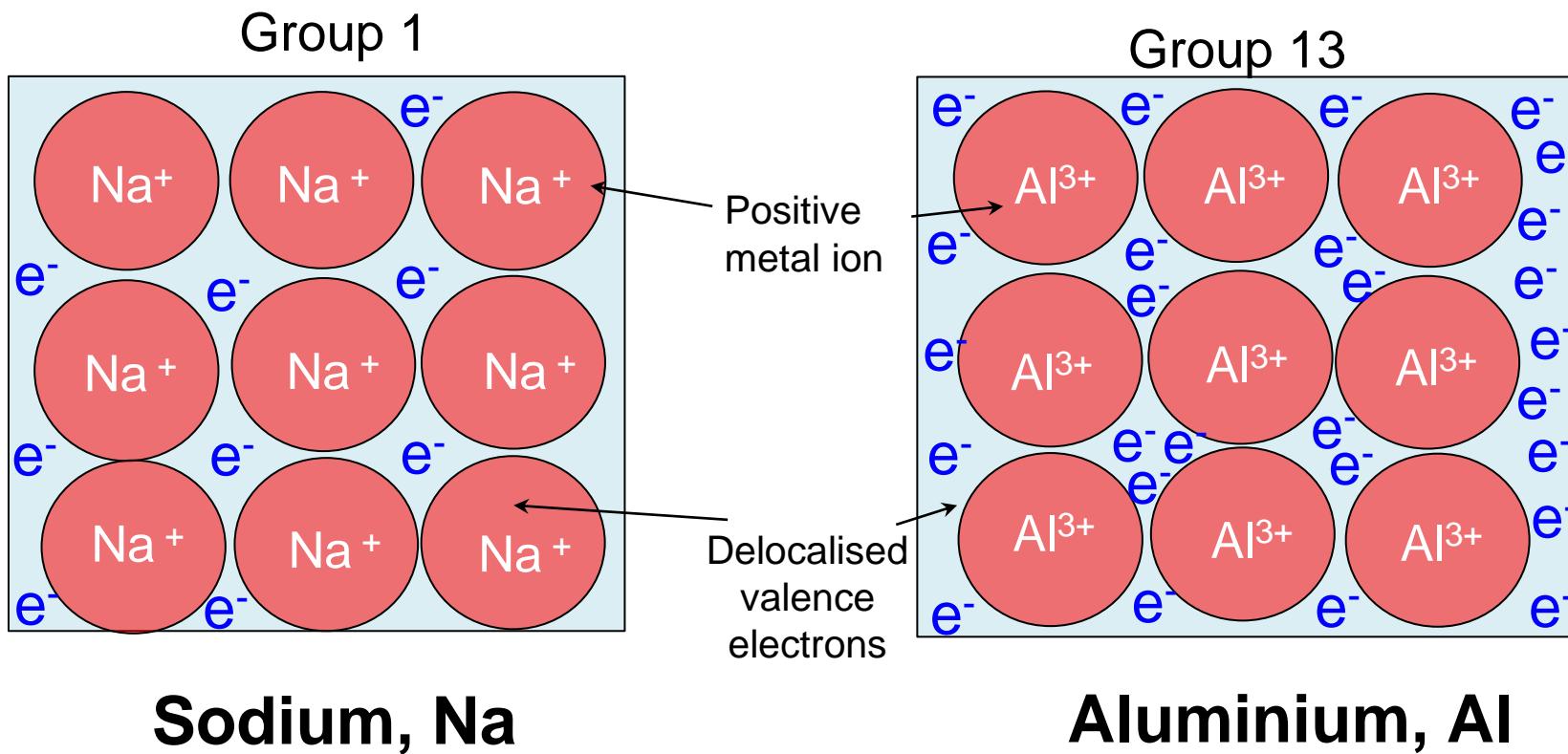
2

Size of positively charged metal ions

- The smaller the cationic size, the stronger metallic bond.

# EXAMPLE:

By using electron sea model, compare melting point of aluminium and sodium. Explain.





- Number of valence electron Al = 3, while Na = 1, thus metallic bond of Al is stronger than Na.
- The strength of metallic bonding is directly proportional to the number of valence electron in the element.
- Therefore, melting point of Al is higher than Na.

# MELTING POINT & BOILING POINT

## Across Period 3

Element	Na	Mg	Al	Si	P	S	Cl	Ar
M.P (°C)	97.8	651	660	1410	44	119	-101	-189
B.P (°C)	892	1107	2450	2360	280	446	-34	-186

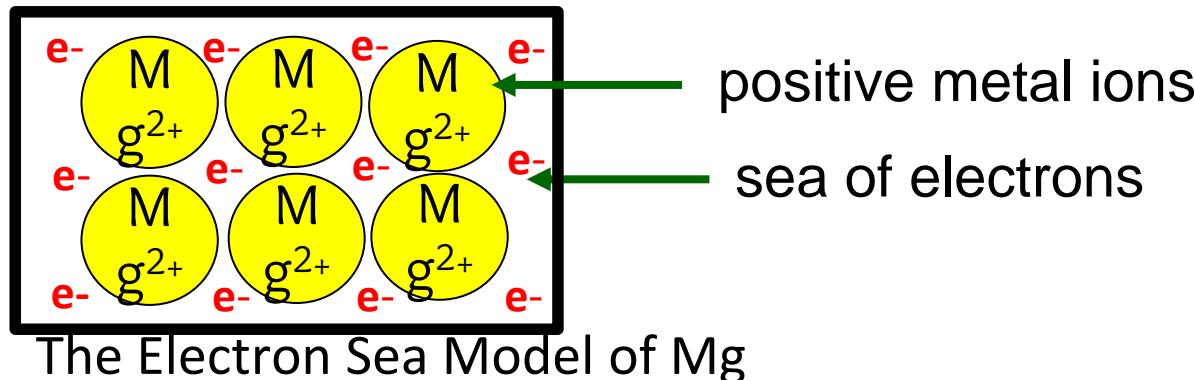
The variations of melting point and boiling point are due to the:

- ✓ Types (strength) of **chemical bonds**.
- ✓ **Structure** of molecules.
- ✓ Types of **intermolecular forces**.

# MELTING POINT & BOILING POINT

## Metal/metallic structure (Na to Al)

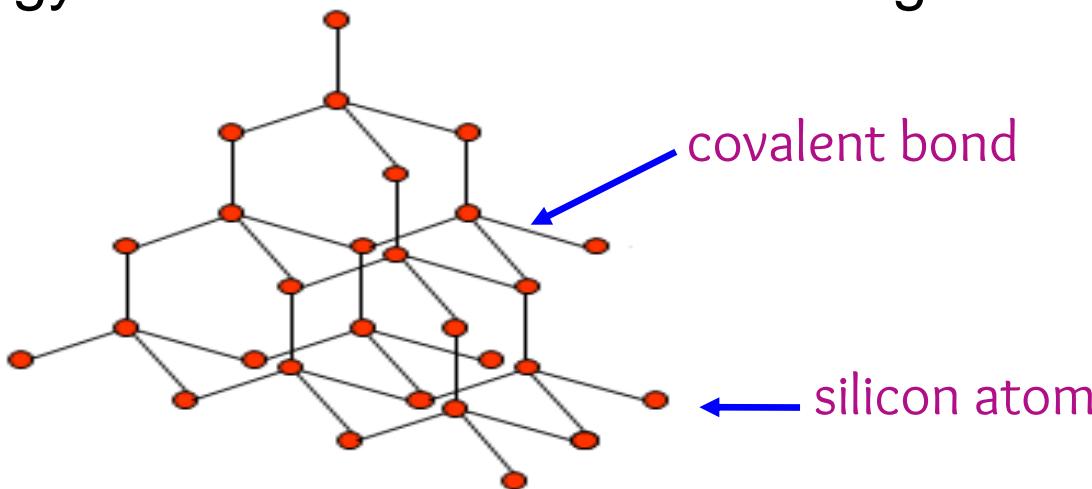
- Metallic bond is an **electrostatic forces** between **positive metal ions** and **sea of valence electrons**.
- The strength of metallic bonding is proportional to the number of **valence electrons**.
- As the metallic bond stronger, the melting / boiling point is higher.
- Valence electrons of **Na, Mg, Al** are **1, 2 and 3** respectively. Thus, **melting point and boiling point increase from Na to Al.**



# MELTING POINT & BOILING POINT

## Giant Covalent (Si)

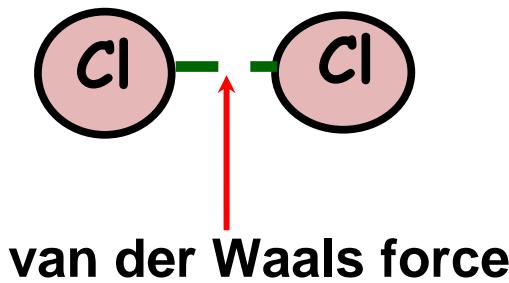
- Si exist in the form of **giant covalent / network solid** (covalently bonded atoms).
- Si has **strong covalent bonds** holding the atoms together in three-dimensional array.
- Each Si is **tetrahedrally covalent bonded** to four other Si atoms infinitely.
- High energy is needed to break the strong covalent bonds.



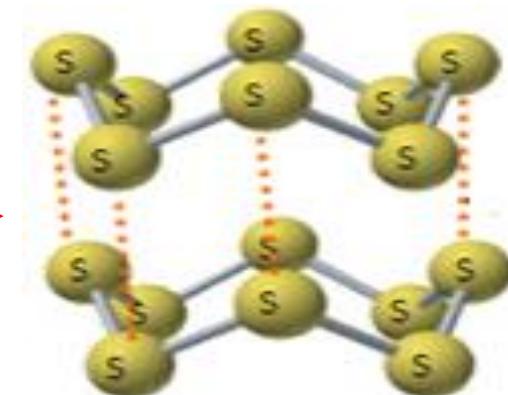
# MELTING POINT & BOILING POINT

## Simple Covalent (P to Ar)

- The non-metal elements  $P_4$ ,  $S_8$ ,  $Cl_2$  exist as molecules and  $Ar$  as monoatom.
- The **covalent bond** between the atoms is very strong but the intermolecular forces (**van der Waals**) is very weak.
- The strength of van der Waals forces is proportional to **molecular size** (relative molecular weight).
- As the molecular size:  $Ar < Cl_2 < P_4 < S_8$  so, the strength of van der Waals forces increases from Ar to S.
- Melting / boiling point** :  $Ar < Cl < P < S$



van der Waals force →



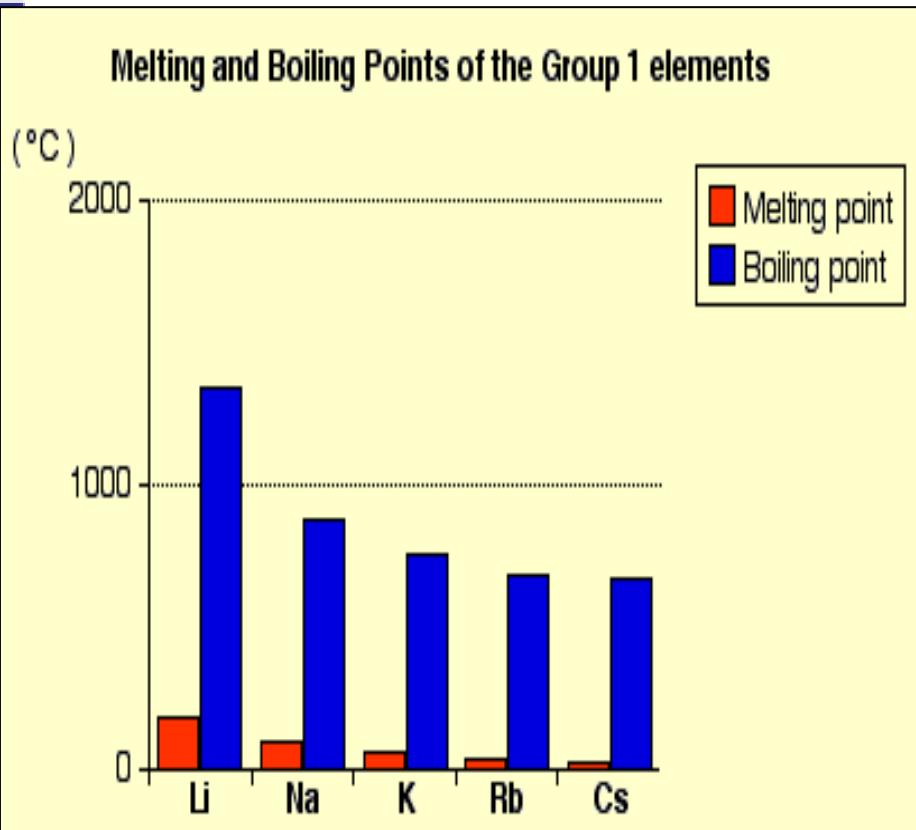
# MELTING POINT & BOILING POINT

Down a Group 1

DECREASE

1
Li 3
Na 11
K 19
Rb 37
Cs 55

	Melting point [°C]	Boiling point [°C]
Li	180	1340
Na	98	881
K	64	765
Rb	39	688
Cs	28	705



# MELTING POINT & BOILING POINT

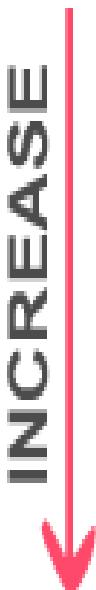
---

## Descending Group 1

- Atomic size **increase**.
- Distance between nucleus and valence electrons **increase**.
- Strength of electrostatic forces between positively charge ion and the electron sea become **weaker**.
- Strength of metallic bond **decrease**.
- Less energy** is needed to break the bond.
- Melting/boiling point decrease**.

# MELTING POINT & BOILING POINT

Down a Group 17



17	Melting point [°C]	Boiling point [°C]
F	-217	-88
Cl	-101	-34
Br	-76	0
I	114	185

# MELTING POINT & BOILING POINT

---

## Descending Group 17

- The size of molecules **increases**, the intermolecular forces (van der Waals) become **stronger**.
- Therefore, **more energy** is needed to overcome the attraction.
- Thus, **melting and boiling point increase**.