

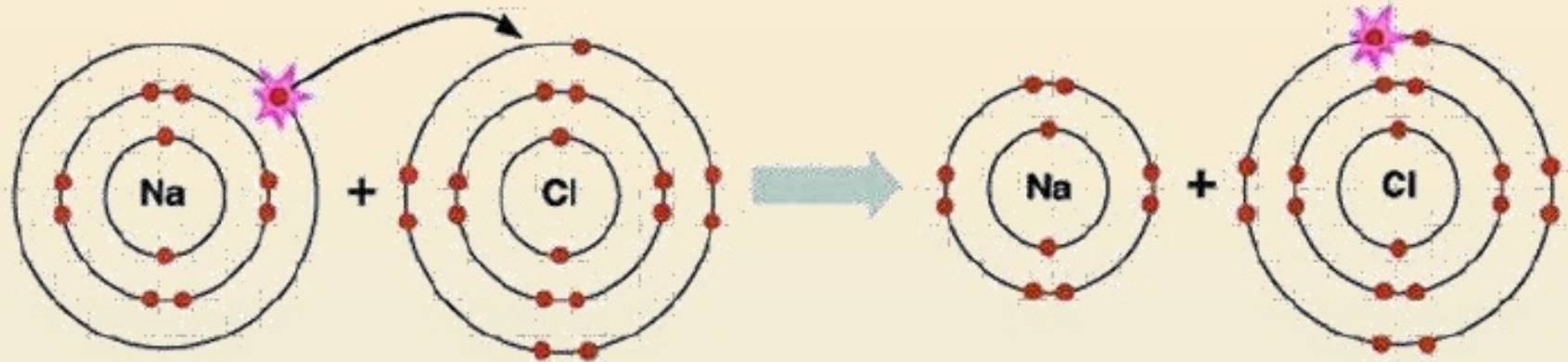
**Government Arts College, CBE**  
**Department of chemistry**  
**Dr. M. Shanthamani**

## Unit-I

# CHEMICAL BONDING

- A **chemical bond** - attraction between atoms, ions or molecules that enables the formation of **chemical** compounds.
- The **bond** may result from the electrostatic force of attraction between oppositely charged ions as in **ionic bonds**
- The sharing of electrons as in **covalent bonds**.

# Ionic Bonding



A sodium  
atom

A chloride  
atom

A sodium  
cation

A chloride  
anion

**Na**

+

**Cl**

**Na<sup>+</sup>**

+

**Cl<sup>-</sup>**

# CA Standards

☐ *Students know* atoms combine to form molecules by sharing electrons to form covalent or metallic bonds or by exchanging electrons to form ionic bonds.

☐ *Students know* salt crystals, such as NaCl, are repeating patterns of positive and negative ions held together by electrostatic attraction.

# Bonds

- Forces that hold groups of atoms together and make them function as a unit.
  - ❖ Ionic bonds - transfer of electrons
  - ❖ Covalent bonds - sharing of electrons

# The Octet Rule - Ionic Compounds

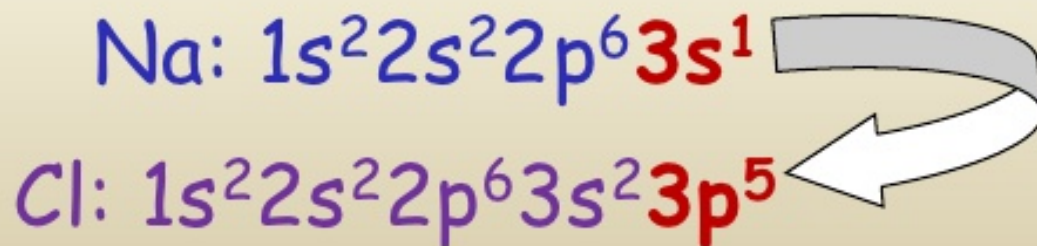
Ionic compounds form so that each atom, by gaining or losing electrons, has an octet of electrons in its highest occupied energy level.

Metals lose electrons to form positively-charged cations

Nonmetals gains electrons to form negatively-charged anions

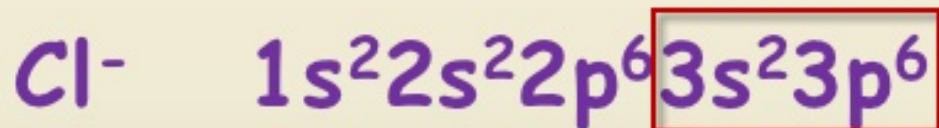
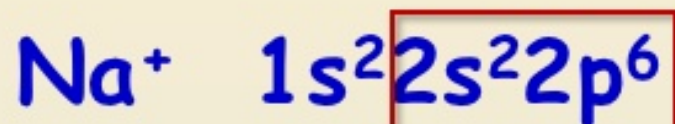
## Ionic Bonding: The Formation of Sodium Chloride

- ❑ Sodium has 1 valence electron
- ❑ Chlorine has 7 valence electrons
- ❑ An electron transferred gives each an octet



# Ionic Bonding: The Formation of Sodium Chloride

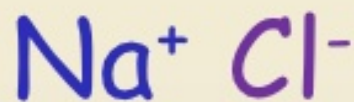
This transfer forms ions, each with an octet:





# Ionic Bonding: The Formation of Sodium Chloride

The resulting ions come together due to electrostatic attraction (opposites attract):



The net charge on the compound must equal zero

# Examples of Ionic compounds

$Mg^{2+}Cl^{-}_2$  **Magnesium chloride:** Magnesium loses two electrons and each chlorine gains one electron

$Na^{+}_2O^{2-}$  **Sodium oxide:** Each sodium loses one electron and the oxygen gains two electrons

$Al^{3+}_2S^{2-}_3$  **Aluminum sulfide:** Each aluminum loses three electrons (six total) and each sulfur gains two electrons (six total)

| <b>Metal</b> | <b>Monatomic Cations</b> | <b>Ion name</b> |
|--------------|--------------------------|-----------------|
| Lithium      | $\text{Li}^+$            | Lithium         |
| Sodium       | $\text{Na}^+$            | Sodium          |
| Potassium    | $\text{K}^+$             | Potassium       |
| Magnesium    | $\text{Mg}^{2+}$         | Magnesium       |
| Calcium      | $\text{Ca}^{2+}$         | Calcium         |
| Barium       | $\text{Ba}^{2+}$         | Barium          |
| Aluminum     | $\text{Al}^{3+}$         | Aluminum        |























*Recall.....*

**IONIC BOND-** Transfer of electrons

Ex- NaCl

**COVALENT BOND-** Sharing of electrons,

Ex-Cl-Cl

**METALLIC BOND** –Exchangeable of electrons

# Properties of Ionic Compounds

- Crystalline solids
- High melting and boiling points
- Conduct electricity when melted
- Many soluble in water but not in nonpolar liquid

# Properties of Covalent Compounds

- Gases, liquids, or solids
- Low melting and boiling points
- Poor electrical conductors in all phases
- Many soluble in non polar liquids but not in water
- **Are brittle**
- When 2 atoms bond covalently the resulting particle is a molecule



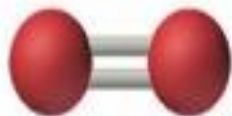


## What Have You Learned?

- What are the two extreme cases of bonds?
- Do covalent bonds lose or gain electrons? (Yes or No).
- Why do atoms bond?



Single bond



Double bond

## Chemical bond

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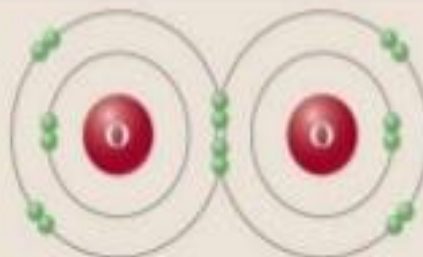
Single covalent bond  
hydrogen gas



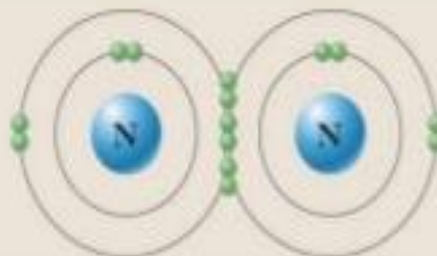
covalent bond



Double covalent bond  
oxygen gas

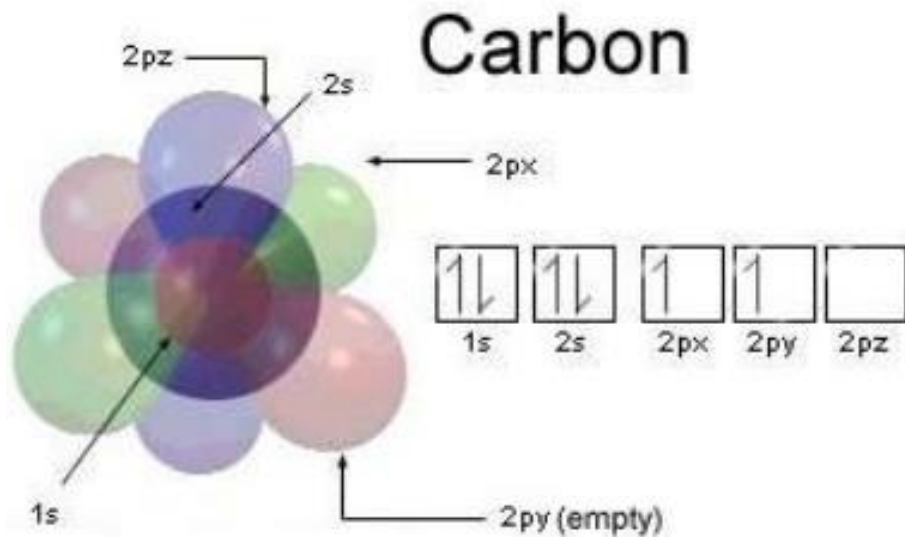
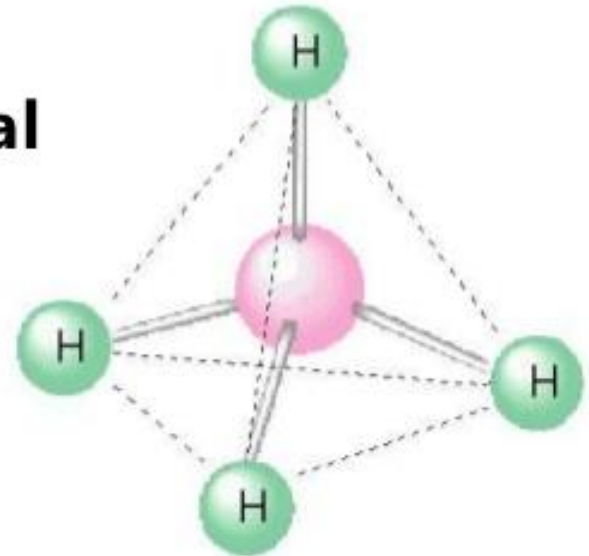


Triple covalent bond  
nitrogen gas



Triple bond

**Recall : methane, CH<sub>4</sub> – tetrahedral shape (4 equal covalent bonds)**



**Carbon has an electron arrangement  $1s^2 2s^2 2p^2$**

**There is a contradiction here . . . . .**



s



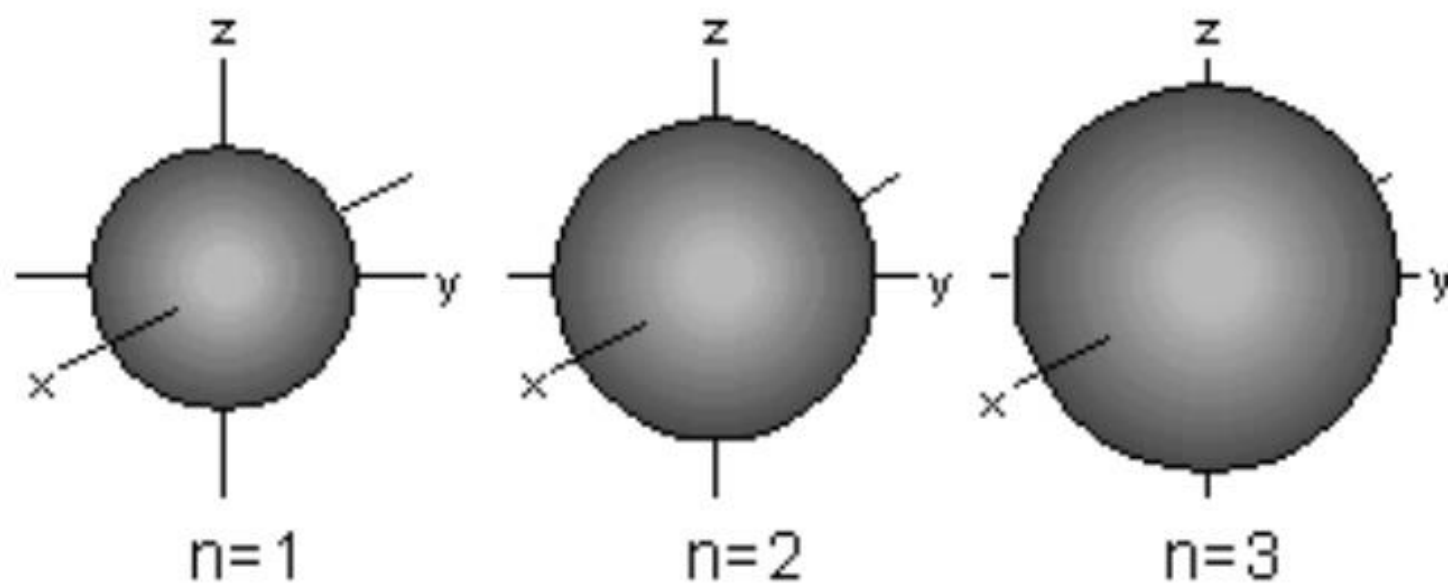
p



d

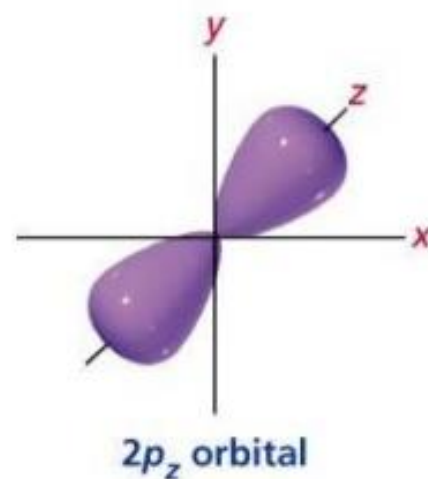
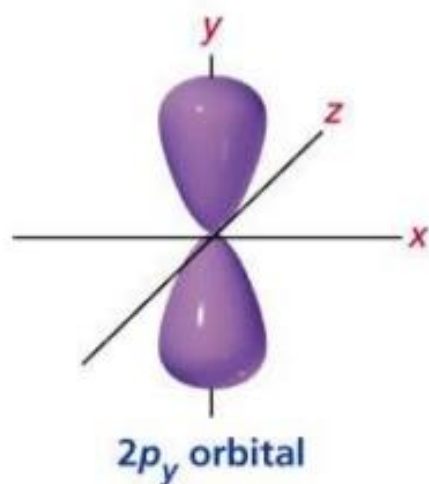
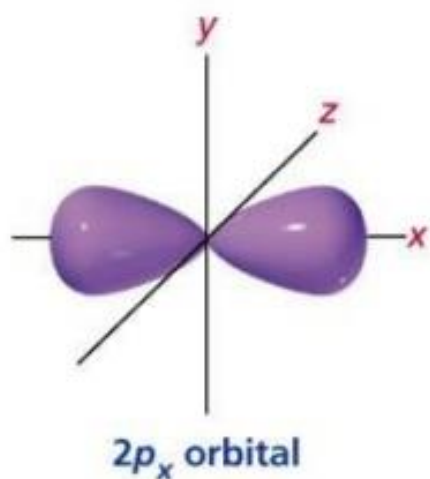
shutterstock

## Recall: the s orbital shape

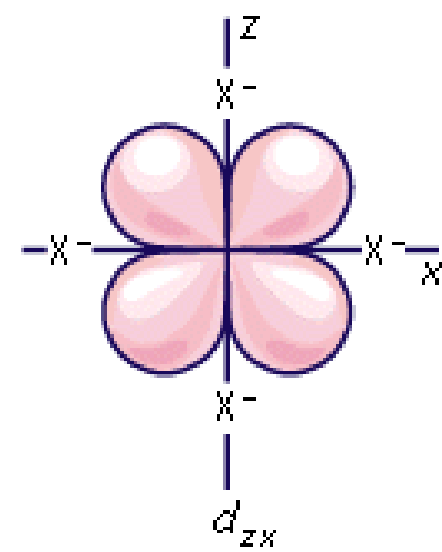
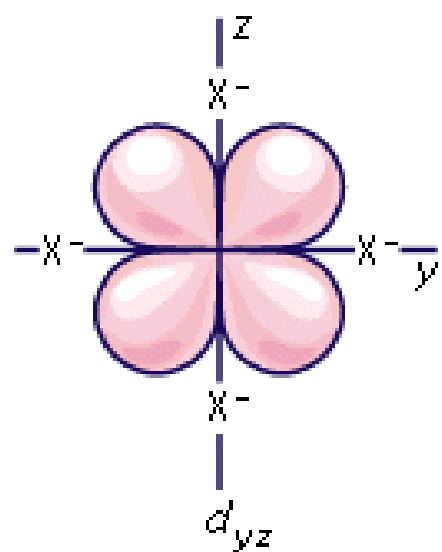
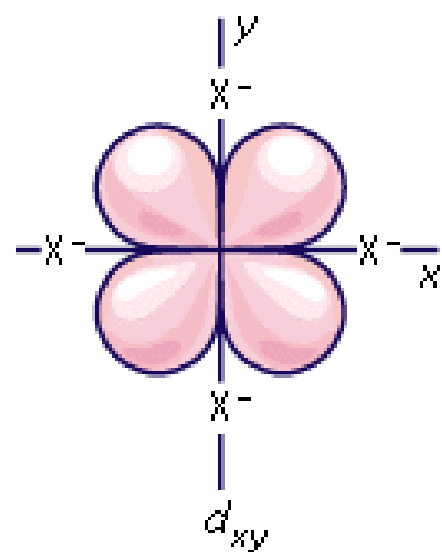
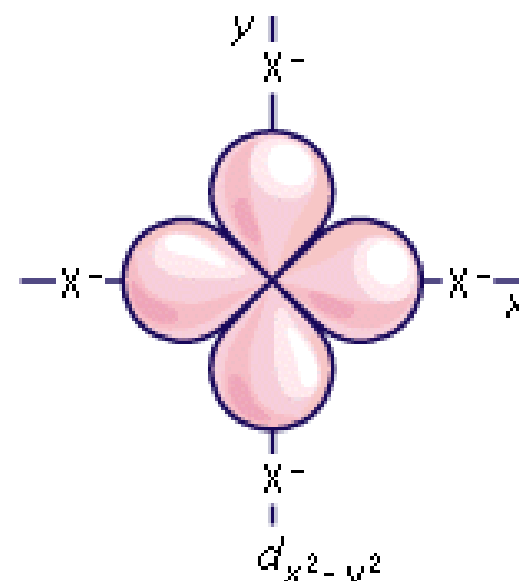
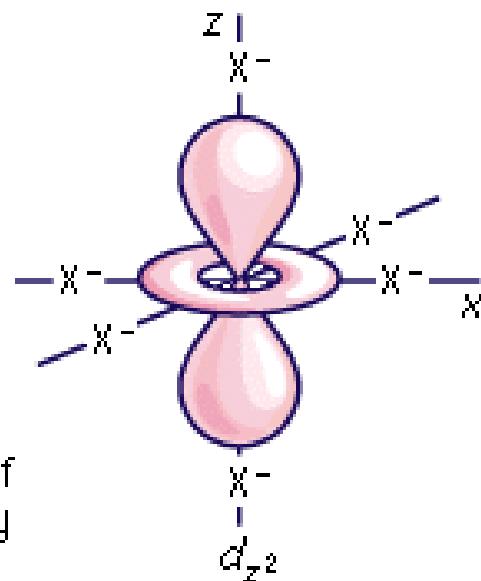


**ONE s orbital in each energy level**

## Recall: the p orbital shape



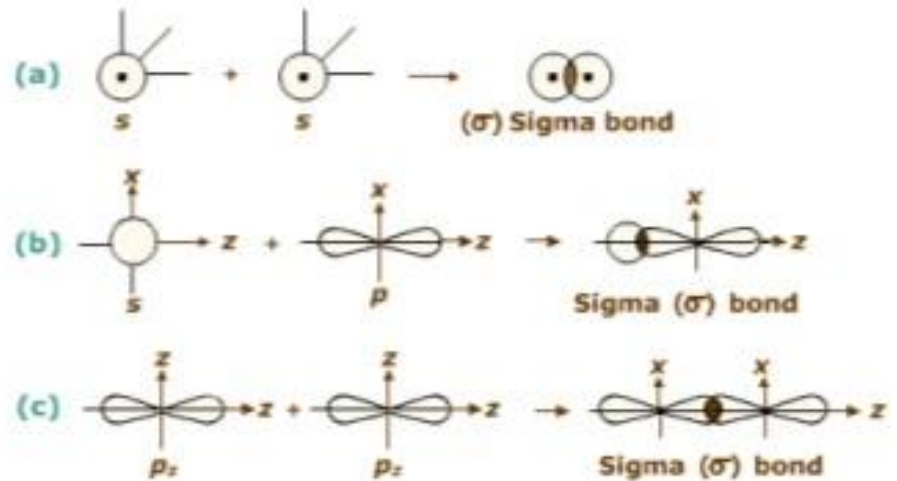
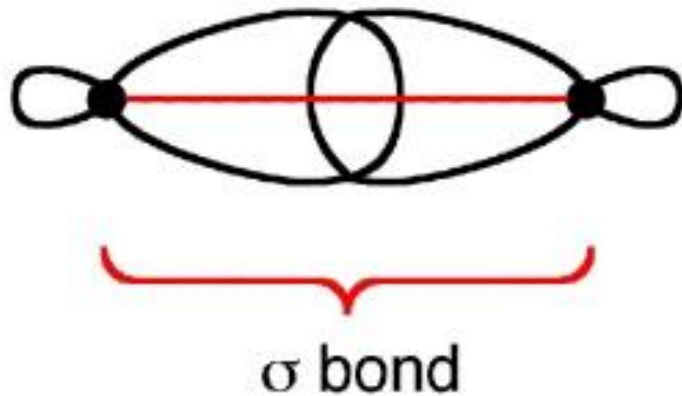
**THREE p orbitals in each energy level (beginning  $n = 2$ )**



The symbols X<sup>-</sup> represent some or all of a set of six octahedrally located anions.

## Sigma bond

In chemistry, **sigma bonds ( $\sigma$  bonds)** are the strongest type of covalent chemical bond. They are formed by head-on overlapping between atomic orbitals. Sigma bonding is most clearly defined for diatomic molecules.

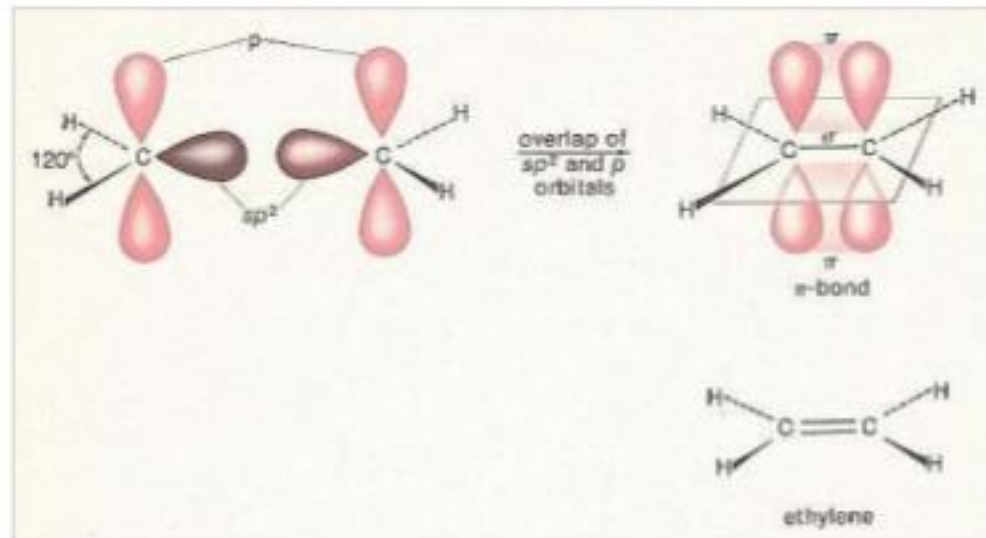
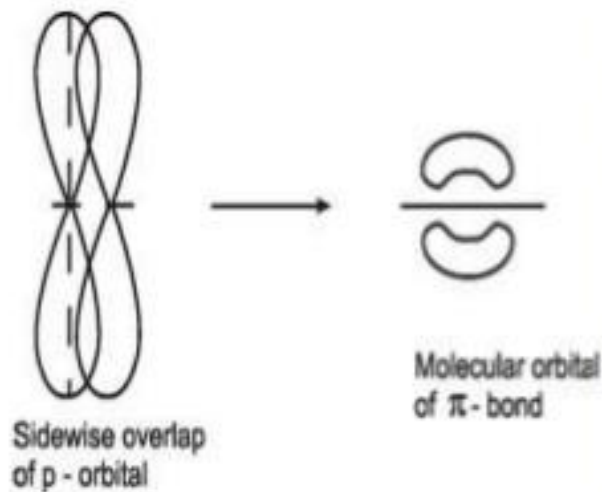


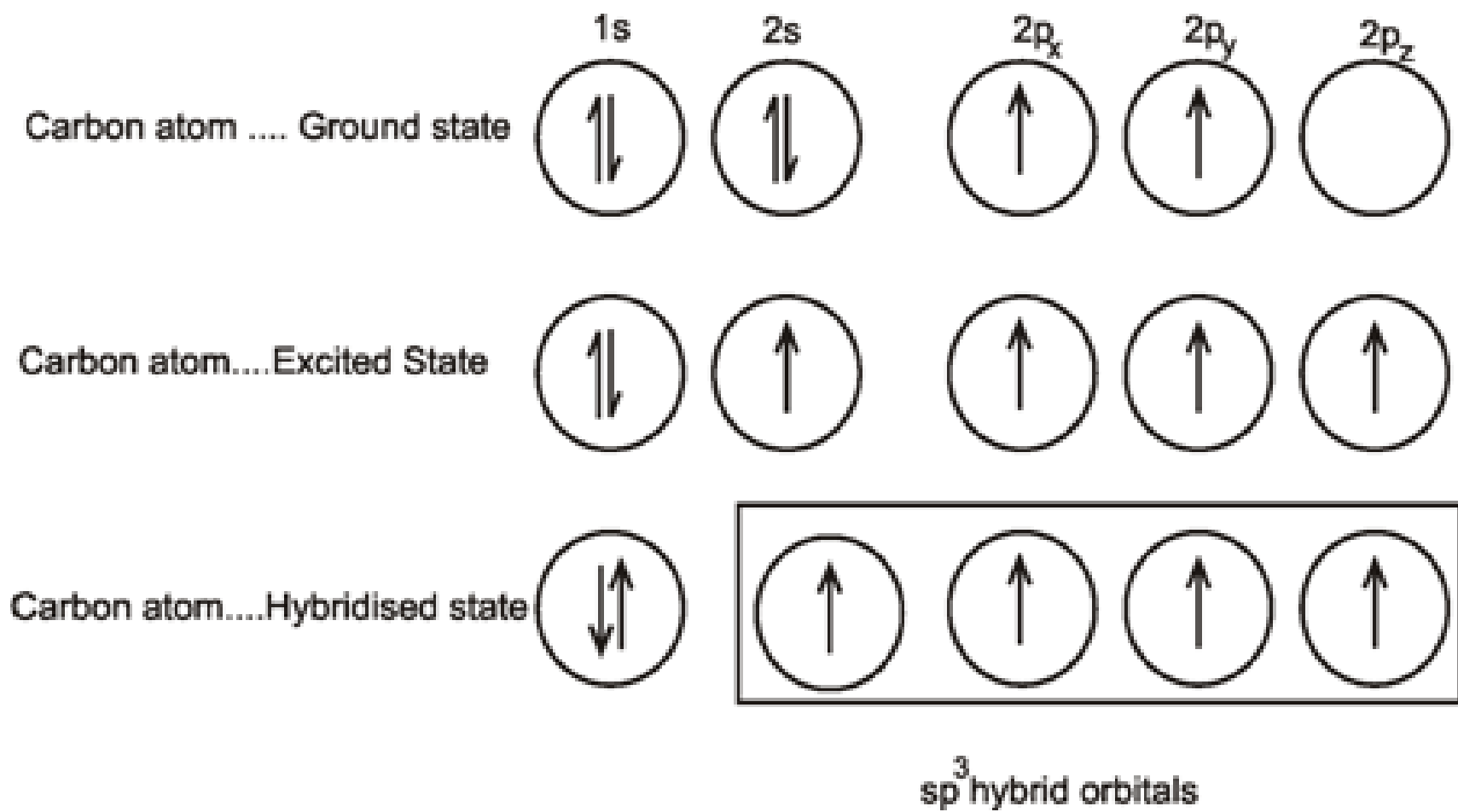
Formation of a sigma bond due to (a) The  $s - s$  overlap  
(b) The  $s - p$  overlap (c) The  $p_z - p_z$  overlap



# $\pi$ bond

Pi bonds ( **$\pi$  bonds**) are covalent chemical bonds where two lobes of one involved atomic orbital overlap two lobes of the other involved atomic orbital. Each of these atomic orbitals is zero at a shared nodal plane, passing through the two bonded nuclei.





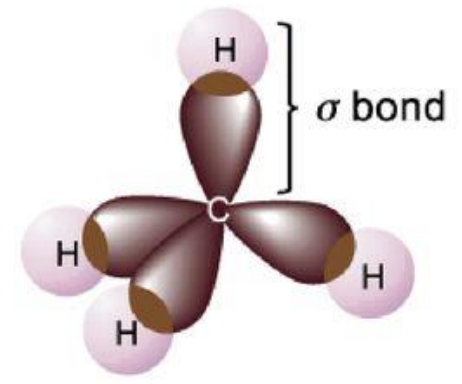
Methane (CH<sub>4</sub>)



Four  $sp^3$  hybrid orbitals of a carbon atom

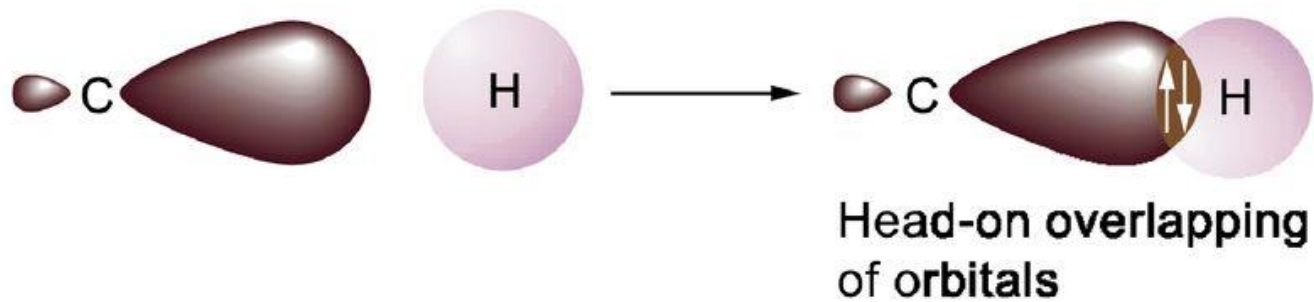
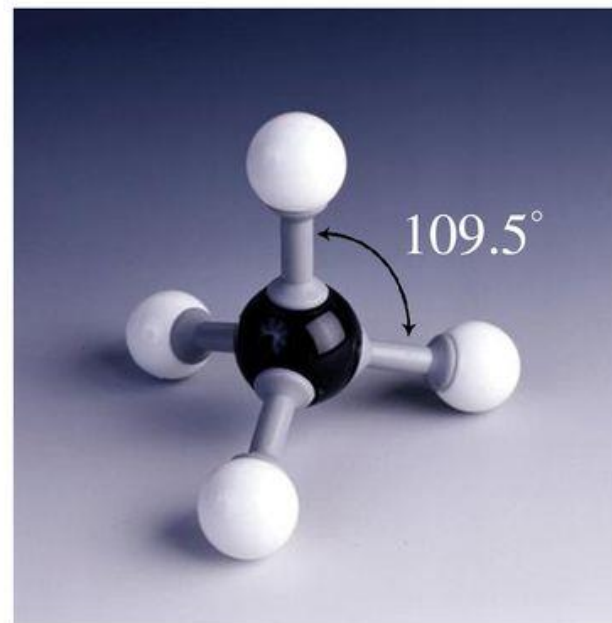
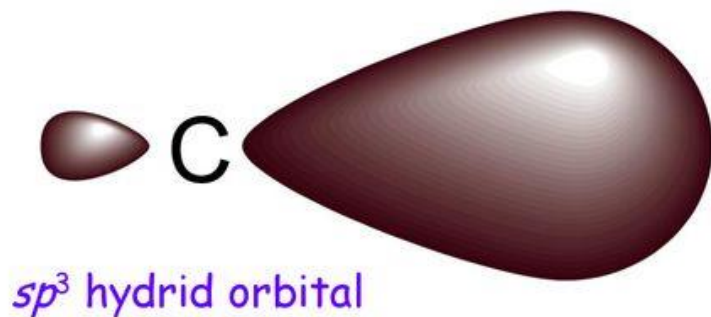


Four 1s orbitals of four hydrogen atoms

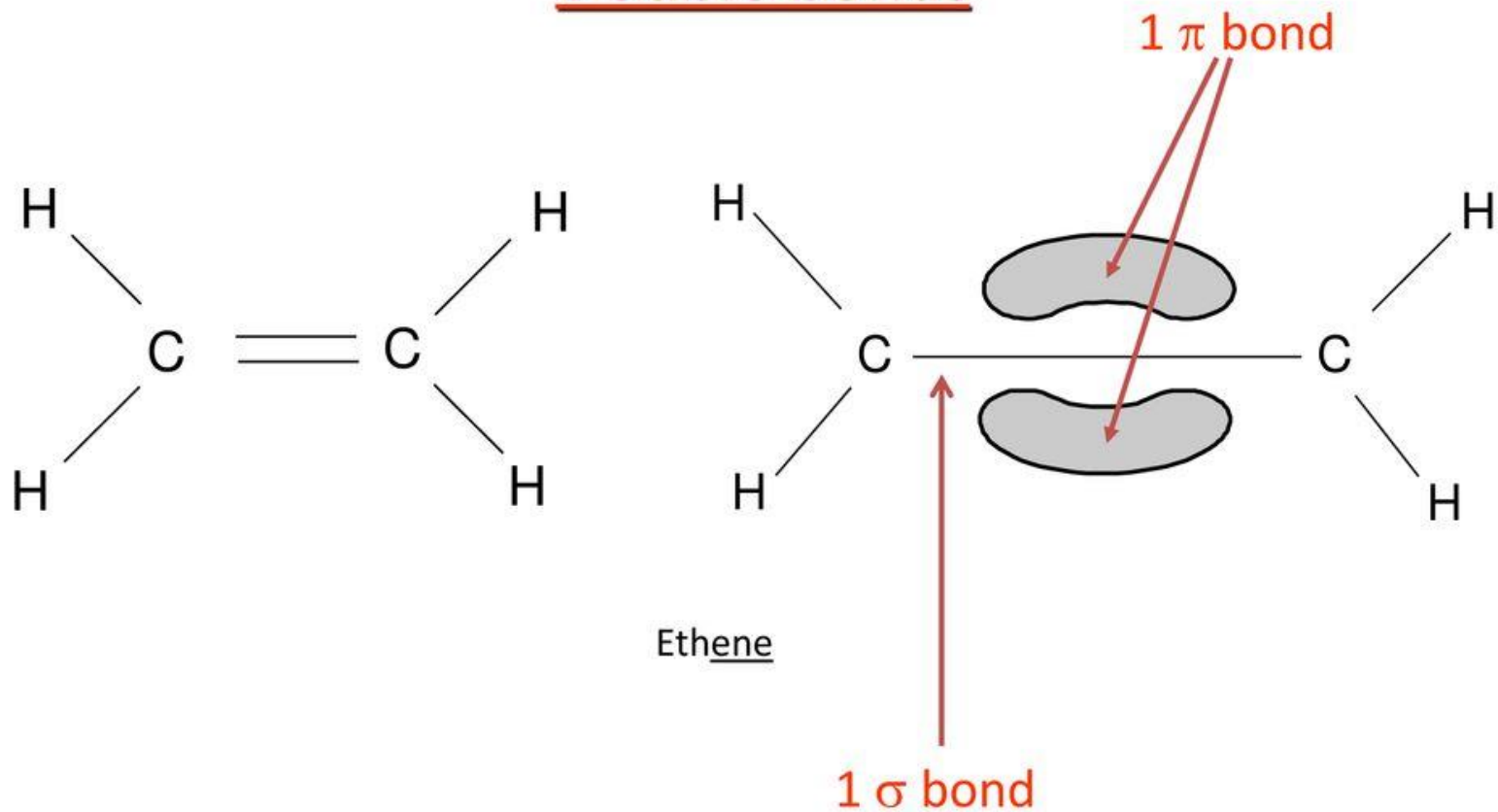


Overlapping of orbitals in a methane molecule

# New Shape for New Orbitals



# Alkenes Contain Carbon-Carbon Double bonds



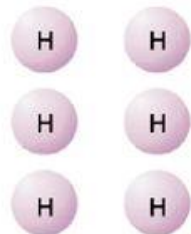
# Ethane ( $C_2H_6$ )



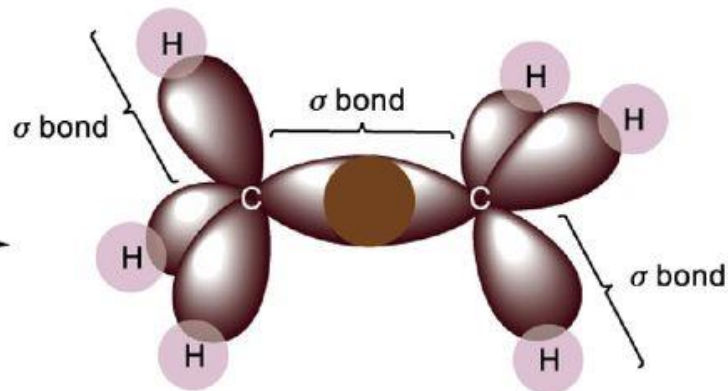
$sp^3$ -hybridized carbon atom



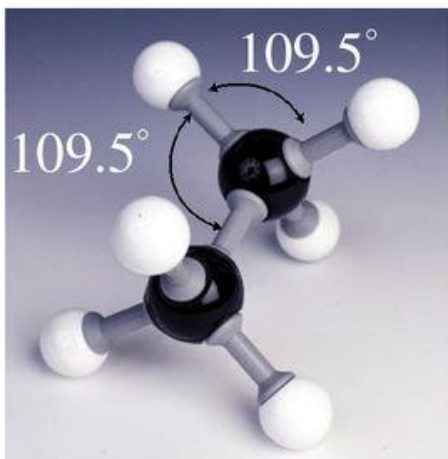
$sp^3$ -hybridized carbon atom



Six 1s orbitals of six hydrogen atoms

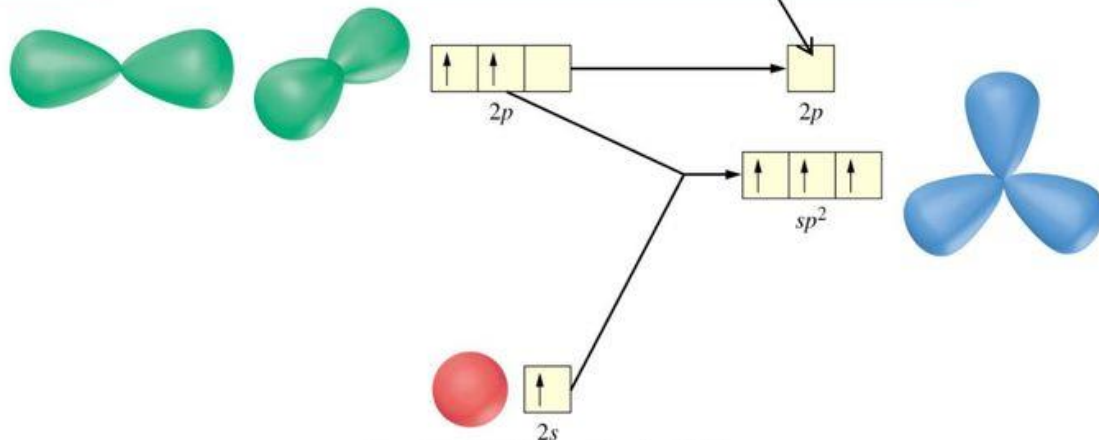


Formation of C-C and C-H  $\sigma$  bonds

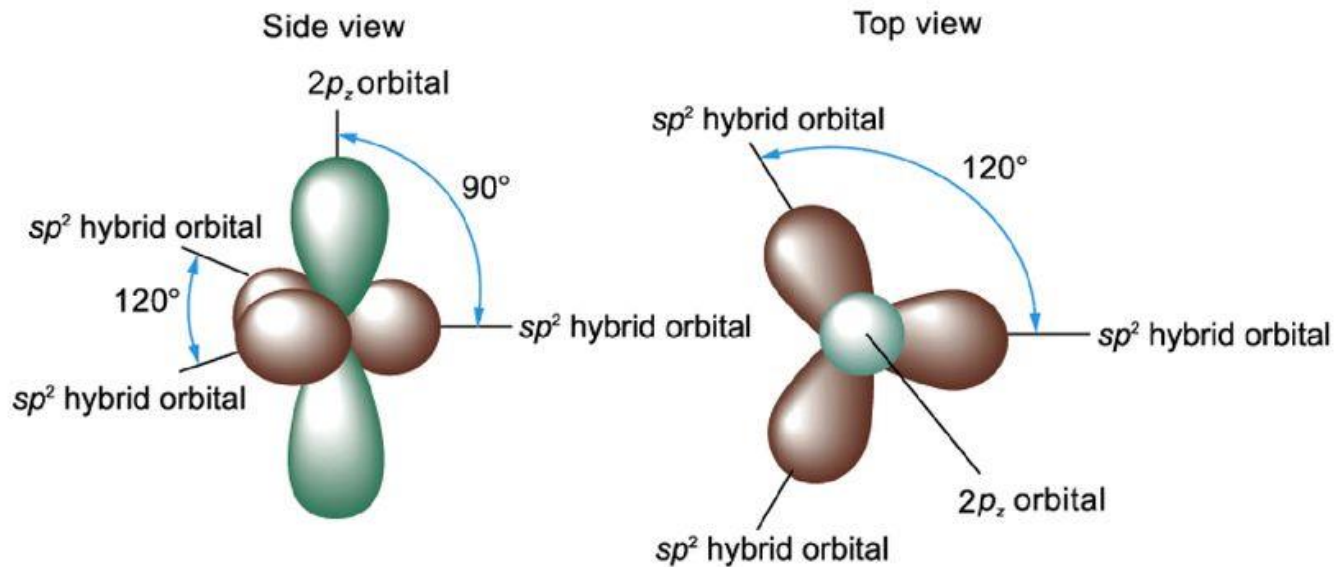


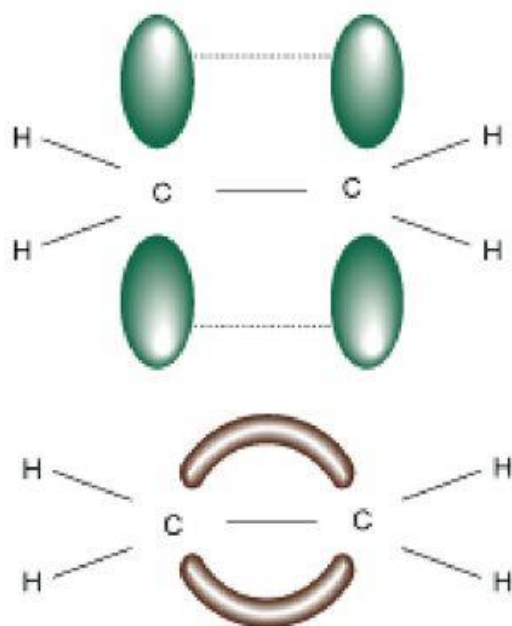
# $sp^2$ Hybridization

# Unhybridized $p$

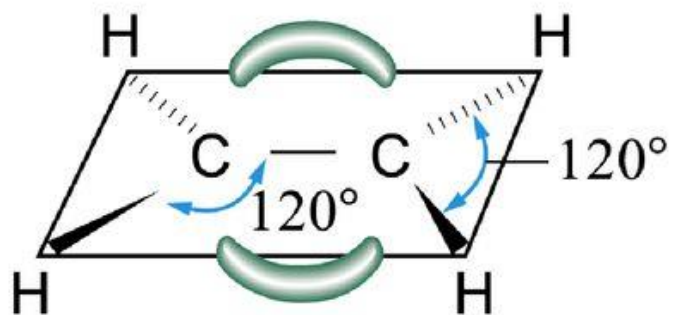
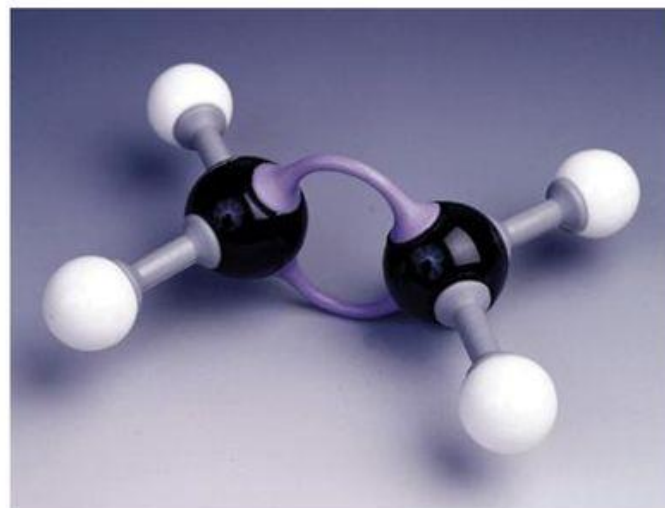


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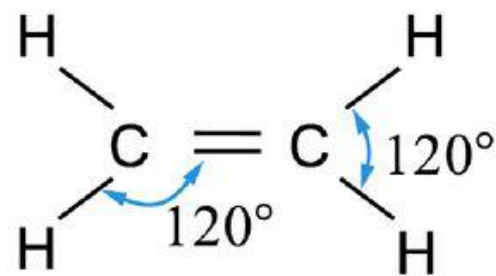




Formation of  $\pi$  bond by the side-way overlap of  $2p_x$  orbitals



or

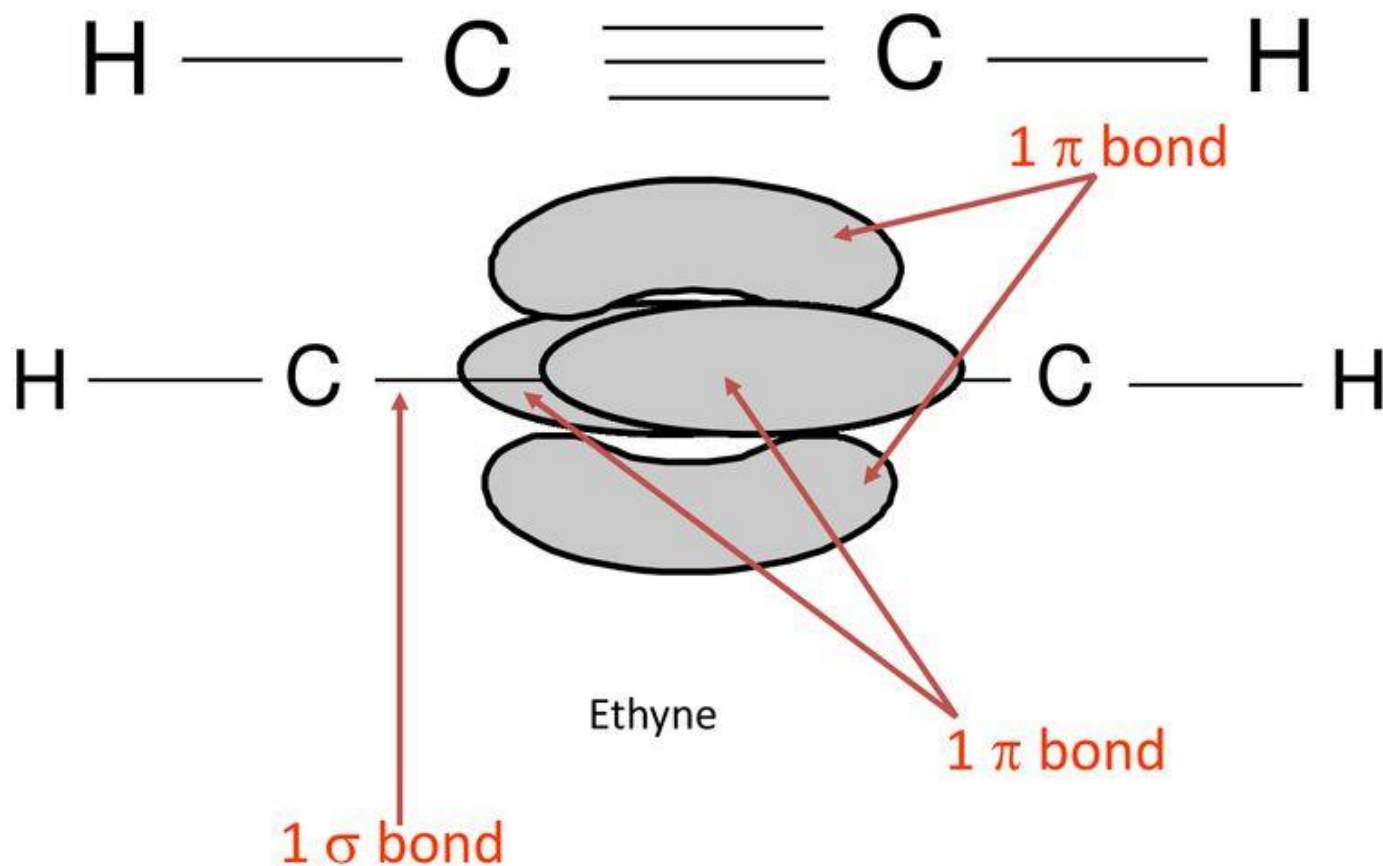




(a) Differences between the  $\sigma$  bond and the  $\pi$  bond in the carbon-carbon double bond:

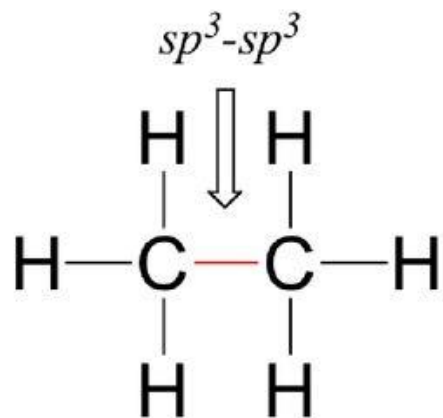
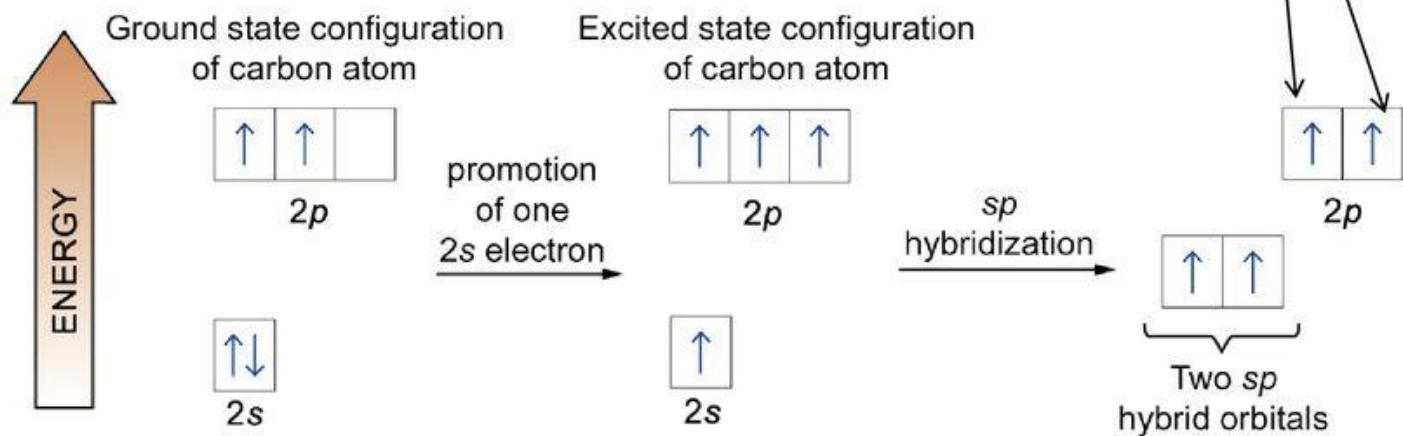
| $\sigma$ bond  | $\pi$ bond   |
|--|--|
| Head-on overlap of the $sp^2$ hybridized orbitals of two carbon atoms            | Side-way overlap of the vacant $p$ orbitals of two carbon atoms                                    |
| The bonding electrons in are localized symmetrically along the internuclear axis | The electrons in the $\pi$ bond appear as two lobes, one above and one below the internuclear axis |
| Stronger   | Weaker   |
| Free to rotate   | Restricted to rotation   |

# Alkynes Contain Carbon-Carbon Triple Bonds

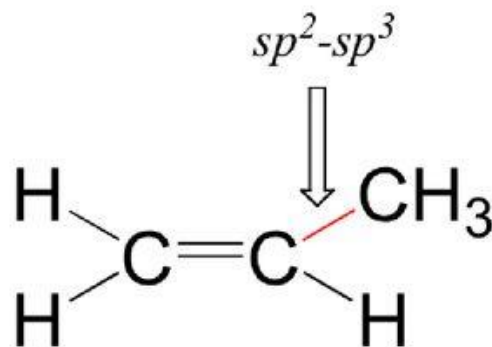


## *sp Hybridization*

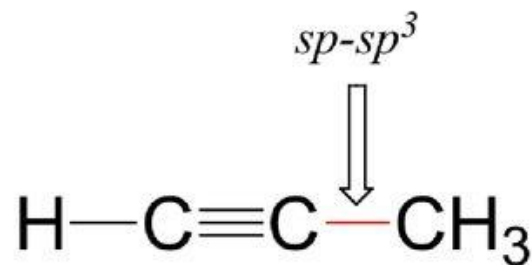
## *2 Unhybridized p for pi bonds*



A



B

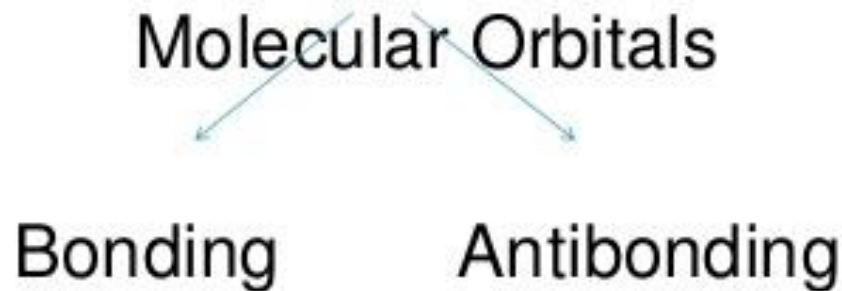


C

# PRINCIPLES OF MOT

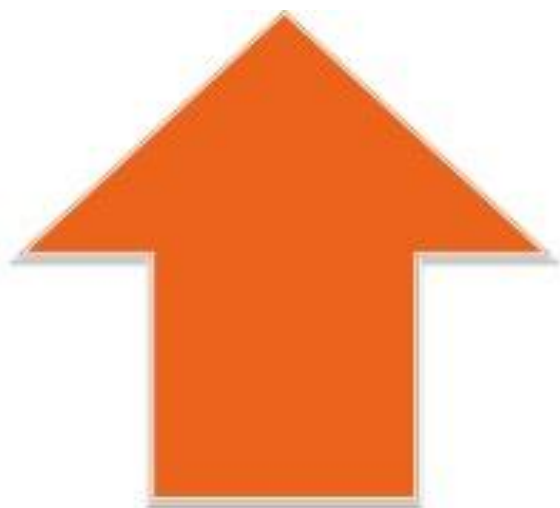
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- In molecules, atomic orbitals combine to form molecular orbitals which surround the molecule.



- 
- Molecular bonds have lower potential energy than in separate atomic orbitals.
  - Thus, electrons prefer to stay in a molecular bond.

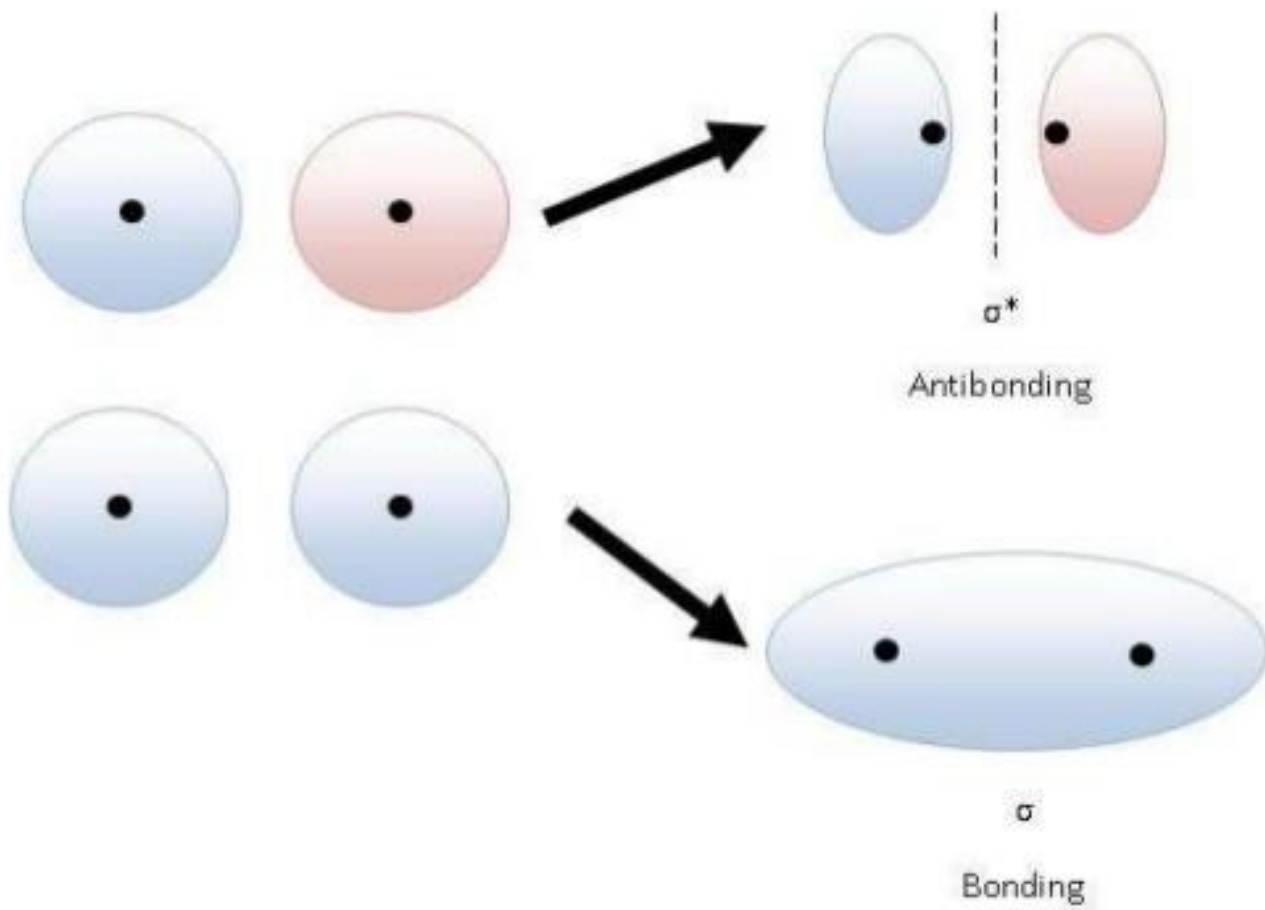




Antibonding  
Molecular  
Orbital



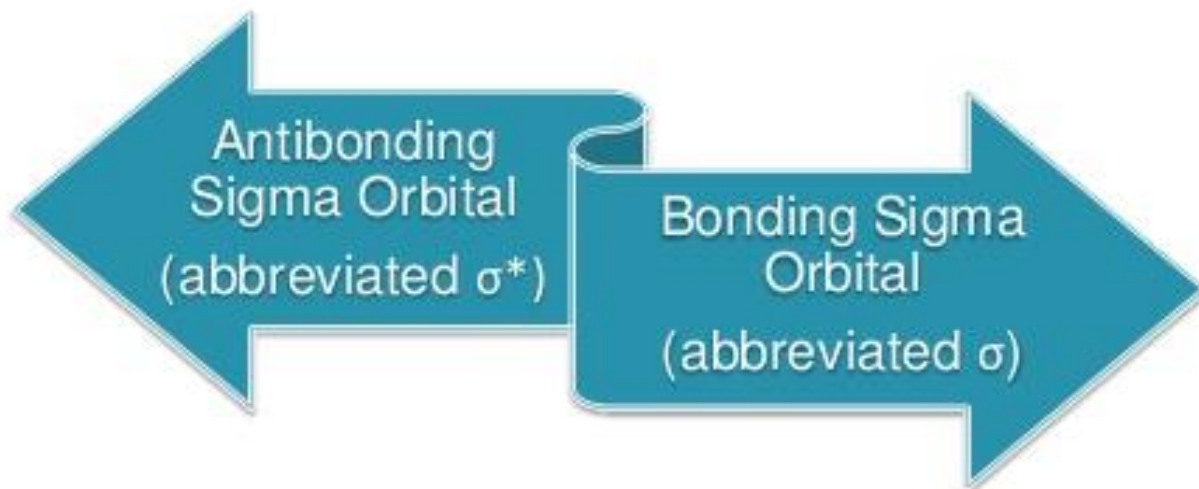
Bonding  
Molecular  
Orbital



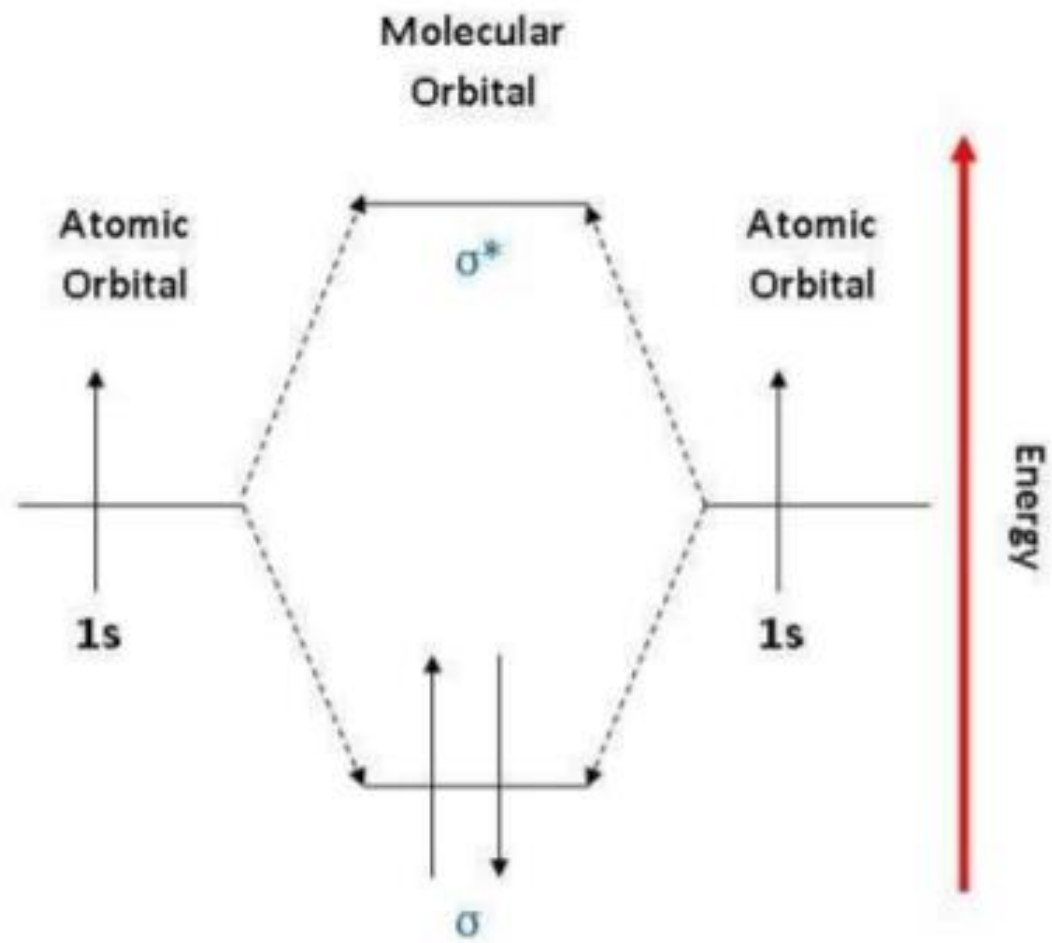
# SIGMA BONDS ( $\sigma$ )

---

- They are symmetrical about the axis
- 

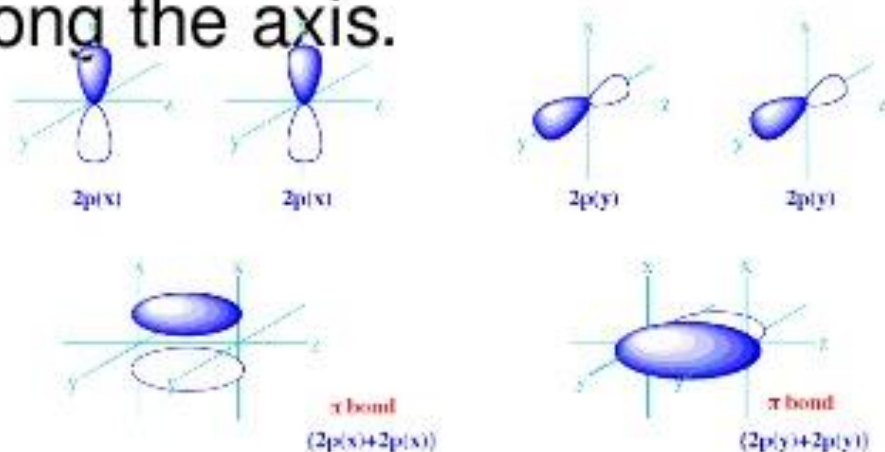






# PI BONDS ( $\pi$ )

- The pi bonding bonds as a side to side overlap, which then causes there to be no electron density along the axis, but there is density above and below the axis.



# DETERMINING BOND ORDER

- Bond Order indicates the strength of the bond. The higher the Bond Order, the stronger the bond.

$$\text{Bond Order} = \frac{1}{2}(a-b)$$

where, a = number of e<sup>-</sup> in bonding Molecular Orbitals

b = number of e<sup>-</sup> in antibonding Molecular Orbitals.

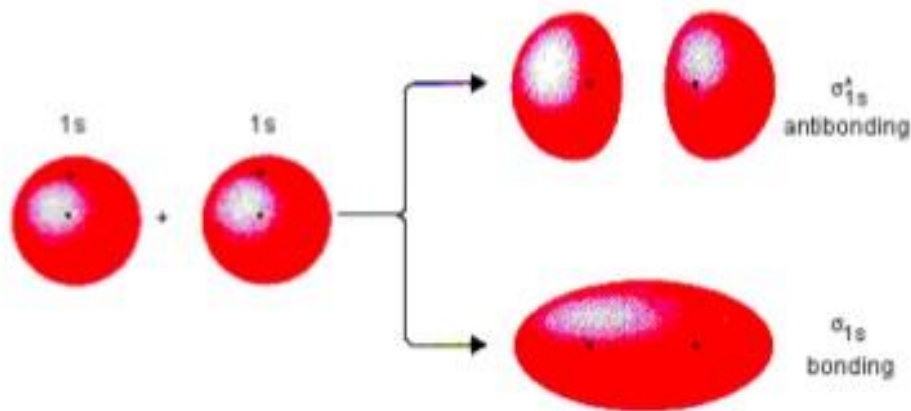
# STABILITY OF THE MOLECULE

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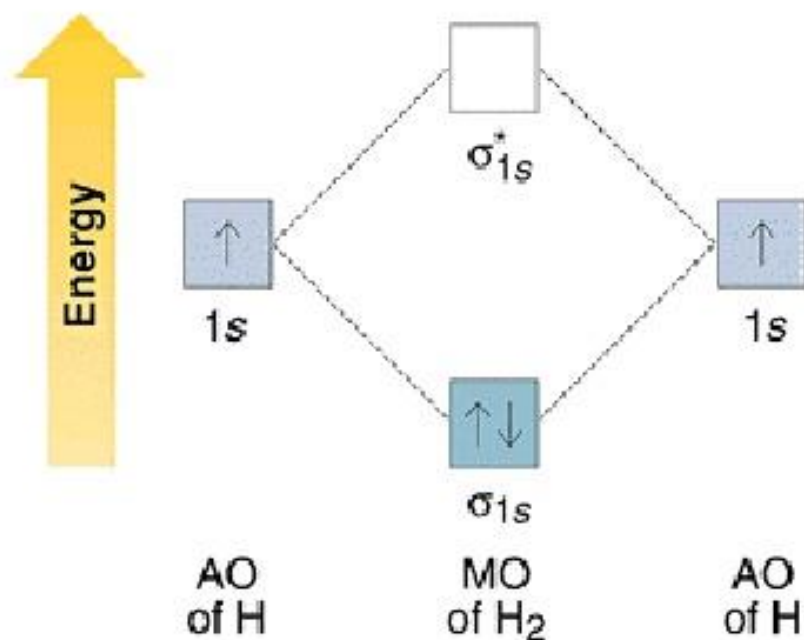
- If the Bond Order is Zero, then no bonds are produced and the molecule is not stable (for example  $\text{He}_2$ ).
- If the Bond Order is 1, then it is a single covalent bond.
- The higher the Bond Order, the more stable the molecule is.

# Molecular Orbital Theory

- Molecular orbitals result from the combination of atomic orbitals. Since orbitals are wave functions, they can combine either constructively (forming a bonding molecular orbital), or destructively (forming an antibonding molecular orbital).
- Consider the  $H_2$  molecule, for example. One of the molecular orbitals in this molecule is constructed by adding the mathematical functions for the two  $1s$  atomic orbitals that come together to form this molecule. Another orbital is formed by subtracting one of these functions from the other



# Electronic configuration, $\sigma^2$ , for $H_2$ molecules

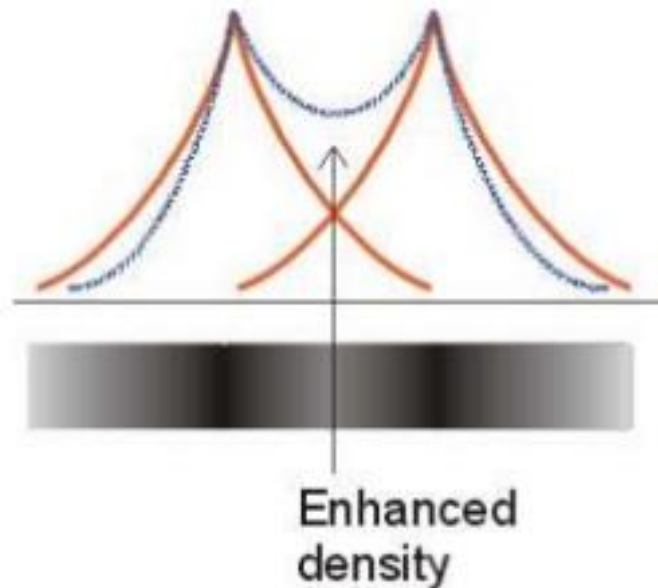


$$H_2 \text{ bond order} = \frac{1}{2} (2 - 0) = 1$$

Generalize the technique of **LCAO**

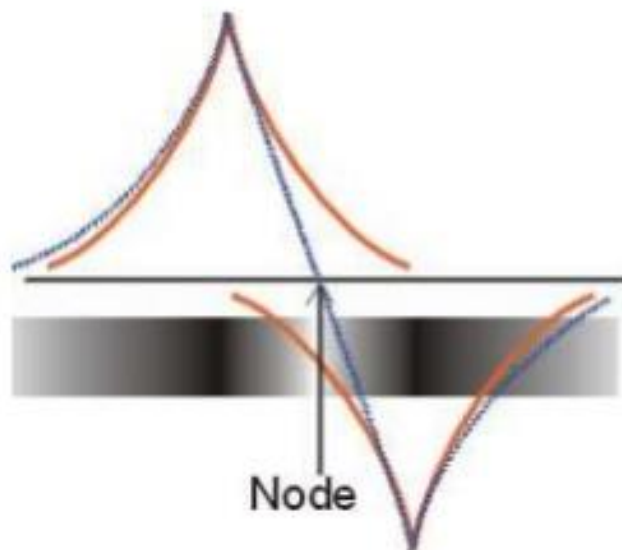
Theories of chemical bonding

## Bonding Molecular Orbital Theory



The bonding orbital results in increased electron density between the two nuclei, and is of lower energy than the two separate atomic orbitals.

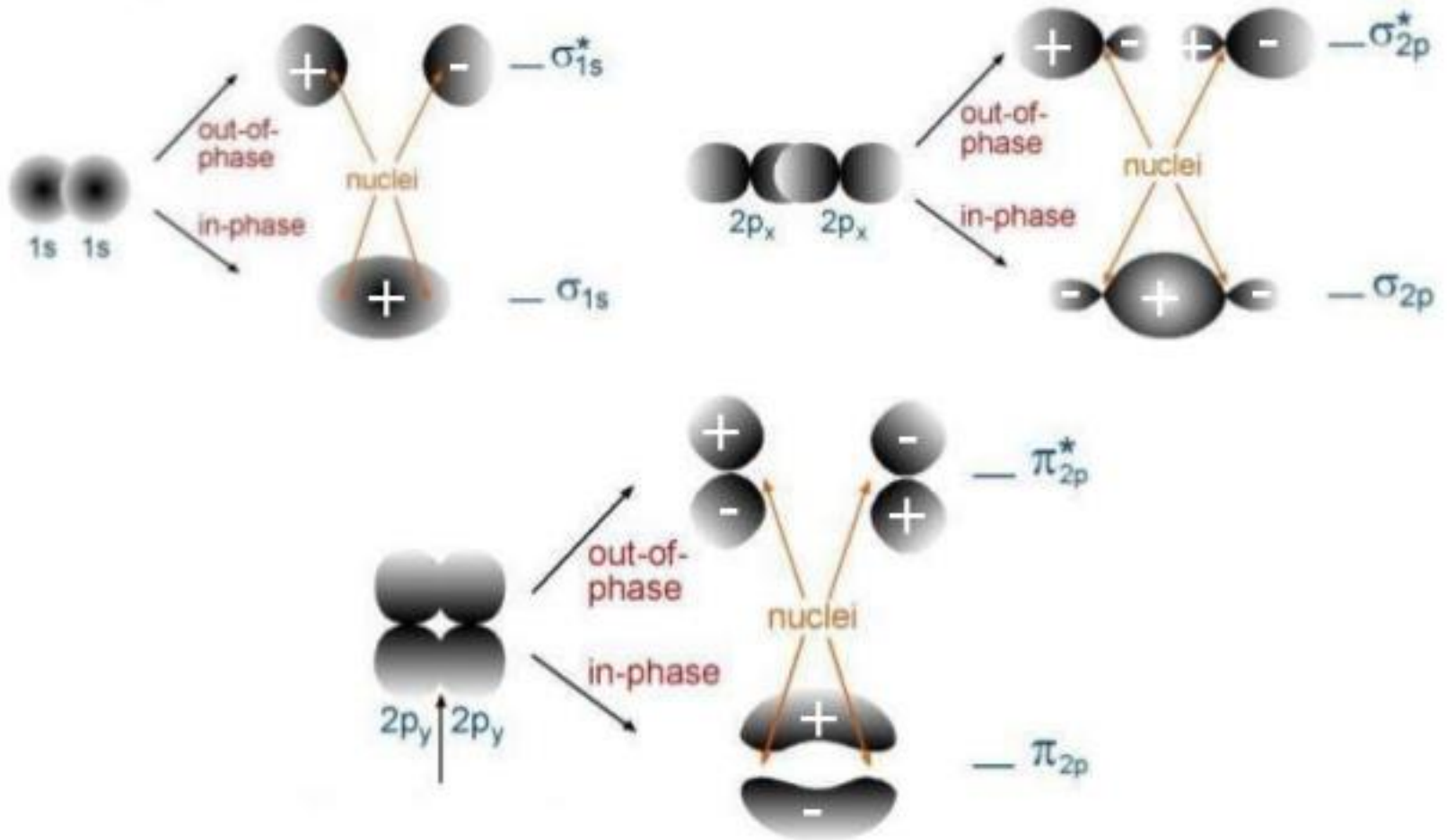
## Antibonding Molecular Orbital Theory



The antibonding orbital results in a node between the two nuclei, and is of greater energy than the two separate atomic orbitals.

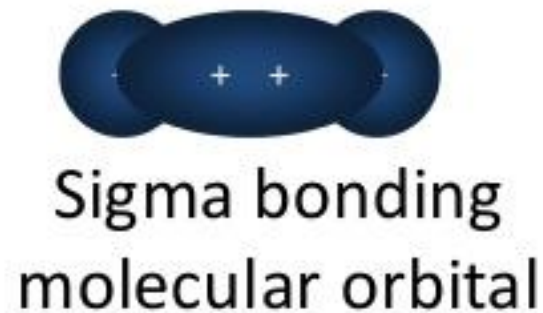


# Overlap of s & p Orbitals



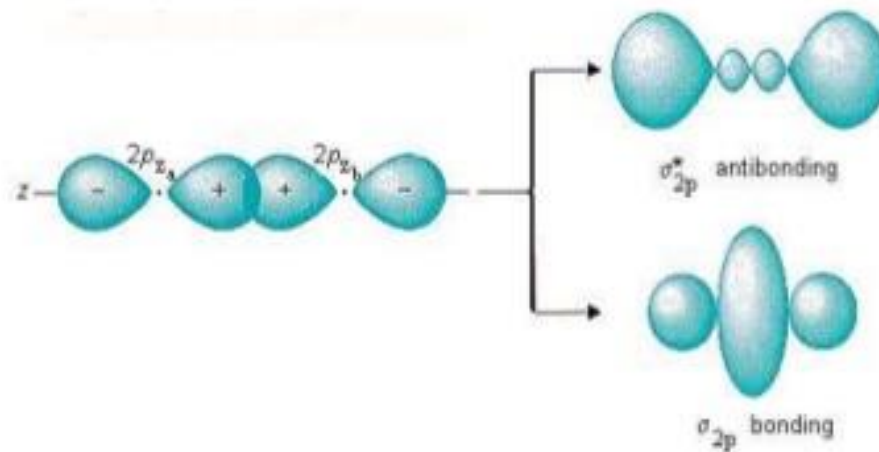
# Sigma bonding orbitals

- From s orbitals on separate atoms



## *Molecular Orbitals of the Second Energy Level*

If we arbitrarily define the  $Z$  axis of the coordinate system for the  $O_2$  molecule as the axis along which the bond forms, the  $2p_z$  orbitals on the adjacent atoms will meet head-on to form a  $\sigma_{2p}$  bonding and a  $\sigma_{2p}^*$  antibonding molecular orbital



# Sigma bonding orbitals

- From p orbitals on separate atoms

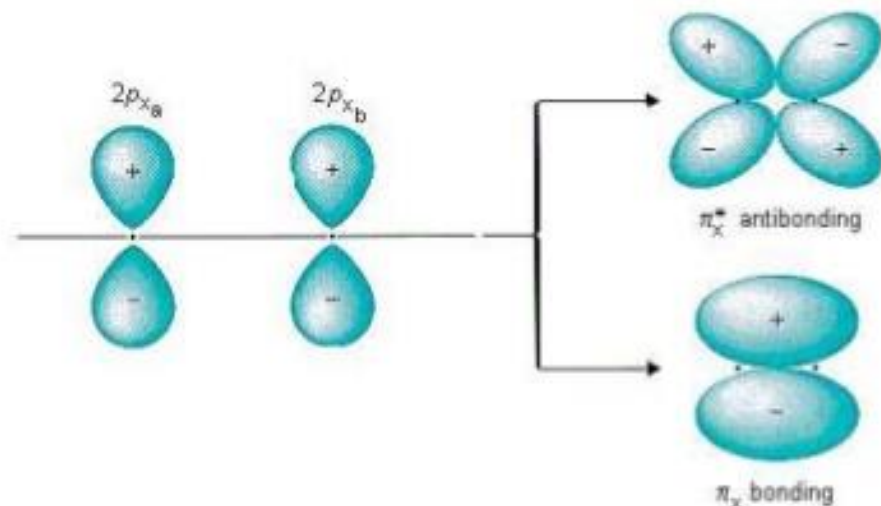


p orbital

p orbital



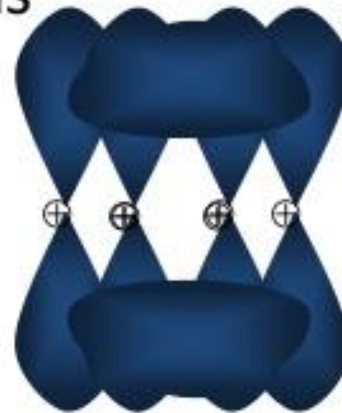
Sigma bonding  
molecular orbital



The  $2p_x$  orbitals on one atom interact with the  $2p_x$  orbitals on the other to form molecular orbitals that have a different shape. These molecular orbitals are called *pi* ( $\pi$ ) orbitals because they look like *p* orbitals when viewed along the bond.

## Pi bonding orbitals

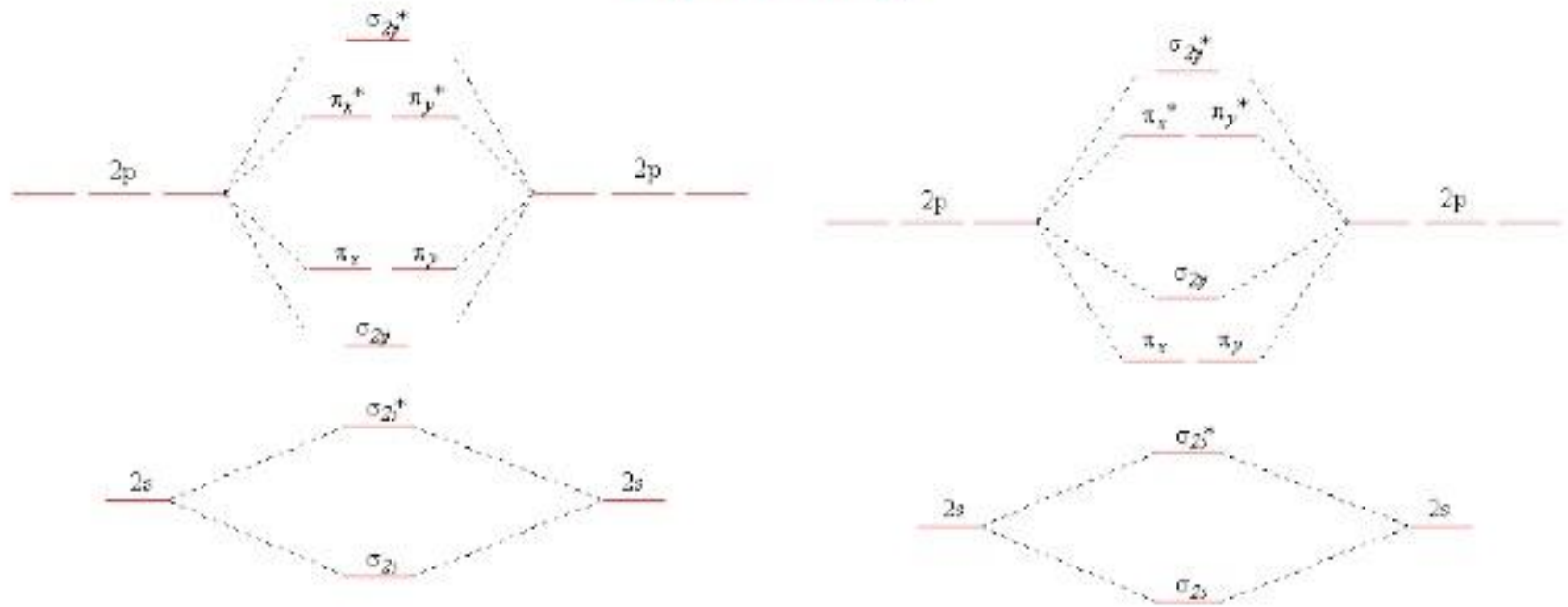
- P orbitals on separate atoms



Pi bonding  
molecular orbital

# Molecular Orbital Diagram

## *s-p* mixing









$\sigma^*1s$



antibonding



bonding MO

$\sigma 1s$

**bond order =**

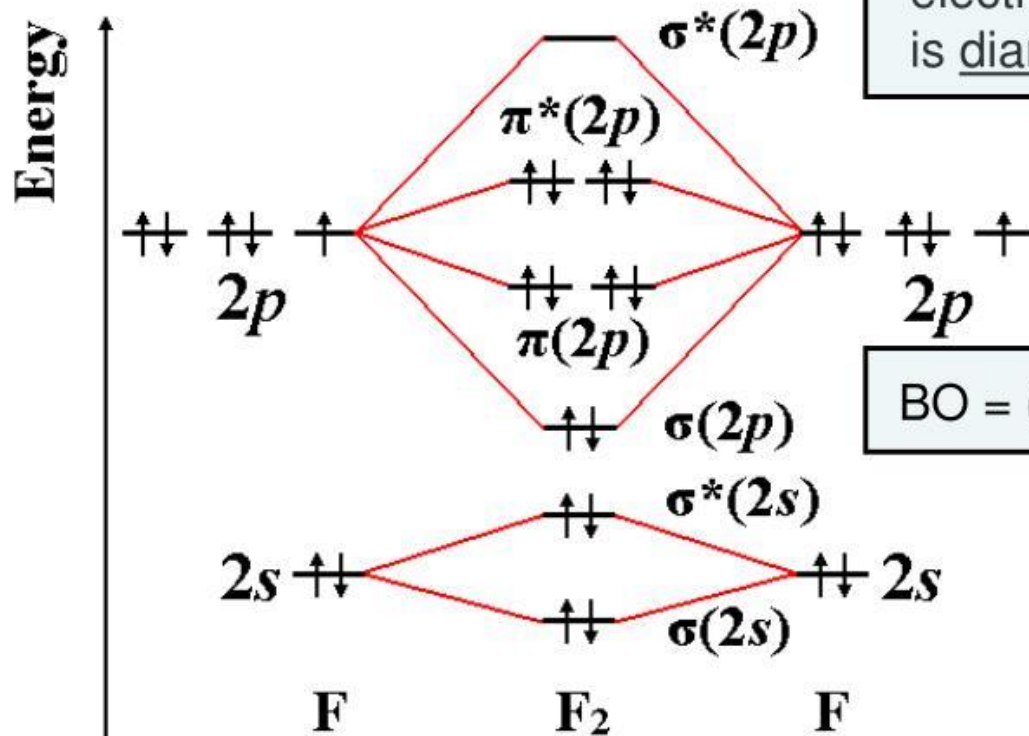
$$\frac{\left( \begin{array}{c} \text{number of electrons} \\ \text{in bonding MO} \end{array} \right) - \left( \begin{array}{c} \text{number of electrons} \\ \text{in anti-bonding MO} \end{array} \right)}{2}$$

2

$$\frac{2 - 0}{2} = 1$$

**bond order = 1**

## F<sub>2</sub> molecule, bond order = 1



F<sub>2</sub> has no unpaired electrons, and so is diamagnetic

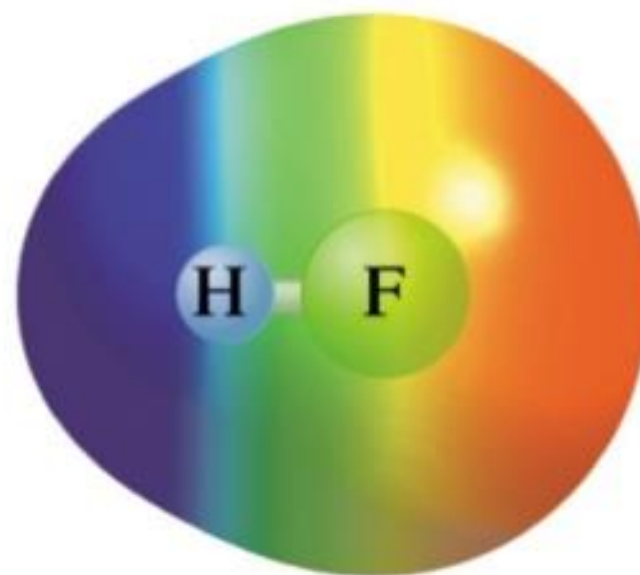
**MO diagram for difluorine (F<sub>2</sub>) molecule.**

*Thank you*

# **PARTIAL IONIC CHARACTER**

# Dipoles and Dipole Moments

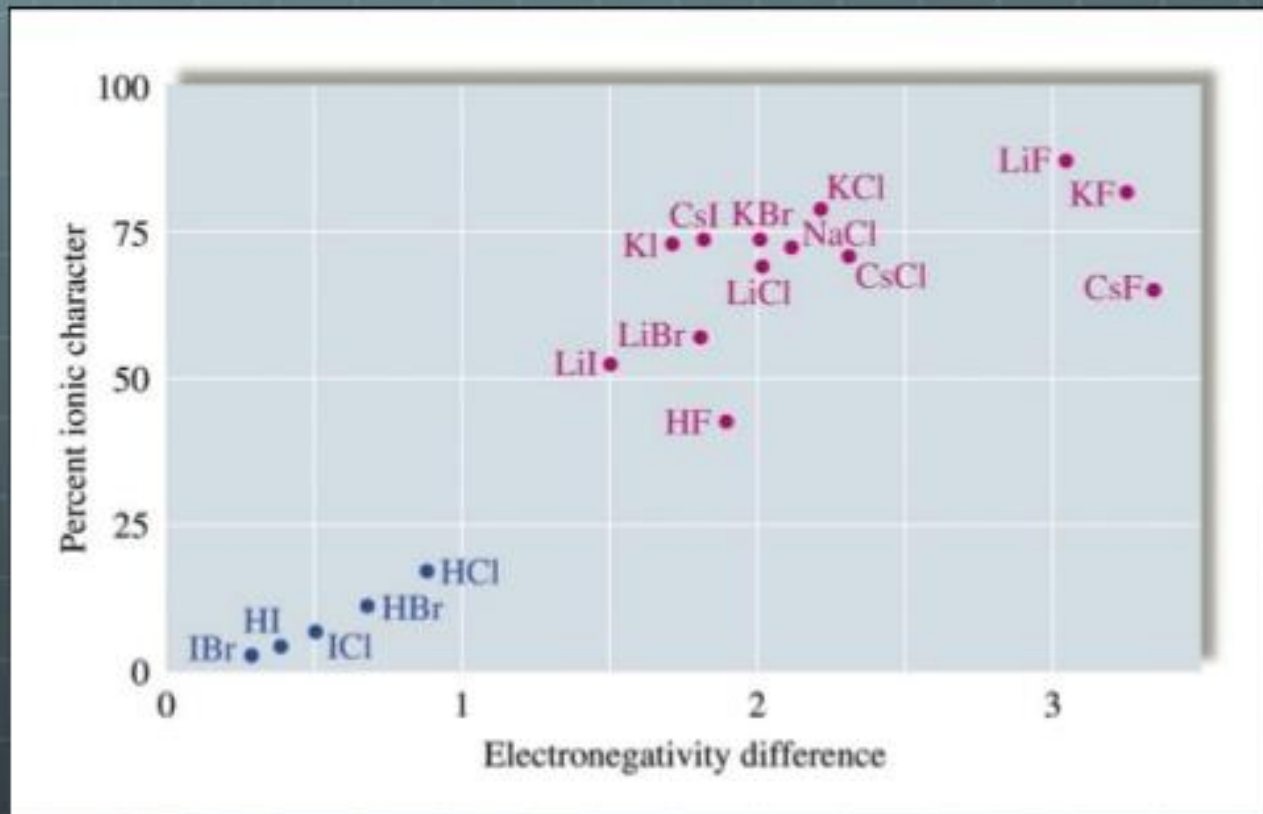
- 🌐 Electrostatic potential diagram shows variation in charge. Red is the most electron rich region and blue is the most electron poor region.



# Dipoles and Dipole Moments

- 🌐 Dipole moments are when opposing bond polarities don't cancel out.

# Bond Character



# Bond Energy

**TABLE 8.5 Bond Lengths for Selected Bonds**

| Bond | Bond Type | Bond Length (pm) | Bond Energy (kJ/mol) |
|------|-----------|------------------|----------------------|
| C—C  | Single    | 154              | 347                  |
| C=C  | Double    | 134              | 614                  |
| C≡C  | Triple    | 120              | 839                  |
| C—O  | Single    | 143              | 358                  |
| C=O  | Double    | 123              | 745                  |
| C—N  | Single    | 143              | 305                  |
| C=N  | Double    | 138              | 615                  |
| C≡N  | Triple    | 116              | 891                  |

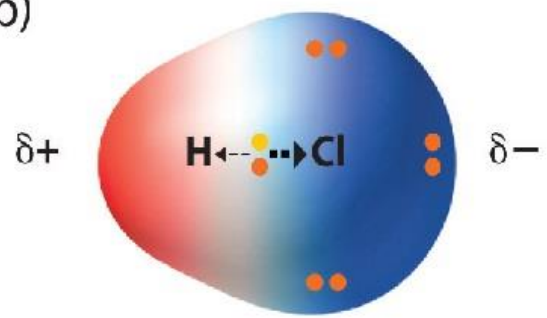


(a)



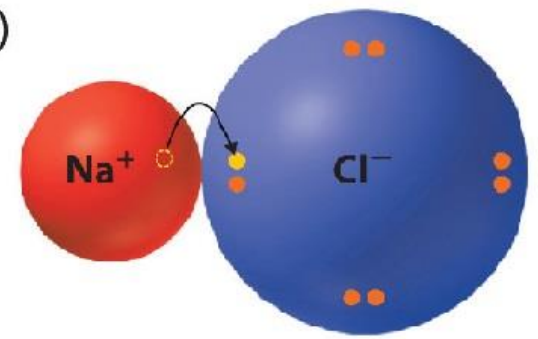
**Nonpolar covalent bond**  
 Bonding electrons shared equally between two atoms.  
 No charges on atoms.

(b)

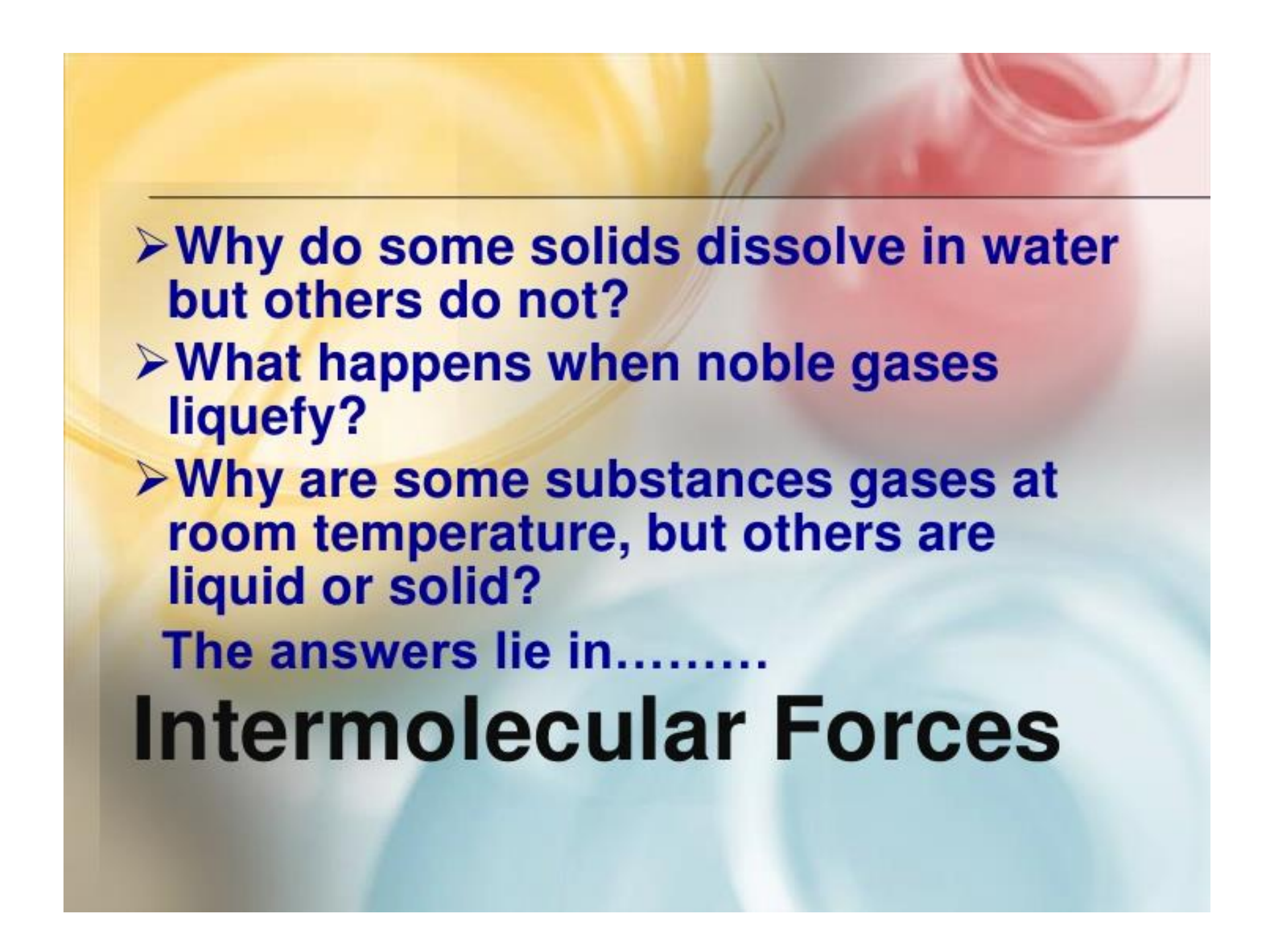


**Polar covalent bond**  
 Bonding electrons shared unequally between two atoms.  
 Partial charges on atoms.

(c)



**Ionic bond**  
 Complete transfer of one or more valence electrons.  
 Full charges on resulting ions.

- 
- A background image showing laboratory glassware, including a yellow beaker on the left and a red flask on the right, with a blue-tinted circular pattern at the bottom.
- 
- **Why do some solids dissolve in water but others do not?**
  - **What happens when noble gases liquefy?**
  - **Why are some substances gases at room temperature, but others are liquid or solid?**

**The answers lie in.....**

# **Intermolecular Forces**

- **Intermolecular forces** may be attractive or repulsive.
- **Johannes D van der Waals**, Dutch, was the first to postulate intermolecular forces in developing a theory to account for properties of real gases.





- **van der Waals forces include**

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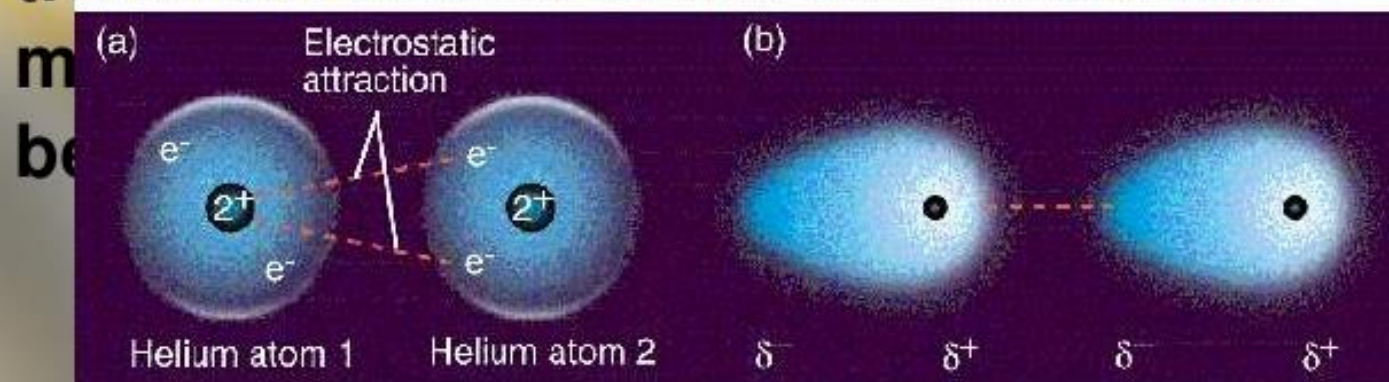
- London forces
- Dipole - dipole forces
- Dipole - induced dipole forces

- **Other intermolecular forces are**

- Ion - dipole interactions
- Ion - induced dipole interactions
- Hydrogen Bonding

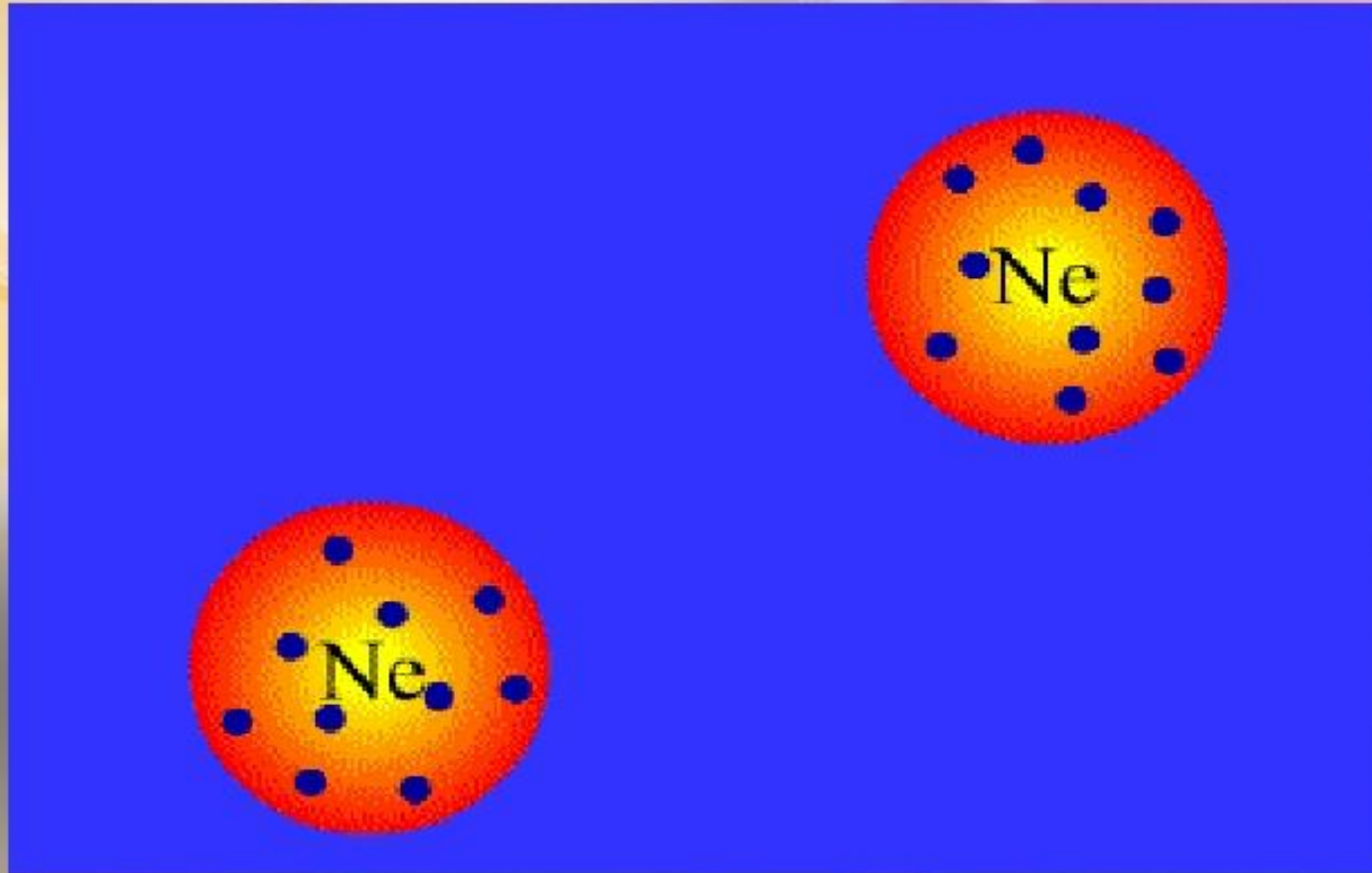
# LONDON FORCES (DISPERSION FORCES)

These arise from temporary variations in electron density in atoms and molecules. At any instant, the electron distribution may be unsymmetrical and hence produce an instantaneous dipole. This can cause an induced transient dipole in the neighbouring

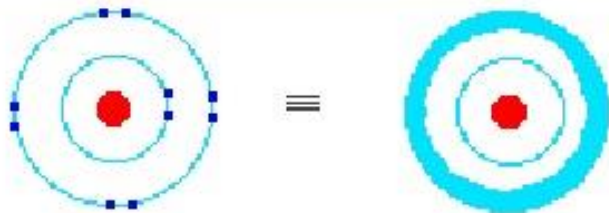


# LONDON FORCES

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- **Dispersion forces are present between all molecules , whether polar or non-polar.**
- **Dispersion forces are stronger in molecules that are easily polarizable.**
- **Larger and heavier molecules exhibit stronger dispersion forces than smaller and lighter ones.**



Neon

no permanent dipole

# MAGNITUDE OF DISPERSION FORCES

- The cylindrical shape of *n*-pentane has greater surface area. Hence, *n*-
- The spherical shape of neopentane has lesser surface area. So, it has less attractive forces.



*n*-Pentane  
(bp = 309.4 K)

on

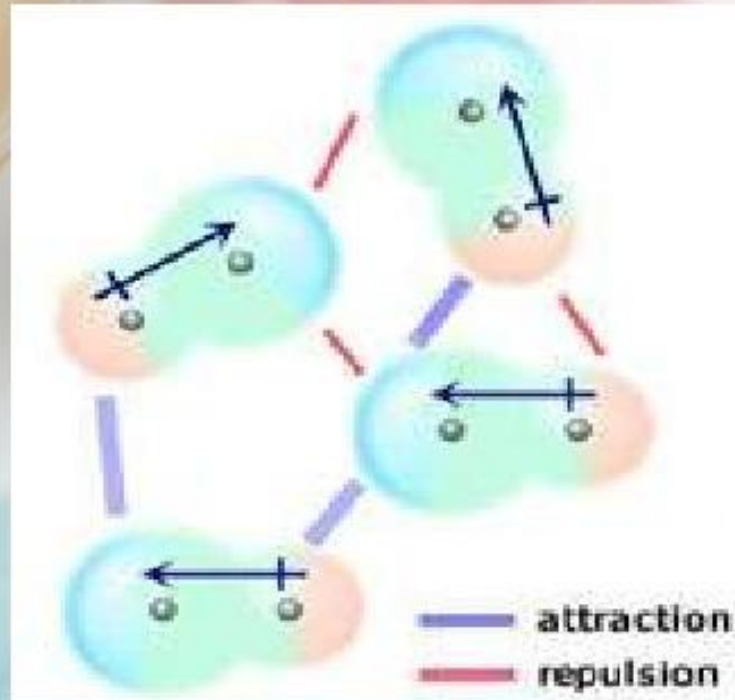


Neopentane  
(bp = 282.7 K)

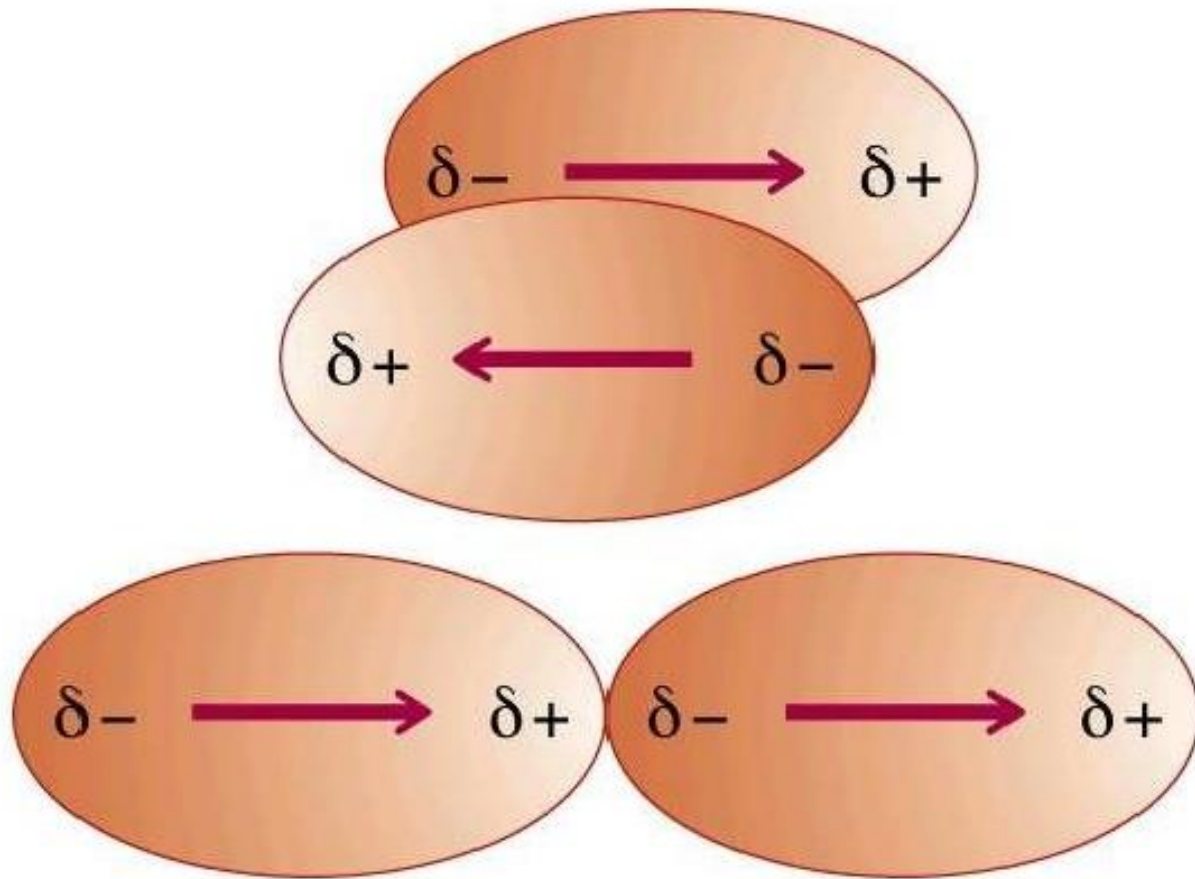


# DIPOLE-DIPOLE FORCES (KEESOM FORCES)

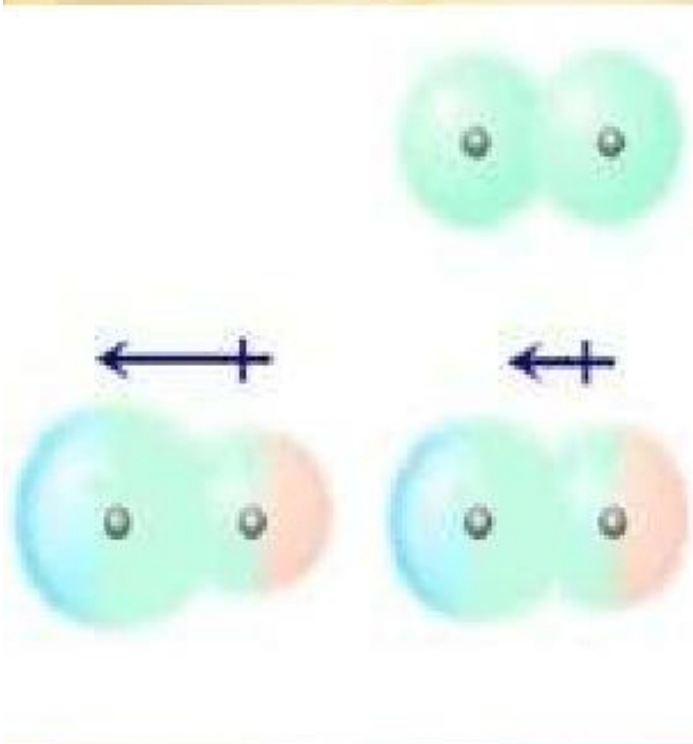
These forces arise due to interaction between oppositely charged ends of polar molecules. Greater the dipole moment of molecules, greater are the



# FORCES



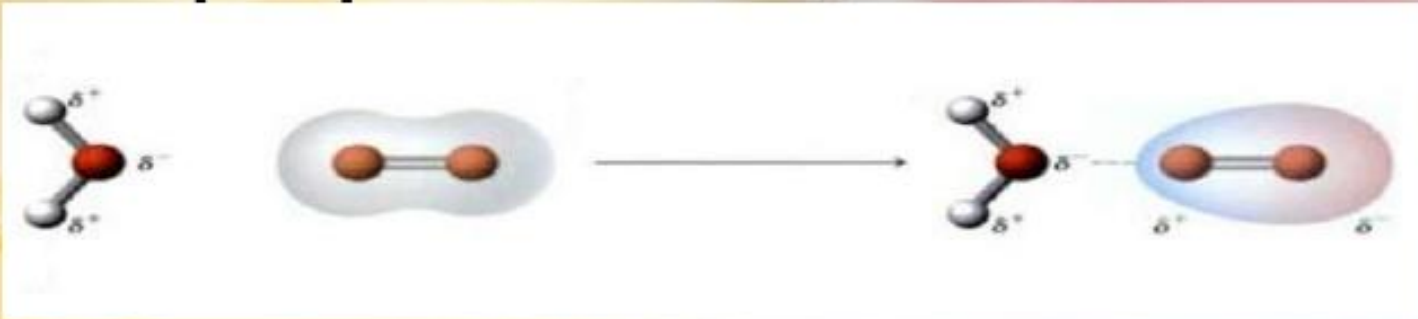
# DIPOLE-INDUCED DIPOLE FORCES



These operate between polar molecules having permanent dipole and the molecules having no permanent dipole. The polar molecule induces a dipole in the neighbouring non-polar molecule. The interaction energy depends on

- Dipole moment of polar molecule

- **Oxygen gas can dissolve in water because the permanent dipole in water can induce a dipole in oxygen**

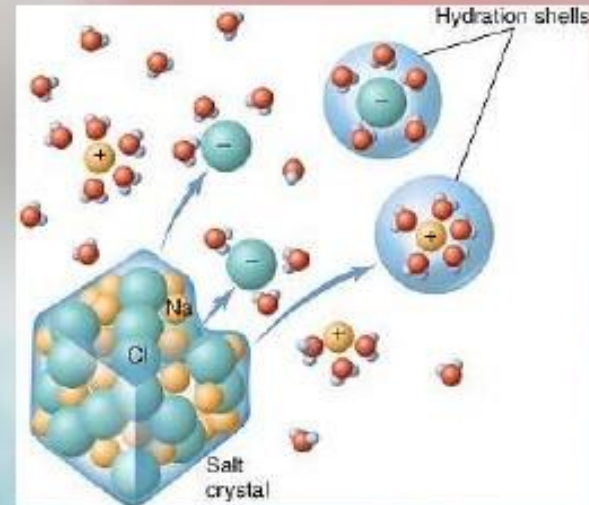


- **Non-polar iodine dissolves in polar ethanol due to dipole-induced dipole forces**

# INTERACTIONS

These interactions depend on

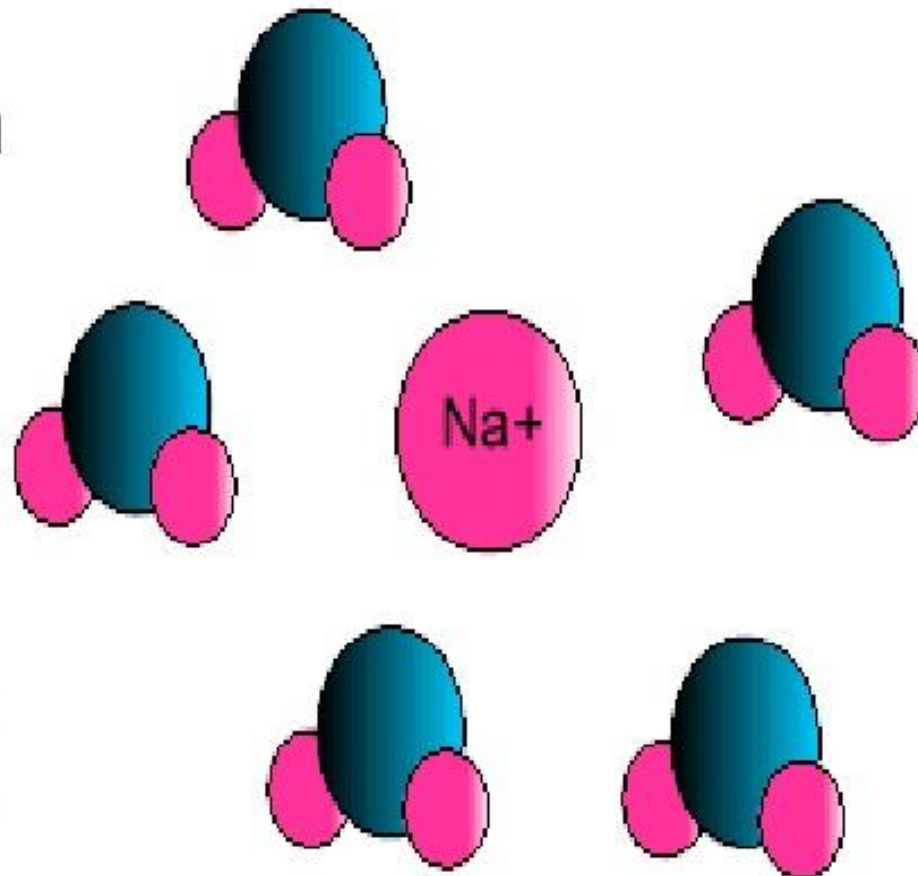
- Charge and size of ion
- Magnitude of dipole moment of polar molecule



**Hydration**

**Of**

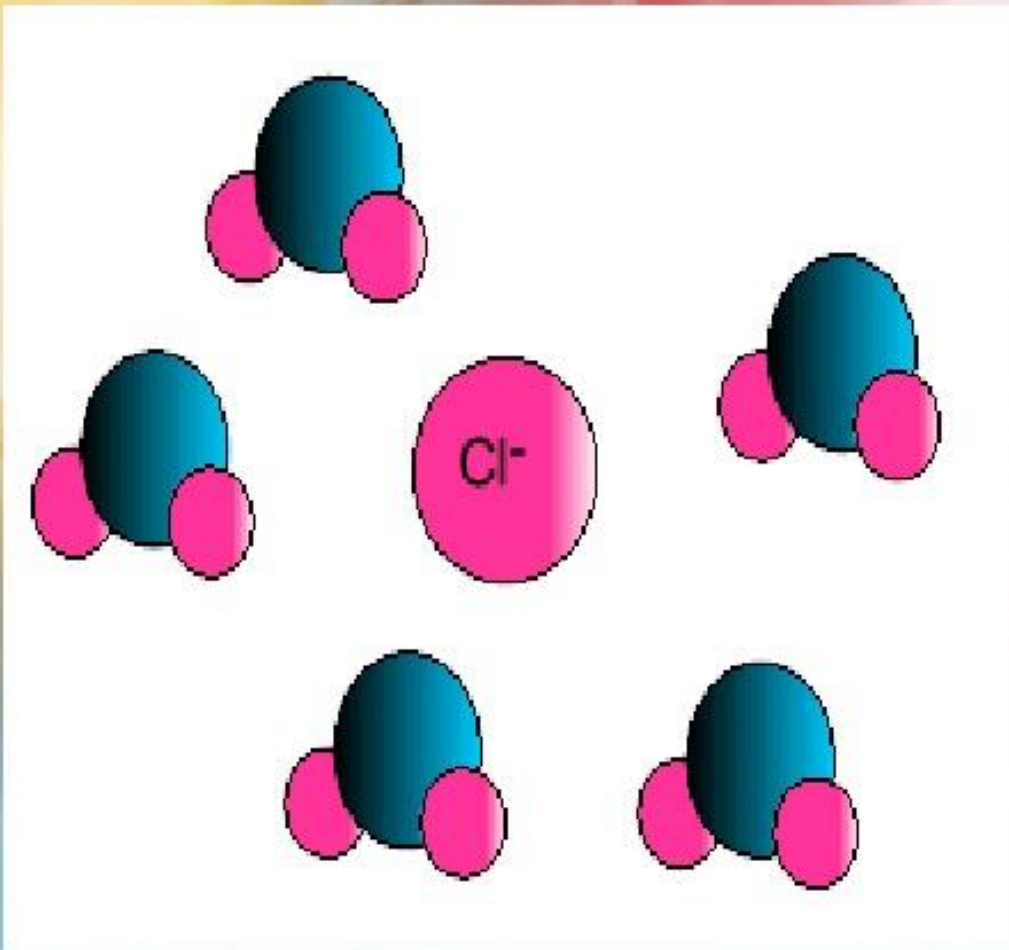
**Sodium  
ions**



**Hydration**

**of**

**Chloride  
Ions**

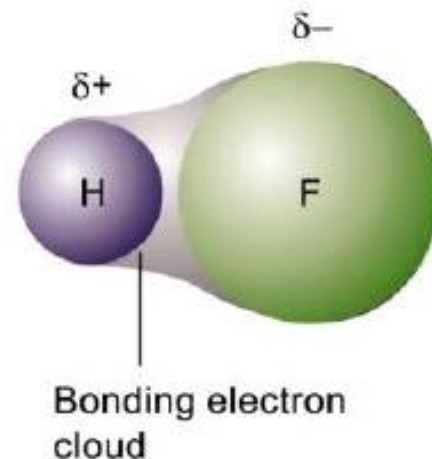


# **HYDROGEN BONDING**



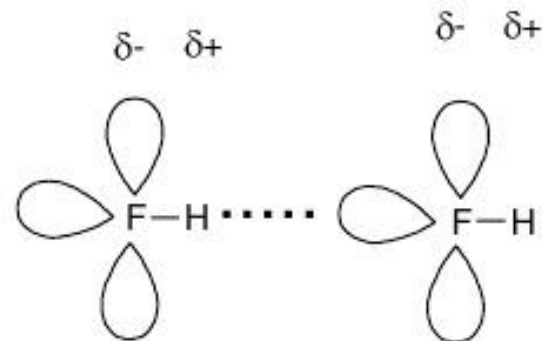
# Hydrogen bonding

- When hydrogen is bonded to a highly electronegative atom (such as **nitrogen**, **oxygen**, **fluorine**), the bonding electron pair is drawn towards the **electronegative** atom



# Hydrogen bonding

- Hydrogen has no **inner shell** electron and is very small in size, the positive charge density developed is **high**
- The nucleus of hydrogen atom is exposed to attraction by nearby electron cloud, a **lone pair electrons** on the electronegative atom



# Hydrogen bonding

- Definition:
  - Electrostatic **attraction** between **hydrogen** atoms bonded to small, strongly **electronegative** atoms (N, O and F) and the **lone pair electrons** on these electronegative atoms

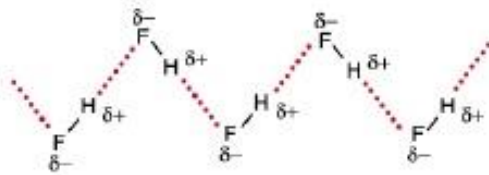


# Hydrogen Bonding

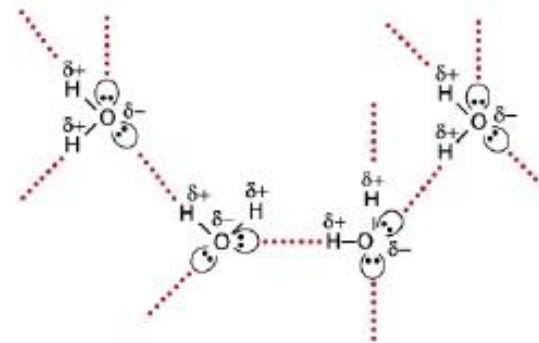
- Essential requirements for formation of hydrogen bond:
  - A hydrogen atom **must be directly bonded to a highly electronegative atom** (e.g. F, O and N)
  - An **unbonded pair of electrons (lone pair electrons)** is presented on the electronegative atom

# Hydrogen bonding

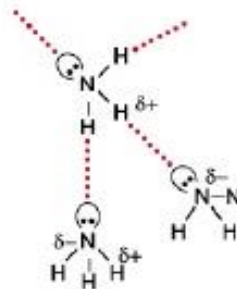
## ■ Examples



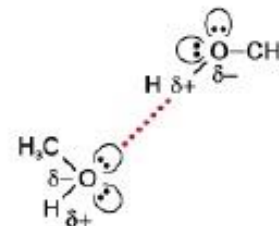
Hydrogen fluoride (HF)



Water (H<sub>2</sub>O)



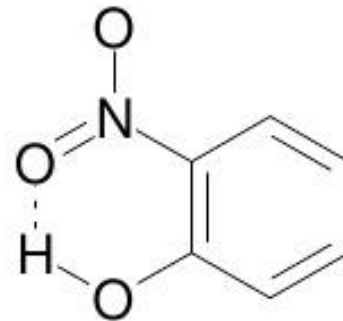
Ammonia (NH<sub>3</sub>)



Methanol (CH<sub>3</sub>OH)

# Special Notes

- Intermolecular hydrogen bond:
  - Hydrogen bond formed **between two molecules**
- Intramolecular hydrogen bond:
  - Hydrogen bond formed **between two different atoms in the same molecule**
- Intermolecular hydrogen bond is stronger than van der Waals' forces



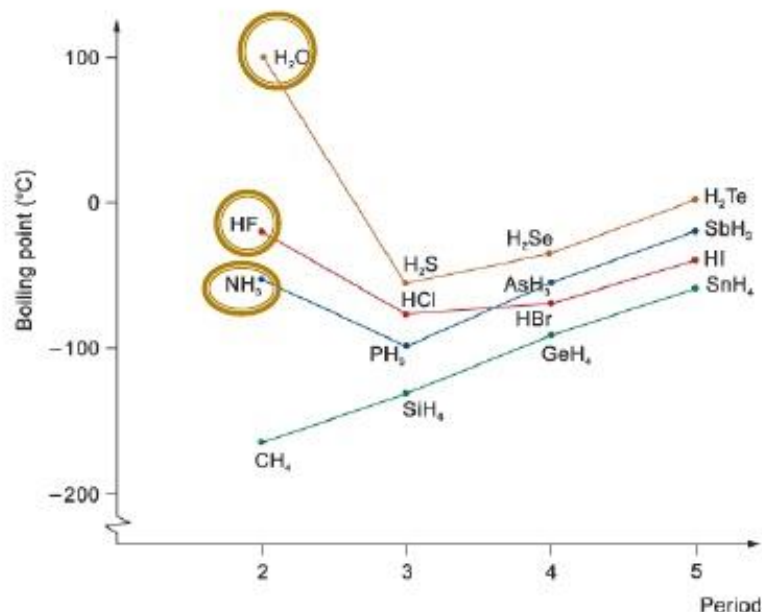
# Importance of Hydrogen Bonding in Physical Phenomena

- Anomalous Properties of the second period hydrides

Questions:

1. Why do  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HF}$  have abnormally high boiling point?

2. Explain why the order of boiling point is  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$ .



# Q1: Why do $\text{NH}_3$ , $\text{H}_2\text{O}$ and $\text{HF}$ have abnormally high boiling point?

- Explanation:
  - N, O and F are highly **electronegative** atoms
    - Formation of **intermolecular hydrogen bonds** in their hydrides.
  - Intermolecular hydrogen bonds are much **stronger** than van der Waals' forces
  - More energy is needed to break the hydrogen bonds in  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$



## Q2: Explain why the order of boiling point is $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$

### ■ Explanation

|                      | No. of H atoms available for hydrogen bond formation | No. of lone pair electrons available | No. of hydrogen bonds can form per molecule |
|----------------------|--|--------------------------------------|---|
| $\text{NH}_3$        | 3  | 1                                    | 1   |
| $\text{H}_2\text{O}$ | 2  | 2                                    | 2   |
| HF                   | 1  | 3                                    | 1   |

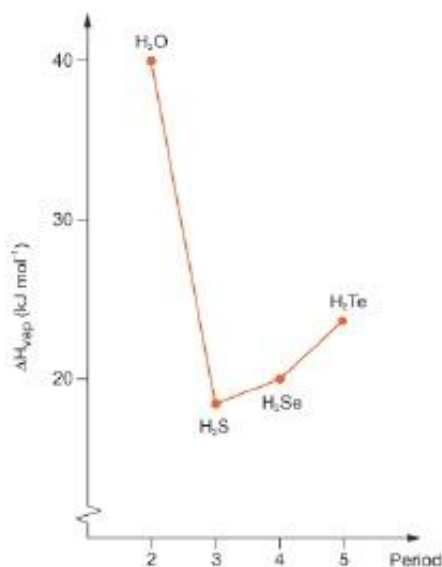
- $\text{H}_2\text{O}$  can form **2** hydrogen bond per molecule
- $\text{NH}_3$  and HF can form only **1** hydrogen bond per molecule
- The boiling point of  $\text{H}_2\text{O}$  is higher than  $\text{NH}_3$  and HF

## Q2: Explain why the order of boiling point is $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$

- Comparing N and F, **F** is more electronegative
- The intermolecular hydrogen bond formed between **HF** molecules is stronger than **NH<sub>3</sub>**
- HF has a higher boiling point than NH<sub>3</sub>

# Importance of Hydrogen Bonding in Physical Phenomena

- Enthalpy of vaporization
  - Energy required to vaporized **one mole** of liquid



**Question:**  
Explain why  $\text{H}_2\text{O}$  has the largest enthalpy of vaporization than  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ .

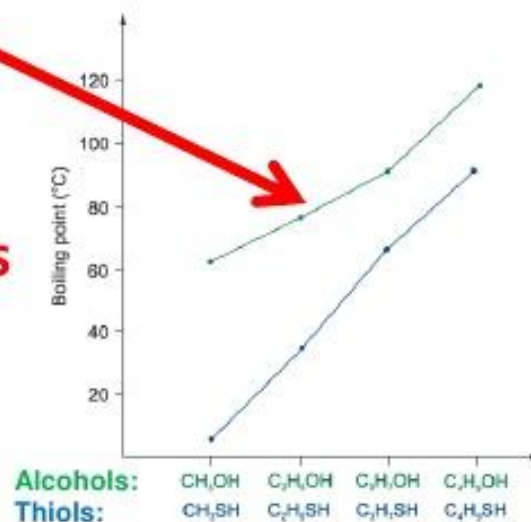
■ Explanation:


- In  $\text{H}_2\text{O}$ , there are **intermolecular hydrogen bonds** between molecules
- However, in  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the interaction between molecules is **dipole-dipole interactions**
- The strength of hydrogen bond is **stronger** than **dipole-dipole interactions**
- To break the hydrogen bonds, **more** energy is required
- $\text{H}_2\text{O}$  has the largest enthalpy change of vaporization

# Importance of Hydrogen Bonding in Physical Phenomena

## ■ Boiling Point and Solubility of Alcohols

- The boiling points of alcohols are higher than the thiols because there are **intermolecular hydrogen bonds** between alcohol molecules, but only **dipole-dipole interactions** between molecules of thiols



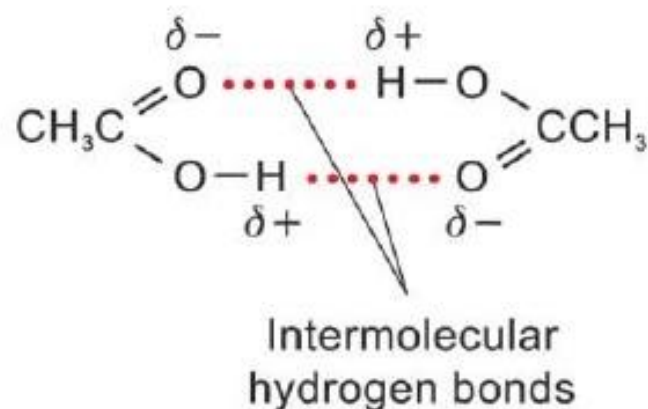
- 
- 
- Alcohols of low molecular masses are **soluble** in water because they can form **intermolecular hydrogen bonds** with water molecules

# Importance of Hydrogen Bonding in Physical Phenomena

- Dimerization of Carboxylic Acid
  - It happens when carboxylic acids are dissolved in **non-polar** solvents or in **vapour** state

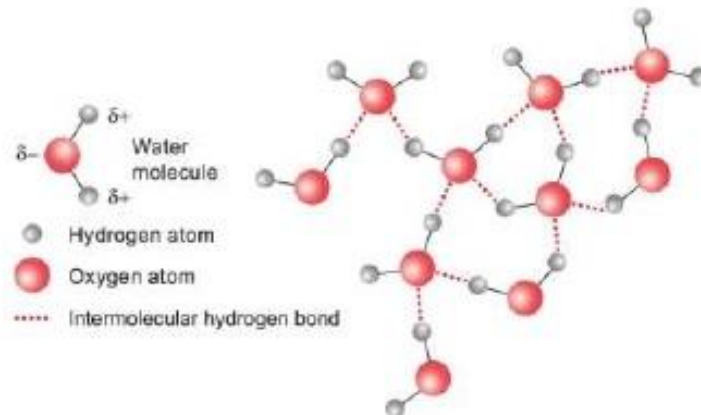
E.g. Ethanoic acid ( $\text{CH}_3\text{COOH}$ )

- Ethanoic acid molecules form **dimers** through the formation of **intermolecular hydrogen bonds**




# Importance of Hydrogen Bonding in Biochemistry

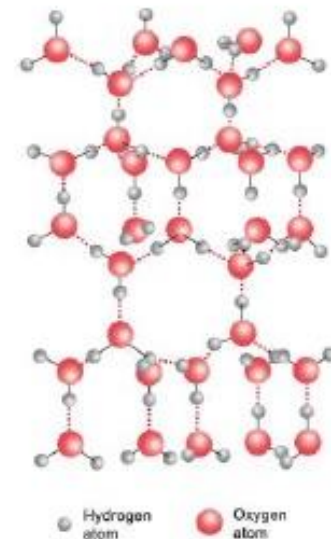
- Hydrogen bonding in ice and water
  - **Intermolecular hydrogen bonds** exist in both water and ice
  - In water, molecules are in constant motion. **Intermolecular hydrogen bonds** are formed and broken continuously.
  - The arrangement of molecules is **random**





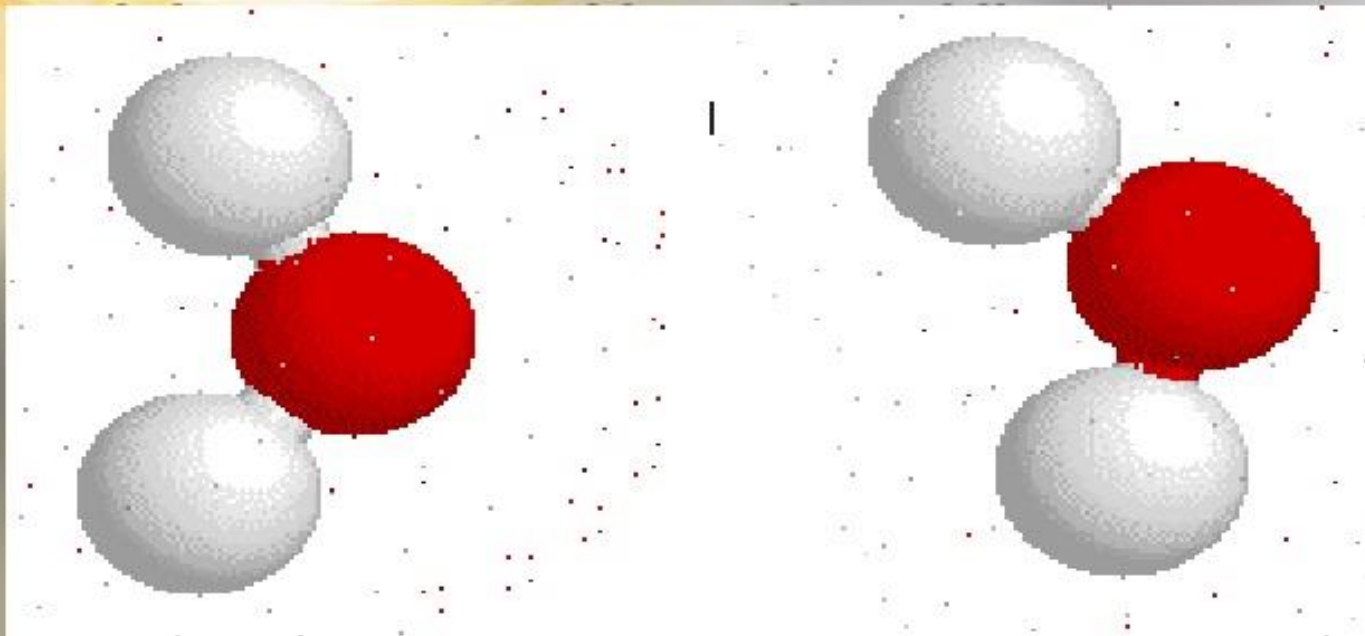
- 
- 
- In ice, the molecular motion is **restricted**. The molecules are arranged in a way to form the **maximum** number of hydrogen bonds

- Each  $\text{H}_2\text{O}$  molecule is **tetrahedrally** bonded to 4 other  $\text{H}_2\text{O}$  molecules by hydrogen bonds
  - Creates an **open structure** and gives rise to a **lower** density of ice than water
  - Insulates the water below and prevents complet solidification → keep fish survive in polar regions



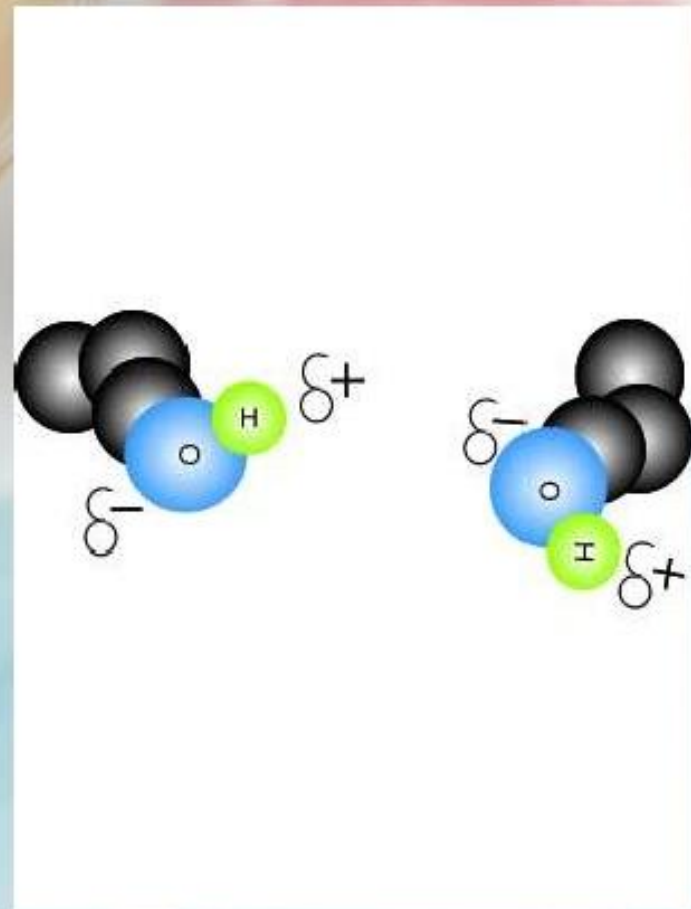
# HYDROGEN BONDING

- It is an electrostatic force of attraction that exists between covalently bonded hydrogen atom of one molecule and the electronegative atom of another molecule.



# CONDITIONS FOR HYDROGEN BOND FORMATION

- A hydrogen atom attached to a relatively electronegative atom is a hydrogen bond donor. This electronegative atom is usually **fluorine, oxygen, or nitrogen**.
- An electronegative atom such as fluorine, oxygen, or nitrogen is a



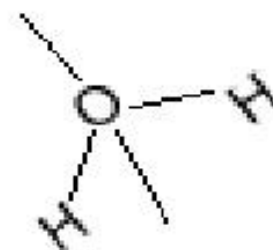
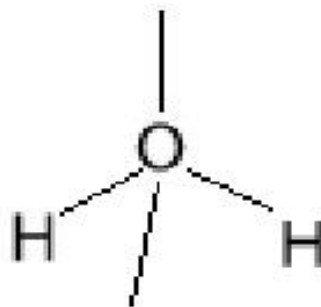
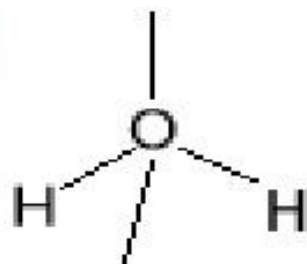
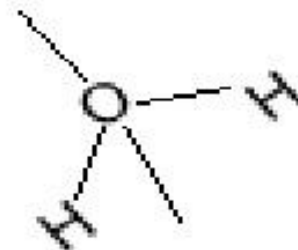
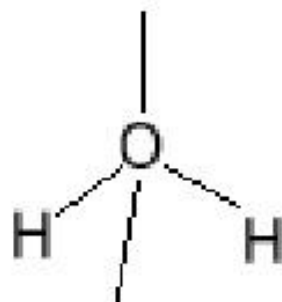
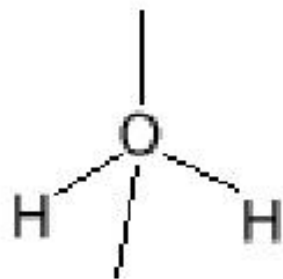
*INTERMOLECULAR  
HYDROGEN BOND*

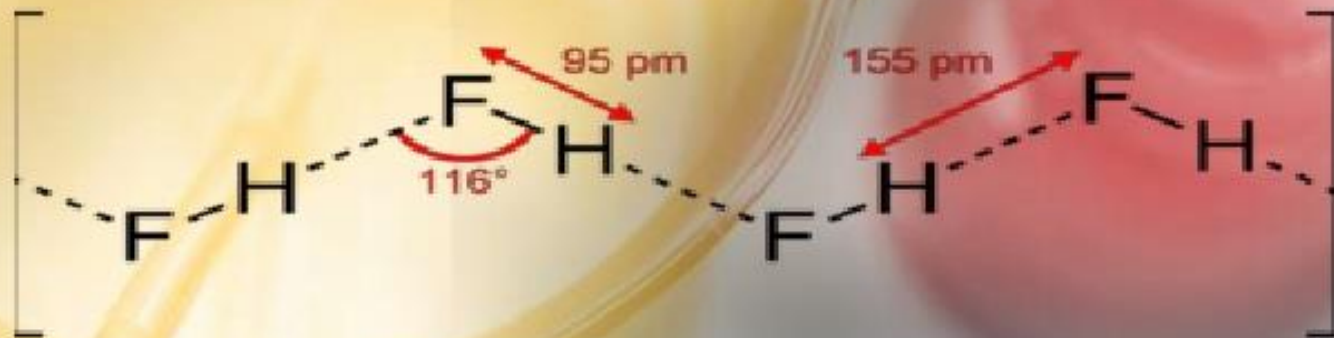
- It is formed between two different molecules of the same or different substances, eg.
- Hydrogen bond between molecules of ammonia
- Hydrogen bond between molecules of water and alcohol

*INTRAMOLECULAR  
HYDROGEN BOND*

- It is formed between the hydrogen atom and a highly electronegative atom present in different bonds within the same molecule, eg.
- o-salicylaldehyde
- o- nitrobenzoic acid

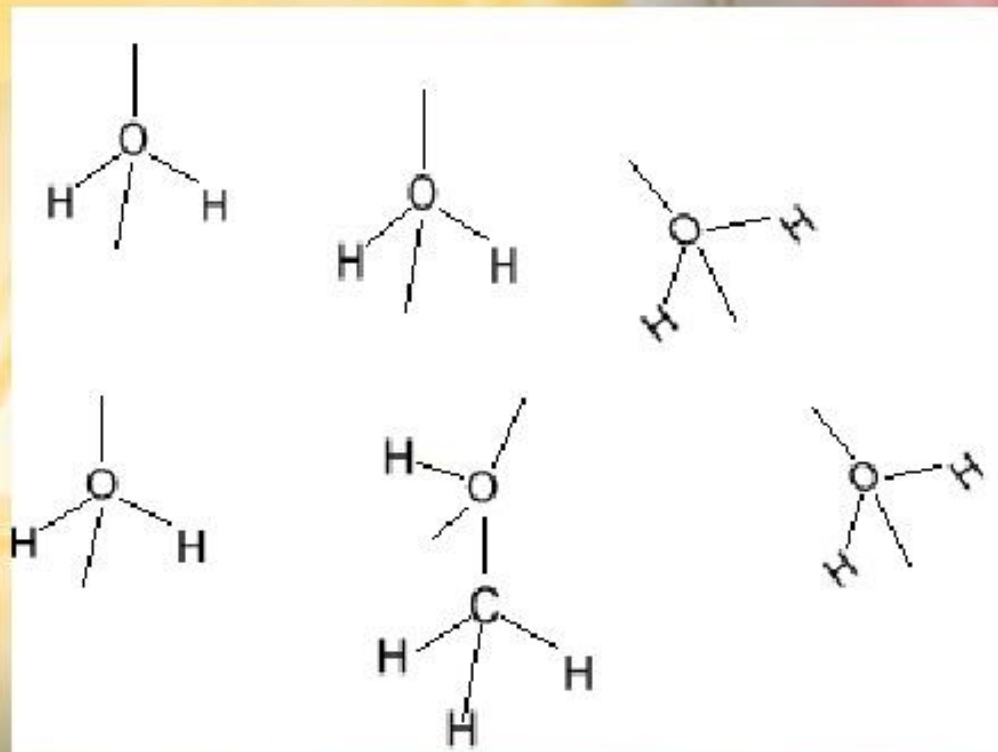
# ASSOCIATION OF WATER MOLECULES





### HYDROGEN FLUORIDE

IN THE SOLID STATE , HYDROGEN FLUORIDE CONSISTS OF LONG ZIG-ZAG CHAINS OF MOLECULES ASSOCIATED TOGETHER BY HYDROGEN BONDING. HENCE, HYDROGEN FLUORIDE MOLECULE CAN ALSO BE REPRESENTED AS  $(HF)_N$ . HOWEVER, IN GASEOUS OR LIQUID STATE , THE CHAIN BECOMES LINEAR.

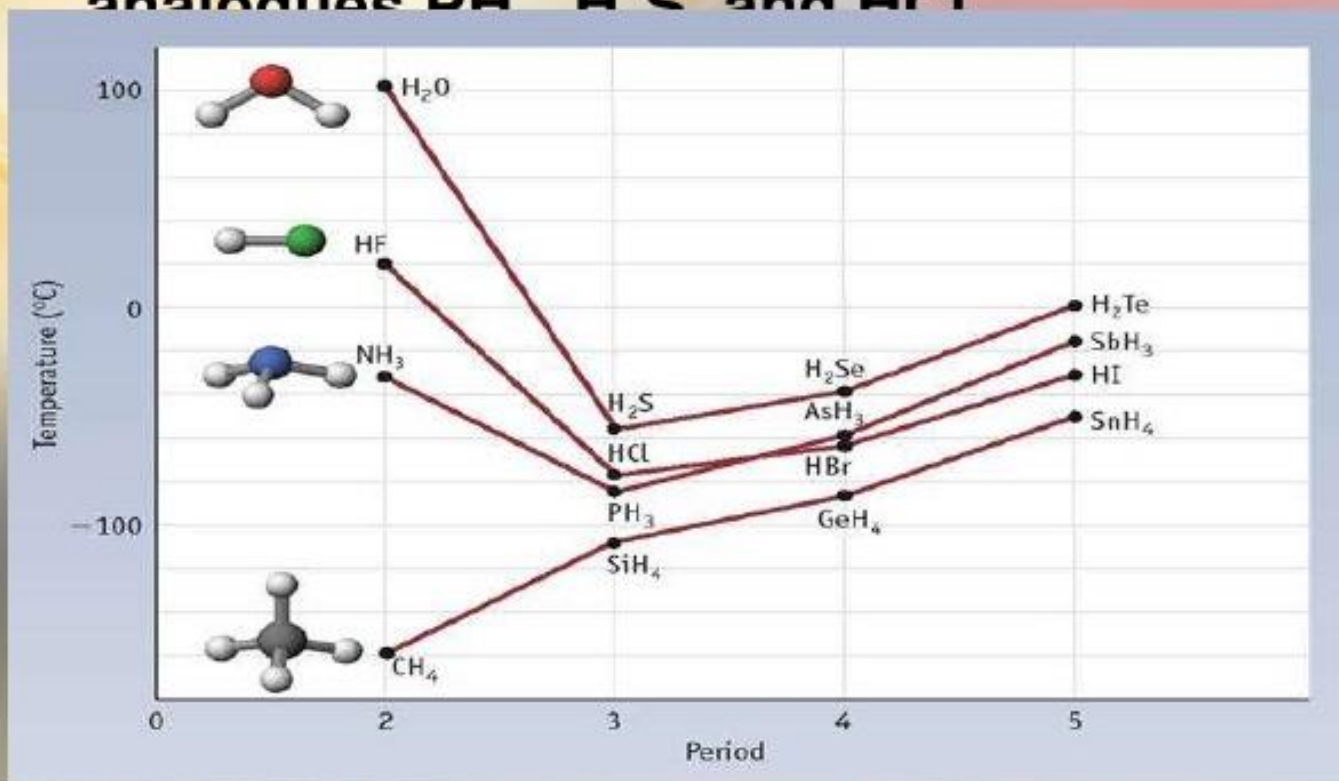


**ALCOHOLS HAVE HIGH MISCIBILITY IN WATER DUE TO FORMATION OF INTERMOLECULAR HYDROGEN BONDS BETWEEN WATER AND ALCOHOL MOLECULES.**



# HIGHER MELTING AND BOILING POINTS

- Dramatically higher boiling points of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$  compared to the heavier analogues  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$



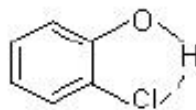
# HYDROGEN BONDING CAUSES

- Higher boiling point in ethanol as compared to diethyl ether
- Higher viscosity of sulphuric acid and glycerol
- Water is a liquid, whereas  $\text{H}_2\text{S}$  is a gas
- Dimerisation of acetic acid molecules

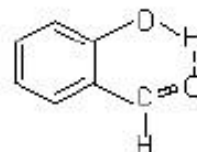


# INTRAMOLECULAR HYDROGEN BONDING

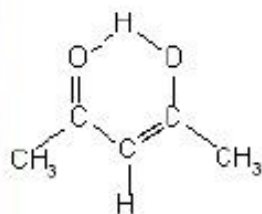
When hydrogen bonding exists within the molecule it is called intramolecular hydrogen bonding. In such type of hydrogen bonding two groups of the same molecule link through hydrogen bond, forming a stable five or six membered ring structure *e.g.*, salicylaldehyde, *o*-chlorophenol, acetone, ethyl acetoacetate etc.



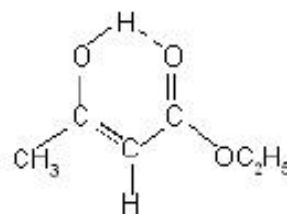
*o*-Chlorophenol



Salicylaldehyde

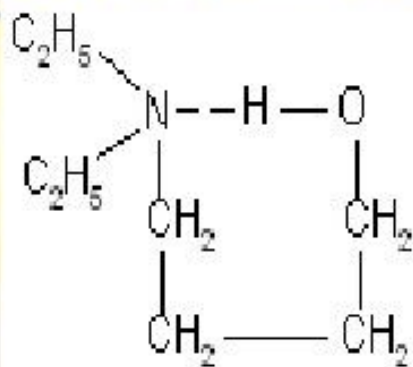


Acetylacetone

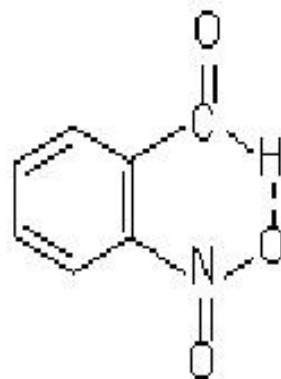


Ethyl acetoacetate

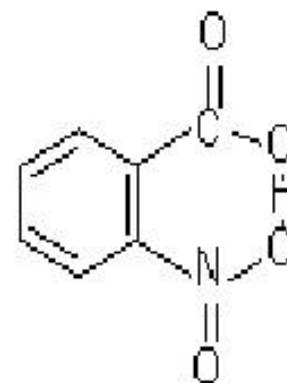
This intramolecular hydrogen bonding was first called chelation (after the Greek word "Chela" meaning, claw) because in the same molecule the formation of a ring hydrogen bonding is a pincer like action resembling the closing of a Crab's claw. Some more examples of intramolecular hydrogen bonding are :



Amino alcohol

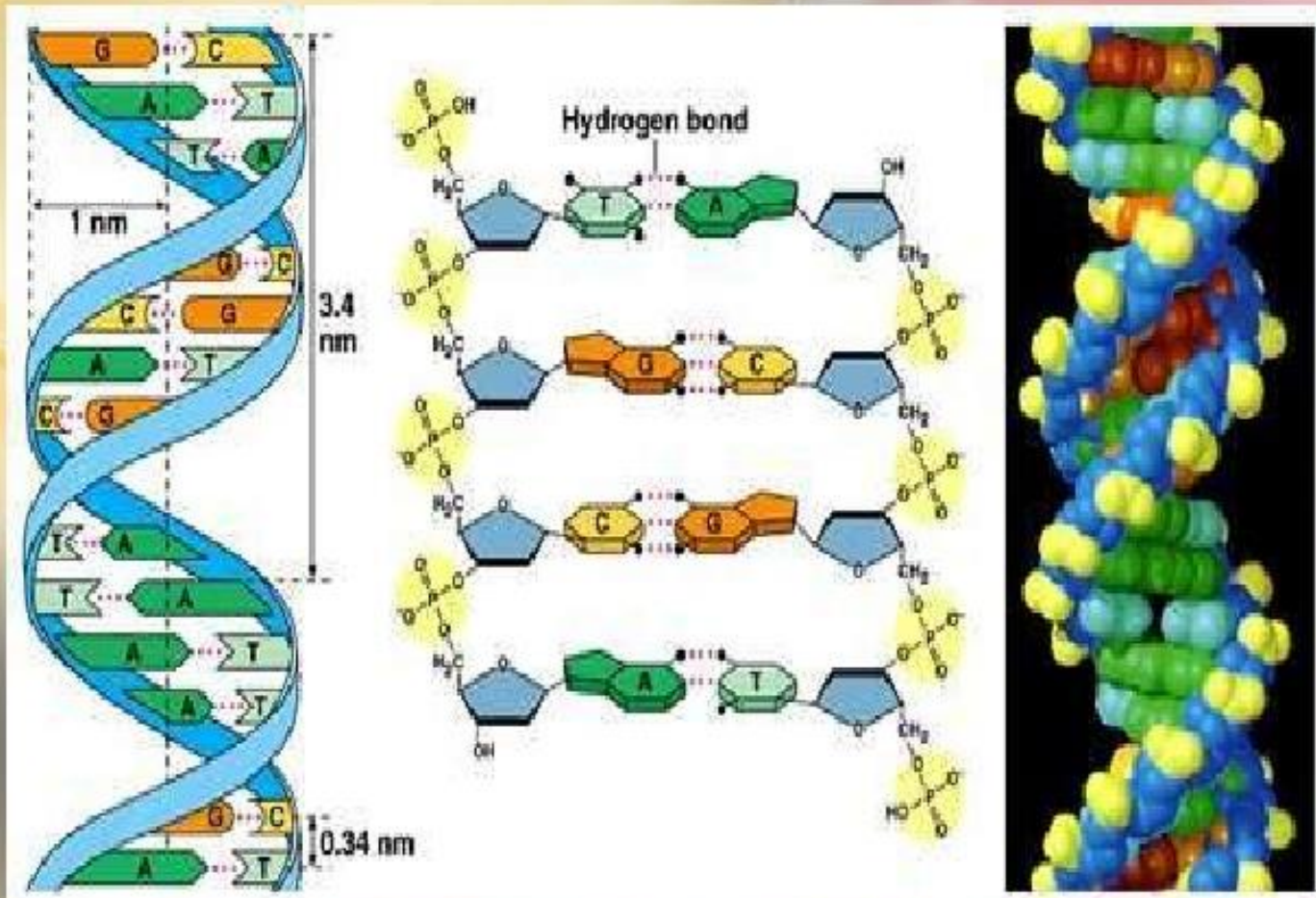


o - Nitrobenzaldehyde



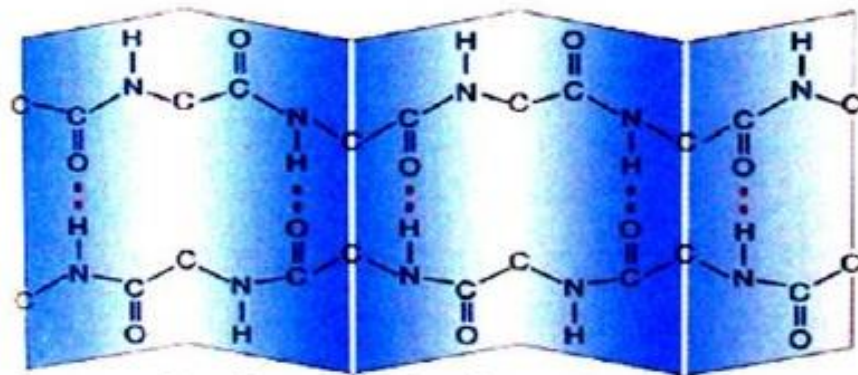
o - Nitrobenzoic acid

# HYDROGEN BONDING IN DNA

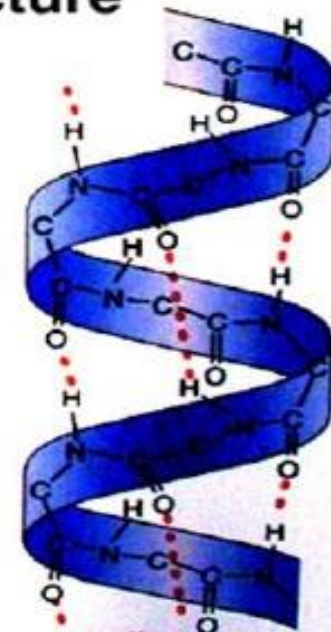


# SECONDARY STRUCTURE OF PROTEINS-HYDROGEN BONDING

secondary structure

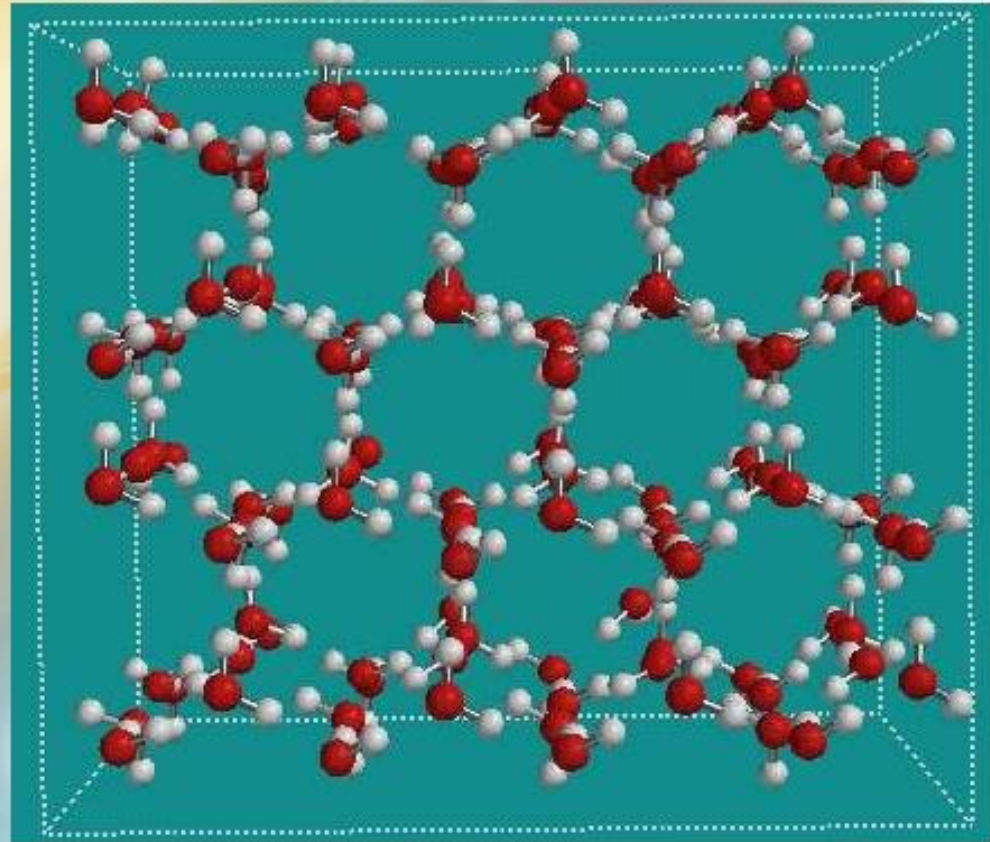


$\beta$  pleated sheet



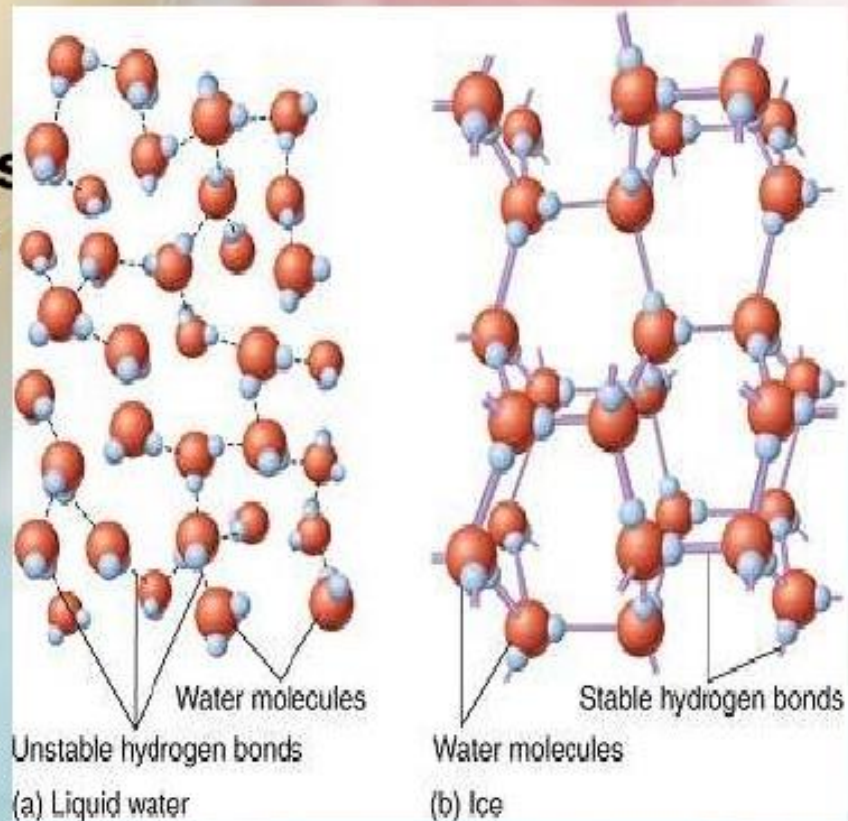
alpha helix

**CAGE  
LIKE  
STRUCTURE  
OF  
WATER  
MOLECULES  
IN ICE  
CAUSES  
LOWER  
DENSITY  
OF ICE**








# UNIQUE NATURE OF WATER

- When ice melts, this cage like structure collapses and the molecules move closer.
- Hence, for the same mass of water, volume decreases and density increases. Hence ice has lower density than water at 273K



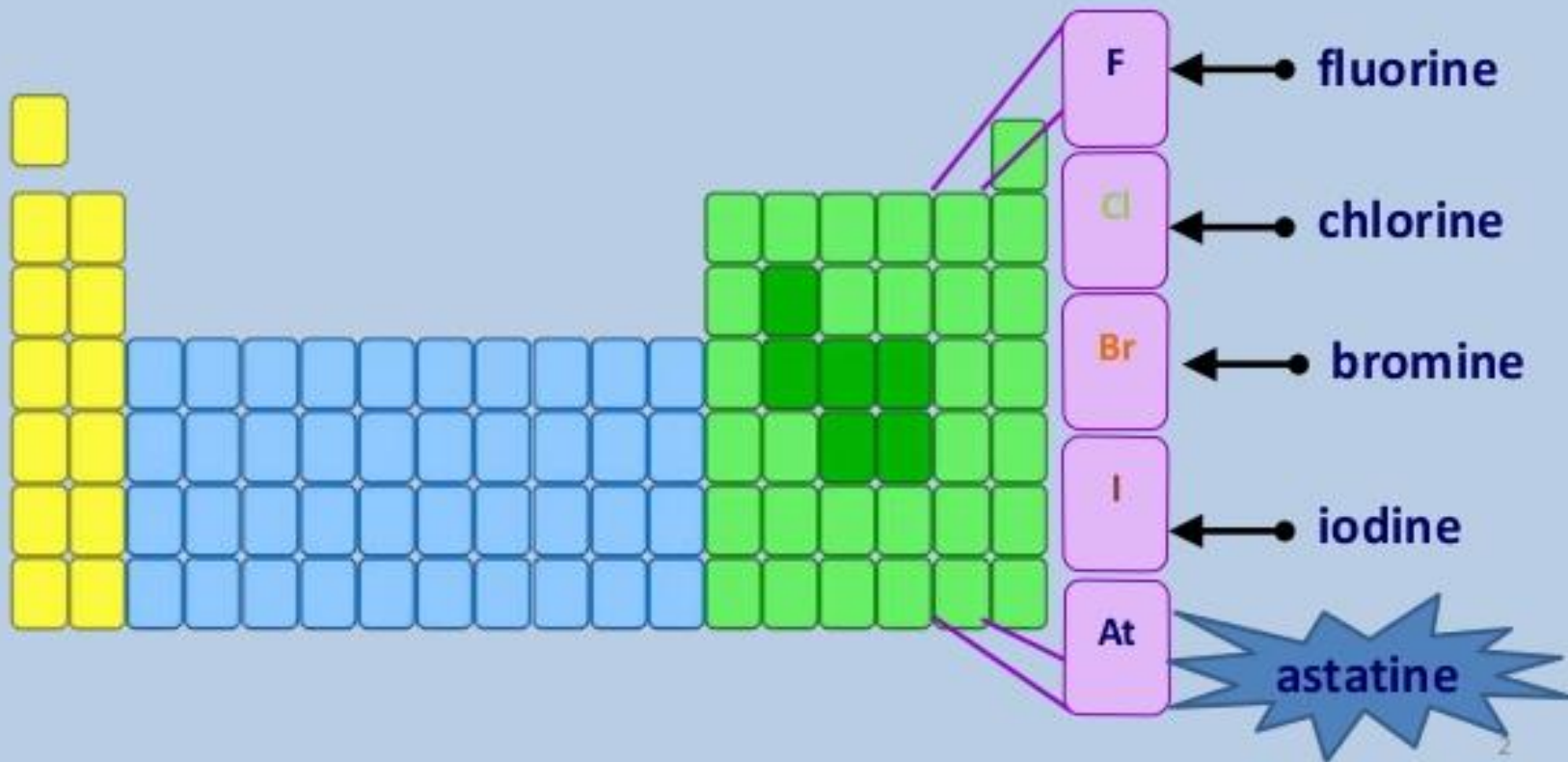


# COMPARISON OF INTERMOLECULAR FORCES

| Force                  | Model   | Basis of Attraction                                       | Energy (kJ/mol) | Example  |
|------------------------|---|---|-----------------|--|
| Ion-dipole             |    | Ion charge–<br>dipole charge                              | 40–600          | $\text{Na}^+ \cdots \text{O} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{H} \end{array}$  |
| H bond                 | $\delta^- \quad \delta^+ \quad \delta^-$<br>—A—H·····:B—                            | Polar bond to H–<br>dipole charge<br>(high EN of N, O, F) | 10–40           | $\begin{array}{c} \text{:}\ddot{\text{O}}\text{—H} \\   \\ \text{H} \end{array} \cdots \begin{array}{c} \text{:}\ddot{\text{O}}\text{—H} \\   \\ \text{H} \end{array}$ |
| Dipole-dipole          |    | Dipole charges  | 5–25            | $\text{I—Cl} \cdots \text{I—Cl}$   |
| Ion–induced dipole     |    | Ion charge–<br>polarizable $e^-$<br>cloud                 | 3–15            | $\text{Fe}^{2+} \cdots \text{O}_2$   |
| Dipole–induced dipole  |   | Dipole charge–<br>polarizable $e^-$<br>cloud              | 2–10            | $\text{H—Cl} \cdots \text{Cl—Cl}$  |
| Dispersion<br>(London) |  | Polarizable $e^-$<br>clouds                               | 0.05–40         | $\text{F—F} \cdots \text{F—F}$   |

# **INTER HALOGEN COMPOUNDS**

The elements in group 17 of the periodic table, on the right, are called the **HALOGENS**.



## Why the name ..... HALOGEN??

- \* Halogen-metal compounds are salts occurring in sea water (e.g. NaCl; sodium chloride),
- \* *halos* = sea salts; *genes*=born.

## *Electron configuration of halogens*

***Fluorine***       ***$1s^2 2s^2 2p^5$***

***Chlorine***       ***$[\text{Ne}]3s^2 3p^5$***

***Bromine***       ***$[\text{Ar}]3d^{10} 4s^2 4p^5$***

***Iodine***       ***$[\text{Kr}]4d^{10} 5s^2 5p^5$***

***Astatine***       ***$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$***

# Interhalogen Compounds

- These covalent compounds are formed when two different halogens react .
- These are formed due to the electronegativity difference among the halogens.

## Classification:

- Interhalogens have the general formula  $AX_n$  where  $n=1, 3, 5$  &  $7$ .

Type AX eg: ClF, BrF, BrCl, ICl, IBr

Type  $AX_3$ : eg : ClF<sub>3</sub>, BrF<sub>3</sub>, ICl<sub>3</sub>

Type  $AX_5$  eg: BrF<sub>5</sub> ClF<sub>5</sub>

Type  $AX_7$  eg: IF<sub>7</sub>

**When representing the compound, the less electronegativity element has to be written first.**

## Iodine mono chloride ..... ICl

is formed by passing chlorine over solid iodine at temperature below 0 °C.



- It is a red-brown chemical compound
- melts near room temperature.
- Because of the difference in the electronegativity of iodine and chlorine, **ICl** is highly polar ;  $\text{I}^+\text{Cl}^-$
- \* In organic synthesis, estimation of **iodine No.** of oils and as a source of  $\text{I}^+$ .

## 1. Iodine monochloride, ICl:

### Preparation:

- It is formed by mixing  $I_2$  and  $Cl_2$  in equal amounts.



- By heating  $I_2$  with  $KClO_3$



- By heating  $ICl_3$  at  $68^\circ C$

### Properties:

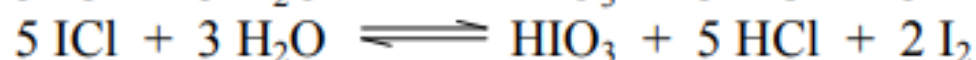
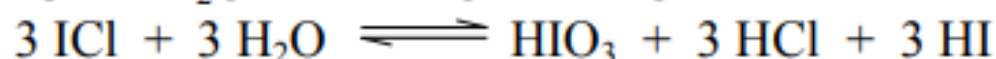
- i. It is dark liquid with b. p.  $97.4^\circ C$ .



ii. ICl exists in two solid form as given below:

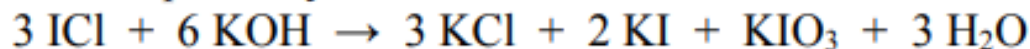
- Solid form: This form melts at  $27.2^{\circ}\text{C}$  and is obtained as needle like crystals on cooling the liquid rapidly.
- Metastable form: This form melts at  $14^{\circ}\text{C}$  and is obtained as a black solid on cooling the liquid slowly at  $100^{\circ}\text{C}$ .

iii. Hydrolysis: ICl dissolve in water and gets hydrolyzed as:

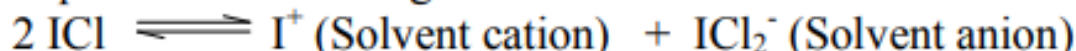


The hydrolysis can be prevented adding HCl

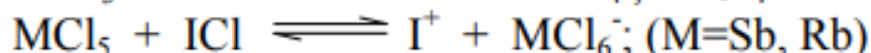
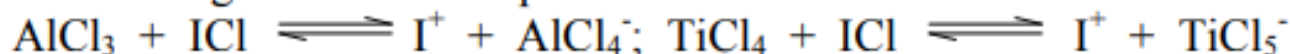
iv. ICl decomposed by excess of KOH as:



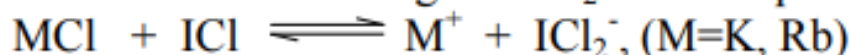
v. In liquid state ICl undergoes auto-ionization as:



Metal halide give  $\text{I}^+$  ions in liquid ICl hence it behaves as Lewis acid.



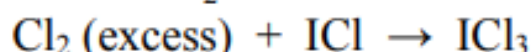
Alkali metal chloride gives  $\text{ICl}_2^-$  ion in liquid ICl and therefore acts as bases.



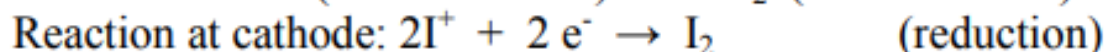
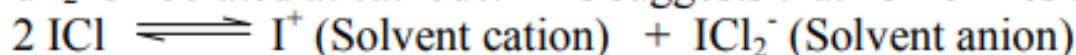
vi. Bromide like KBr,  $[(\text{CH}_3)_4\text{N}]\text{Br}$  etc. , reacts with ICl, polyhalide ion is produced.



vii. Excess of  $\text{Cl}_2$  convert ICl into  $\text{ICl}_3$



viii. When molten ICl is electrolyzed, a mixture of  $\text{I}_2$  and  $\text{Cl}_2$  is liberated at anode and  $\text{I}_2$  is liberated at cathode. This suggests that ICl ionizes as:



## Uses:

- A solution of ICl is used as catalyst in the oxidation of As(III) oxide by ceric sulphate and for preparation of polyhalides.
- The solution of ICl in glacial acetic acid is used for determining the iodine value of oil by Wiz's method.

## Structure of ICl- Its linear in shape



$$7 + 7 \\ = \textcircled{14}$$

Iodine Chloride



## Bromine trifluoride... BrF<sub>3</sub>

- It is obtained by mixing bromine vapor and fluorine in a stream of nitrogen at 20°C.



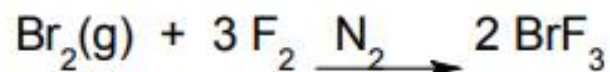
It is a straw-colored liquid with a pungent odor.

It is a powerful [fluorinating agent](#)

It is used to produce [uranium hexafluoride](#) (UF<sub>6</sub>) in the processing and reprocessing of nuclear fuel.

### Preparation:

- It is obtained by mixing  $\text{Br}_2$  vapour with  $\text{F}_2$  in presence of  $\text{N}_2$



- By action of  $\text{ClF}_3$  on  $\text{Br}_2$  at  $10^0 \text{ C}$ .



### Properties:

- i. It is fuming liquid with b. p.  $125.8^0 \text{ C}$ , is very reactive and non corrosive liquid.
- ii. It reacts with  $\text{Br}_2$  to form  $\text{BrF}$  :  $\text{BrF}_3 + \text{Br}_2 \rightarrow 3 \text{BrF}$
- iii. *Auto-ionisation*:  $2 \text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$   
The substance making available  $\text{BrF}_2^+$ , due to above mode of auto-ionisation; acts as acids.  
Examples:  $\text{AuF}_3 + \text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{AuF}_4^-$   
 $\text{MF}_4 (\text{M}=\text{Ge}, \text{Sn}, \text{Ti}) + 2 \text{BrF}_2^+ \rightleftharpoons 2 \text{BrF}_2^+ + \text{MF}_6^{2-}$   
The substance making available  $\text{BrF}_4^-$  acts as bases.  
Examples:  $\text{MF} (\text{M}=\text{Li}, \text{K}, \text{Ag}) + \text{BrF}_3 \rightleftharpoons \text{M}^+ + \text{BrF}_4^-$
- iv. *Neutralisation reactions*: These reactions are those in which a compound containing  $\text{BrF}_2^+$  ion reacts with that having  $\text{BrF}_4^-$  ion and salt and solvent are formed.

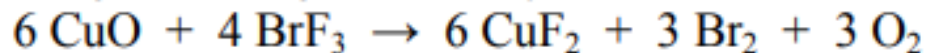
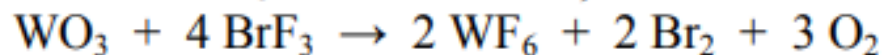
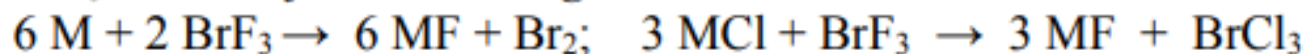
Acid

Base

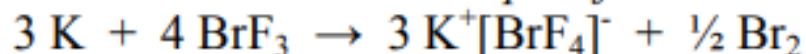
Salt

Solvent

v.  $\text{BrF}_3$  is useful *fluorination agent* as follow.

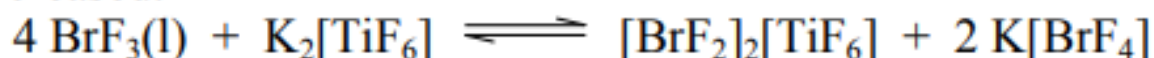


vi. *Redox reactions and complex formation:*

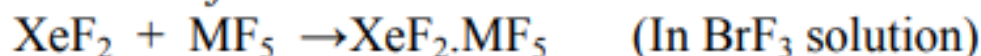


ZXC

vii. *Solvolysis reaction:* In these reaction the concentration of  $[\text{BrF}_2]^+$  and  $[\text{BrF}_4]^-$  is increased.



viii. *Formation of adducts:*



$\text{BrF}_3$  hydrolysed by water with formation of bromine oxy-fluoride.



### Uses:

- For preparation of polyhalides.
- For preparation of complex compounds by acid-base reaction, are difficult to prepare by other methods.
- As fluorinating agent.
- For preparation of fluorocomplexes of many metals like Au, Ge, As etc.

Molecule :  $\text{BrF}_3$

$$x = \frac{1}{2} [7 + 3]$$

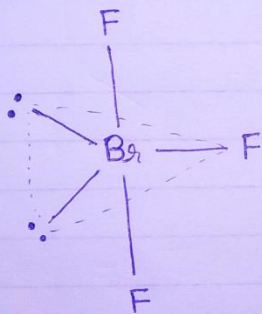
$$x = \frac{10}{2}$$

$$x = 5$$

$\therefore$  Hybridisation =  $sp^3d$   $\Rightarrow$  Trigonal bipyramidal

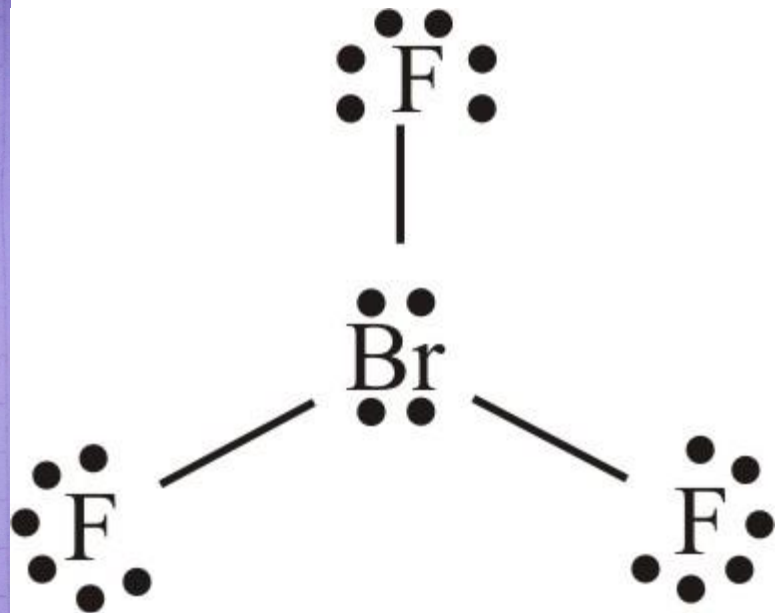
$$\text{l.p.} = 5 - 3 = 2$$

$$\text{b.p.} = 3$$



Geometry = Trigonal bipyramidal

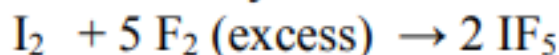
Shape = T-shaped



## 2. Iodine pentafluoride, IF<sub>5</sub>:

### Preparation:

- It is formed by direct combination of I<sub>2</sub> and F<sub>2</sub> (excess):



- By the action of F<sub>2</sub> on I<sub>2</sub>O<sub>5</sub>:  $10 \text{F}_2 + 2 \text{I}_2\text{O}_5 \rightarrow 4 \text{IF}_5 + 5 \text{O}_2$

- By heating I<sub>2</sub> with AgF:  $\text{I}_2 + 10 \text{AgF} \rightarrow 2 \text{IF}_5 + 10 \text{Ag}$

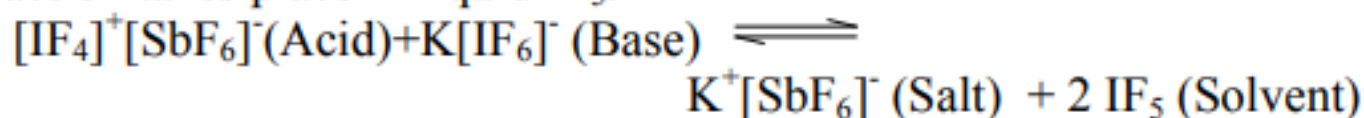
### Properties:

- i. It is colourless liquid with m. p. = 9.6<sup>0</sup> C.

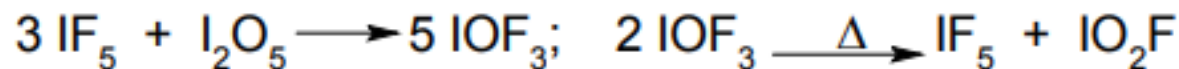
- ii. It is good conductor of electricity as it ionizes as:



Thus, the substances that give IF<sub>4</sub><sup>+</sup> ions in liquid IF<sub>5</sub>, acts as acid and those which produce IF<sub>6</sub><sup>-</sup> ions behave as bases in this solvent. The following acid-base reaction takes place in liquid IF<sub>5</sub>.



- iii. IF<sub>5</sub> reacts with I<sub>2</sub>O<sub>5</sub> to form iodine oxy-fluoride, IOF<sub>3</sub> which is solid and decomposes on heating at 110<sup>0</sup> C.





- i. Hydrolysis of  $\text{IF}_5$  gives halogen acid and oxy-halic acid.  
 $\text{IF}_5 + 3 \text{H}_2\text{O} \rightarrow 5 \text{HF} + \text{HIO}_3$
- v. With  $\text{F}_2$  at  $250^\circ\text{-}300^\circ \text{C}$  temperature gives  $\text{IF}_7$ .



### USES

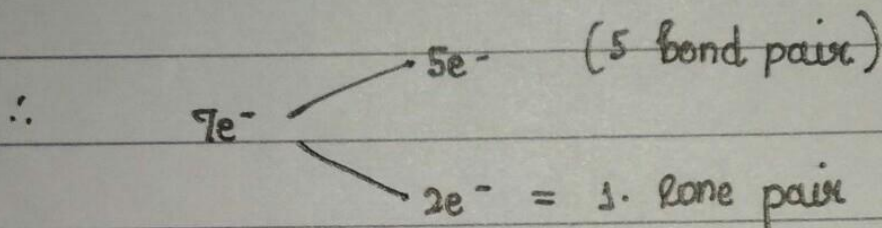
It is used as an ionising solvent.

$IF_5$

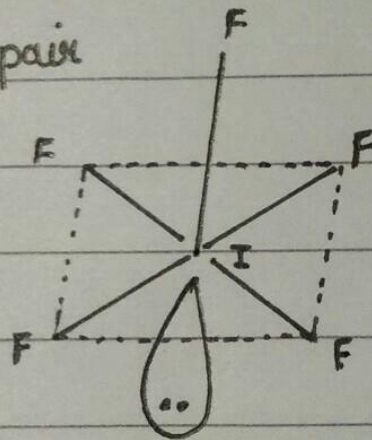
Hybridisation of Central atom =  $\frac{1}{2} [V + M - C + A]$

$$H = \frac{1}{2} [7 + 5 - 0 + 0] = \frac{12}{2}$$

$$H = 6 = sp^3d^2$$

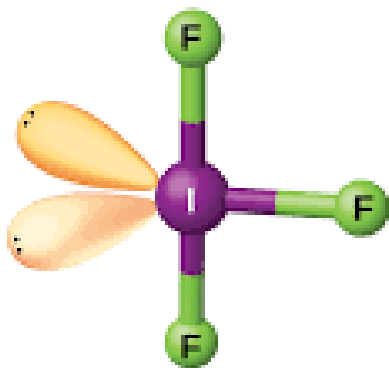
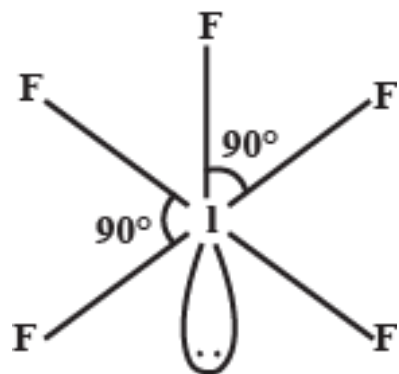


Hybridisation structure =

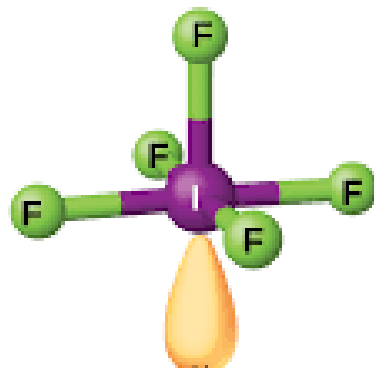


Hybridisation shape = Square pyramidal

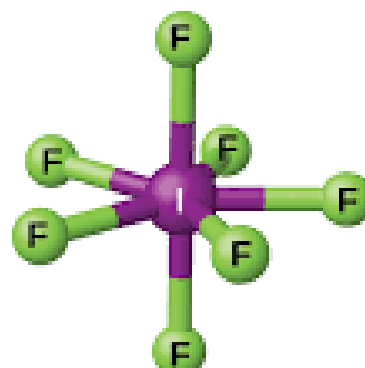
## STRUCTURE OF IF<sub>5</sub>



IF<sub>3</sub>



IF<sub>5</sub>



IF<sub>7</sub>

*Thank you*

# Interhalogen compounds

## INTERHALOGEN COMPOUNDS

The binary covalent compounds formed by halogens amongst themselves are known as interhalogen compounds. They have the general formula,  $AX_n$  where A is a large halogen atom and X is a smaller halogen atom. The value of n is 1,3,5 and 7. Some examples are given in the table.

| S.No. | Type   | Example                     |
|-------|--------|-----------------------------|
| 1.    | $AX$   | $ClF, BrF, BrCl, ICl, IBr$  |
| 2.    | $AX_3$ | $ClF_3, BrF_3, IF_3, ICl_3$ |
| 3.    | $AX_5$ | $ClF_5, BrF_5, IF_5$        |
| 4.    | $AX_7$ | $IF_7$                      |

- (i) In naming the compound, the less electronegative element is mentioned first.

4.



- (i) In naming the compound, the less electronegative element is mentioned first.
- (ii) All interhalogen compounds are diamagnetic, since  $n$  is odd.
- (iii) Iodine alone forms all types of interhalogen compounds mainly due to its big size and electropositive nature.
- (iv) It is found that the greater the difference in the electronegativity values of the two halogens, the stronger is the bond between them.

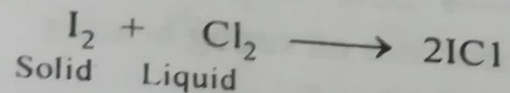
We shall discuss few interhalogen compounds in detail.

MONOCHLORIDE ICl

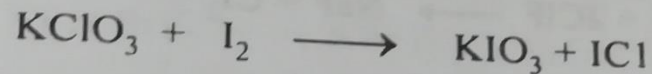
## Interhalogens of AX type

### Iodine monochloride

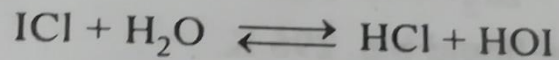
**Preparation.** (i) It can be prepared by the direct combination of liquid chlorine with solid iodine under controlled conditions of temperature and pressure.



(ii) It may also be obtained by heating iodine with potassium chlorate.



**Properties.** (i) It is a reddish oil and is readily hydrolyzed by water.



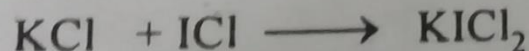
(ii) It is also decomposed by sodium hydroxide.



(iii) When electricity is passed through iodine monochloride, iodine is liberated at the cathode and chlorine at the anode, indicating that the compound is a chloride of monovalent positively charged iodine.

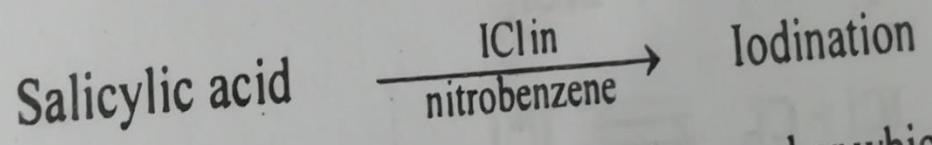
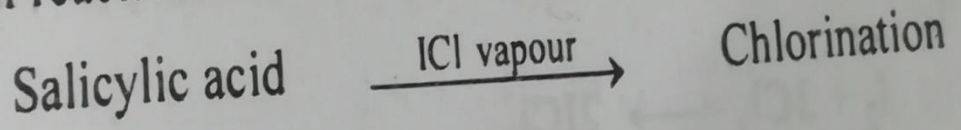


(iv) With alkali metal halides it gives polyhalides.

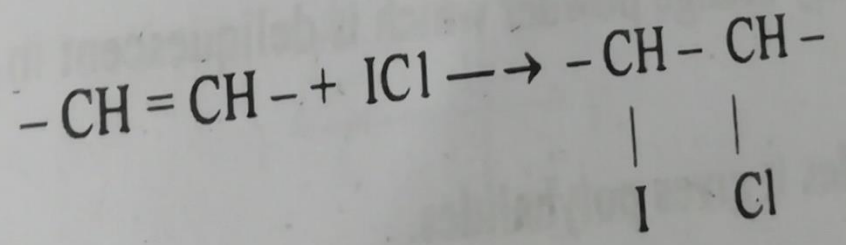




Uses. (i) It is used to iodinate organic compounds, though chlorination may also occur depending on the condition of reaction.



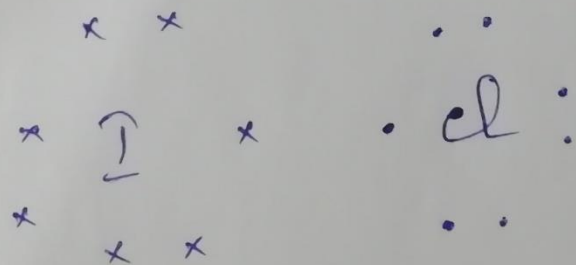
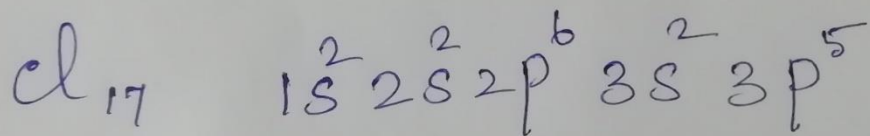
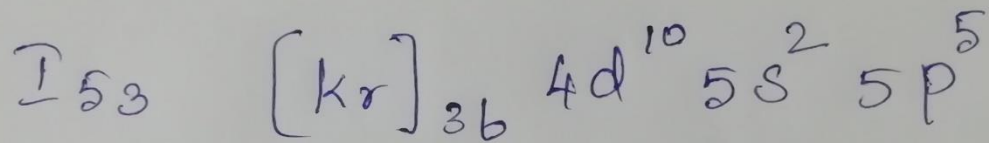
(ii) It is used as Wij's reagent in the estimation of iodine number which is a measure of unsaturation of fats and oils.





# Iodine Monochloride ICl

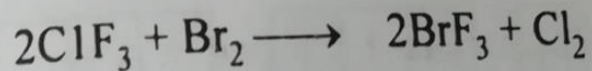
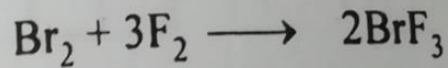
## Structure



Linear structure.

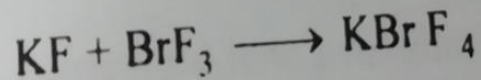
## Bromine trifluoride, $\text{BrF}_3$

**Preparation.** It is obtained by mixing bromine and fluorine vapours or by the action of  $\text{ClF}_3$  on bromine at 238 K.

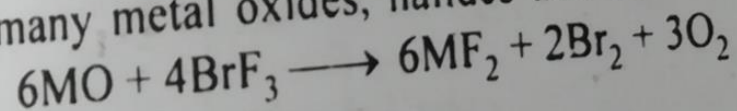


**Properties.** (i) Bromine trifluoride is a greenish-yellow fuming liquid having b.p. 400 K.

(ii) With alkali fluorides it forms polyhalides.

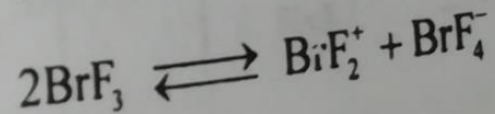


(iii) It converts many metal oxides, halides and even metals to their respective fluorides.



where M is a divalent metal.

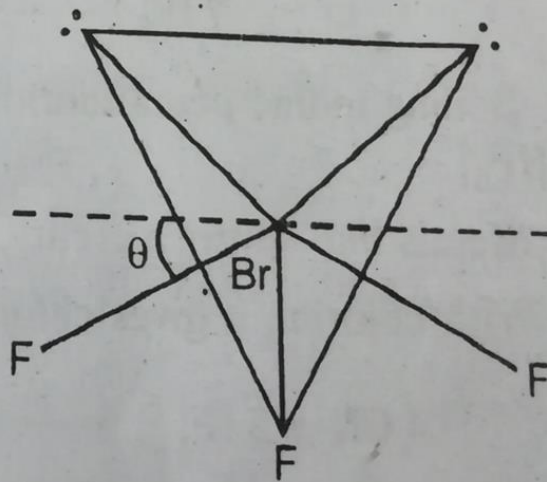
(iv) It ionizes considerably as



... involves  $sp^3 d$  hybridisation. The T shape structure can be

Structure  $\text{BrF}_3$

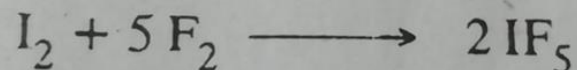
In bromine trifluoride molecule, ten electrons are present in the valency shell of the bromine atom. Out of these, two pairs are lone pairs. The expected geometry is trigonal bipyramidal. But due to the presence of the two lone pairs, the shape is distorted. To avoid repulsion, the bonding pairs contract and it has a *bent T shape*. It makes use of  $sp^3d$  - hybridisation.



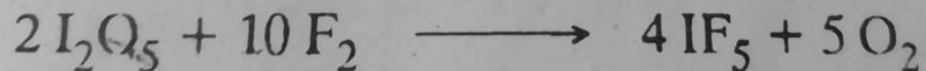
## ✓ IODINE PENTAFLUORIDE, $\text{IF}_5$

### Preparation

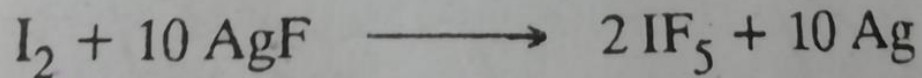
- (a) It is prepared by passing fluorine (diluted with nitrogen) over iodine in a heated quartz tube :



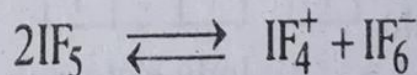
- (b) It is formed by the action of fluorine on  $\text{I}_2\text{O}_5$  :



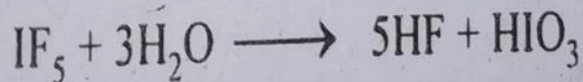
- (c) It can also be obtained by heating  $\text{I}_2$  with silver fluoride :



Properties. (i) Liquid  $\text{IF}_5$  conducts electricity and self-ionizes.



(ii) It undergoes hydrolysis as



(iii) Complex salts are formed by heating  $\text{IF}_5$  with alkali halides.



### Structure of iodine pentafluoride

$\text{IF}_5$  is formed by  $sp^3d^2$  hybridisation and hence is octahedral in structure as shown below

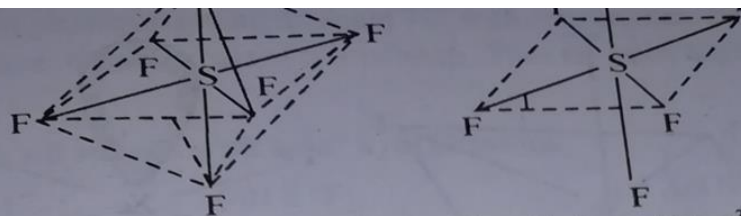
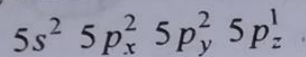


Fig. 3.37. Octahedral molecule of sulphur hexafluoride formed by  $sp^3d^2$  hybridisation.

**(ii) Shape of iodine pentafluoride  $IF_5$ .**

It is a case of  $sp^3d^2$  hybridisation. At. no. of iodine is 53. Its outer electronic configuration is



In the excited state two electrons from  $5p$  orbitals are excited to  $5d$  orbitals, thereby giving five single electrons for the formation of five bonds with fluorine.  $5s$ ,  $5p_x$ ,  $5p_y$ ,  $5p_z$  and two  $d$ -orbitals ( $sp^3d^2$ ) hybridise to give equivalent orbitals oriented octahedrally.

However one position is occupied by a lone pair. Therefore actual shape is square pyramidal (Fig. 3.38).

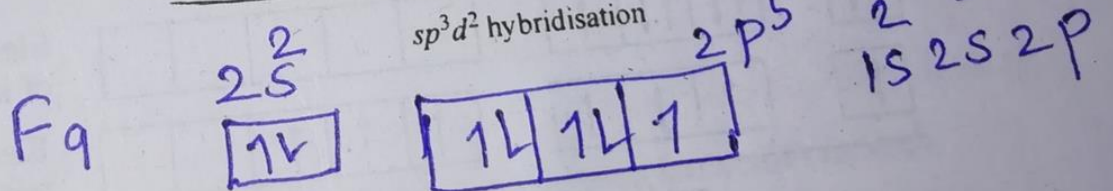
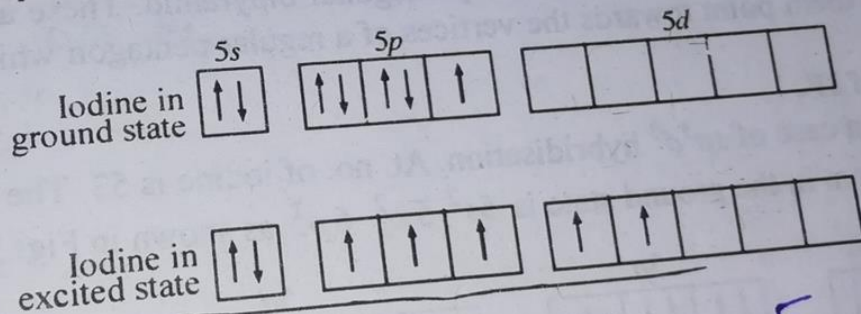
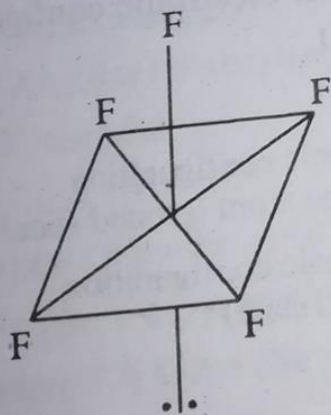


Fig. 3.38. Shape of  $IF_5$  molecule.

ic configuration in the

b) It is also formed by heating iodine with potassium chlorate.



### Properties

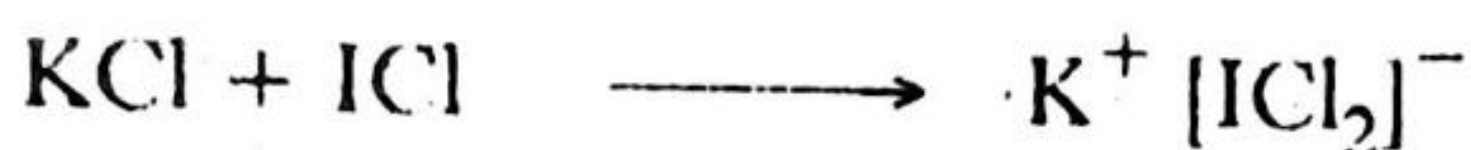
It is a dark red liquid but solidifies on standing at 290 - 300 K. It exists in two forms - stable and metastable form.

It is readily hydrolysed forming hypoiodite and iodate ions.



When current is passed through ICl, iodine is liberated at the cathode and chlorine at the anode.

Alkali metal chlorides like KCl dissolve in it.

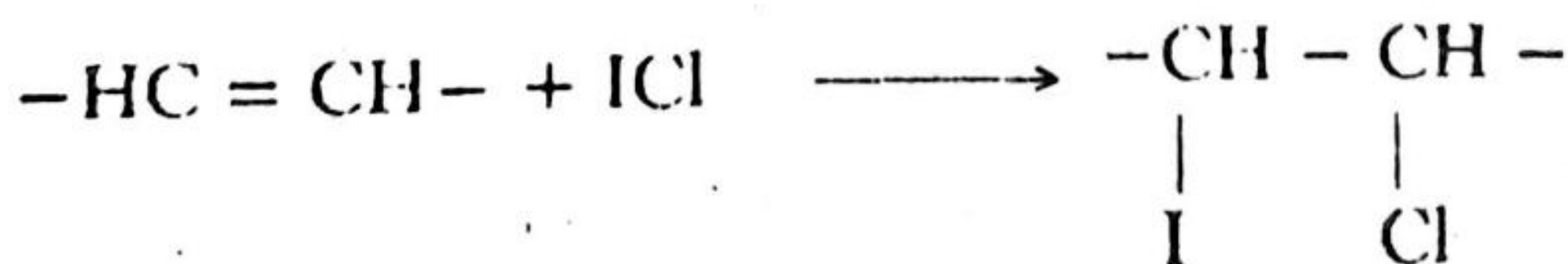


It is used to iodinate organic compounds. Chlorination may also occur depending on the condition.



### Uses

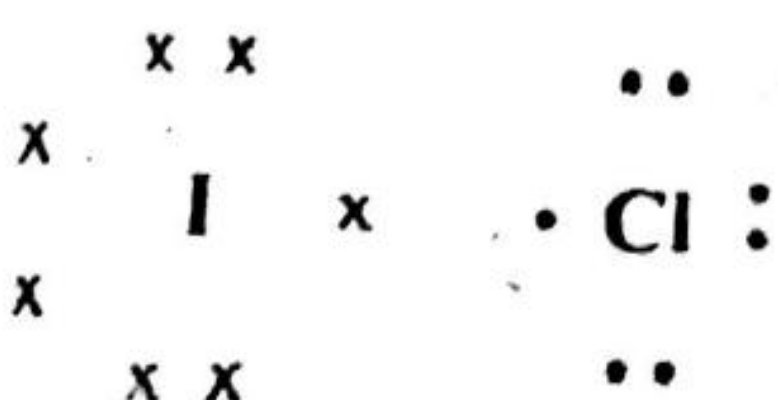
- (1) Liquid ICl is used as an ionising solvent.
- (2) It finds use as *Wij's reagent* in the estimation of iodine value of fats and oils.



- (3) It is used to iodinate organic compounds.

### Structure

It has the following linear structure :



## BROMINE TRIFLUORIDE, $\text{BrF}_3$

### Preparation

(a) It is prepared by mixing bromine vapour and fluorine in a stream of nitrogen :



(b) It is also formed by the action of  $\text{ClF}_3$  on bromine at 283 K :



### Properties

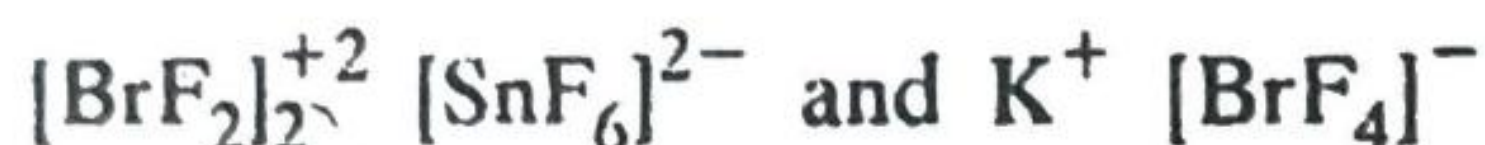
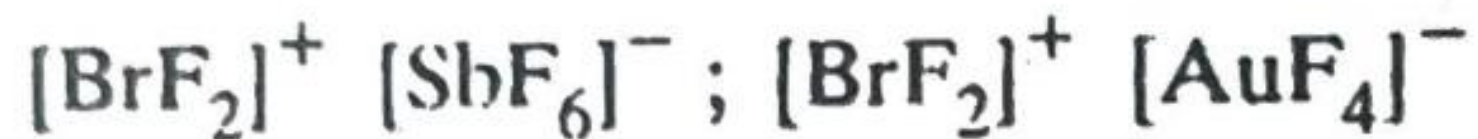
*chlorine tri  
fluoride*

It is a colourless liquid (b.p. 400 K). It has got high electrical conductivity.

It undergoes auto-ionisation as -



It reacts with metals and metallic oxides forming salts containing  $\text{BrF}_2^+$  and  $\text{BrF}_4^-$  groups. For example,



It converts many metal oxides and chlorides into fluorides as it is a good fluorinating agent :



It is decomposed violently by water giving bromine, oxygen, bromic acid ( $\text{HBrO}_3$ ) and hydrofluoric acid :



It displaces oxygen from oxides like  $\text{SiO}_2$ ,  $\text{CuO}$  etc.



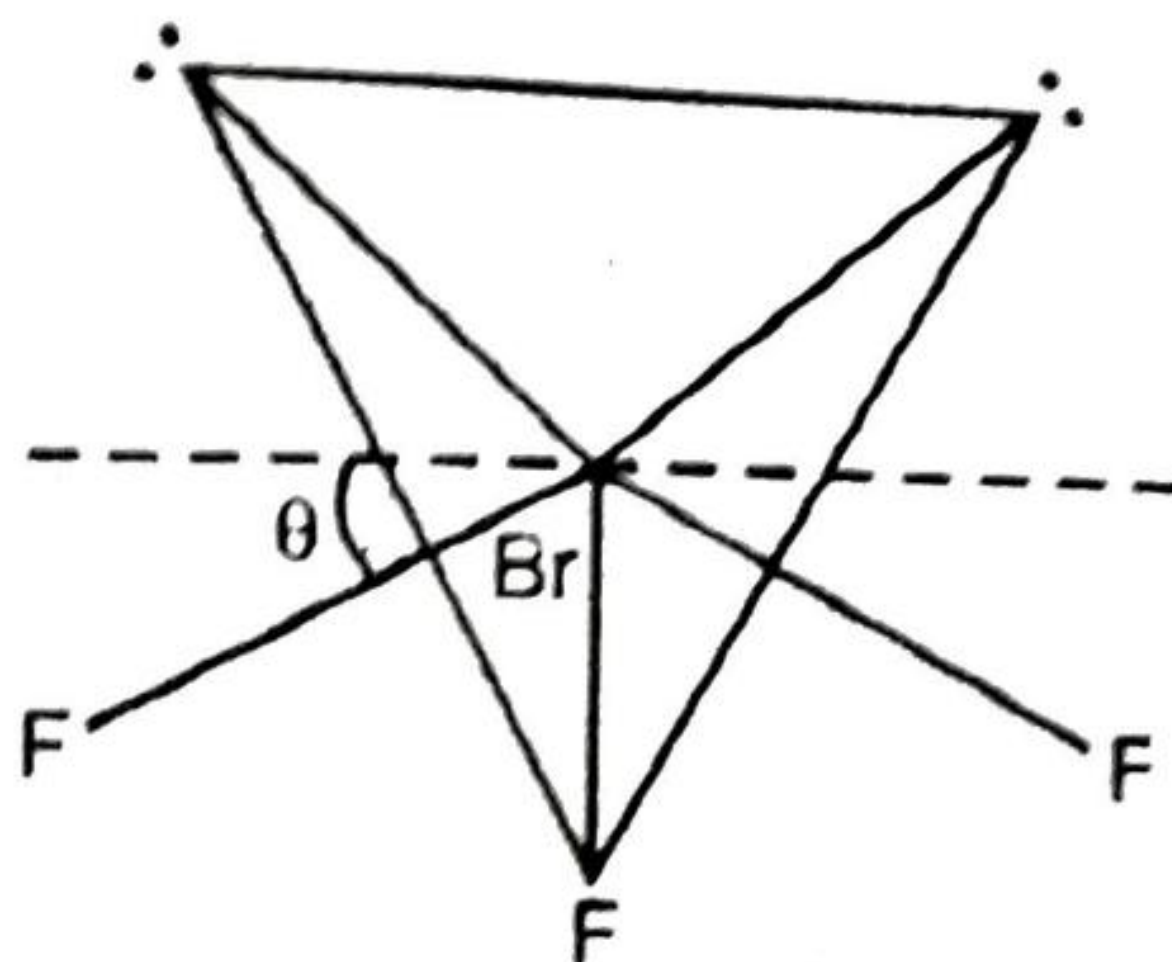
### Uses

- (1)  $\text{BrF}_3$  is used as a solvent.
- (2) It is a good fluorinating agent.



## Structure

In bromine trifluoride molecule, ten electrons are present in the valency shell of the bromine atom. Out of these, two pairs are lone pairs. The expected geometry is trigonal bipyramidal. But due to the presence of the two lone pairs, the shape is distorted. To avoid repulsion, the bonding pairs contract and it has a *bent T shape*. It makes use of  $sp^3d$  - hybridisation.



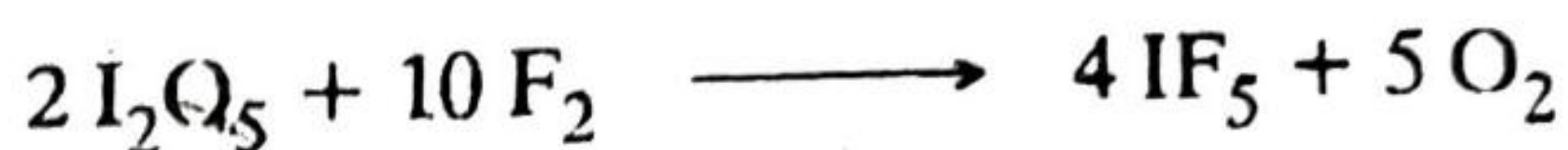
## IODINE PENTAFLUORIDE, $IF_5$

### Preparation

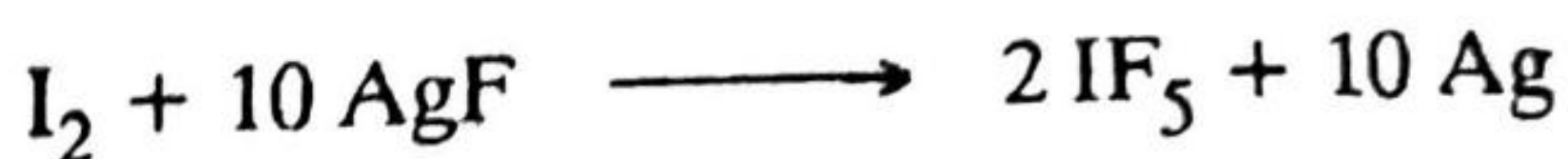
- (a) It is prepared by passing fluorine (diluted with nitrogen) over iodine in a heated quartz tube :



- (b) It is formed by the action of fluorine on  $I_2O_5$  :

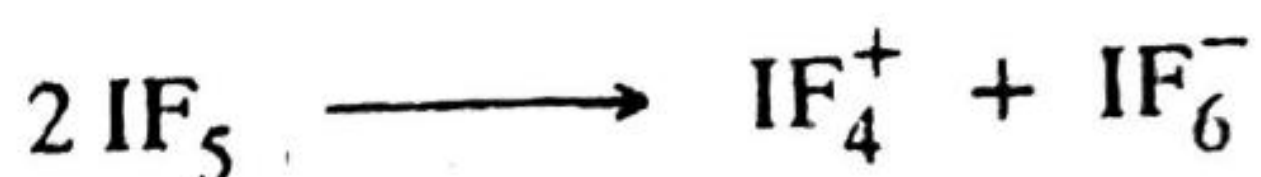


- (c) It can also be obtained by heating  $I_2$  with silver fluoride :

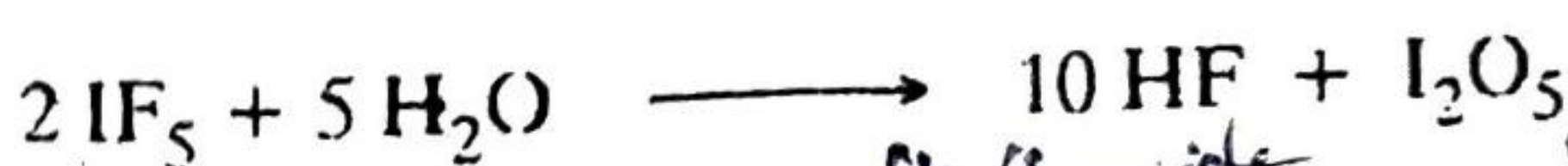


### Properties

It is a colourless liquid (b.p. 330 K). It is a good conductor of electricity as it undergoes self ionisation as



It reacts with water to form iodic and hydrofluoric acids :



*Hydrofluoric acid*  
*Iodic pentoxide*

When heated to about 773 K it decomposes to iodine and iodine heptafluoride.



Boiling iodine pentafluoride dissolves potassium fluoride to give,  $\text{K}^+ [\text{IF}_6]^-$

Metals like silver, mercury, iron, copper are slowly attacked by  $\text{IF}_5$ . With chlorine it gives chlorine trifluoride.



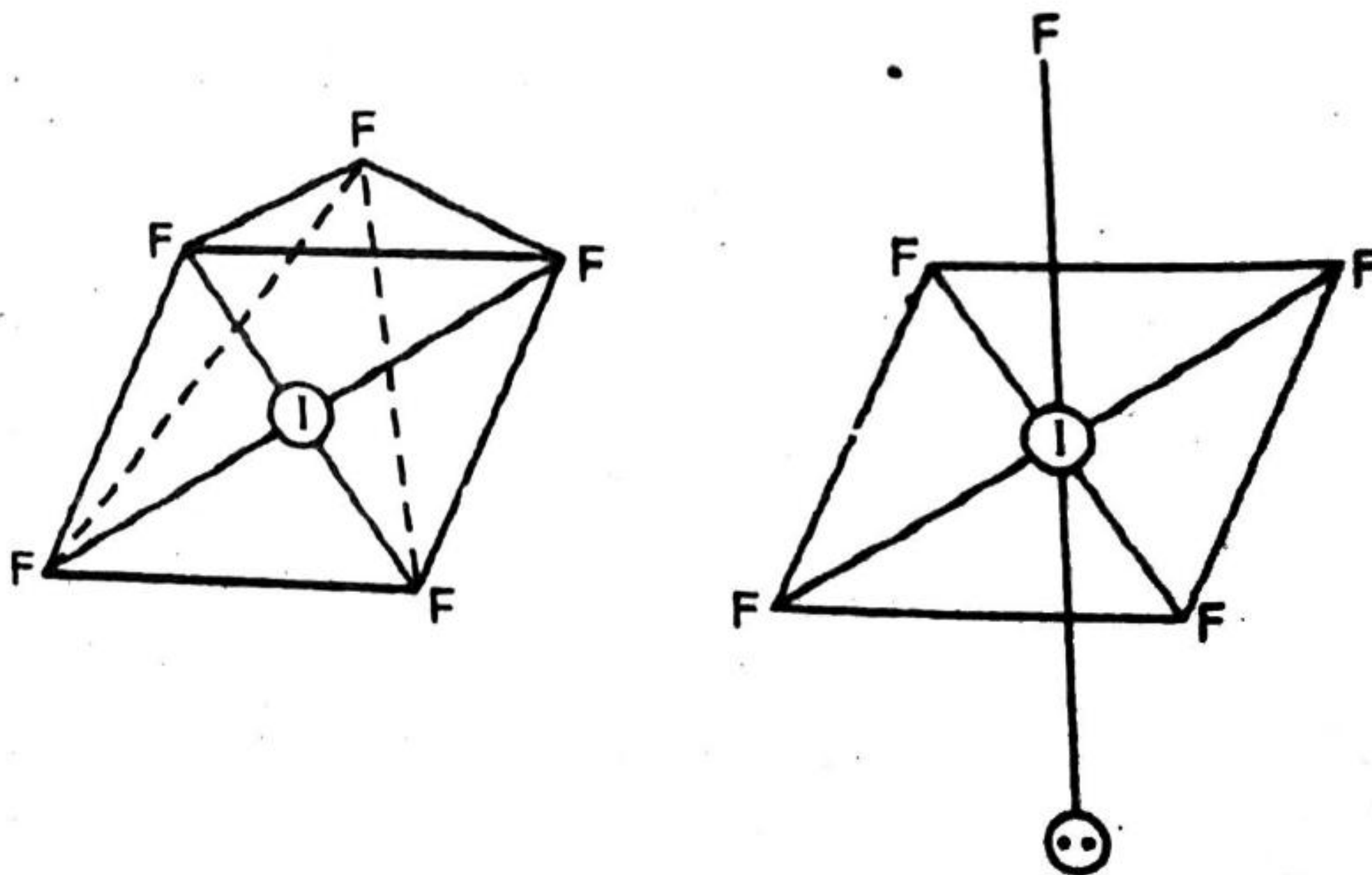
The alkali metals, sulphur, bromine react when heated.

### Uses

$\text{IF}_5$  is used as an ionising solvent.

### Structure

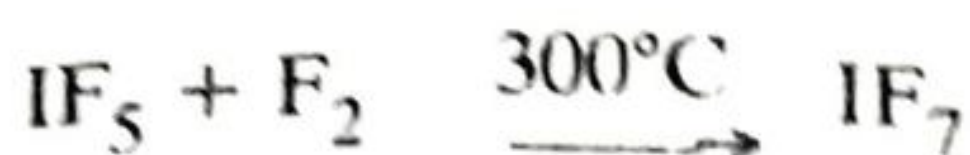
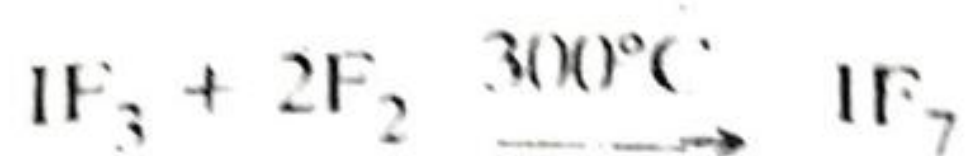
There are six pairs of electrons around the central atom, iodine. Of these one is a lone pair. Therefore, the expected geometry of octahedron is slightly distorted and the molecule has a square pyramidal structure.



### Chemistry of iodine heptafluoride, $\text{IF}_7$

#### Preparation

- (i) It can be prepared by passing fluorine over  $\text{IF}_3$  or  $\text{IF}_5$  at  $300^\circ\text{C}$ .



(ii) It can be prepared from the following reaction.



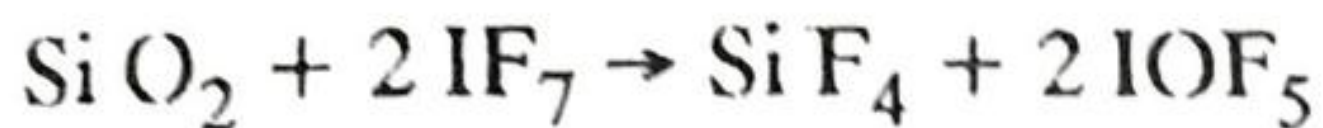
(iii) It can also be prepared by passing excess fluorine over gaseous iodine at  $300^\circ\text{C}$



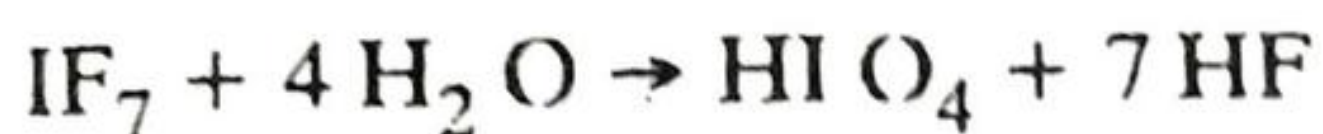
### Properties

It is a colourless gas with m.p.  $6.5^\circ\text{C}$ . It is diamagnetic in nature.

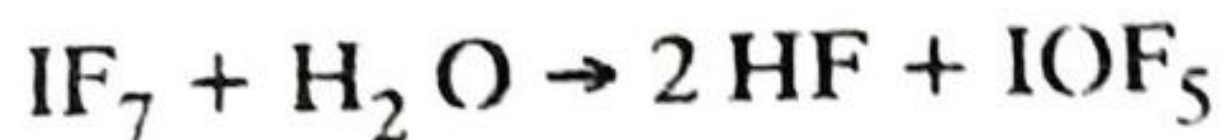
$\text{IF}_7$  is a stronger fluorinating agent than  $\text{IF}_5$ . It reacts with most elements in cold or on warming including glass or silica at  $100^\circ\text{C}$



Vapours of  $\text{IF}_7$  undergo smooth hydrolysis to  $\text{HIO}_4$  and  $\text{HF}$



An oxofluoride ( $\text{IOF}_5$ ) is formed with less amount of water at room temperature.



It reacts with most metals (except the platinum group), non metals including  $\text{Cl}_2$  and  $\text{I}_2$ , water (to give periodate and fluoride ions), many inorganic compounds and a variety of organic materials.

It explodes when heated with hydrogen.

Two of seven fluorine atoms present in  $\text{IF}_7$  can easily be removed.

### Uses

It is used as a fluorinating agent.

