

# Chemical Bonding

## Introduction

Atoms are generally not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g.,  $H_2$ ,  $O_2$ ,  $P_4$ .

Most of the molecules are cluster of atom.

Molecule will only be formed if it has lower energy and is more stable, than the individual atoms.

## Chemical Bond

- A force when acts between two or more atoms to hold them together as a stable molecule, the bond thus formed is chemical bond.
- It is group of two or more atoms involving redistribution of electrons among them.
- This process accompanied by decrease in energy.
- Decrease in energy  $\propto$  Strength of the bond.
- Therefore molecules are more stable than atoms.

**Ex.**  $Cl_2$ ,  $HCl$ ,  $NaCl$  etc.

## Cause of Chemical Combination

### (1) Tendency to acquire minimum energy

- (a) When two atoms comes closer, nucleus of one atom attracts the electron of another atom.
- (b) When net result is attraction, the total energy of the system (molecule) decreases and chemical bond forms.
- (c) Bond formation is an exothermic process.

## Definition

- ♦ The forces of attraction which holds the atoms together within a molecule is called Chemical Bond.

## Concept Ladder



Attraction  $\propto 1/\text{energy}$   
 $\propto$  Stability

## Rack your Brain



How do atoms combined to form molecules?

## Concept Ladder



Inert gas elements do not participate in the bond formation because they have stable electronic configuration and have minimum energy.



**(2) Tendency of acquire noble gas configuration**

- (a) Atom combines to acquire noble gas configuration.
- (b) (b) In formation of bond only outermost electron i.e. ns, np and (n-1)d electrons participate.

**How atom combine to form molecule.**

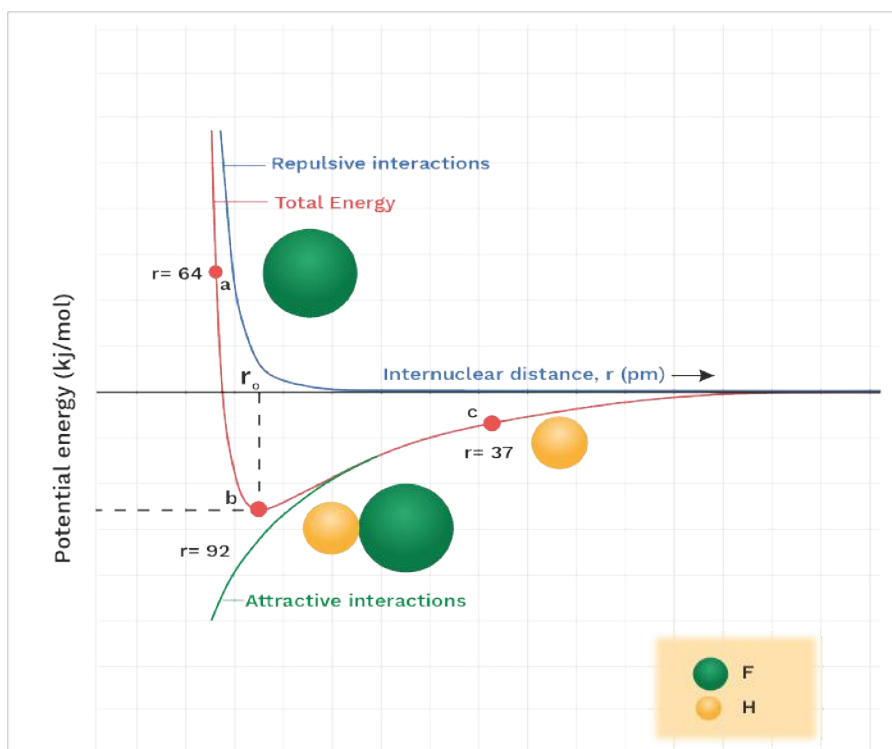
- (i) To obtain stable octet configuration or inert gas configuration.
- (ii) Decrease in Potential Energy — When two atoms approaches to each other then there is force of repulsion due to nucleus of two atoms & also force of attraction between nucleus of one atom & electron of another atoms.

**Rack your Brain**

Why inert gases are generally unreactive?

**Rack your Brain**

Why do atoms form bonds?







- At point (b) force of attraction is dominating so PE decreases & when PE becomes min. then bond is formed. When atom is made more closer, repulsion increases. Hence, after point (b) PE increases.
- During molecule formation attraction > repulsion PE decreases.
- ● Between two atoms, when at any particular distance the PE is minimum or when they combine then the distance or length between them is termed as bond length.

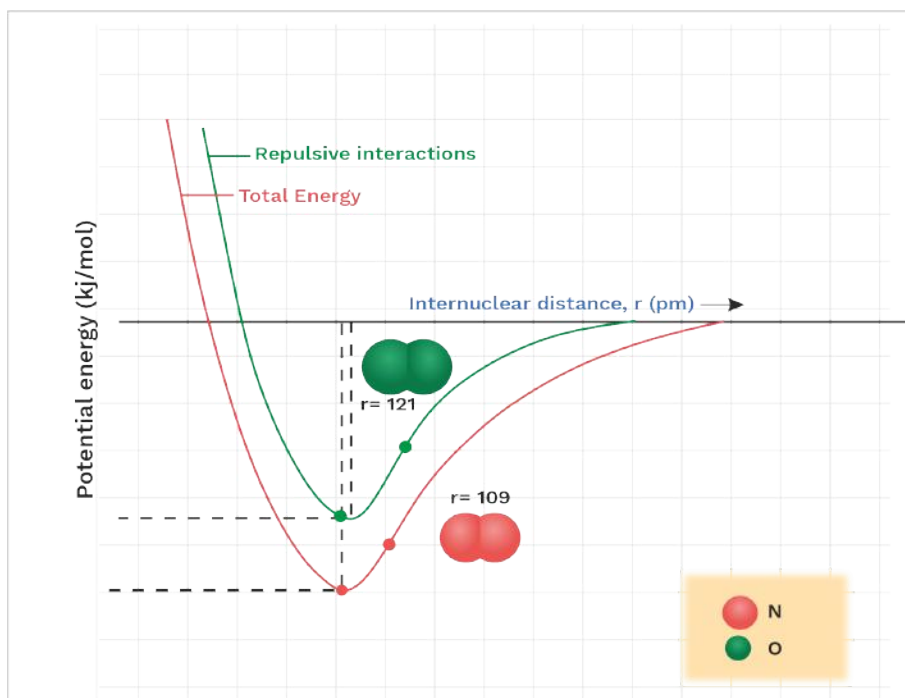
**Note :**

- The time at which molecule is formed, there is decrease in potential energy.
- For graph  $N_2$  molecule is more stable than  $O_2$ .

**Concept Ladder**



Energy is absorbed to break bonds. Energy is released when new bonds form. Bond making is an exothermic process.







- $\text{He}_2$  molecule has no graph on PE-axis, as they exist in the form of atom only not in molecule. So for all inert gases there is no graph on PE-axis.
- Between two atoms, when at any particular distance the PE is minimum or when they combine with each other.

### Lewis symbol

To represent the Lewis symbol of a particular element valence electron is represented as a dot. Some examples of Lewis symbol of various elements are given in the table.

### Concept Ladder



Lewis octet rule is acquire inert gas configuration atoms loose or gain electron or share electron.

LEWIS SYMBOL OR ELECTRON DOT SYMBOLS		
Element	Electronic Configuration	Lewis Symbol
Hydrogen	1	$\cdot\text{H}$
Helium (He)	2	$\ddot{\text{He}}$
Lithium (Li)	2, 1	$\dot{\text{Li}}$
Carbon (C)	2, 4	$\cdot\dot{\text{C}}\cdot$
Nitrogen (N)	2, 5	$:\dot{\text{N}}\cdot$

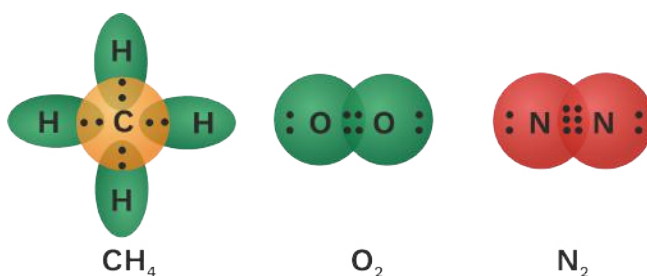




## Octet Rule

Tendency of atoms to achieve 8 electrons in their outer most shell is known as Lewis octet Rule (except in case of Hydrogen) for this atom can gain, loose or share the electrons.

Ex.



### Rack your Brain

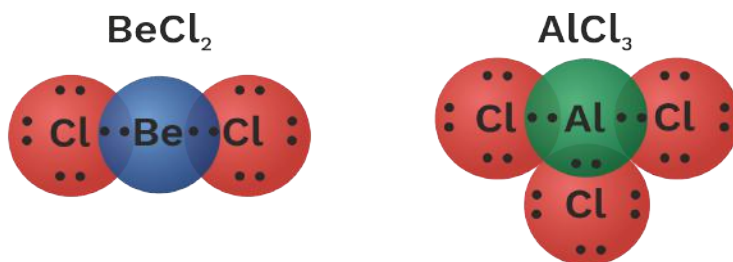


Does CO satisfy the octet rule?

## Exceptions of Octet Rule :

- (1) **Electron Deficient Molecules:** Those molecules having less than 8 e<sup>-</sup>.

Ex:



Be has only 4 electrons      Al has only 6 electrons

- (2) **Odd Electron Molecules :** In molecules with odd number of electron like nitrogen dioxide,  $\text{NO}_2$  and nitric oxide,  $\text{NO}$ , the octet rule is not satisfied for all the atoms

E.g.  $\ddot{\text{N}} = \ddot{\text{O}}$  ,  $\ddot{\text{O}} = \ddot{\text{N}} - \ddot{\text{O}} \cdot$

- (3) Some noble gases (example Xe and Kr) also combine with  $\text{O}_2$  and F to form a no. of compounds like  $\text{XeF}_2$ ,  $\text{XeOF}_2$ ,  $\text{KrF}_2$  etc., Octet Rule does not account for the shape of molecules.

### Concept Ladder



$\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBR}_3$ ,  $\text{BI}_3$  all are covalent compounds and not follow octet rule.

$\text{AlF}_3$  is ionic compound and  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{AlI}_3$  are covalent compound.



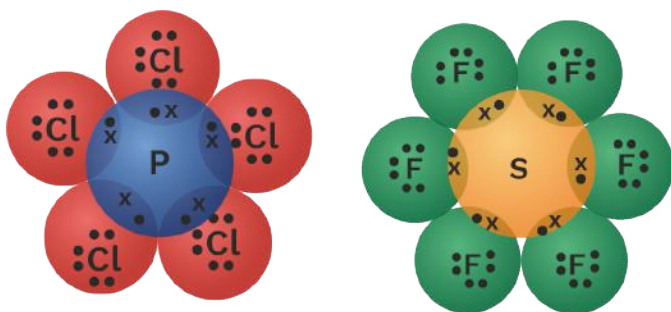


(4) It does not explain the relative stability and energy of the molecules.

(5) **Electron Efficient Molecules:** Those molecules in which central atom has more than eight electrons.

E.g.  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ ,  $\text{SF}_4$ ,  $\text{XeF}_4$

These Compounds also known as Hypervalent Compound.



Species	Valence $e^-$
$\text{PCl}_5$	10
$\text{SF}_6$	12
$\text{IF}_7$	14
$\text{SF}_4$	10
$\text{XeF}_4$	12

### Concept Ladder



**d-block metal ion generally contain 9 to 17  $e^-$**



They follow octet rule in their maximum oxidation state  $[\text{Sc}^{+3}, \text{Ti}^{+4}, \text{V}^{+5}, \text{Cr}^{+6}, \text{Mn}^{+7}]$

### Rack your Brain



Which of the following compounds  $\text{Mn}$ ,  $\text{Mn}^{+2}$ ,  $\text{Mn}^{+4}$ ,  $\text{Mn}^{+7}$  respectively follow the octet rule?

### Concept Ladder



**Pseudo inert gas configuration**



Cations which contain 18 electrons in outermost orbit

E.g.  $\text{Ga}^{+3}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Sn}^{+4}$ ,  $\text{Cd}^{+2}$  etc.

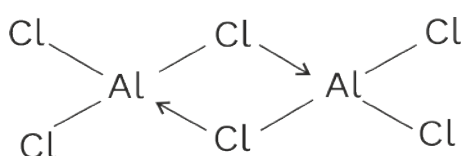
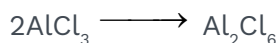




**Q.1**  $\text{AlF}_3$  is an ionic compound but the rest of the members are covalent.

**A.1** Aluminium has some metallic character, so it can form an ionic bond with fluorine because fluorine is the most electronegative element.

**Dimer Formation**



When two molecules are combined to form a noble compound then it is called a dimer.

**Q.2** Octet rule is followed by :

- (1)  $\text{Al}_2\text{Cl}_6$       (2)  $\text{AlF}_3$       (3) Both      (4) None of these

**A.2** (3)  $\text{Al}_2\text{Cl}_6$  (dimer)

**Q.3** Which compound does not exist or forms a dimer :

- (1)  $\text{Al}_2\text{Cl}_6$       (2)  $\text{Al}_2\text{Br}_6$       (3)  $\text{Ga}_2\text{Cl}_6$       (4)  $\text{Al}_2\text{F}_6$

**A.3** (4)  $\text{Al}_2\text{F}_6$  forms an ionic compound

**Note :**  $\left. \begin{array}{l} \text{Dimer of } \text{AlCl}_3 \text{ } \text{Al}_2\text{Cl}_6 \\ \text{Dimer of } \text{AlBr}_3 \text{ } \text{Al}_2\text{Br}_6 \end{array} \right\} \text{Coordinate bond}$

**Polymer:**

When 'n' number of molecules combined to form a stable compound then it is called a polymer.

**Ex :** PVC, Nylon





**Q.4**  $\text{BeCl}_2$  follows octet rule in :

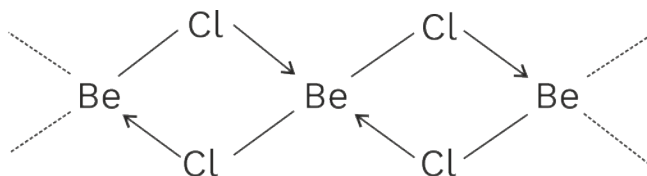
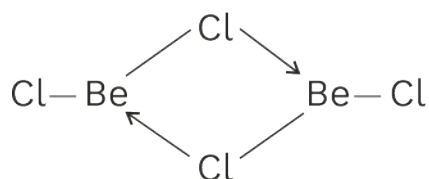
- (1) Monomer (2) Dimer  
(3) Polymer (4) All

**A.4**



Valence electrons = 4

“Does not exist”



Valence electrons = 8

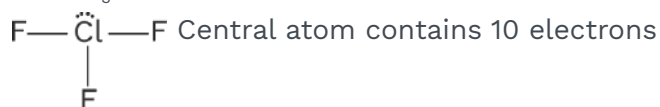
For  $\text{BeCl}_{2(g)}$  octet is not completed but for  $\text{BeCl}_{2(s)}$  octet is completed.

**Q.5**

Which is super octet.

- (1)  $\text{BF}_3$  (2)  $\text{PF}_3$   
(3)  $\text{ClF}_3$  (4) None of these

**A.5**



Central atom contains 10 electrons

**Duplet configuration**  $\text{H}^-$ ,  $\text{Li}^+$ ,  $\text{Be}^{+2} \rightarrow$  All are duplets

**Q.6**

In which compound both ions follows octet rule

- (1)  $\text{NaH}$  (2)  $\text{NaF}$   
(3)  $\text{MgO}$  (4) 2 & 3

**A.6**

(4)  $\text{NaH}$  or  $\text{Na}^+\text{H}^-$  - does not follows octet

$\left. \begin{array}{l} \text{NaF or Na}^+\text{F}^- \\ \text{MgO or Mg}^{2+}\text{O}^{2-} \end{array} \right\}$  Follows octet





**Q.7** Vanadium ( $Z = 23$ ), in which of the following octet rule passed?

- (1)  $V^{+2}$                       (2)  $V^{+3}$   
(3)  $V^{+4}$                       (4)  $V^{+5}$

**A.7** (4), the electronic configuration of vanadium is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

In case of  $V^{+2}$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$  and for  $V^{+3}$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

In case of  $V^{+5}$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6$

**Q.8** Pseudo inert gas configuration present in

- (1)  $Cu^+$                       (2)  $Ag^+$   
(3)  $Zn^{+2}$                       (4) All

**A.8** (4)

Some noble gases (example Xe and Kr) also combine with  $O_2$  and F to form a number of compounds like  $XeF_2$ ,  $KrF_2$ ,  $XeOF_2$  etc.,

**Q.9** Which compound does not exist

- (1)  $KrF_2$                       (2)  $XeF_2$   
(3)  $NeF_2$                       (4)  $XeO_2F_2$

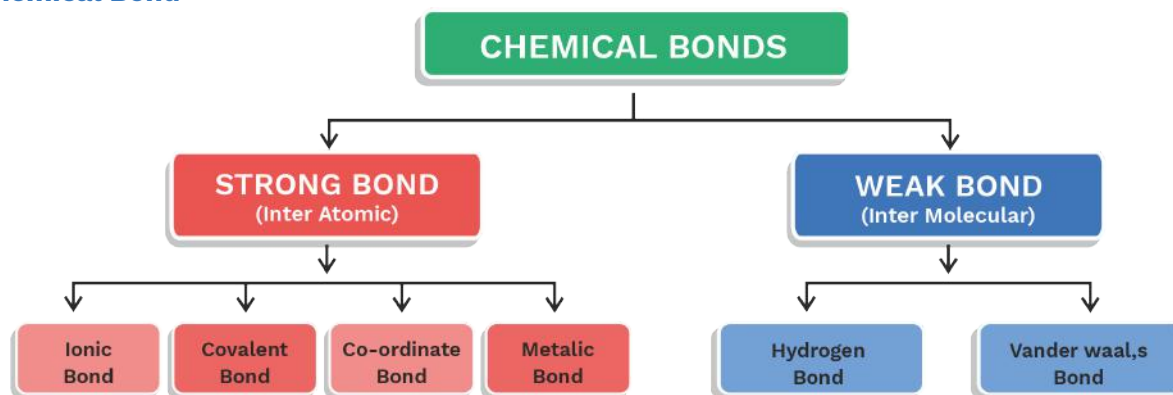
**A.9** (3), Only Kr & Xe form (Inert-gas) compounds

Octet Rule does not account for the shape of molecules.

It does not explain the relative stability and energy of the molecules.



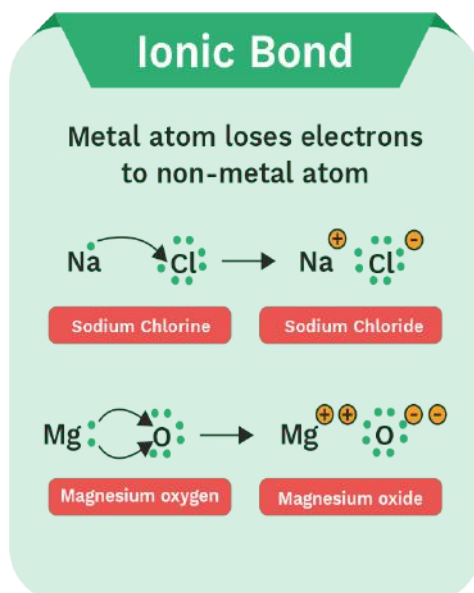
## Chemical Bond



### (1) Ionic Bond or Electrovalent Bond

- It is formed by complete transfer of  $e^-$ s from one to another atom, so as to complete their octet by acquiring 8 electrons or duplet in case of  $H_2$ ,  $Li_2$  etc. and hence acquire the nearest stable noble gas configuration.

**Ex :**  $NaCl$ ,  $MgCl_2$  etc.



### Concept Ladder



The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element.

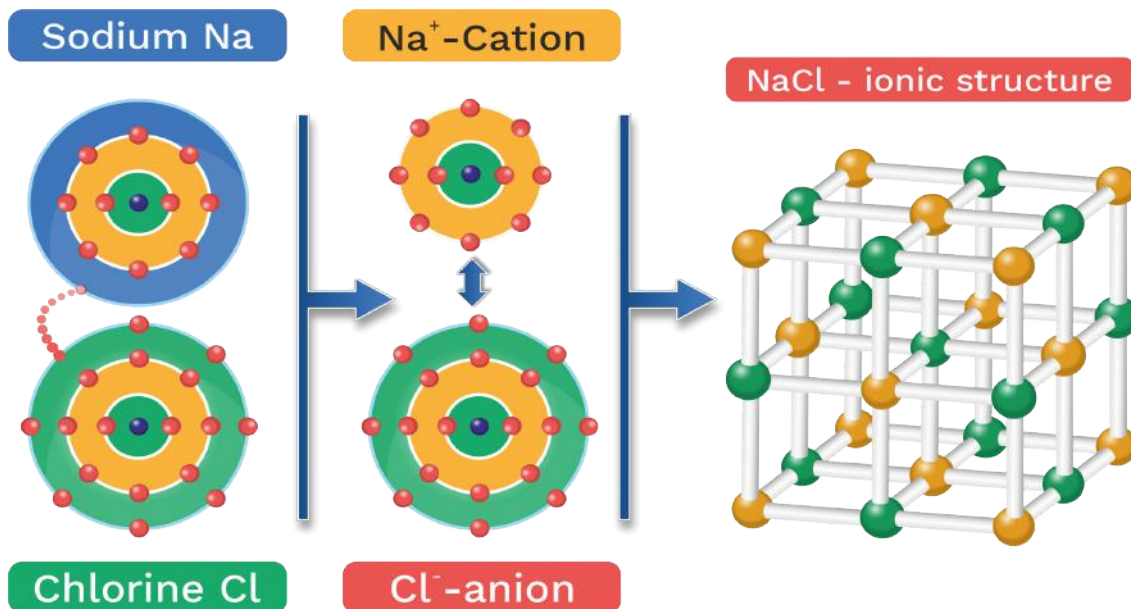
### Previous Year's Question



Bond formed in crystal by anion and cation is [AIPMT]

- (1) Ionic                      (2) Metallic  
(3) Covalent                (4) Dipole

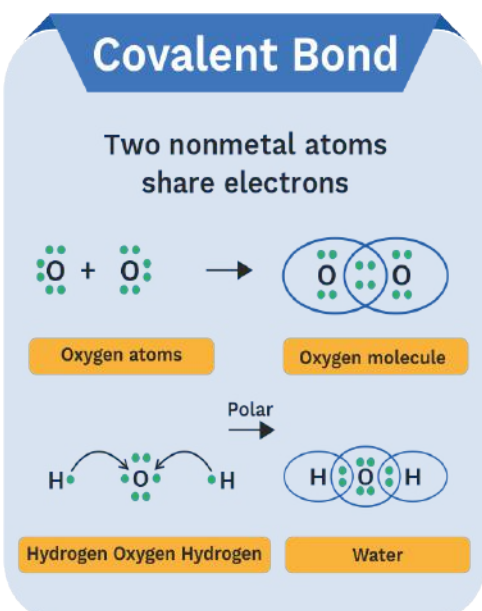




**(2) Covalent bond :**

- Covalent linkage and the no. of electrons contributed by each atom is known as covalency.

**Ex :** CO<sub>2</sub>, CCl<sub>4</sub>, NCl<sub>3</sub>, CS<sub>2</sub> etc.



**Definition**

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called **covalent bond**

**Previous Year's Question**

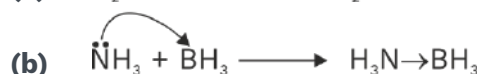
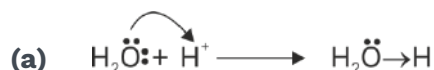
Ionic and covalent bonds are present in **[AIPMT]**

(1) CCL<sub>4</sub>      (2) CaCl<sub>2</sub>  
(3) NH<sub>4</sub>Cl      (4) H<sub>2</sub>O

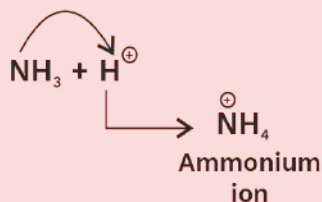


**(3) Coordinate bond :**

- It is formed when shared pair of electrons comes only from one atom. There is no mutual sharing of electrons.

**Ex:****Coordinate Bond**

formed by two atoms sharing a pair of electrons in which both electrons come from the same atom.



It is also called dative bond or dipolar bond.

**(4) Metallic bond :**

- Metallic bonding arises from the electrostatic force of attraction between conduction electrons and positively charged metal ions (Kernels)

**Definition**

The one that donates electron is called donor atom and other is called acceptor. The bond is also called dative bond.

**Previous Year's Question**

Which one of the following molecules has a coordinate bond [AIPMT]

- |                            |                     |
|----------------------------|---------------------|
| (1) $\text{NH}_4\text{Cl}$ | (2) $\text{AlCl}_3$ |
| (3) $\text{NaCl}$          | (4) $\text{Cl}_2$   |

**Concept Ladder**

- Ionic bonding: Stability through transfer of electrons.
- Covalent bonding : Stability through mutual sharing of electrons.

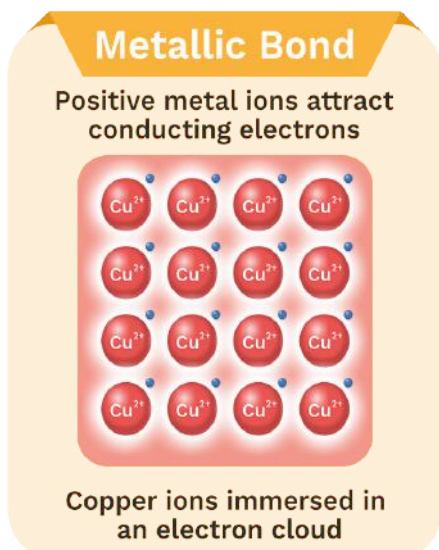
**Rack your Brain**

Which one stronger ionic or covalent bond?

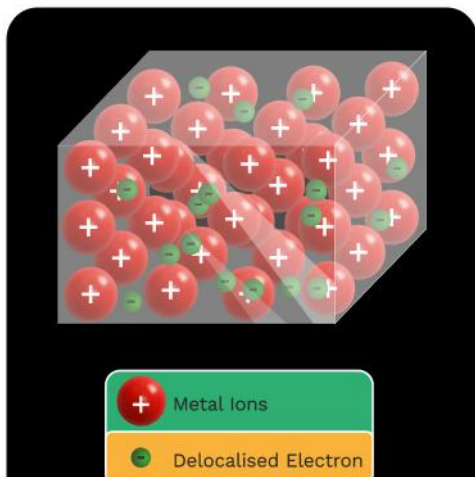




**Ex :**  $\text{Na}_{(s)}$ ,  $\text{Cu}_{(s)}$  etc.



- Metals are malleable and ductile.
- Metallic lustre is due to oscillation of surface electron by absorption of light energy.
- Metals are good conductor of heat and electricity due to presence of mobile electrons.
- Conductivity Order =  $\text{Ag} > \text{Cu} > \text{Au} > \text{Al}$ .



### Concept Ladder



Metallic bonding loosely bound and mobile electrons surround the positive nuclei of metal atoms.

### Previous Year's Question



Which of the following does not apply to metallic bond **[AIPMT]**

- (1) Overlapping valency orbitals
- (2) Mobile valency electrons
- (3) Delocalized electrons
- (4) Highly directed bonds

### Concept Ladder



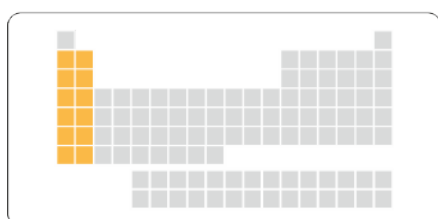
The strength of Metallic Bond is directly related to the positive charge on the metal ion.





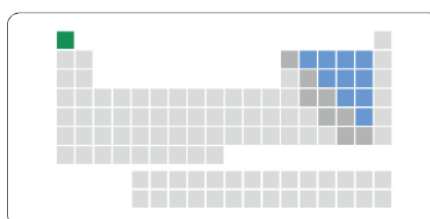
## CHEMICAL BONDING ROAD MAP

1A 2A		3A 4A 5A 6A 7A 8A							
■ Hydrogen	■ Metals	■ Metalloids	■ Nonmetals	■ Group 18					
H	Li Be								He
Na Mg									
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr									
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe									
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn									
Fr Ra Ac Rf Ha Sg Ns Hs Mt									
Pr Nd Pm Sm Eu Ce Gd Tb Dy Ho Er Tm Yb Lu									
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr									



Groups 1 and 2 Metals

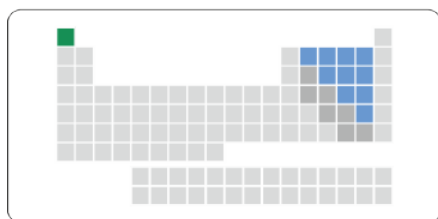
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NonMetals and H

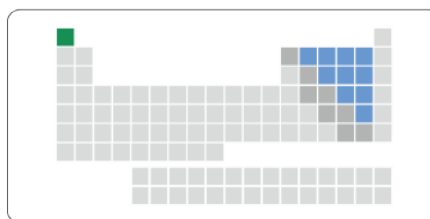
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**Ionic  
Bonding**



NonMetals and H

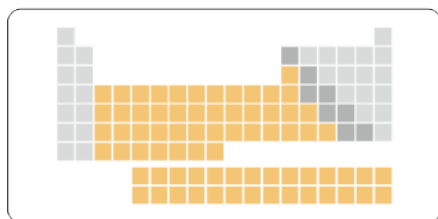
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NonMetals and H

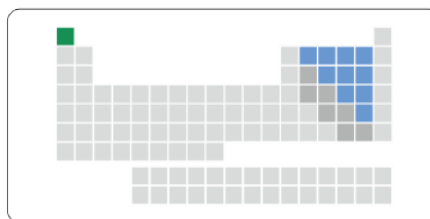
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**Covalent  
Bonding**



Other Metals

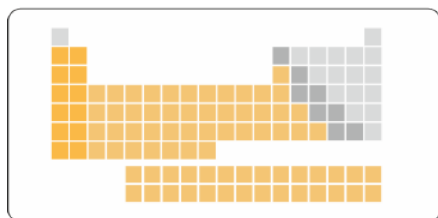
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NonMetals and H

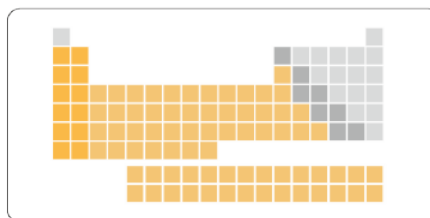
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**Polar  
Bonding**



Metals

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Metals

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**Metallic  
Bonding**

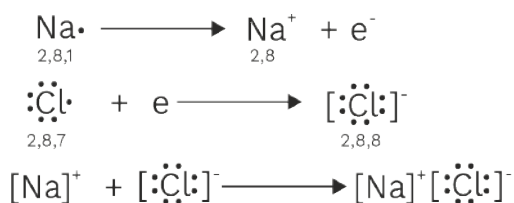




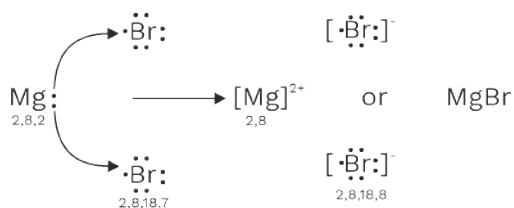
## Ionic Bond or Electrovalent Bond

Number of e<sup>-</sup>s added or lost in the formation of an electrovalent linkage is termed as the **electrovalence** of the element.

### Ex. 1 Formation of NaCl



### Ex.2



- (Metal is generally s-block having low EN and non metal having high EN)
- Difference in EN is greater than 1.7 for the formation of ionic bond.
- IA, IIA & IIIA group form ionic bond with VA, VIA & VIIA group elements. Strong ionic bond are formed by IA & IIA elements in IIIA Al, Ga, In, Tl forms ionic bond & from non metals VIIA group is best.
- Elements from IA & VII A form strongest bond due to large DEN.
- From IA → Cs & from VIIA → F form strongest among all elements from Periodic Table.
- Distance between the two elements in periodic table is directly proportional to the ionic character of bond.
- % ionic character  $16\Delta + 3.5\Delta^2$ , where  $\Delta$  is the electronegativity difference.

### Concept Ladder



- Ionic bond is formed between opposite ions.
- Ionic bond formed between metal and nonmetal



### Previous Year's Question



Which forms a crystal of NaCl

[AIPMT]

- (1) NaCl molecules
- (2) Na<sup>+</sup> and Cl<sup>-</sup> ions
- (3) Na and Cl atoms
- (4) None of these

### Rack your Brain



Why in s-block compounds Li, Mg and Be not ionic in nature?

### Concept Ladder



Ionic compounds do not have molecular formula. It has only empirical formula. eg. NaCl is the empirical formula of sodium chloride.







- Compounds of Mg like  $\text{MgH}_2$ ,  $\text{MgF}_2$ ,  $\text{MgO}$  &  $\text{Mg}_2\text{C}_3$  ionic in nature
- Similarly **compounds of Be has only one ionic compound ( $\text{Be}_2\text{C}$ )**
- All acids are covalent in gaseous or pure state but have ionic & conducting nature in water. Ex. –  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  etc.



### Rack your Brain



Why ionic bond is non directional?

**Q.10** To find Ionic character in  $\text{NaCl}$

**A.10** EN for Na–0.9, EN for Cl–3

$$\Delta \text{EN} = 3 - 0.9 = 2.1$$

$$\begin{aligned} \text{Percentage ionic character} &= 16\Delta + 3.5\Delta^2 \\ &= 16 \times 2.1 + 3.5 \times (2.1)^2 \\ &= 49.13 \end{aligned}$$

**Q.11** Type of bond present in  $\text{HCl}$

- |              |                    |
|--------------|--------------------|
| (1) Ionic    | (2) Electrovalent  |
| (3) Covalent | (4) Polar Covalent |

**A.11** (4) Polar Covalent

#### Note :

(a) Trend in Ionic character;  $\text{LiCl} < \text{NaCl} < \text{KCl} < \text{RbCl} < \text{CsCl}$

(b) Ionic character  $\text{NaI} < \text{NaBr} < \text{NaCl} < \text{NaF}$ , greater the  $\Delta\text{EN}$  greater will be the ionic character





**Q.12** Write down the order of covalent character in MF, MCl, MBr, MI

**A.12** Ionic character –  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$  and

Covalent character  $\text{MF} < \text{MCl} < \text{MBr} < \text{MI}$

Covalent character is opposite of ionic character

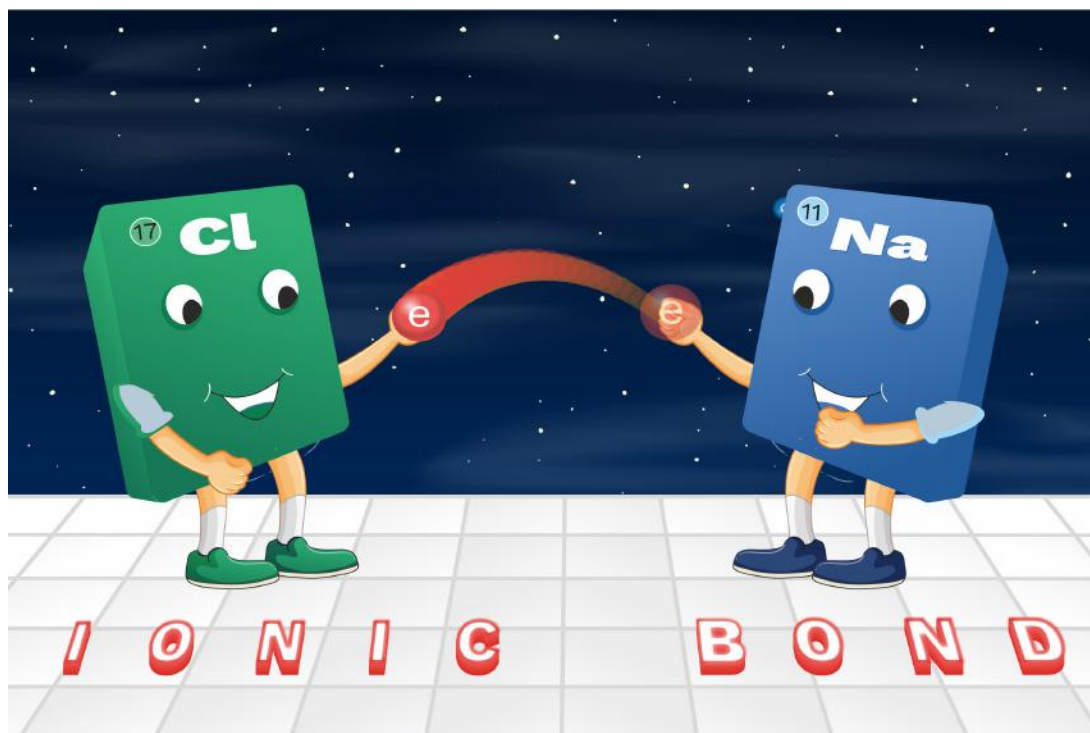
**Q.13** Among NaCl, MgS & AlP which has the lowest Ionic character

**A.13** Ionic character –  $\text{NaCl} > \text{MgS} > \text{AlP}$ , AlP has the lowest ionic character

**Q.14** Which has more ionic character, KCl or CuCl

**A.14** In KCl, K belongs to s-block and  $\Delta\text{EN}$  of KCl  $>$   $\Delta\text{EN}$  of CuCl

( $\therefore$  Ionic character  $\propto \Delta\text{EN}$ )

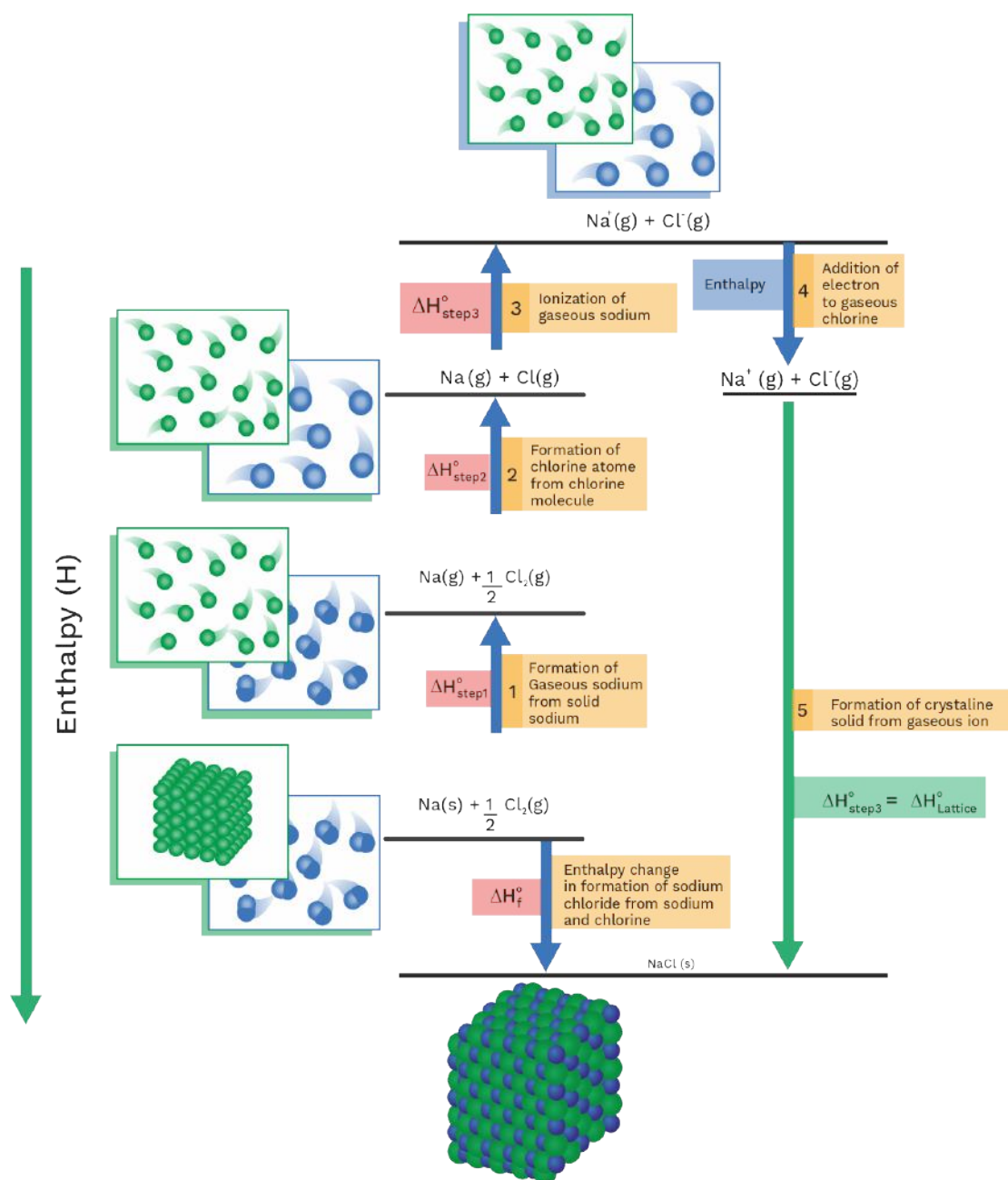






## Born-Haber Cycle

$$\Delta H_f^\circ = \Delta H_{(\text{sub})} + \frac{1}{2} \Delta H_{(\text{diss})} + \text{I.E} - \text{E.A} - U, \text{ where } U \text{ is lattice energy}$$



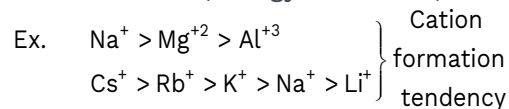




## Conditions for ionic bond formation

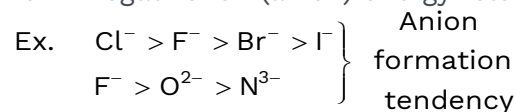
### (a) Ionisation energy (I.E.)

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the positive ion or cation. (energy absorbed)



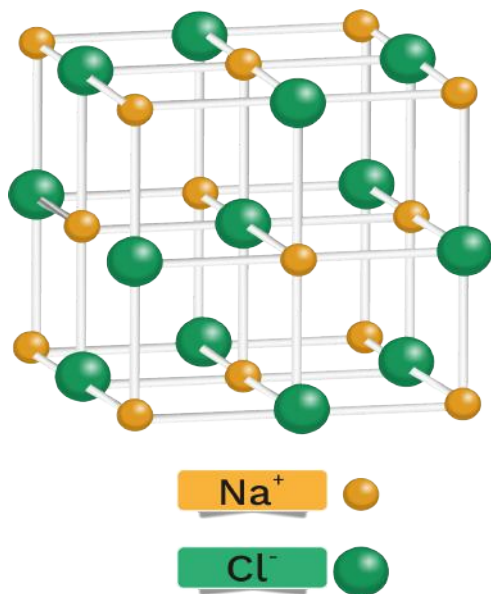
### (b) Electron affinity (E.A.)

Amount of energy released when an electron is added to an isolated gaseous atom to form negative ion (anion) energy released.



### (c) Lattice energy (L.E.)

Amount of energy released when one mole of crystal lattice is formed. Higher lattice energy  $\rightarrow$  Greater will be the stability of strength of ionic compound.



### Concept Ladder



Lesser Ionisation energy  $\rightarrow$   
Greater tendency to form cation.

### Concept Ladder



Higher electron affinity  $\rightarrow$   
Greater tendency to form anion.

### Definitions

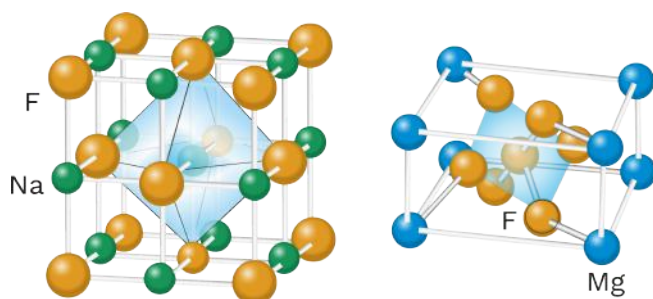
Lattice energy – energy required to separate a mole of an ionic solid into gaseous ions. Higher the lattice energy, greater will be the stability or strength of ionic compound.

### Concept Ladder



$$\text{Lattice energy (U)} \propto \frac{Z^+Z^-}{r^+ + r^-}$$





### Concept Ladder



Favourable condition for ionic bond -  
 Low Sublimation Energy  
 Low Ionization Energy  
 Low Bond Dissociation Energy  
 High Electron Affinity.  
 High Lattice Energy.

### Factors affecting lattice energy

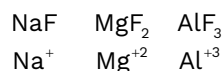
Magnitude of charge  $U \propto z^+z^-$   
 (Ionic charge) Lattice energy  $\propto$   
 Magnitude of charge

Size of Cation :- Lattice energy  $\propto \frac{1}{r^+ + r^-}$

### Factors affecting lattice energy

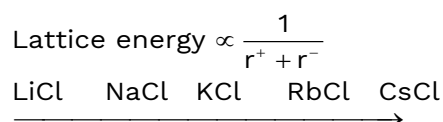
#### (i) Magnitude of charge :

Lattice energy ( $U$ )  $\propto Z^+Z^-$  (Ionic charges of cation and anion)



- 
- Lattice energy increases
  - Size of cation decreases

#### (ii) Size of Cation



- Size of cation increasing
- Lattice energy decreases
- Size of anion is constant

### Concept Ladder



Melting point, solubility, hardness, thermal stability of ionic compound are affected by lattice energy

### Previous Year's Question



Among the following, which compound will show the highest lattice energy [AIPMT]

- |         |         |
|---------|---------|
| (1) KF  | (2) NaF |
| (3) CsF | (4) RbF |





**Q.15** Which parameter is not involved in the Born-Haber cycle.

- (1) Sublimation Energy    (2) Dissociation Energy  
(3) Ionisation energy    (4) Electronegativity

**A.15** (4) Electronegativity

**Note:**

Formation of compound takes place when energy released is greater than absorbed  
i.e. Energy released > Energy absorbed ( $\Delta H_f^\circ = -U$ )

**Q.16** Which reaction represents LE for magnesium fluoride

- (1)  $\text{Mg(g)} + \text{F}_2\text{(g)}$                       (2)  $\text{Mg(g)} + 2\text{F(g)}$   
(3)  $\text{Mg}^{+2}\text{(g)} + \text{F}^-\text{(g)}$                       (4)  $\text{Mg}^{+2}\text{(g)} + 2\text{F}^-\text{(g)}$

**A.16.** (4), During release of LE ions will combine to form magnesium fluoride so option (1) and (2) are not correct as they represent atomic form of elements. In option (3) two fluorine atoms are required so option (4) is the correct option.

Ex.  $\text{LiF} < \text{MgF}_2 < \text{MgO} < \text{Al}_2\text{O}_3$  (lattice energy)

$\text{LiH} > \text{NaH} > \text{KH} > \text{CsH}$  (size of cation increases lattice energy decreases)

$\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$  (size of anion increases lattice energy decreases)

$\text{NaF} < \text{MgF}_2 < \text{AlF}_3$  (lattice energy)

## Properties of Ionic Compound

### (a) Physical State

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction. Ionic bond is non-directional in nature because the electrostatic bond is

act in all directions.

Covalent and coordinate bonds are directional in nature

### Concept Ladder



Hardness of ionic compound  
 $\propto \text{LE} \propto \text{charge} \propto 1/\text{size}$ .

**Q17** Why does the physical state of halogens vary down the group that is  $\text{F}_2$ ,  $\text{Cl}_2$  are gaseous  $\text{Br}_2$  is liquid and  $\text{I}_2$  is in solid state.





**A.17.** On moving down the group mass increases, Vander's wall forces of attraction  $\propto$  mass. So forces increases and molecules comes closer to each other.

**Q.18** Directional bond is present in

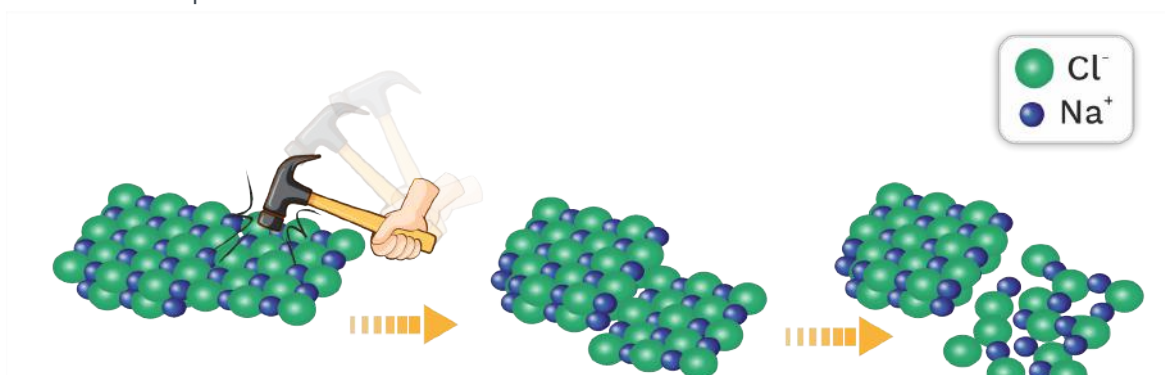
(1) NaCl(s) (2) Na(s)

(3) CCl<sub>4</sub>(l) (4) None

**A.18** (3), NaCl(s) – ionic bond, Na(s) – Metallic bond, CCl<sub>4</sub>(l) – Covalent bond

**(b) Brittleness**

Ionic compound are hard and brittle in nature. Brittle means the can be break into smaller particles



**Ex.** (i) CaO > SrO > BaO (Size increases, Lattice energy decreases so hardness decreases)

(ii) NaF < MgF<sub>2</sub> < AlF<sub>3</sub> (size decreases,

lattice energy increases so hardness increases)

**Q.19** Na(s) is soft metal but NaCl is hard. Why?

**A.19** In case of sodium metallic bonding is their but in case of NaCl strong electrostatics forces of attraction between the ions are there.

**(c) Conductivity**

It depends on ionic mobility.

In solid state – No free ions – Bad conductor of electricity.

**Concept Ladder**



Solid state < fused < Aqueous solution (conductivity order)







In fused state or aqueous solution Due to free ion – Good conductor of electricity.

**Note** (a) Increase in size mobility decreases hence conductivity decreases.

(b) Smaller cation become largest in  $H_2O$

(hydrated size) due to more hydration and become least conducting.

**Q.20.** Which one conducting in nature

(1) NaCl(s)

(2) Fused  $AlBr_3$

(3) Molten sulphur

(4) Na(s)

**A.20** (4), Na(s)

#### Explanation

(i) NaCl(s) – Non conducting

(ii)  $AlBr_3$  – Covalent in nature

(iii) Molten Sulphur – non metal

(iv) Na(s) – Metal (it contains free electrons)

#### Exception:

Nonmetals are not conducting but graphite is conducting because it has free electron

#### (d) Ionic reaction

(a) Ionic compounds shows ionic reaction and covalent compounds shows – molecular reaction.

(b) Ionic reactions are faster than molecular reaction because of free ions.

**Ex.** When NaCl is added in  $AgNO_3$  solution, white ppt of Ag/Cl is formed at once.

#### (e) Isomorphism

(1) The two compounds are termed as isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.

(2) They have similar crystal structure.

#### Concept Ladder



$$\text{Conductivity} \propto \text{Mobility} \\ \propto 1/\text{size of atom}$$



#### Previous Year's Question



When NaCl is dissolved in water, the sodium ion becomes

[AIPMT]

- |                |              |
|----------------|--------------|
| (1) Oxidized   | (2) Reduced  |
| (3) Hydrolysed | (4) Hydrated |

#### Rack your Brain



Why is  $NaHCO_3$  ionic?

#### Previous Year's Question



Which one is least ionic in the following compounds

[AIPMT]

- |              |              |
|--------------|--------------|
| (1) AgCl     | (2) KCl      |
| (3) $BaCl_2$ | (4) $CaCl_2$ |



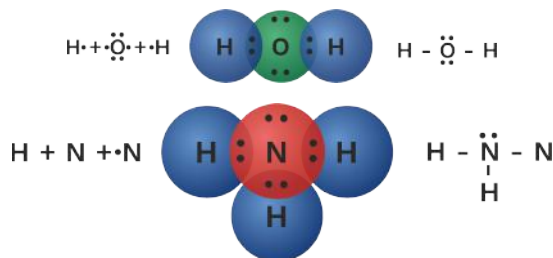
**Example.**

	Na <sup>+</sup>	F <sup>-</sup>	Mg <sup>2+</sup>	O <sup>-2</sup>
Valency	+1,	-1	+2,	-2
Electronic configuration	2, 8	2, 8	2, 8	2, 8
Similarly	Ca <sup>+2</sup>	2Cl <sup>-1</sup>	2K <sup>+1</sup>	S <sup>-2</sup>
	2, 8, 8	2, 8, 8	2, 8, 8	2, 8, 8

**Covalent bond:**

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octets or duplets in case of elements having only one shell is called **covalent bond or covalent linkage** and the number of electrons contributed by each atom is known as **covalency**.

- It is formed between non-metal and non-metal (CO<sub>2</sub>, Cs<sub>2</sub>, CCl<sub>4</sub> etc.)
- Less electropositive metal and non-metal (SnCl<sub>4</sub>, FeCl<sub>3</sub> etc.)
- Electrons which are not participate in bond formation are known as lone pair (lp) or non-bonded electron pair or unshared electron pair.

**Examples :****Concept Ladder**

Ionic bond non-directional and does not show stereo isomerism

**Previous Year's Question**

Which of the following statements is correct for covalent bond

[AIPMT]

- (1) Electrons are shared between two atoms
- (2) It may be polar or non-polar
- (3) Direction is non-polar
- (4) Valency electrons are attracted

**Concept Ladder**

Less electropositive metal cannot lose electron easily. Covalent bond is formed by equal sharing of electrons.



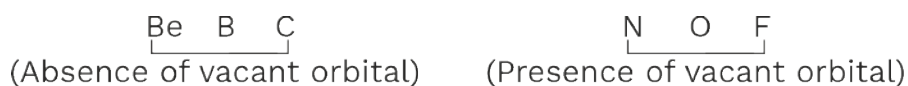


### Orbital concept of Covalent bond

- One orbital can hold maximum of  $2e^-$  with opposite spin



- Half filled orbital has tendency to get paired
- For N, O and F, there is no vacant orbital is present, only half filled orbital is present so promotion of electron is not possible.



- Completion of octet is not essential condition but full fill ment of half-filled orbital is essential condition.

**Ex.** Be form  $\text{BeF}_2$  and  $\text{BeH}_2$  in its excited state and it has total 4 electrons in its outer most shell after formation of bond.

- For  $2^{\text{nd}}$  period elements promotion of electrons is not possible in excited state as the is no availability of 2d subshell.

### Nitrogen (E.C $-1s^2 2s^2 2p^3$ )



### Previous Year's Question



Which one is the electron deficient compound

[AIIMS]

- |                    |                    |
|--------------------|--------------------|
| (1) $\text{ICl}$   | (2) $\text{NH}_3$  |
| (3) $\text{BCl}_3$ | (4) $\text{PCl}_3$ |

### Rack your Brain



Is HCl is ionic or covalent?

### Previous Year's Question



Ionic and covalent bonds are present in

[AIPMT]

- |                            |                          |
|----------------------------|--------------------------|
| (1) $\text{CCl}_4$         | (2) $\text{CaCl}_2$      |
| (3) $\text{Na}_4\text{Cl}$ | (4) $\text{H}_2\text{O}$ |





- For the formation of ammonia ( $\text{NH}_3$ ), no need of excited state as it has already 3 unpaired electron in its ground state.

### Phosphorus (E.C $-1s^2 2s^2 2p^6 3s^2 3p^3$ )



### Characteristics of Covalent compounds

- (i) **Physical State** : Covalent molecules exist as gases or liquids due to weak forces of attraction (Vander Waal's forces and Hydrogen Bonding) and some exist as soft solids.

**Eg.** Sulphur, Phosphorus, Iodine (Soft Solids).  
 $\text{F}_2$  and  $\text{Cl}_2$  (gas),  $\text{Br}_2$  (liquid).

- (ii) **Conductivity** : Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self-ionisation can conduct electricity.

**Eg.**  $\text{H}_2\text{O}$ , liq.  $\text{NH}_3$  etc.  
 Free ions are formed which can conduct electricity. Exceptions : Graphite, HCl in water.

- (iii) **Isomerism** : Covalent bond is rigid and directional, so it shows isomerism.

**Eg.** Organic compounds.

### Fajan's Rule

- Every ionic compound has some covalent character
- $\text{CsF}$  has maximum ionic character but contains 0.1% of covalent character due to polarisation.

### Concept Ladder



In case of nitrogen  $\text{NH}_3$ ,  $\text{NCl}_3$  can be formed but  $\text{NH}_5$ ,  $\text{NCl}_5$  are not possible as it has no vacant 2d orbital.

### Rack your Brain



Are acids covalent or ionic?

### Previous Year's Question



Covalent compounds are generally ..... in water

[AIPMT]

- (1) Soluble (2) Insoluble  
 (3) Dissociated (4) Hydrolysed





- Change in shape of  $e^-$  cloud of anion by cation is known as Polarisation or deformation or distortion



### Polarizability

- Tendency of anion to get polarise.
- Anions having large size has high tendency to get polarize as outer most electrons has less force of attraction with nucleus.  
Ex.  $F^- < Cl^- < Br^- < I^-$  (as size increases polarizability increases)

### Factor affecting polarisation

A molecule is predominantly covalent if

- Smaller the size of cation.
- larger the size of anion.
- greater the charge on cation and anion.
- ion does not have inert gas configuration, but it possesses pseudo inert gas configuration (18 electrons in the ultimate shell).

LiCl	Size of cation $\uparrow$	BeCl <sub>2</sub>
NaCl	Polarization $\downarrow$	MgCl <sub>2</sub>
KCl	Covalent character $\downarrow$	CaCl <sub>2</sub>
CsCl	Ionic Character $\uparrow$	BaCl <sub>2</sub>

### Note

- In s-block compounds, BeCl<sub>2</sub> has maximum covalent character & CsCl has minimum covalent character.
- To find either ionic character or covalent character always use polarization.

### Rack your Brain



Why are covalent bonds strongest?

### Concept Ladder



Polarizing power is favour by small cation & large anion. Small sized cation has large Zeff (effective nuclear charge) so has more ability to polarize near by anion or distort election cloud of nearly anion.

### Previous Year's Question



Which of the followonig have both polar and non-polar bonds

[AIIMS]

- |                                   |                        |
|-----------------------------------|------------------------|
| (1) C <sub>2</sub> H <sub>6</sub> | (2) NH <sub>4</sub> Cl |
| (3) HCl                           | (4) AlCl <sub>3</sub>  |



- (c) Polarizing power of cation is expressed in ionic potential ( $\phi$ ).
- (d) Covalent character  $\propto$  polarisation  $\propto$  Ionic potential ( $\phi$ )  $\propto$  charge/size.
- (e) Along the period covalent character increases,  $\phi$  increases and polarizing power increasing.

### Concept Ladder



Covalent character  $\propto$   
polarisation  $\propto$  charge on  
cation  $\propto$  size of anion



**Q.21** Which has maximum covalent character?

- (1)  $\text{AlF}_3$                       (2)  $\text{AlCl}_3$                       (3)  $\text{AlBr}_3$                       (4)  $\text{AlI}_3$

**A.21** (4),  $\text{AlI}_3 - \text{AlF}_3 < \text{AlCl}_3 < \text{AlBr}_3 < \text{AlI}_3$  (Covalent character)





**Q.22** Among  $\text{FeCl}_2$  and  $\text{FeCl}_3$ , which one has high polarizing power.

**A.22**  $\text{FeCl}_2 < \text{FeCl}_3$  (polarizing power)

In  $\text{FeCl}_2$ , the charge on Fe is +2 whereas in  $\text{FeCl}_3$ , Fe has +3 charge

Polarizing power  $\propto$  charge

**Q.23** Which cation polarizes more  $\text{CN}^-$  ion

(1)  $\text{K}^+$  (2)  $\text{Rb}^+$  (3)  $\text{Cs}^+$  (4)  $\text{Ag}^+$

**A.23** (4),  $\text{K}^+$  and  $\text{Ag}^+$  has similar size but  $\text{Ag}^+$  has pseudo configuration so it has more ability to polarize  $\text{CN}^-$

### Hydration Energy

- Amount of release energy during hydration of one mole of ionic solid.
- Polarity of solvent increases,  $\epsilon_r$  increases ( $\epsilon_r$  for  $\text{H}_2\text{O}$  is 81) then solubility of ionic compound increases.

### Concept Ladder



Factor affecting hydration energy

Hydration Energy  $\propto Z^+Z^-$

Hydration Energy  $\propto \frac{1}{r^+} + \frac{1}{r^-}$

**Q.24** Maximum mobility in aqueous solution is

(1)  $\text{Al}^{+3}$  (2)  $\text{Li}^+$  (3)  $\text{Be}^{+2}$  (4)  $\text{Rb}^+$

**A.24** (4)

### Solubility

(a) Solubility of metal + non metal compounds  
 $\text{M}^+\text{X}^-_{(s)} + (x+y)\text{H}_2\text{O} \rightarrow \text{M}^+(\text{H}_2\text{O})_x + \text{X}^-(\text{H}_2\text{O})_y$

;  $\Delta S = +ve$

$\Delta G = \Delta H - T\Delta S$

(I) If  $\Delta H = -ve$

(Hydration Energy > Lattice Energy, compound will be soluble)

(II) If  $\Delta H = +ve$

(Hydration Energy < Lattice Energy, compound will be insoluble)

### Rack your Brain



Why lithium ion is highly hydrated?

### Concept Ladder



Generally metal halides are water soluble except chloride,  $\text{Br}^-$ , iodides of Pb, Hg and Ag.





$$(1) \quad \text{Solubility} \propto \frac{\text{Hydration Energy}}{\text{Lattice Energy}}$$

(Mainly applicable for s-block elements)

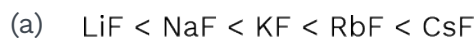
- If common ion smaller in size like  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{OH}^-$  and IIA cations then lattice energy dominates.
- If common ion larger in size like  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{I}^-$ ,  $\text{Br}^-$  and polyatomic anions the hydration energy dominates.

$$(2) \quad \text{Solubility} \propto \frac{1}{\text{Polarisation or covalent character}}$$

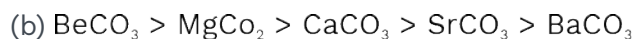
Mainly applicable for Be-Halides, p and d block metals.

$$(3) \quad \text{Solubility in organic solvent} \propto \text{polarisation or covalent character}$$

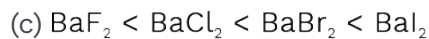
#### Compare solubility order



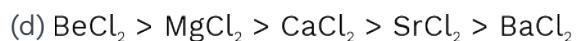
$\xrightarrow{\hspace{2cm}}$   
 Size of cation increases,  
 Lattice Energy Increases



$\xrightarrow{\hspace{2cm}}$   
 Size of cation increases,  
 Hydration Energy decreases



$\xrightarrow{\hspace{2cm}}$   
 Size of anion increases,  
 Lattice Energy decreases



$\xrightarrow{\hspace{2cm}}$   
 Size of Cation increases,  
 Hydration Energy decreases

#### Rack your Brain



Why Alkali metal hydroxides and  $\text{Ba(OH)}_2$  are water soluble, rest are insoluble?

#### Previous Year's Question



Which of the following is least soluble

[AIPMT]

- |                    |                    |
|--------------------|--------------------|
| (1) $\text{BaF}_2$ | (2) $\text{SrF}_2$ |
| (3) $\text{CaF}_2$ | (4) $\text{MgF}_2$ |

#### Concept Ladder



All metal nitrates are water soluble.





- (d) O-nitrophenol > p-nitrophenol

Mostly metal sulphates are water soluble except  $\text{CaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{BaSO}_4$  and  $\text{PbSO}_4$ .





Sol. (d) In case of O-nitrophenol, Intra molecular hydrogen bonding is their but in case of p-nitrophenol inter molecular hydrogen bonding is their greater the intermolecular hydrogen bonding greater will be solubility

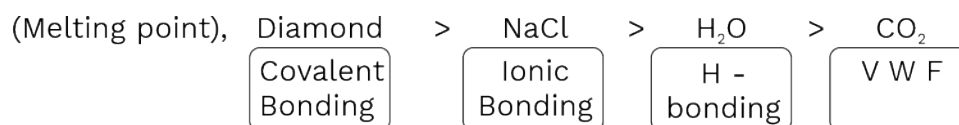
### Concept Ladder



Solubility of organic compounds increases due to H-bonding.



### Melting point and Boiling point



(a) Melting point of metal + non metal compounds

Melting point  $\propto$  Lattice energy (Mainly applicable for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> or F<sup>-</sup>, O<sup>-</sup>, H<sup>-</sup>)

$$\text{Melting point} \propto \frac{1}{\text{Polarisation or covalent character}}$$

Melting point = Ionic > Covalent compounds (except giant molecules)

### Melting Point orders

(a)  $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$   
 $\xrightarrow{\text{Size of cation increases, polarisation decreases}}$

(b)  $\text{NaF} < \text{MgF}_2 < \text{AlF}_3$   
 $\xrightarrow{\text{Charge increases}}$   
 Lattice Energy increases

(c)  $\text{NaCl} > \text{MgCl}_2 > \text{AlCl}_3$   
 $\xrightarrow{\text{Charge increases}}$   
 Polarisation increases

(d)  $\text{CaF}_2 > \text{CaCl}_2 > \text{CaBr}_2 > \text{CaI}_2$  (anion size increases, polarisation increases)

(e)  $\text{Na}_2\text{O} < \text{MgO} < \text{Al}_2\text{O}_3$  (charge increases,

### Rack your Brain



Why NH<sub>3</sub> has more melting point compare to SbH<sub>3</sub>?

### Concept Ladder



For non metallic molecules if intermolecular attraction increases then melting point increases, boiling point increases. Surface tension increases, critical temperature increases, viscosity increases but volatility and vapour pressure decreases.







Lattice Energy increases)

- (f)  $\text{NaF} < \text{MgO} < \text{SCN} < \text{TiC}$  (charge increases, Lattice energy increases)
- (g)  $\text{NaCl} > \text{KCl} > \text{RbCl} > \text{CaCl} > \text{LiCl}$  (size of cation increases, lattice energy decreases)  
Note :  $\text{LiCl}$  is a covalent compound due to small size of lithium.
- (h)  $\text{MgF}_2 > \text{CaF}_2 > \text{SrF}_2 > \text{BaF}_2 > \text{BeF}_2$  (Size of cation increases, lattice energy decreases)  
Note :  $\text{BeF}_2$  is a covalent compound
- (i)  $\text{SnCl}_2 > \text{SnCl}_4$  (charge increases, polarisation increases)
- (j)  $\text{CaCl}_2 > \text{FeCl}_2 > \text{FeCl}_3$  (charge increases, polarisation increases)
- (k) Metal fluoride < Metal oxide (Charge increases, lattice energy increases)

### Melting point and Boiling point of non metallic molecules

- (a)  $\text{CH}_3 - \text{O} - \text{CH}_3$  <  $\text{C}_2\text{H}_5\text{OH}$  (Boiling point)  
(VWF) (H-bonding)
- (b)  $(\text{CH}_3)_2\text{SO}_4$  <  $\text{H}_2\text{SO}_4$  (Boiling point)  
(VWF) (H-Bonding)
- (c)  $\text{H}_2$  <  $\text{CO}_2$  <  $\text{H}_2\text{O}$   
(VWF) (H-bonding)  
(Molecular mass increases, VWF increases)
- (d)  $\text{CH}_3\text{OH}$  <  $\text{H}_2\text{O}$   
(H-Bonding) (H-Bonding)

### Concept Ladder



Hardness = Diamond >  $\text{B}_4\text{C}$  (Artificial) >  $\text{SiC}$  >  $\text{Al}_2\text{O}_3$  carborundum

### Rack your Brain



Why  $\text{SbH}_3$  has more boiling point compare to  $\text{NH}_3$ ?

### Previous Year's Question



Electrovalent compounds do not have

[AIPMT]

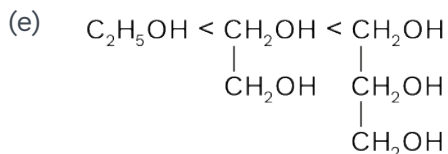
- (1) High M.P. and Low B.P.
- (2) High dielectric constant
- (3) High M.P. and High B.P.
- (4) High polarity



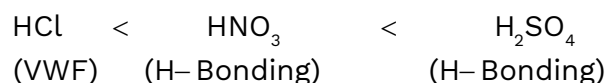


(Surface tension)

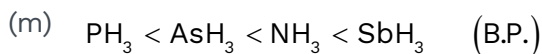
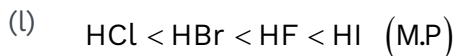
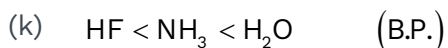
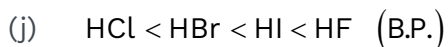
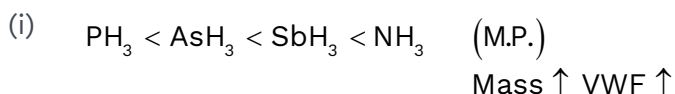
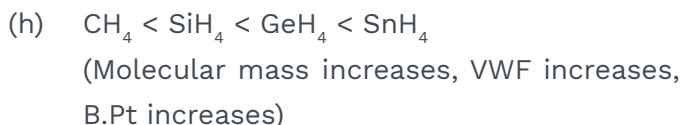
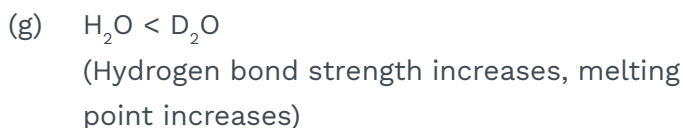
Note:- Extent of hydrogen bonding increases, boiling point increases.



(f)

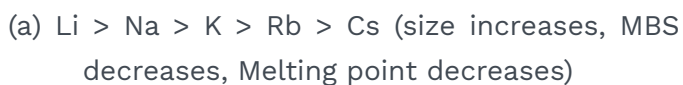


(Melting point)



### Melting point of Metals

Melting point of metals Metallic bond strength (MBS)



### Rack your Brain



Why HF has more boiling point compare to HI?

### Concept Ladder



Giant Molecules = Diamond, Silica ( $\text{SiO}_2$ )<sub>x</sub>, Borazone ( $\text{BN}$ )<sub>x</sub>, Carborundum ( $\text{SiC}$ ), Norbide ( $\text{B}_4\text{C}$ )

### Rack your Brain



Why HI has more melting point compare to HF?



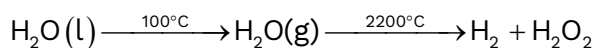


- (b) 3d series < 4d series < 5d series (melting point and boiling point increases,  $Z_{\text{eff}}$  increases)
- (c)  $\text{Zn} > \text{Cd} > \text{Hg}$  (Melting point and boiling Point decreases, interelectronic repulsion increases)
- (d)  $\text{Be} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$  (Melting point decreases, size increases, MBS decreases)

Note:

- Maximum melting point in Boron family  $\longrightarrow \text{B}$
- Minimum melting point in Boron family  $\longrightarrow \text{Ga}$

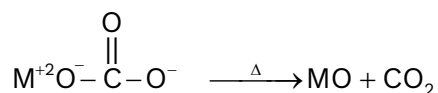
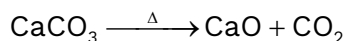
### Thermal Stability



- (1) Thermal stability of halides, hydrides and normal oxides.

$$\text{Thermal stability} \propto \frac{1}{\text{size}}$$

- (2) Thermal stability of compounds having polyatomic anion



$$\text{Thermal stability} \propto \frac{1}{\text{Polarising power}} \propto \frac{\text{Size of cation}}{\text{charge of cation}}$$

- $\text{LiHCO}_3$  and IIA bicarbonates don't exist in solid state due to high polarising power of cation.

### Concept Ladder



Maximum Melting point in all elements  $\longrightarrow \text{C}$  (Diamond). Minimum Melting point in elements  $\longrightarrow \text{He}$ .

### Rack your Brain



Why  $\text{BeCO}_3$  is kept in  $\text{CO}_2$  atmosphere due to thermal stability?

### Concept Ladder

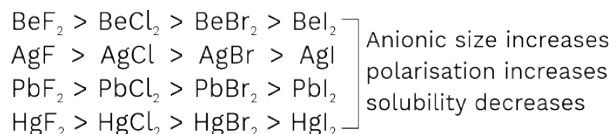


Maximum Melting point in metals  $\longrightarrow \text{W}$  (Tungsten). Minimum Melting point in metals  $\longrightarrow \text{Hg}$





### Thermal stability order



### Covalency

The combining capacity of any element is known as **Valency**.

The main points of the theory are :

- (i) Valency of an atom depends mainly on the number of electrons present in the valence shell. These electrons are named as valency electrons.
- (ii) Noble gases have 8 electrons in the outermost orbit (except He). These gases are chemically inert.
- (iii) Atoms having less than eight electrons in the outermost orbit are chemically active. It is the tendency of these atoms to achieve 8 electrons in the outermost orbit. (Hydrogen, Lithium, Beryllium try to achieve helium configuration.) The number of electrons which take part determines the valency of the atom.
- (iv) There are two ways by which the atoms can acquire noble gas configuration or 8 electrons in the outermost energy level.
  - (a) By losing or accepting electrons.
  - (b) By sharing electrons.

### Concept Ladder



$\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{OH}^-$  of Na, K, Rb, Cs don't decompose (only melt) due to large size of cation.

### Rack your Brain



Why  $\text{XeF}_8$  does not exist?

### Concept Ladder

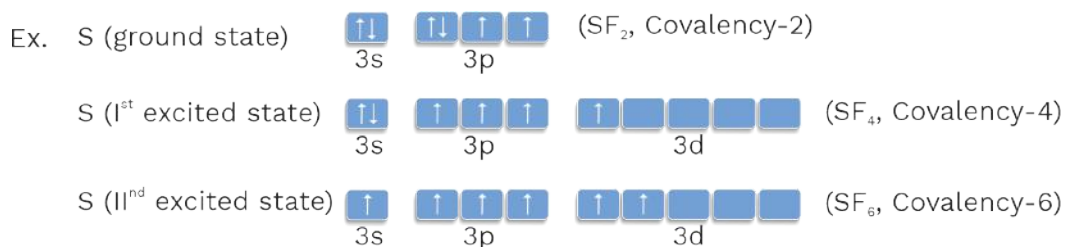


$\text{SF}_3$  does not exist in nature as sulphur has only valency of 2, 4, 6.

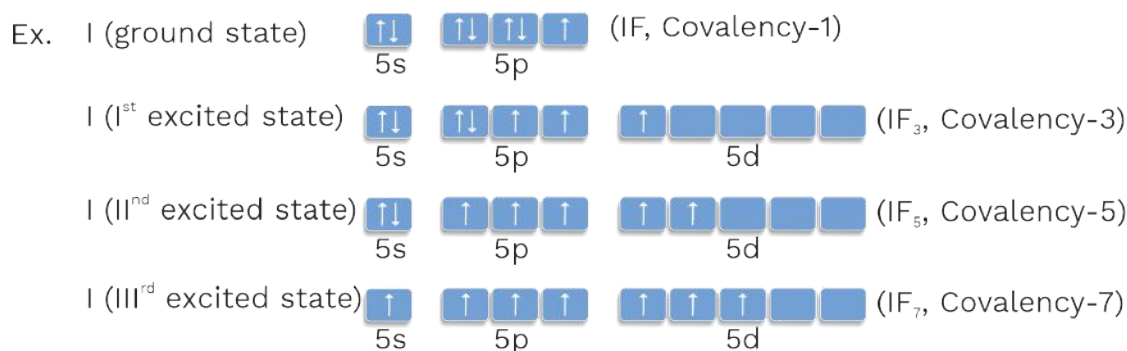




### Sulphur (E.C - $1s^2 2s^2 2p^6 3s^2 3p^4$ )



### Iodine (E.C - $1s^2 2s^2 2p^6 3s^2 3p^4$ )



### Applications of Covalency

- Non existence of compound – Due to absence of 2d orbital the elements of II period can not extend their orbitals or increase their valencies so formation of compound is not possible.
- ClF<sub>3</sub> exists but FCl<sub>3</sub> does not as F belongs to II<sup>nd</sup> period, it has maximum valency of 1 as it can not increase its covalency due to absence of 2d orbital.

#### Concept Ladder



Xe can not form any compound in ground state it can only form compound in its excited state by having covalency of 2, 4, 6 and 8 in its I<sup>st</sup>, II<sup>nd</sup>, III<sup>rd</sup> and IV<sup>th</sup> excited state respectively. (XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub> etc.)





**Q.25**  $\text{PCl}_5$  exists but  $\text{PI}_5$  does not similarly  $\text{SF}_6$  exists but  $\text{SCL}_6$  does not and also  $\text{IF}_7$  exist but  $\text{ICl}_7$  does not

**A.25** It is due to large size of atoms, there will be large steric repulsion due to which formation of compound is not possible.

**Q.26** From the following which compound exists.

- (1)  $\text{NCl}_5$       (2)  $\text{PCl}_5$       (3)  $\text{PI}_5$       (4) All of these

**A.26** (2),  $\text{PCl}_5$  exists

$\text{NCl}_5$  – does not exist as 2d orbital is not present

$\text{PI}_5$  – due to steric repulsion

**Q.27** From the following which compound exists.

- (1)  $\text{SCL}_2$       (2)  $\text{SCL}_4$       (3)  $\text{SCL}_6$       (4) (1) and (2)

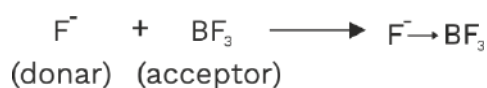
**A.27** (4),  $\text{SCL}_6$  does not exist as size of Cl is large and steric repulsion are there.

- Inert gases are less reactive they can not form compounds. Only Xe and Kr form compounds with elements having high electronegativity (F and O)
- Xe can not form any compound in its ground state as there is no unpaired electron present.

#### Coordinate bond:

- The one that donates electron is called donor atom and other is called acceptor. The bond is also called dative bond.

**Note :** It is a special type of covalent bond in which shared pair of electrons is provided by one atom. In the formation of coordinate bond either a lone pair or a negative charge must be donated



#### Definition

It is formed when shared pair of electrons comes only from one atom. There is no mutual sharing of electrons.

#### Previous Year's Questions



The compound containing coordinate bond is

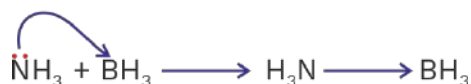
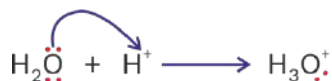
[AIIMS]

- (1)  $\text{SO}_3$       (2)  $\text{O}_3$   
(3)  $\text{H}_2\text{SO}_4$       (4) All of these

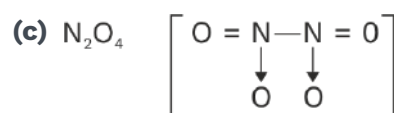
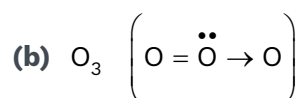




Ex:



Ex. (a)  $\text{N}_2\text{O}$  ( $\text{N} \equiv \text{N} \rightarrow \text{O}$ )



### Formal charge

The Lewis structure of  $\text{O}_3$  may be drawn as :  
The atoms have been numbered as 1, 2 and 3.

The formal charge on :

The central O atom marked (1) =  $6 - 2 - \frac{1}{2}(6) = +1$

The end O atom marked (2) =  $6 - 4 - \frac{1}{2}(4) = 0$

The end O atom marked (3) =  $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent  $\text{O}_3$  along with the formal charges as follows :

### Resonance

For a molecule when a single Lewis structure cannot explain all the properties. The molecule is then supposed to have many structures having similar energy, position of nuclei, bonding and nonbonding pair of electrons. Each structure can explain most of the properties of the molecule, but none can define all the properties of the molecule. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

Resonance structures are represented by a double headed arrow ( $\leftrightarrow$ ).

### Concept Ladder

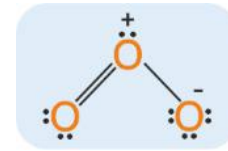
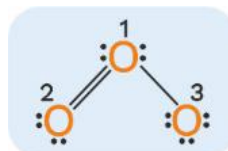


Formal charge =  $V - L - \frac{1}{2}B$

Where, V = Total number of valence electrons in the free atom.

L = Total number of non-bonding (lone pair) electrons.

B = Total number of bonding (shared) electrons.



### Previous Year's Questions



In  $\text{PO}_4^{3-}$  ion, the formal charge on each oxygen atom and P-O bond respectively are

[AIPMT]

(1) -0.75, 1.75

(2) -0.75, 1.0

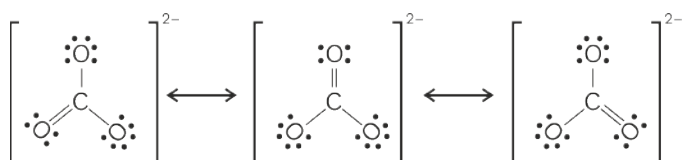
(3) -0.75, 0.6

(4) -3, 1.25

### Definition

When a molecule is represented by two or more hybrid structures and that structure are different in the position of electrons not in atoms is known as Resonance.



**Example****Carbonate ion ( $\text{CO}_3^{2-}$ )**

$$\text{Bond order} = \frac{\left( \begin{array}{c} \text{total number of bond between} \\ \text{two atoms in all the structures} \end{array} \right)}{\text{Total number of resonating structures}}$$

$$\text{Bond order} = \frac{2 + 1 + 1}{3} = 1.33$$

**Valance Shell electron pair repulsion theory (VSEPR)**

Given by Nyholm and Gillespie

- Shape of a molecule depends upon total number of lone pair and bond pair of central atom.
- These electron pair trends to occupy in such a place that their should be minimum repulsion.

**Electron-group Arrangement and Molecular Shape**

The electron-group arrangement is defined by both bonding and nonbonding electron groups. Molecular shape is classified using the designation.



A = central atom

X = surrounding atom

E = nonbonding valence-electron group

p and q are integers

**Concept Ladder****Condition for Resonance**

- (1) Same number of paired and unpaired electrons.
- (2) Same position of atoms.
- (3) Almost equal energy.
- (4) They differ only in the arrangement of electrons in different resonating forms.

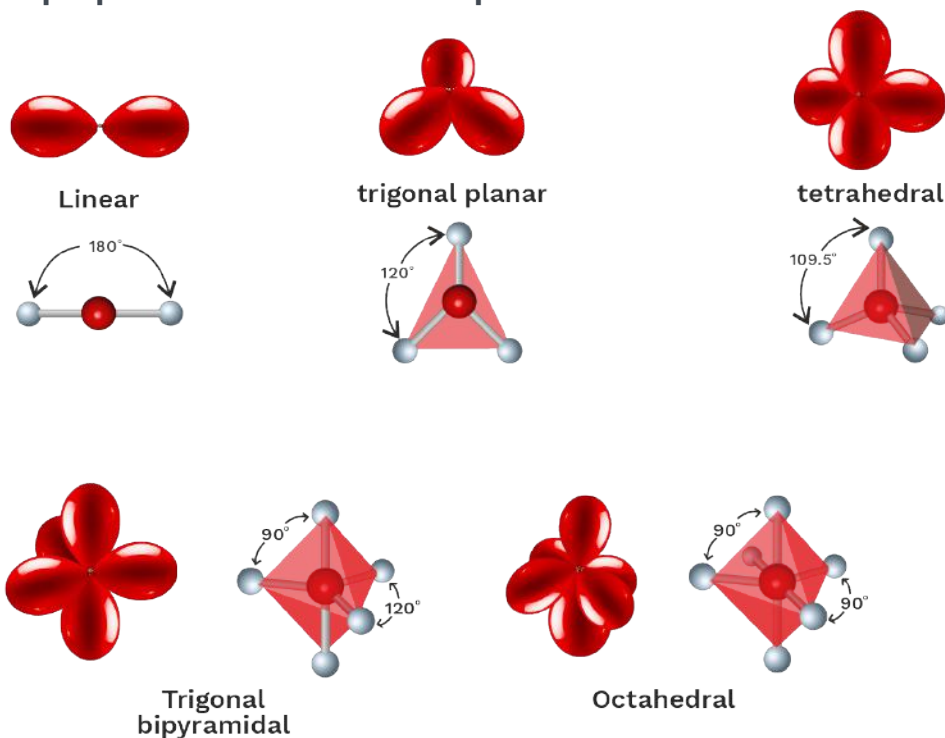
**Concept Ladder****Repulsion Order**

- (a) Lone pair - Lone pair > Lone Pair - Bond Pair > Bond Pair - Bond Pair
- (b) Multiple Bond - Multiple bond > Multiple bond - Single bond > single bond - single bond



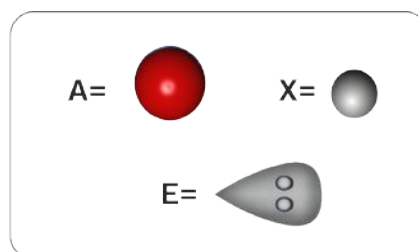
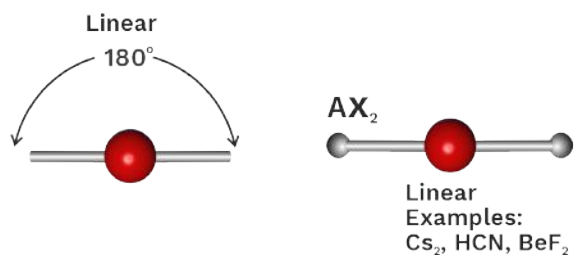


## Electron-group repulsions and molecular shapes



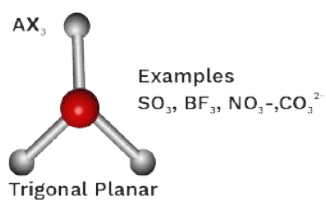
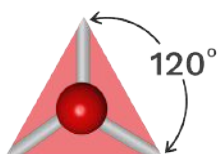
### The single molecular shape of the linear electron-group arrangement.

(1)

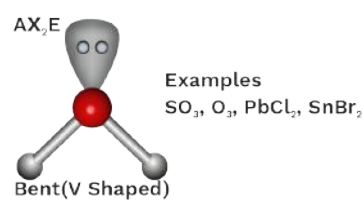


(2)

(A) Trigonal Planar



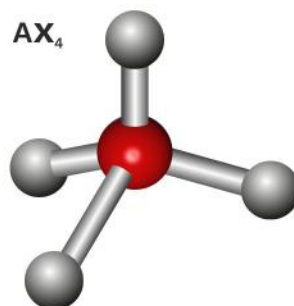
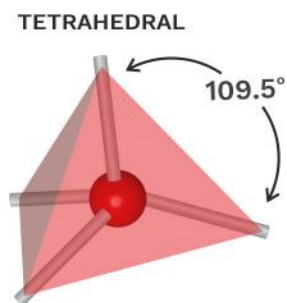
(B)



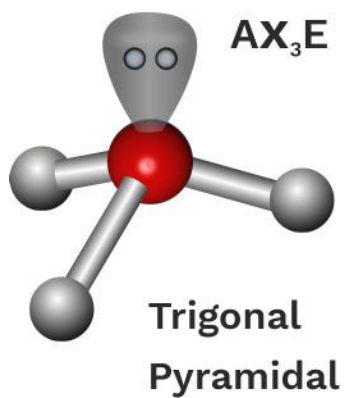




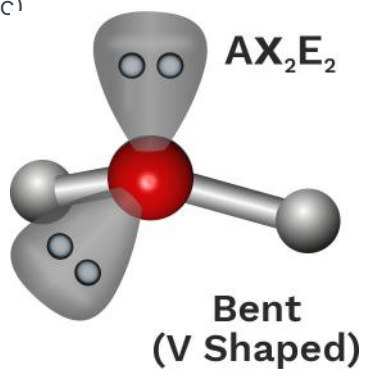
(3) (a)



(b)



(c)



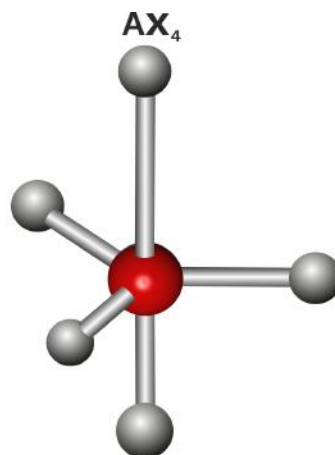
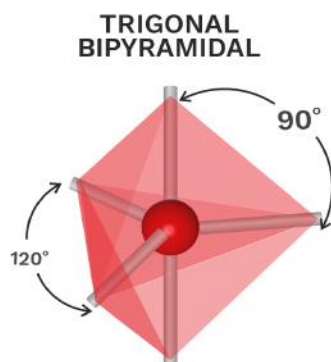
**Ex:** AX<sub>4</sub> : CH<sub>4</sub>, SiCl<sub>4</sub>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>

AX<sub>3</sub>E : NH<sub>3</sub>, PF<sub>3</sub>, ClO<sub>3</sub><sup>-</sup>, H<sub>3</sub>O<sup>+</sup>

AX<sub>2</sub>E<sub>2</sub> : H<sub>2</sub>O, OF<sub>2</sub>, SCl<sub>2</sub>

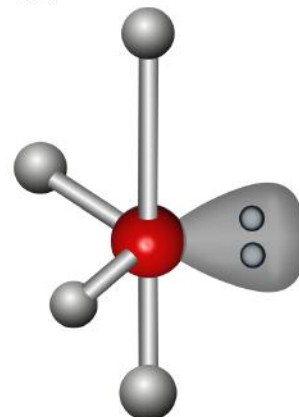
(4)

(A)



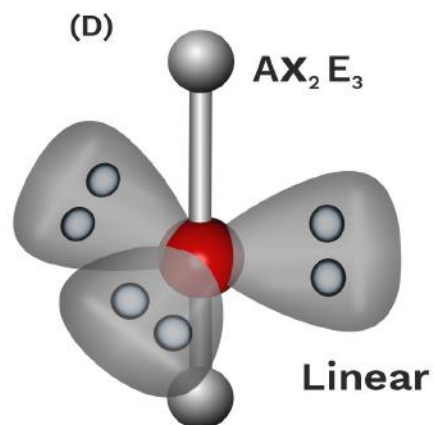
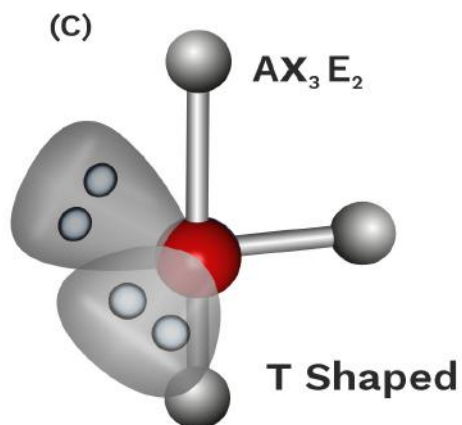
**Trigonal Bipyramidal**

(B)



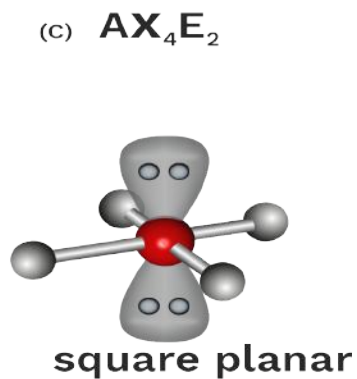
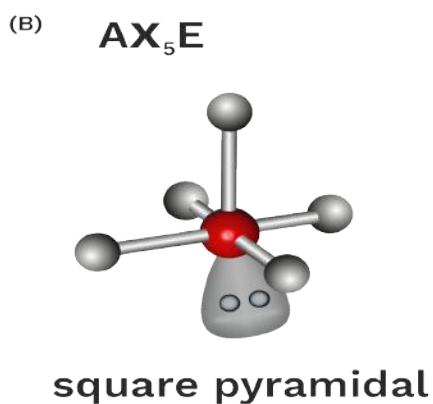
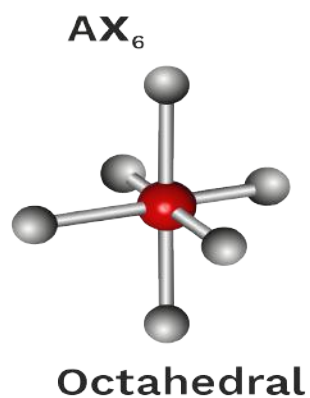
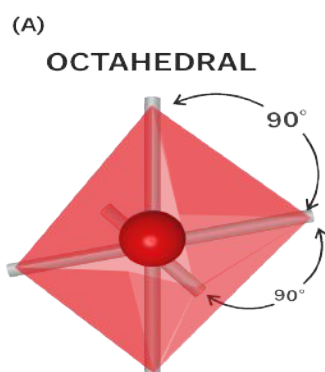
**Seesaw**





**Ex:** (a)  $AX_5$  :  $PF_5$ ,  $AsF_5$ ,  $SOF_4$ , (b)  $AX_4E$  :  $SF_4$ ,  $XeO_2F_2$ ,  $IF_4^+$ ,  $IO_2F_2^-$ , (c)  $AX_3E_2$  :  $ClF_3$ ,  $BrF_3$   
 (d)  $AX_2E_3$  :  $XeF_2$ ,  $I_3^-$ ,  $IF_2^-$ , Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

(5)



**Ex:** (a)  $AX_6$  :  $SF_6$ ,  $IOF_5$  (b)  $AX_5E$  :  $BrF_5$ ,  $TeF_5^-$ ,  $XeOF_4$  (c)  $AX_4E_2$  :  $XeF_4$ ,  $ICl_4^-$





e- Group arrangement (no. of groups)	 Linear(2)		 Trigonal Planar(3)		 Tetrahedral (4)		
Molecular shape (class)	 Linear AX <sub>2</sub>		 Trigonal Planar (AX <sub>3</sub> )	 V shaped or bent (AX <sub>2</sub> E)	 Tetrahedral (AX <sub>4</sub> )	 Trigonal pyramidal (AX <sub>3</sub> E)	 V shaped or bent (AX <sub>2</sub> E <sub>2</sub> )
no. of bonding groups	2		3	2	4	3	2
Bond angle	180°		120°	< 120°	109.5°	< 109.5°	< 109.5°
	Surrounding Atom						

 Trigonal bipyramidal(5)				 Tetrahedral (4)		
 Linear (AX <sub>5</sub> )	 Seesaw (AX <sub>4</sub> E)	 T Shaped (AX <sub>3</sub> E <sub>2</sub> )	 Linear (AX <sub>2</sub> E <sub>3</sub> )	 Octahedral (AX <sub>6</sub> )	 Square pyramidal (AX <sub>5</sub> E)	 Square planar (AX <sub>4</sub> E <sub>2</sub> )
5	4	3	2	6	5	4
90°(ax) 120°(eq)	<90°(ax) <120°(eq)	<90°(ax)	180°	90°	<90°	90°





## Valence bond theory

- Given by Heitler and London.
- Any atom which undergoes covalent bond formation, tries to pay up its unpaired  $e^-$  in ground state or excited state. This pairing of  $e^-$  takes place by combination of 2 atomic orbitals of bonded atoms. This combination is K/A overlapping.

When nature of overlapping is same, but orientation is different, two type of overlapping are possible

- (a) Head to head overlapping – Orbitals approaches to each other along their axis (co-axial overlapping), formation of  $\sigma$  (sigma) bond takes place.

s-s overlapping: s orbital is known directional so it can be combined in any direction.

### Overlapping Inter nuclear Axis type of bond

1.	s-s	Any axis	$\sigma$
2.	s+p <sub>x</sub>	x-axis	$\sigma$
	s+p <sub>y</sub>	y-axis	$\sigma$
	s+p <sub>z</sub>	z-axis	$\sigma$
Any other sp overlapping is not possible			
3.	p <sub>x</sub> +p <sub>x</sub>	x-axis	$\sigma$
	p <sub>y</sub> +p <sub>y</sub>	y-axis	$\sigma$
	p <sub>z</sub> +p <sub>z</sub>	z-axis	$\sigma$
4.	p <sub>x</sub> +p <sub>y</sub>	y or z axis	$\pi$
	p <sub>y</sub> +p <sub>y</sub>	x or z axis	$\pi$
	p <sub>z</sub> +p <sub>z</sub>	x or y axis	$\pi$

## Concept Ladder



If terminal atom are same :  
Eq. bond length > Axial bond length.

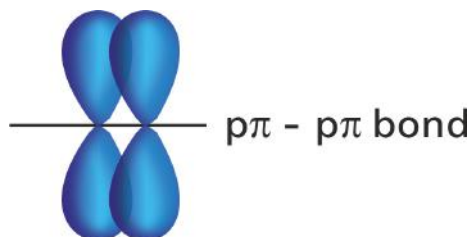
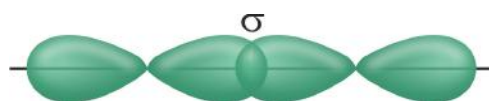
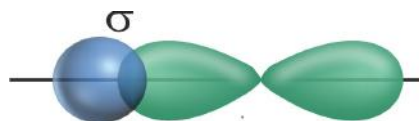
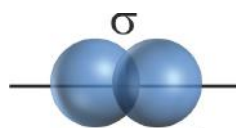
## Previous Year's Questions



Which of the following molecules has more than one lone pair?

[AIIMS-2016]

- (1) SO<sub>2</sub>                      (2) XeF<sub>2</sub>  
(3) SiF<sub>4</sub>                     (4) CH<sub>4</sub>

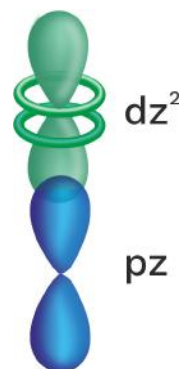






any other pp overlapping is not possible

5.  $p_z + d_{z^2}$  z-axis  $\sigma$



Any other p-d axial overlapping is not possible

6.  $p_x + d_{xy}$  y-axis  $\pi$

$p_y + d_{xy}$  x-axis  $\pi$

7.  $p_x + d_{xz}$  z-axis  $\pi$

$p_z + d_{xz}$  x-axis  $\pi$

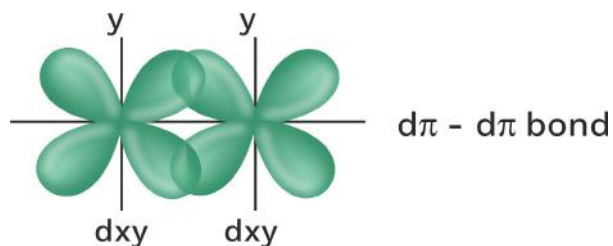
8.  $p_y + d_{yz}$  z-axis  $\pi$

$p_z + d_{yz}$  y-axis  $\pi$

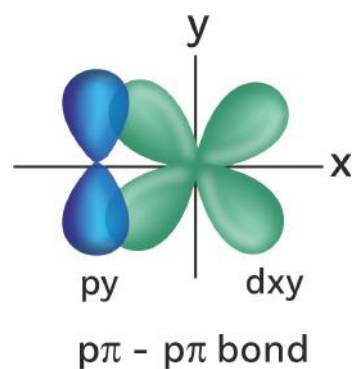
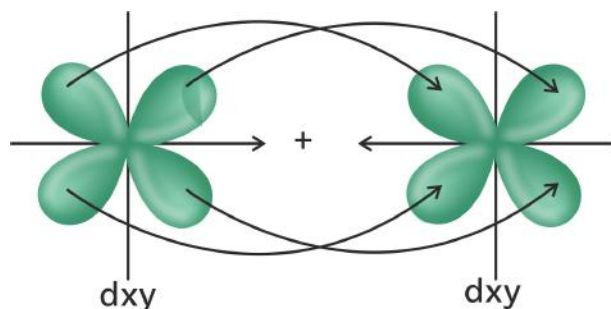
Any other p-d collateral overlapping is not possible

### d-d overlapping

(a)



(b)



### Rack your Brain



Is s orbital directional or non directional?

inter nuclear axis  
z-axis  
 $\delta$ -bond





## Bond Strength and Overlapping

Applicable only when orbitals are given

(a) 
$$\text{Bond Strength} \propto \frac{1}{\text{shall no. of orbitals}}$$

Ex.  $1s-2p > 1s-3p > 1s-4p$  (size increases, B.L increase)

(b) If shall no of orbitals is same then

$\text{B.S} \propto \text{Extent of overlapping} \propto \text{directional properties}$

Ex.  $2p-2p > 2s-2p > 2s-2s$  (B.S) (Directional properties decreases)

(c)  $\pi$  bond strength order

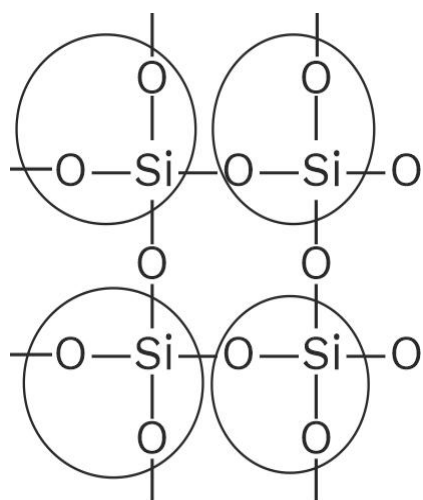
$2p\pi-2p\pi > 2p\pi-3d\pi > 2p\pi-3p\pi > 3p\pi-3p\pi$   
(B.S) (Intermolecular distances increases)

1.  $\text{N} \equiv \text{N}$  exists but  $\text{P} \equiv \text{P}$  doesn't exist.

2.  $\text{O} = \text{C} = \text{O}$  Stable molecule but  $\text{O} = \text{Si} = \text{O}$  doesn't exist

Giant molecule (covalent solid)

Ex:  $(\text{SiO}_2)_n$  polymer



### Concept Ladder



**VBT** assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom.

### Rack your Brain



Is a single or double bond stronger?

### Concept Ladder



Tendency of polymerisation increases with decreasing  $\pi$  bond strength.

### Rack your Brain



$\text{O}_2$  exists but  $\text{S}_2$  does not exist at room temperature. Why?





Sigma bond	Pie bond
i. Formed by coaxial over lapping	i. Formed by collateral overlapping
ii. Formed by hybrid orbital	ii. Formed by unhybridized orbitals
iii. Strong bond	iii. Weak bond
iv. Independent existence	iv. Exist only after the formation of sigma bond
v. Directional in nature	v. Non directional nature
vi. Sigma bond does not participate in resonance	vi. Pie bond take part in resonance
vii. Electron cloud is continuous	vii. Electron cloud is discontinuous and split into two parts i.e. above and below the plane.
viii. Free rotation possible in sigma bond	viii. Restricted rotation

### Hybridisation

- A hypothetical concept given by Pauling.
- Endothermic process.
- Orbital having almost same energy but have diff. shape can participate in hybridisation.
- Hybrid orbitals always form  $\sigma$  bond except benzyne.
- Size or energy or directional property of hybrid orbitals  $\propto \frac{1}{s\text{-character}}$

$sp < sp^2 < sp^3$  size/energy/directional properties (s-character decreases, p-character increases)

### Definition

It is a mixing of atomic orbitals of an atom to form new orbitals which have almost same energy and same shape.

### Concept Ladder





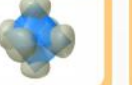


Half filled, full filled or vacant orbitals can participate in hybridisation because it is a mixing of orbitals not electrons.





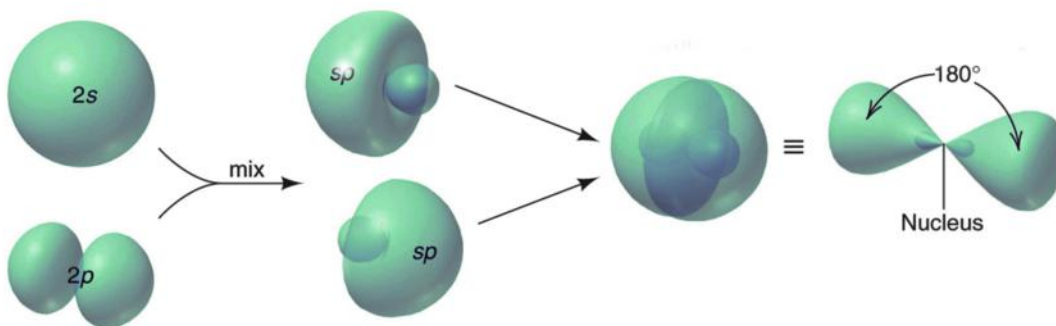


## Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two p	three $sp^2$	four $sp^3$	five $sp^2d$	six $sp^2d^2$
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

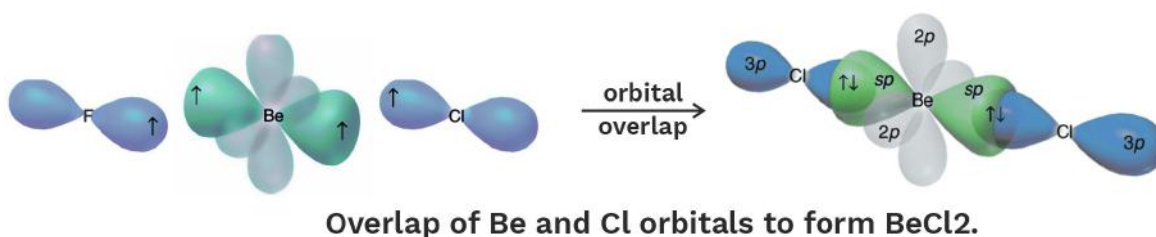
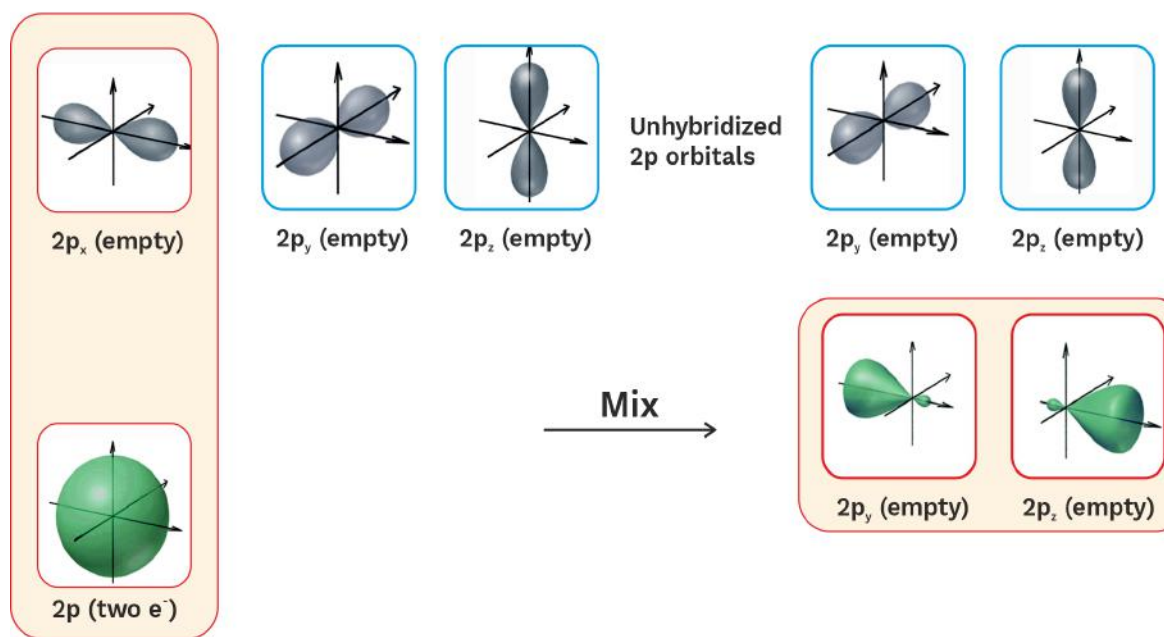
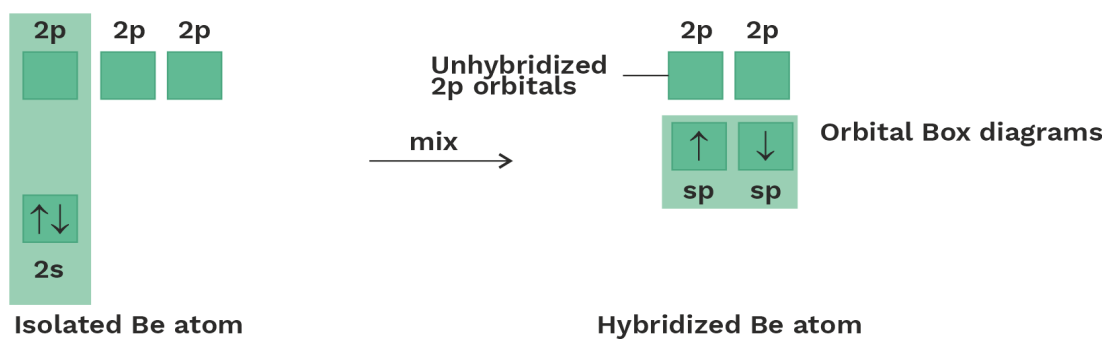
### (1) $sp$ Hybridisation

Ex:  $\text{BeF}_2$



One 2s and one 2p atomic orbital mix to form two hybrid orbitals



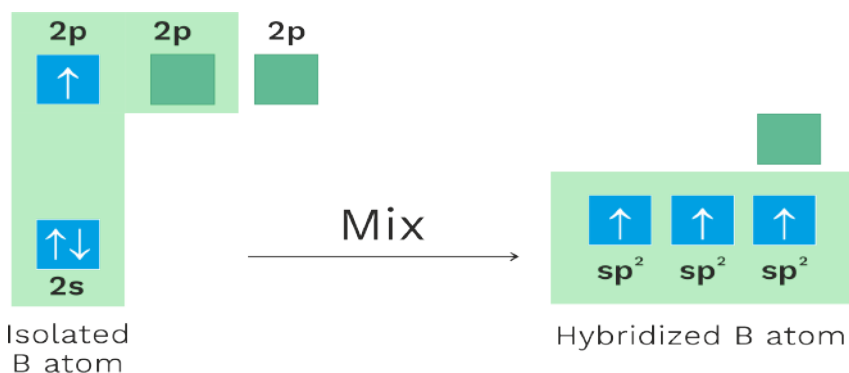






## (2) $sp^2$ Hybridisation

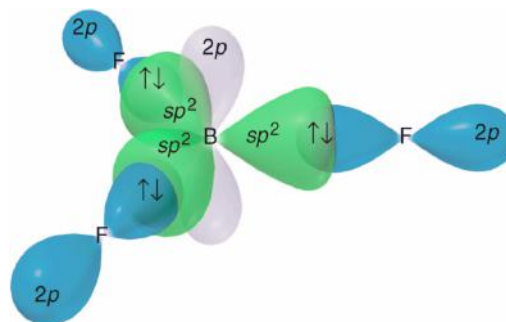
Ex:  $BF_3$



By mixing one s and two p-orbitals gives three  $sp^2$  hybrid orbitals. The third 2p orbital remains unhybridized.

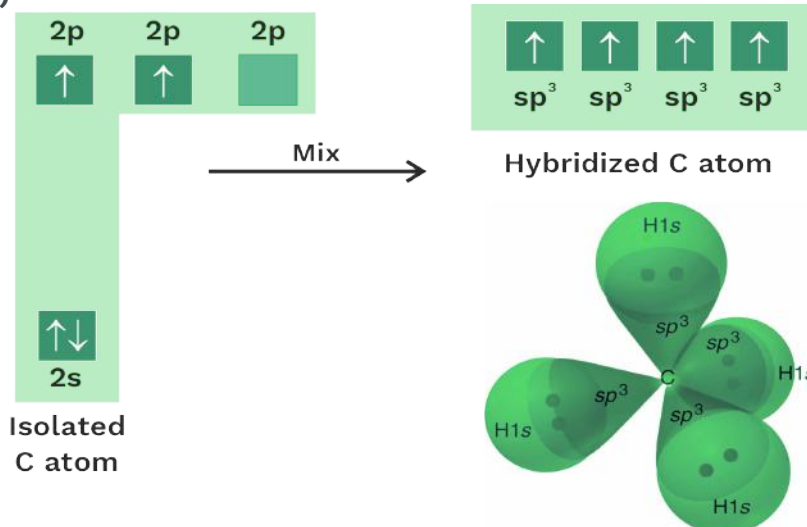
The three  $sp^2$  orbitals to be pointed at the corners of an equilateral triangle, their axes are  $120^\circ$  apart.

Each half-filled  $sp^2$  orbital overlaps with the half-filled 2p orbital of a fluorine atom.



## (3) $sp^3$ Hybridisation

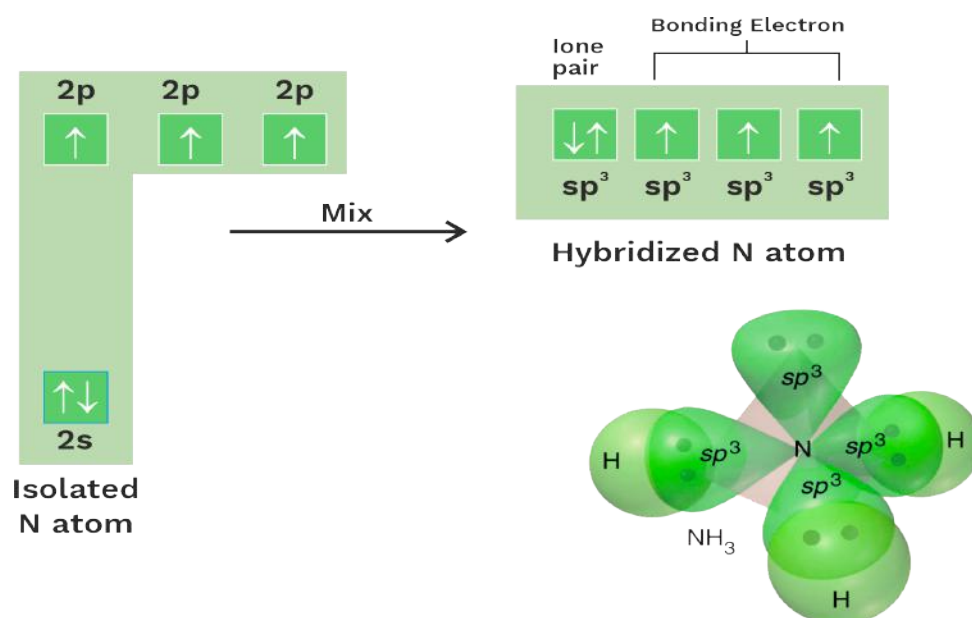
Ex:  $CH_4$  (Methane)



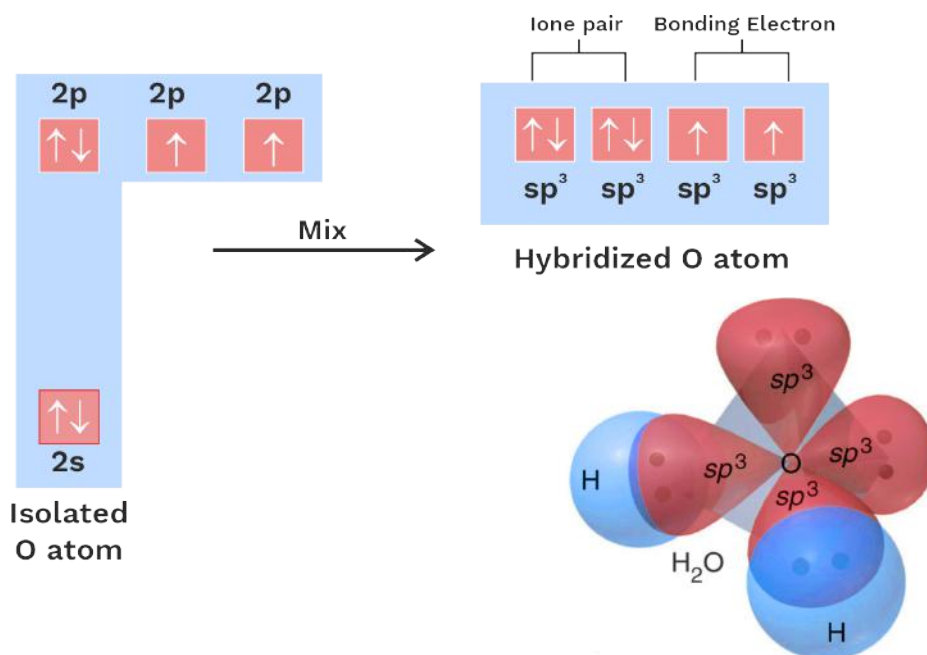




$\text{NH}_3$



$\text{H}_2\text{O}$

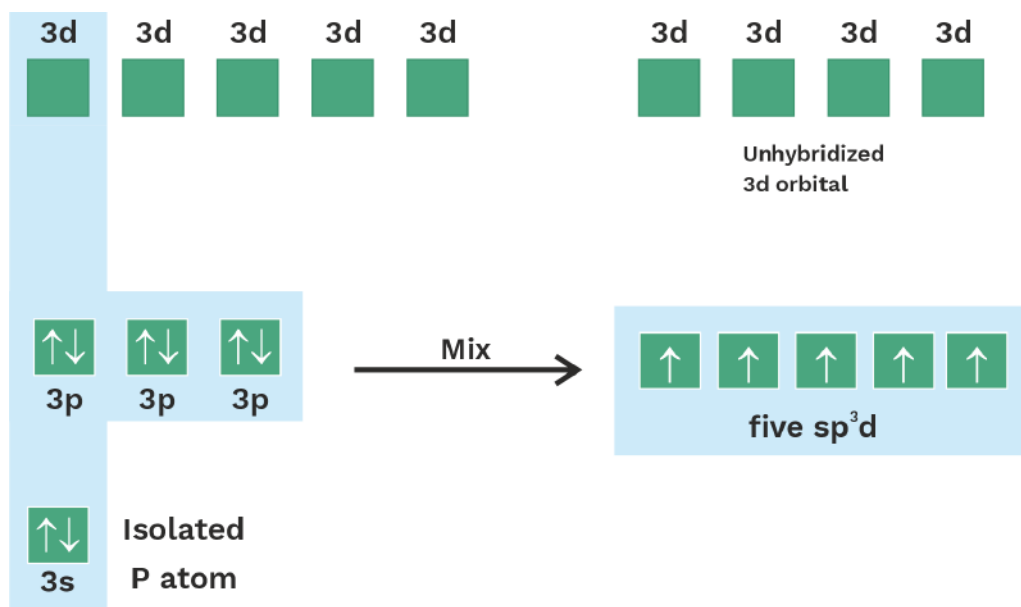




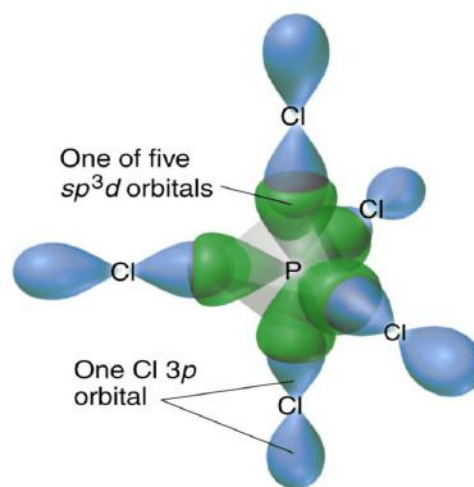
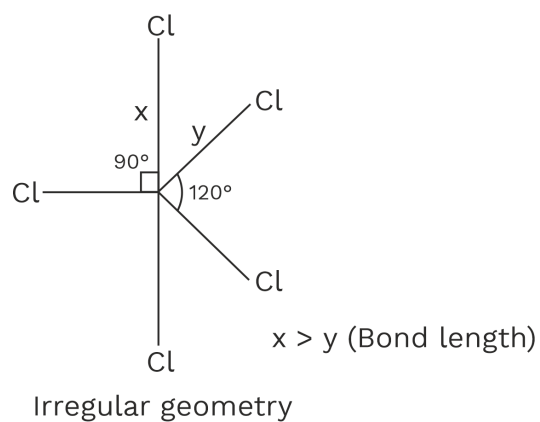


#### (4) $sp^3d$ Hybridisation

Ex:  $PCl_5$



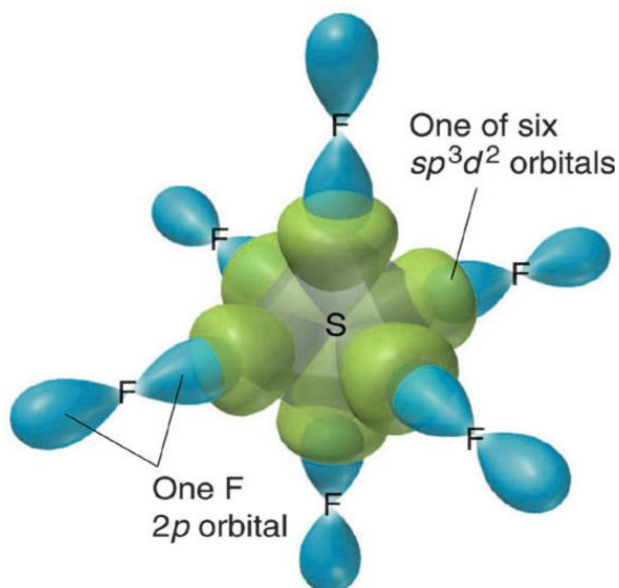
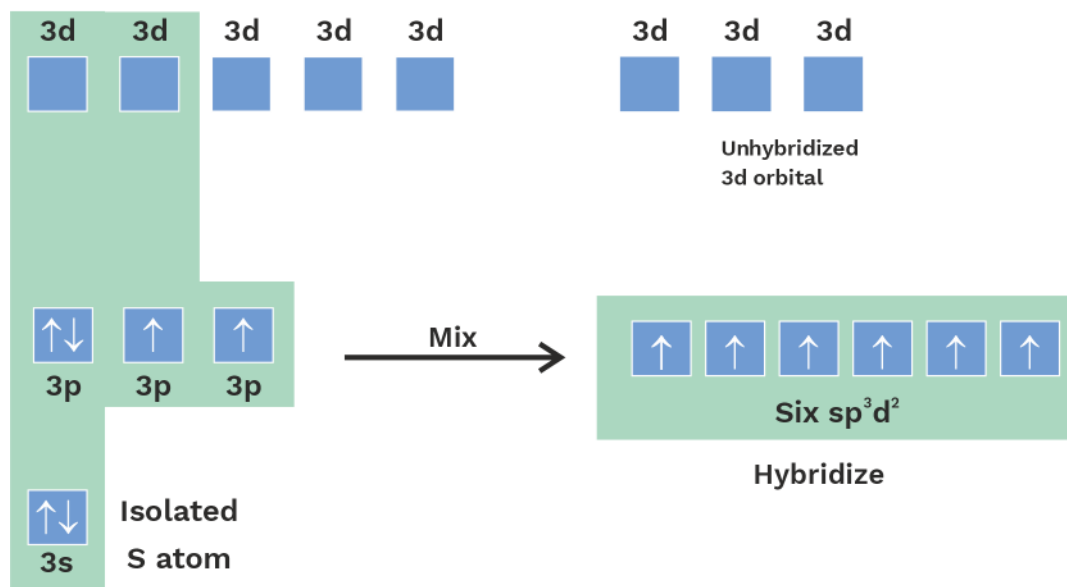
The formation of more than 4 bonding orbitals requires d-orbital involvement in hybridization.





## (5) $sp^3d^2$ Hybridisation

Ex:



### Concept Ladder



#### Position of LP & Multiple Bond

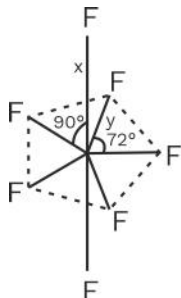
- (a)  $sp$ ,  $sp^2$ ,  $sp^3$  hybridisation = anywhere
- (b)  $sp^3d$  = always at equatorial position
- (c)  $sp^3d^2$  = always at axial position



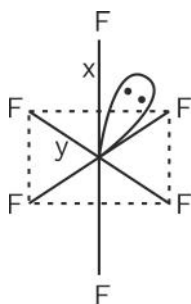


### SOME IMPORTANT EXAMPLES

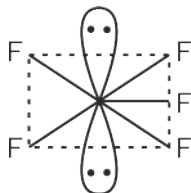
- (1)  $\text{PCl}_3\text{F}_2$   
 $\sigma = 7$ ,  $\text{lp} = 0$   
 $\text{sp}^3\text{d}^3$ , PBP  
 Non planar  
 $x < y$   
 no  $\pi$  bond.



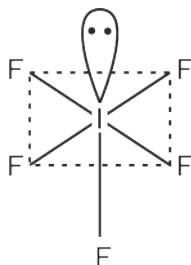
- (2)  $\text{XeF}_6$   
 $\sigma = 6$ ,  $\text{lp} = 1$   
 $\text{sp}^3\text{d}^3$ , PBP  
 Distorted octahedral  
 Non planar  
 $x < y$   
 no  $\pi$  bond.



- (3)  $\text{XeF}_5^-$   
 $\sigma = 5$ ,  $\text{lp} = 2$   
 $\text{sp}^3\text{d}^3$ , PBP  
 Pentagonal planar  
 no  $\pi$  bond  
 All BL are identical.



- (4)  $\text{IF}_5$   
 $\sigma = 5$ ,  $\text{lp} = 1$   
 $\text{sp}^3\text{d}^2$ , SBP  
 Square pyramidal  
 Non planar  
 no  $\pi$  bond  
 Not identical



- (5)  $\text{XeF}_4$   
 $\sigma = 4$ ,  $\text{lp} = 2$   
 $\text{sp}^3\text{d}^2$ , SBP

### Concept Ladder



#### Bent Rule

More EN atom occupies that position of hybrid orbitals which has less s-character.  
 Less EN atom & lp occupies that position of hybrid orbitals which has more s-character.

### Rack your Brain



What is the shape  $\text{XeF}_2$ ?

### Previous Year's Questions



Which of the following molecules can central atom said to adopt  $\text{sp}^2$  hybridisation

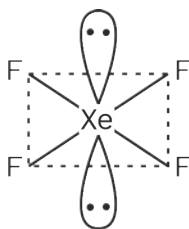
[AIPMT]

- (1)  $\text{BeF}_2$  (2)  $\text{BCl}_3$   
 (3)  $\text{C}_2\text{H}_2$  (4)  $\text{NH}_3$

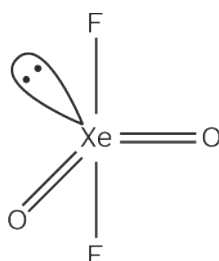




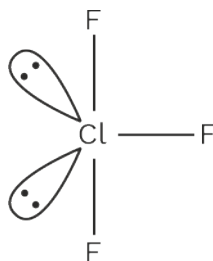
square planar  
no  $\pi$  bond  
Identical.



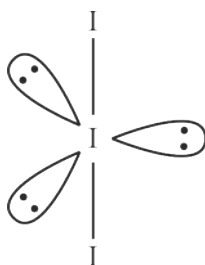
- (6)  $\text{XeO}_2\text{F}_2$   
 $\sigma = 4$ ,  $\text{lp} = 1$   
 $\text{sp}^3\text{d}$ , TBP  
 Distorted octahedral  
 non planar  
 $x < y$   
 no  $\pi$  bond



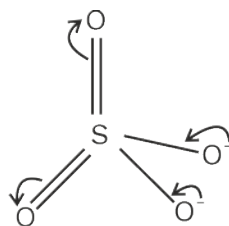
- (7)  $\text{ClF}_3$   
 $\sigma = 3$ ,  $\text{lp} = 2$   
 $\text{sp}^3\text{d}$ , TBP  
 T-shape  
 planar  
 no  $\pi$  bond



- (8)  $\text{I}_3^-$   
 $\sigma = 2$ ,  $\text{lp} = 3$   
 $\text{sp}^3\text{d}$ , TBP  
 Linear  
 Planar  
 no  $\pi$  bond  
 Identical



- (9)  $\text{SO}_4^{2-}$   
 $\sigma = 4$ ,  $\text{lp} = 0$   
 $\text{sp}^3$ , Tetrahedral



$$\text{B.O.} = \frac{6}{4} = 1.5$$

### Previous Year's Questions



Which of the following hybridisation results in non-planar orbitals

[AIPMT]

- (1)  $\text{sp}^3$  (2)  $\text{dsp}^2$   
 (3)  $\text{sp}^2$  (4)  $\text{sp}$

### Concept Ladder



v-shape, T-shape, linear, Trigonal planar, square planar & pentagonal planar are planar shape. Rest are non planar.

### Previous Year's Questions



Which of the following molecules has trigonal planar geometry

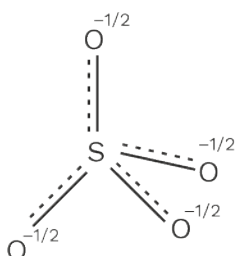
[AIPMT]

- (1)  $\text{IF}_3$  (2)  $\text{PCl}_3$   
 (3)  $\text{NH}_3$  (4)  $\text{BF}_3$

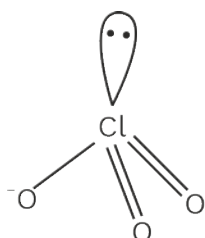




Tetrahedral  
Non planar  
 $p\pi - p\pi$   
Identical

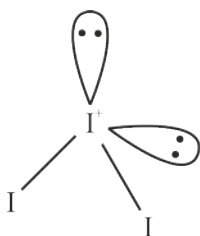


- (10)  $\text{ClO}_3^-$   
 $\sigma = 3$ ,  $\text{lp} = 1$   
 $\text{sp}^3$ , Tetrahedral  
 Pyramidal  
 Non planar  
 $p\pi - p\pi$   
 Identical

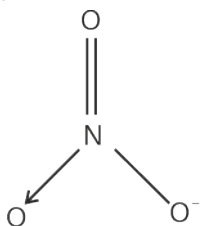


$$\text{F.C.} = -\frac{1}{3} \quad \text{B.O.} = \frac{5}{3}$$

- (11)  $\text{I}_3^+$   
 $\sigma = 2$ ,  $\text{lp} = 2$   
 $\text{sp}^3$ , Tetrahedral  
 v shape  
 Planar  
 no  $\pi$  bond  
 Identical



- (12)  $\text{NO}_3^-$   
 $\sigma = 3$ ,  $\text{lp} = 0$   
 $\text{sp}^2$ , Trigonal planar  
 Trigonal planar  
 Planar  
 $p\pi - p\pi$   
 Identical



$$\text{F.C.} = \frac{-2}{3} \quad \text{B.O.} = \frac{4}{3} = 1.33$$

### Previous Year's Questions



In which of the following molecules are all the bond not equal

[AIPMT]

- (1)  $\text{AlF}_3$  (2)  $\text{NF}_3$   
 (3)  $\text{ClF}_3$  (4)  $\text{BF}_3$

### Concept Ladder



Orbitals having non bonded unpaired electron and d-orbitals are present at higher energy level. They participate in hybridisation only when terminal atoms have high EN. ( $\text{EN} > 2.5$ )

### Previous Year's Questions



Which of the two ions from the list given below that have the geometry that is explained by the same hybridisation of orbitals,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{SCN}^-$ .

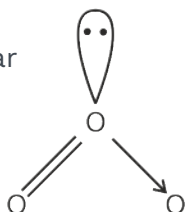
[AIPMT]

- (1)  $\text{NO}_2^-$  and  $\text{NH}_2^-$   
 (2)  $\text{NO}_2^-$  and  $\text{NO}_3^-$   
 (3)  $\text{NH}_4^+$  and  $\text{NO}_3^-$   
 (4)  $\text{SCN}^-$  and  $\text{NH}_2^-$



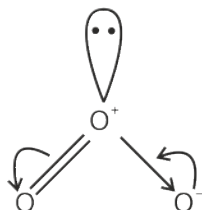
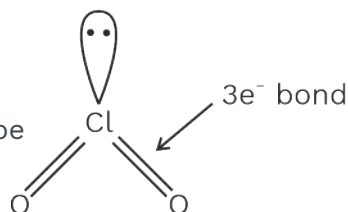
(13)  $O_3$  $\sigma = 2, \quad lp = 1$  $sp^2, \quad \text{Trigonal planar}$  $v\text{-shape,} \quad \text{planar}$  $p\pi - p\pi$ 

Identical

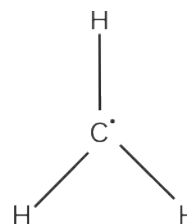


$$F.C. = \frac{-1}{2}, \frac{-1}{2}, +1$$

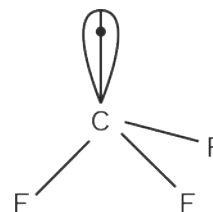
$$B.O. = \frac{3}{2} = 1.5$$

(14)  $ClO_2$  $\sigma = 2, \quad lp = 1$  $sp^2, \quad v\text{-shape}$ **Hybridisation state of odd  $e^-$  species**(1)  $\dot{C}H_3$  $\sigma = 3$  $lp = 0.5$ Steric number =  $3.5 \approx 3$ 

(because of terminal atom is less electronegative)

so we consider l.p. is  $\approx 0$ )(2)  $\dot{C}F_3$  $\sigma = 3$  $lp = 0.5$ Steric number =  $3.5 \approx 4$ 

(because of terminal atom is more electronegative)

so we consider l.p. is  $\approx 1$ )**Concept Ladder**

d-orbital can't participate in hybridisation due to less EN of terminal atom.

Do not exists

$PH_5, SH_4, XeH_2 = sp_3d$

$SH_6, XeH_4 = sp^3d^2$

$XeH_6, IH_7 = sp^3d^3$

**Rack your Brain**

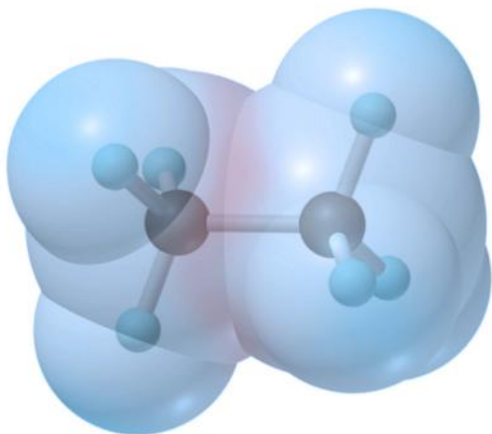
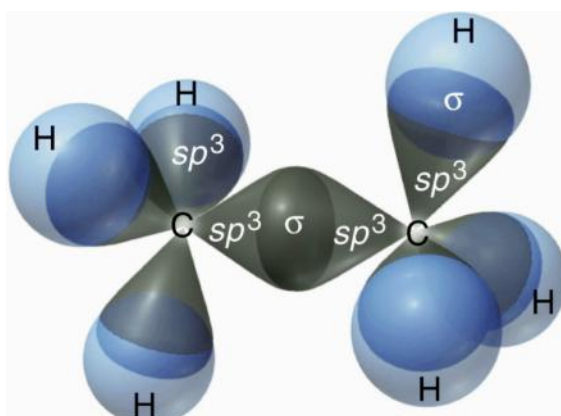
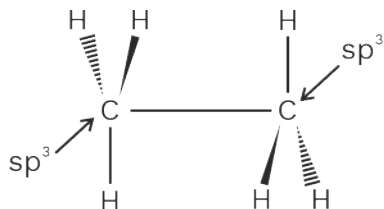
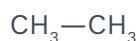
What is the hybridisation of  $\dot{N}O_2$  and  $\dot{C}lO_3$ ?





## Hybridisation of Alkane, Alkene and Alkyne

### (1) Ethane ( $\text{C}_2\text{H}_6$ )



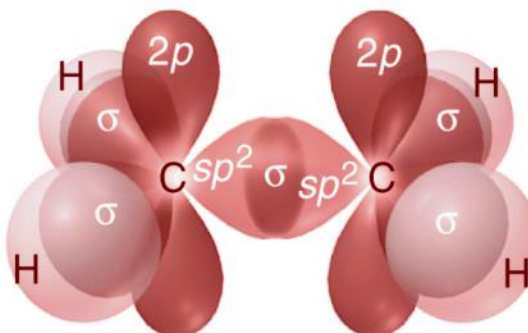
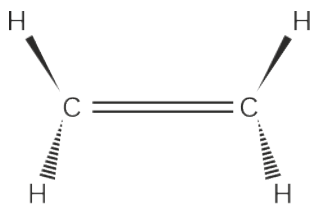
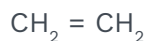
For all sigma bonds there is relatively even distribution of electron density.

### Concept Ladder

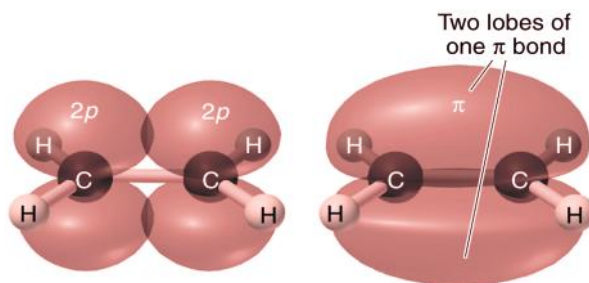
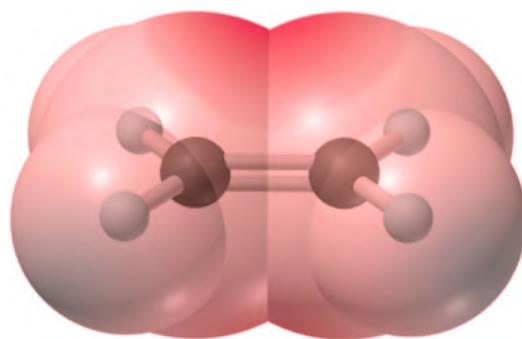


s character is the contribution of sigma type bond in a hybridization  $sp^3 = 25\%$  s character,  $75\% = p$ -character  $sp^2 = 33\%$  s-character,  $66\%$  p-character  $sp = 50\%$  s-character,  $50\%$  p-character. The more s-character a bond has, the stronger and shorter the bond is.

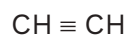
### (2) Ethene ( $\text{C}_2\text{H}_4$ )







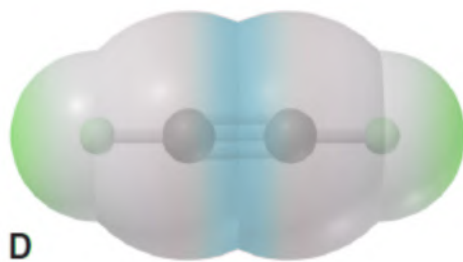
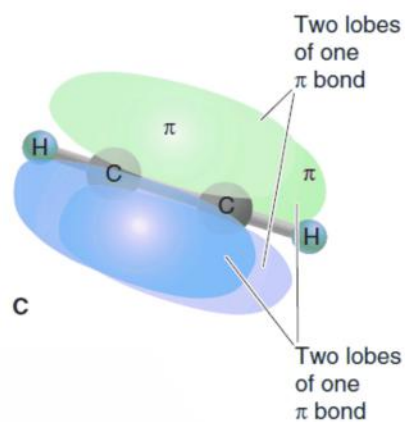
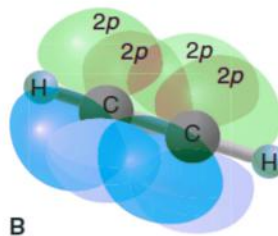
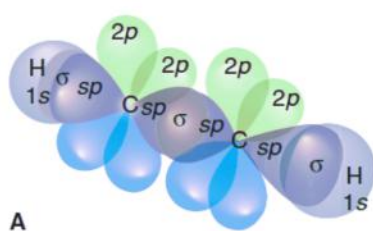
**(3) Ethyne (C<sub>2</sub>H<sub>2</sub>)**



**Rack your Brain**



Which has stronger bond compare to alkane, alkene or alkyne?



**Concept Ladder**



Bond length of		
alkane	alkene	alkyne
1.54Å	1.34Å	1.21Å





A single bond is more than twice as weak as a double bond, because a  $\pi$  bond is weaker than a  $\sigma$  bond.

### Bond Parameter

**Bond Length, Bond Strength, Bond Angle, Bond Energy, Bond Dissociation Energy, Atomic Size and s-character**

$$\text{B.S. or B.E. or BDE} \propto \frac{1}{\text{B.L.}} \propto \frac{1}{\text{Size}} \propto s\text{-character} \propto \text{B.O.}$$

BE or BDE (Not BL) of 2nd periodic single bonded atoms also depend upon lp-lp repulsion.

**Ex:** (1)  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$  BE/BDE

lp-lp repulsion

(2)  $\begin{array}{c} \text{N} & \text{N} \\ | & | \\ \text{N} & \text{N} \end{array} < \begin{array}{c} \text{P} & \text{P} \\ | & | \\ \text{P} & \text{P} \end{array}$  BE/BDE

lp-lp repulsion

Catenation  $\propto$  B.E.

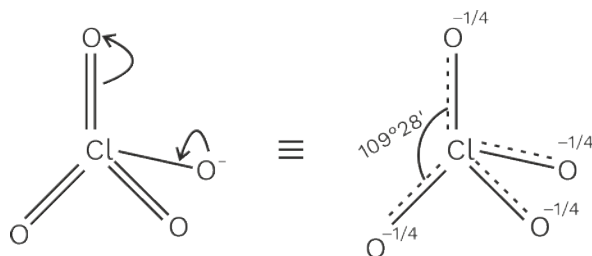
**Ex:**  $\text{C} - \text{C} > \text{Si} - \text{Si} \geq \text{Ge} - \text{Ge} > \text{Sn} - \text{Sn}$

Size  $\uparrow$

B.C.  $\downarrow$

Catenation  $\rightarrow$

**Ex:** (1)  $\text{ClO}_4^-$



$$\text{B.O.} = \frac{7}{4} = 1.75$$

### Previous Year's Questions



Which of the following molecule has highest bond energy?

[AIIMS]

- (1)  $\text{F}-\text{F}$  (2)  $\text{N}-\text{N}$   
(3)  $\text{C}-\text{C}$  (4)  $\text{O}-\text{O}$

### Concept Ladder



If species have equal stable resonating structure than B.L., B.S., B.D., B.A. and F.C. depends upon resonance hybrid.

### Previous Year's Questions

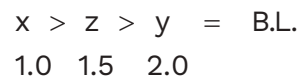


Which of the following compounds possess the  $\text{C}-\text{H}$  bond with the lowest bond dissociation energy?

[AIIMS]

- (1) Toluene  
(2) Benzene  
(3) n-Pentane  
(4) 2,2-Dimethylpropane



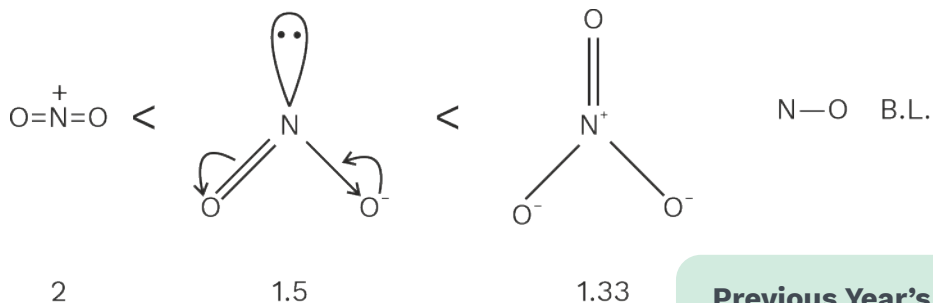


Why C—O bond length in carboxylate ion is equal?

**Q.** Compare given properties —

(1)  $\text{H}_2\text{O}_2 > \text{O}_3 > \text{O}_2$        $\text{O}-\text{O}$  B.L.  
           1        1.5    2.0      B.O. ↑

(2)



(3)

$$\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^- \quad \text{F.C. on oxygen}$$

$$\frac{-3}{4} \quad \frac{-2}{4} \quad \frac{-1}{4}$$

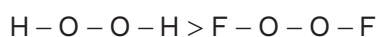

**A :** Bond energy and bond dissociation energy have identical value for diatomic molecules.

**R :** Greater the bond dissociation energy, less reactive is the bond.



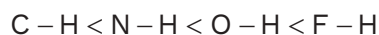


(4)



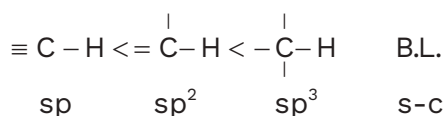
O-O (B.L.)  
size ↓ B.L. ↓

(5)



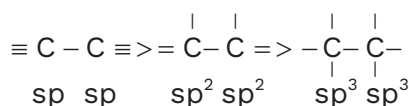
B.S. or B.E.  
size ↓ B.L. ↓

(6)



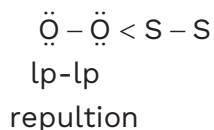
B.L.  
s-character ↓

(7)



B.S.  
s-character ↓

(8)

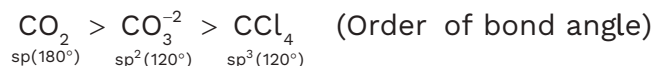


Catenation

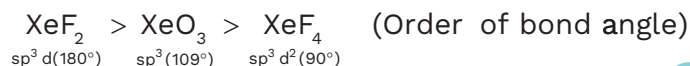
**Bond Angle**

(1) Hybridisation state

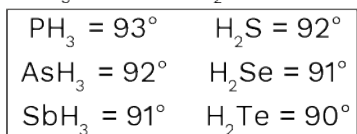
(a)



(b)

**Drago's Rule :-**

This rule is applicable only when Central atom has lone pair.



Bond angle  $\approx 90^\circ$   
No hybridization

**Previous Year's Questions**

Which of the following is correct regarding bond angles?

- (i)  $\text{SO}_2 < \text{H}_2\text{O}$  (ii)  $\text{H}_2\text{S} < \text{SO}_2$   
(iii)  $\text{SO}_2 < \text{H}_2\text{S}$  (iv)  $\text{SbH}_3 < \text{NO}_2^+$

**[AIIMS]**

- (1) ii and iv (2) i, ii and iv  
(3) i and iii (4) None of these

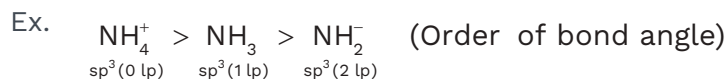
**Concept Ladder****Drago's Rule**

Elements of 3rd period and below 3rd period don't show hybridisation when they are bonded with less EN atom like hydrogen.

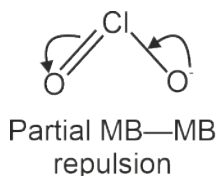
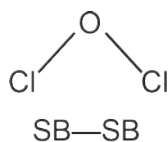
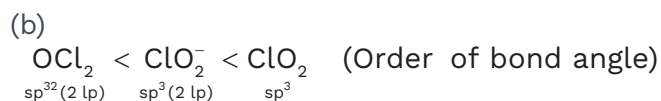
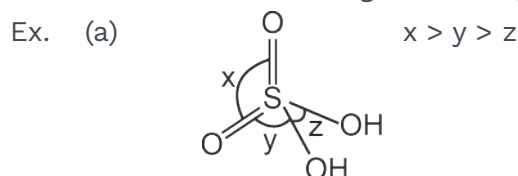




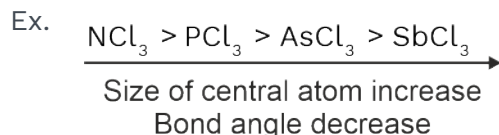
(2) Bond angle  $\propto \frac{1}{\text{number no lone pair}}$



(3) Multi Bond — Multi Bond  
 or Multi Bond — Single Bond repulsion.

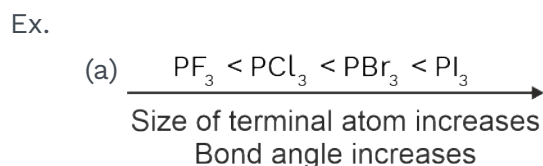


(4) Bond angle  $\propto \frac{\text{EN of Central atom}}{\text{Size of Central atom}}$   
 Steric repulsion increase, Bond Angle increase



(5) Bond angle  $\propto \frac{\text{size of Terminal atom}}{\text{EN of Terminal atom}}$

(EN of terminal atom only for F atom)



### Previous Year's Questions



Decreasing order of bond angle is  
**[AIIMS]**

- (1)  $\text{BeCl}_2 > \text{NO}_2 > \text{SO}_2$
- (2)  $\text{BeCl}_2 > \text{SO}_2 > \text{NO}_2$
- (3)  $\text{SO}_2 > \text{BeCl}_2 > \text{NO}_2$
- (4)  $\text{SO}_2 > \text{NO}_2 > \text{BeCl}_2$

### Rack your Brain



Why  $\text{PH}_3$  does not show the bond angle  $109^\circ 28'$ ?

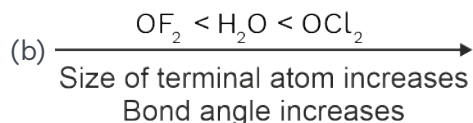
### Previous Year's Questions



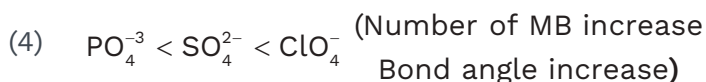
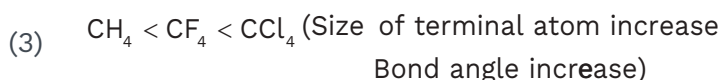
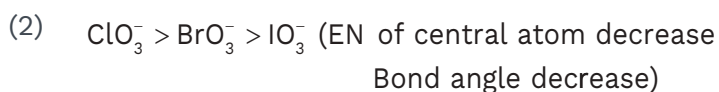
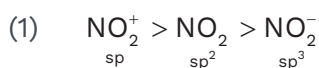
The correct order of increasing bond angles in the following triatomic species is  
**[NEET]**

- (1)  $\text{NO}_2^+ < \text{NO}_2 < \text{NO}_2^-$
- (2)  $\text{NO}_2^+ < \text{NO}_2^- < \text{NO}_2$
- (3)  $\text{NO}_2^- < \text{NO}_2^+ < \text{NO}_2$
- (4)  $\text{NO}_2^- < \text{NO}_2 < \text{NO}_2^+$





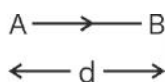
Q. Compare bond angle



### Dipole Moment (D.M.)

- Polarity of a bond depends upon  $\Delta\text{EN}$  but polarity of a molecule depends upon DM.
- Dipole moment is a product charge and internuclear distance.

$$\mu = q \times d$$



unit = debye

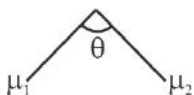
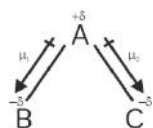
$$1 \text{ debye} = 10^{-18} \text{ esu.cm}$$

$$1 \text{ debye} = 3.33 \times 10^{-30} \text{ C}\cdot\text{m}$$

- Dipole moment is vector quantity and its direction is from positively charged atom to negatively charged atom.



- Dipole moment of a molecule is vector sum of all dipole moments of lp's and bp's.



### Concept Ladder



Central atom and terminal atom are applicable only when Central atom form difference type of bond or central atom has lone pair.

### Previous Year's Questions



Which of the following are arranged in the decreasing order of dipole moment?

[AIIMS]

- (1)  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{F}$
- (2)  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$
- (3)  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{F}$
- (4)  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$

### Concept Ladder



If molecular has v-shape, T-shape, pyramidal shape, then it will be polar.

**Ex:**  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{PCl}_3$ ,  $\text{ClF}_3$ ,  $\text{BrF}_3$  etc.



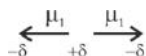


$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

$$\theta = 0^\circ \quad \mu = \mu_1 + \mu_2 \quad (\text{Max. dipole moment})$$

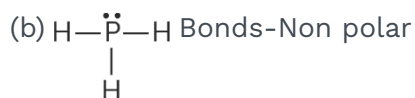
$$\theta = 180^\circ \quad \mu = \mu_1 - \mu_2 \quad (\text{Min. dipole moment})$$

$$\theta \propto \frac{1}{\text{Dipole moment}}$$



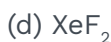
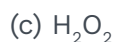
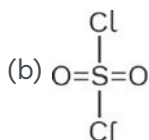
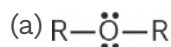
**Ex:** (a)  $\text{O}=\text{C}=\text{O}$  Bonds-polar but molecular is non polar.

$$\mu = \mu_1 - \mu_1$$

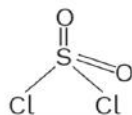
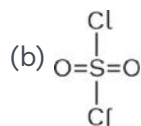


But molecular is polar due to its lp.

**Q.** Which of the following molecule is non polar?



**A.** (a)  $\text{R}-\ddot{\text{O}}-\text{R} \rightarrow \text{V-shape}$

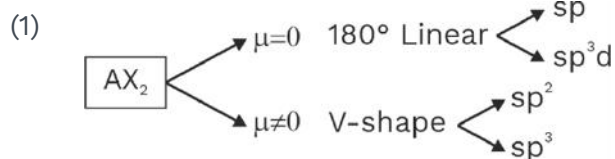


$\mu \neq 0$   
Non-polar

(c)  $\text{H}_2\text{O}_2$  — Half open book like structure ex.  $\text{O}_2\text{F}_2$ ,  $\text{S}_2\text{F}_2$ ,  $\text{S}_2\text{Cl}_2$ .

(d)  $\text{XeF}_2 \rightarrow \text{sp}^3\text{d}$

### Dipole Moment and Geometry



### Concept Ladder



If central atom doesn't have any lone pair and all terminal atom are same then molecule will be Non polar.

**Ex:**  $\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{PCl}_5$ ,  $3\text{F}_6$ ,  $\text{IF}_7$ ,  $\text{B}_2\text{H}_6$ ,  $\text{Al}_2\text{Cl}_6$  etc.

### Previous Year's Questions



The dipole moment is minimum in

[AIIMS]

- (1)  $\text{NH}_3$  (2)  $\text{NF}_3$   
 (3)  $\text{SO}_2$  (4)  $\text{BF}_3$

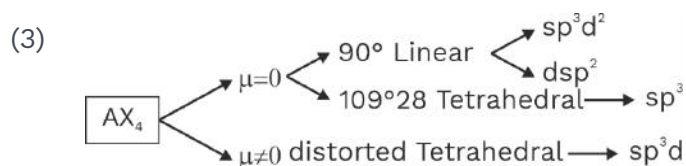
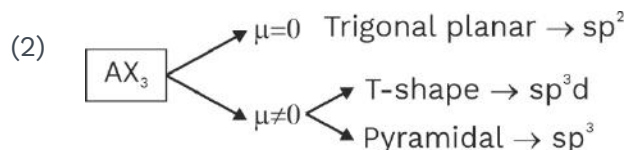
### Concept Ladder



If central atom has only 1 lone pair then molecule will be polar.

**Ex:**  $\text{XeF}_6$ ,  $\text{SF}_4$ ,  $\text{TeCl}_4$ ,  $\text{SO}_2$ ,  $\text{NF}_3$  etc.





$$\% \text{Ionic character} = \frac{\mu_{\text{obs.}}}{\mu_{\text{theo}}} \times 100$$

$$\mu_{\text{obs}} = \text{given (debye)}$$

$$\mu_{\text{Theo}} = q \times d$$



$$q = 1.6 \times 10^{-19} \text{ C}$$

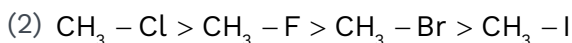
$$\text{or } q = 4.8 \times 10^{-10} \text{ e.s.u}$$

**Q.** Compare dipole moment.



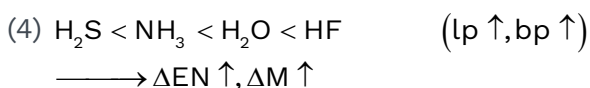
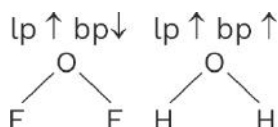
$$\mu = q \times d$$

( $\Delta EN \Rightarrow$  dominating factor)



$$\mu = q \times d$$

(Size  $\Rightarrow$  dominating factor)



### Previous Year's Questions



The correct order of dipole moment is

[AIIMS]

- (1)  $CH_4 < NF_3 < NH_3 < H_2O$
- (2)  $NF_3 < CH_4 < NH_3 < H_2O$
- (3)  $NH_3 < NF_3 < CH_4 < H_2O$
- (4)  $H_2O < NH_3 < NF_3 < CH_4$

### Previous Year's Questions



Which of the following bonds will be most polar?

[AIPMT]

- (1) N—Cl
- (2) O—F
- (3) N—F
- (4) N—N



**Molecular Orbital theory (MOT)**

Initially developed by Robert S. Mullikan.

Molecular Orbitals

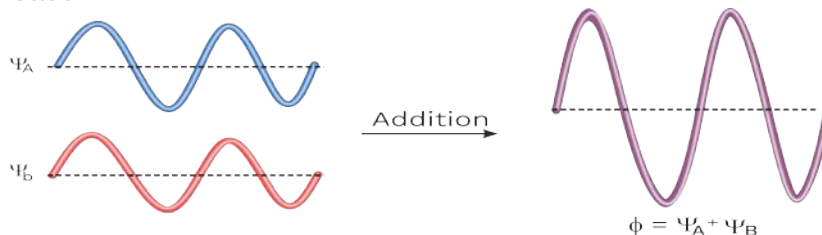
Bonding Molecular Orbitals (BMO)

Anti-bonding Molecular Orbitals (ABMO)

Molecular bonds have lower P.E. than in separate atomic orbitals. Thus, electrons prefer to stay in a molecular bond.

**Drawbacks of VBT**

1. It can't explain paramagnetic nature of  $O_2$ .
2. It can't explain bonding of odd electron species.
3. It can not explain existence of  $H_2^+$ ,  $He_2^+$  etc.
  - A hypothetical concept given by Pauling.
  - Both VBT and MOT are based upon combination of atomic orbitals.
  - According to VBT, orbitals which have unpaired electron can combine with each other but according to MOT, all atomic orbitals which have same energy and same symmetry can combine with each other.
  - According to VBT 1 atomic orbital + 1 atomic orbital = 1 molecular orbital
  - According to MOT 1 atomic orbital + 1 atomic orbital = 2 molecular orbitals (Antibonding molecular orbital (ABMO), Bonding molecular orbital (BMO))

**Linear Combination of Atomic Orbitals (LCAO)****Case I****Concept Ladder****Principle of MOT**

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

**Rack your Brain**

Which molecular orbital is more stable in orbital diagram?

**Previous Year's Questions**

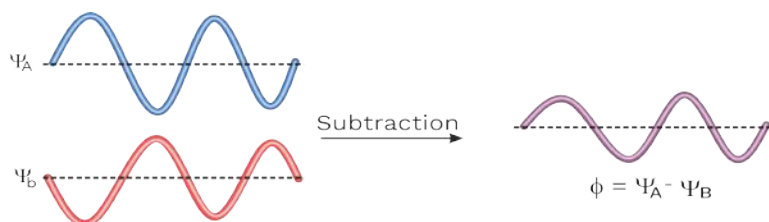
Which one of the following species does not exist under normal conditions? **[AIPMT]**

- (1)  $Be_2^+$
- (2)  $Be_2$
- (3)  $B_2$
- (4)  $Li_2$





### Case II



#### Difference between bonding and antibonding molecular orbital

Bonding molecular orbital	Antibonding molecular orbital
$\phi_b = \Psi_A + \Psi_B$	$\phi_a = \Psi_A - \Psi_B$
Wave functions are added	Wave functions are subtracted
Electron density between the nuclei increases	Electron density between the nuclei decreases
Energy is less	Energy is more
No nodal plane	Has nodal plane
Represented by $\sigma, \pi, \delta$ etc.	Represented by $\sigma^*, \pi^*, \delta^*$ etc.

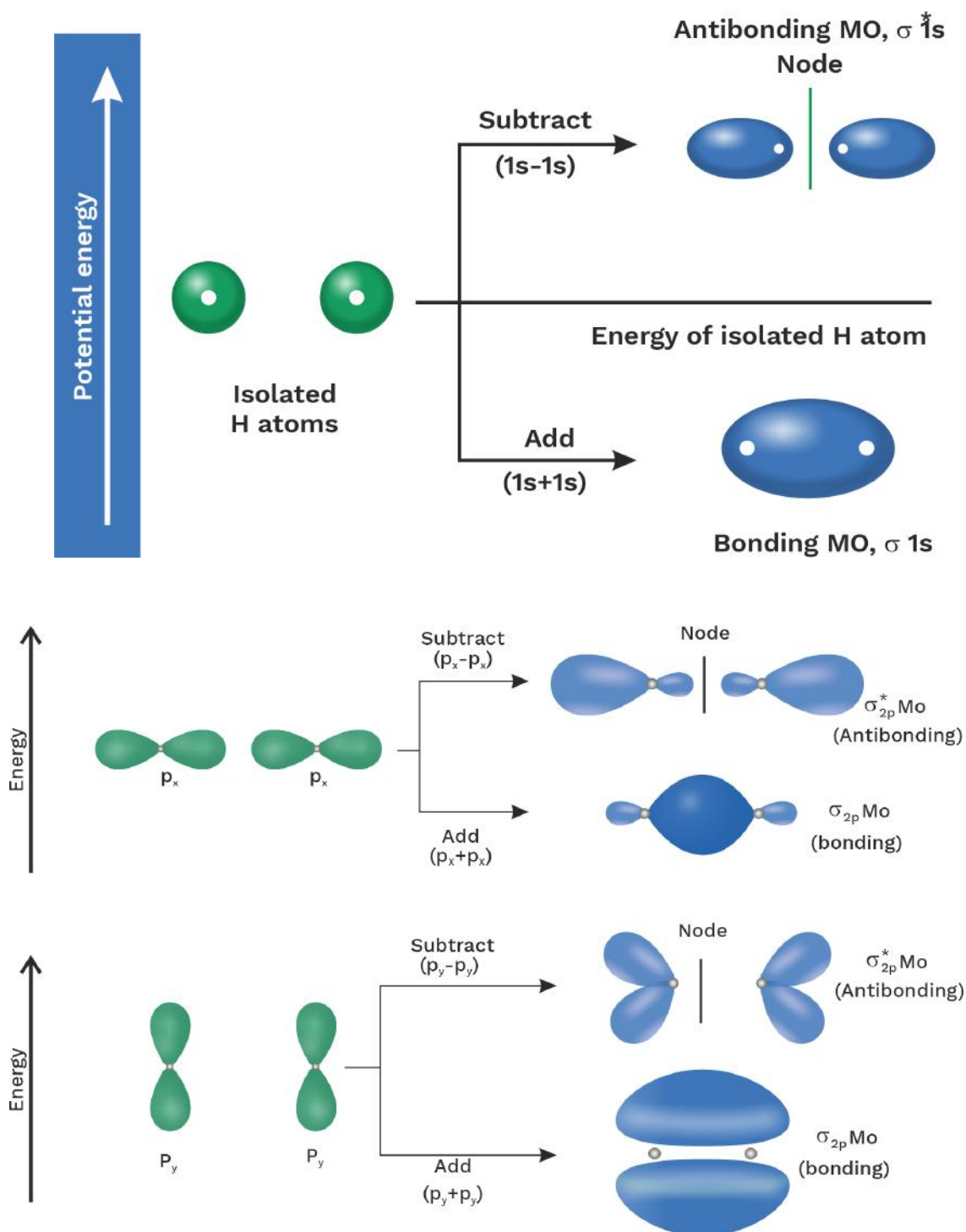
#### Difference between atomic and molecular orbital

Atomic orbital	molecular orbital
Monocentric	Polycentric
Less stable	More stable

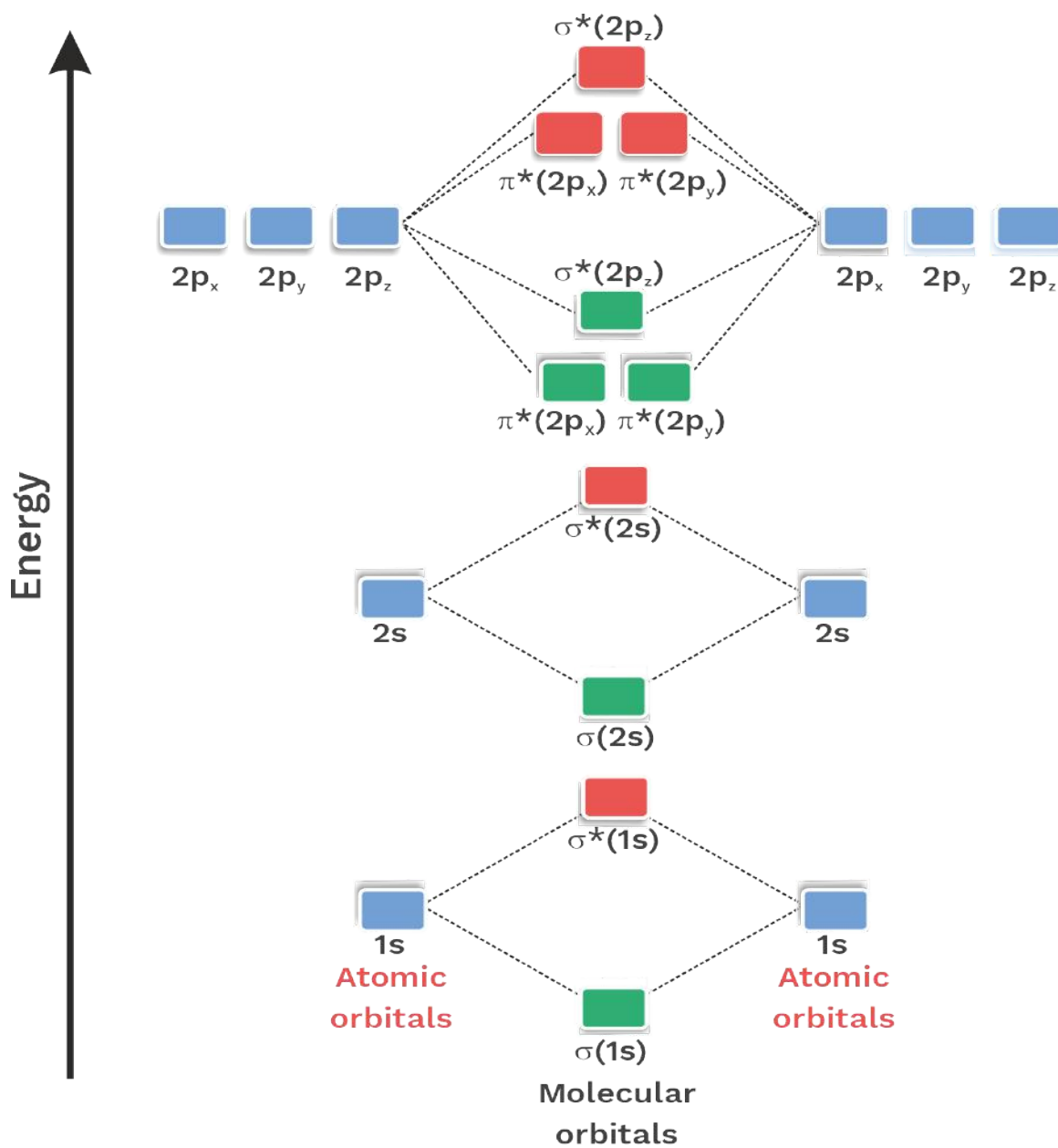




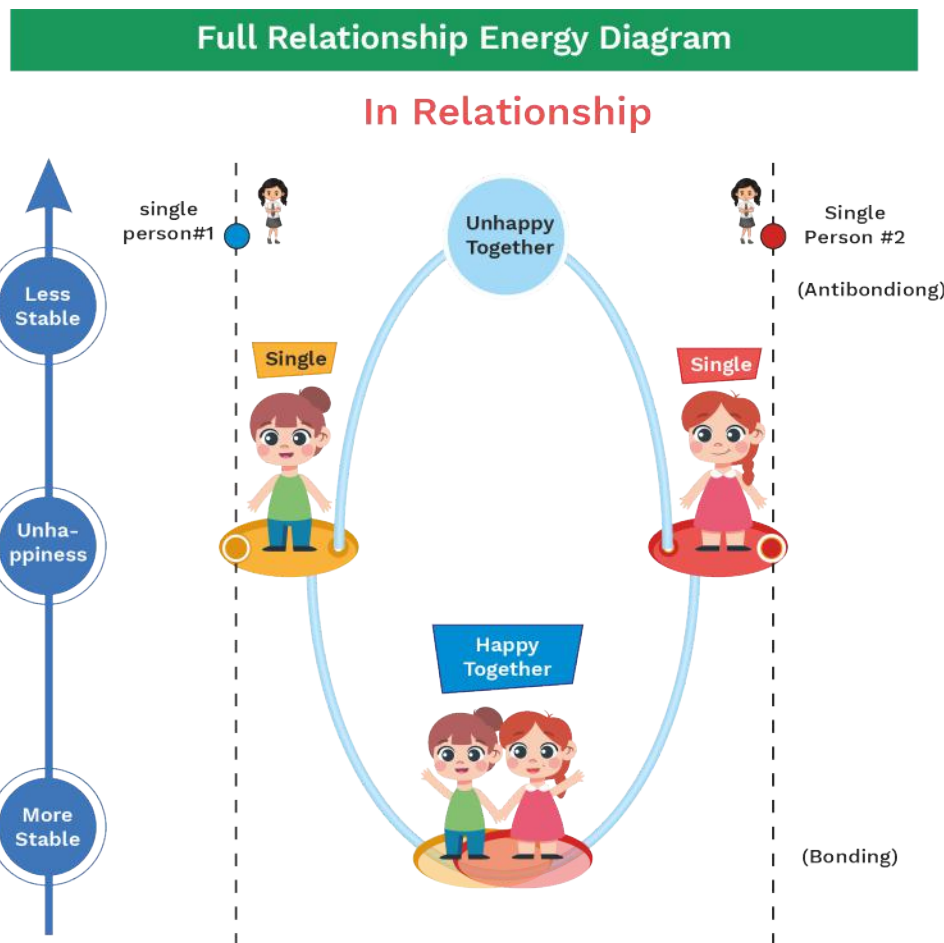
### Energy Level Diagram for Molecular Orbitals









**Bond order**

It is half of the difference between the number of electrons present in the bonding and the antibonding orbitals.

$$\text{Bond order} = \frac{\text{Number of } e^- \text{ in BMO} - \text{Number of } e^- \text{ in AMO}}{2} \quad \text{Or } \text{B.O} = \frac{N_b - N_a}{2}$$

**Note :**

If  $N_b > N_a$  (bond order positive) Molecules will stable

**If  $N_b < N_a$  (bond order is negative or zero) molecules will unstable.**





### Magnetic character

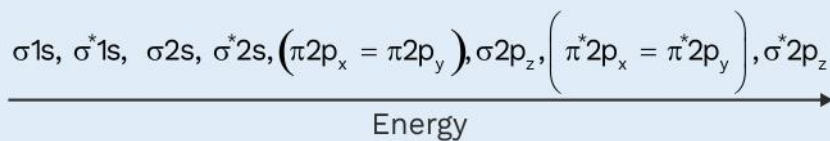
- (a) **Diamagnetic:** If all the electrons in the molecules or ion are paired.
- (b) **Paramagnetic:** If the molecule has any unpaired electron or electrons, it is paramagnetic in nature.

#### Note:

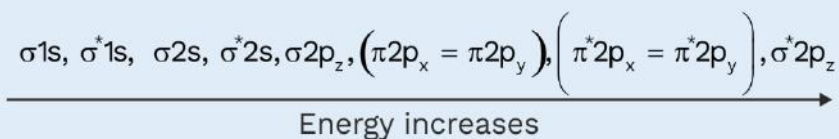
**greater the no. of unpaired electrons present in the molecule or ion greater is the paramagnetic nature.**

Magnetic moment =  $\sqrt{n(n+2)}$  B.M. Where n is the number of unpaired electrons.

The energy for first ten molecular orbitals for  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$



For  $\text{O}_2$ ,  $\text{F}_2$ ,  $\text{Ne}_2$



### Previous Year's Question



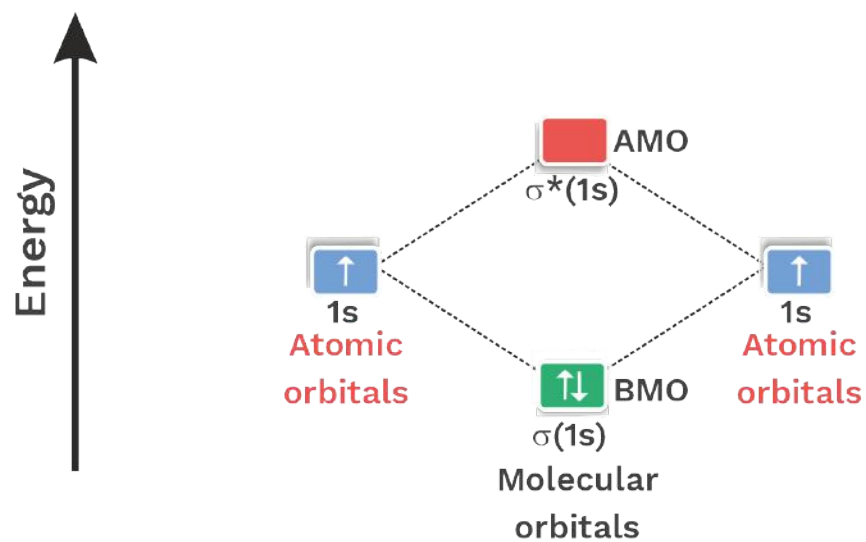
Which of the following is paramagnetic [NEET]

- (1)  $\text{CN}^-$
- (2)  $\text{NO}^+$
- (3)  $\text{CO}$
- (4)  $\text{O}_2^-$



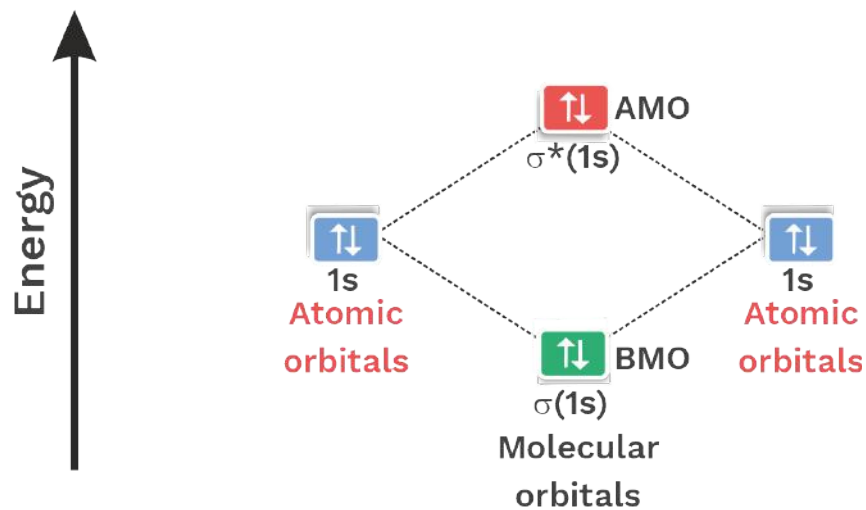


### Energy Level Diagram for H<sub>2</sub>



$$\text{H}_2 \text{ bond order} = 1/2(2 - 0) = 1$$

### Energy Level Diagram for He<sub>2</sub>

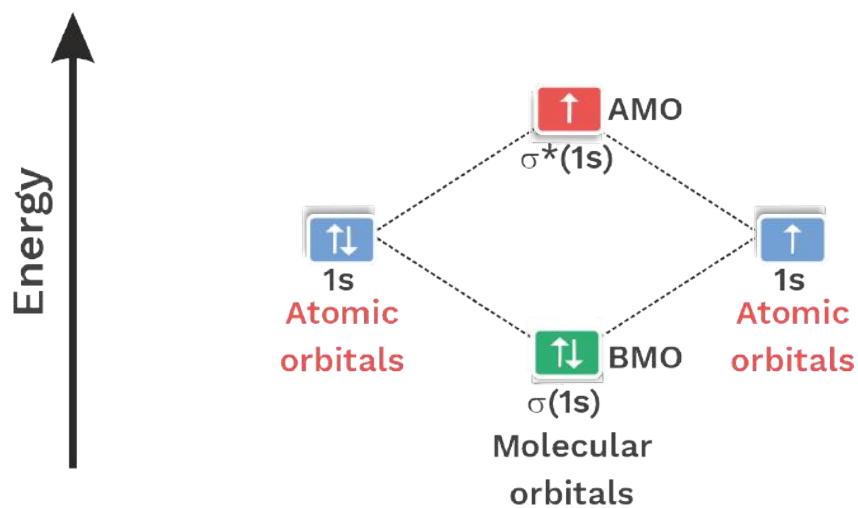


$$\text{He}_2 \text{ bond order} = 1/2(2 - 2) = 0$$



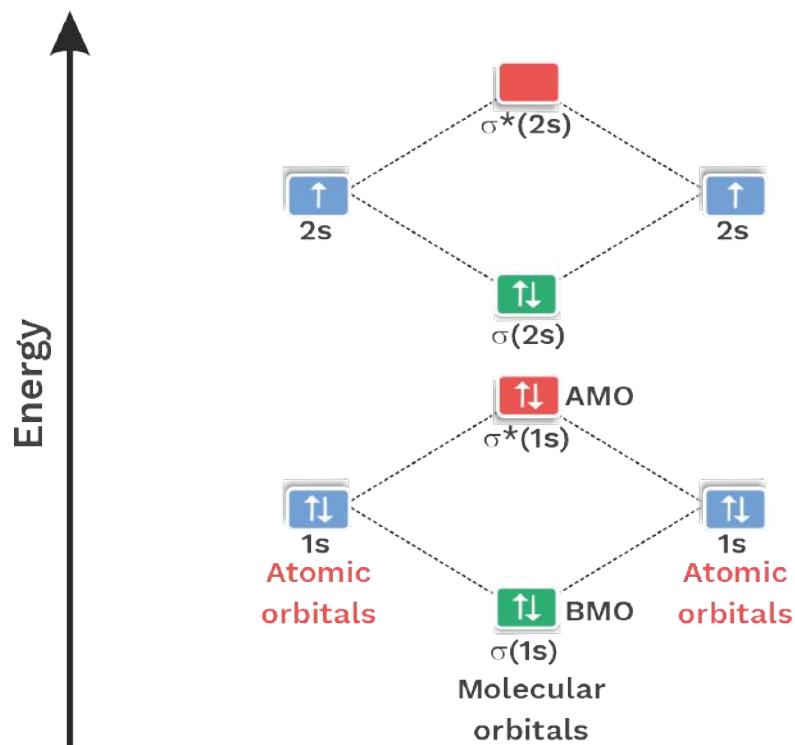


### Energy Level Diagram for $\text{He}_2^+$



$$\text{He}_2^+ \text{ bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

### Energy Level Diagram for $\text{Li}_2$

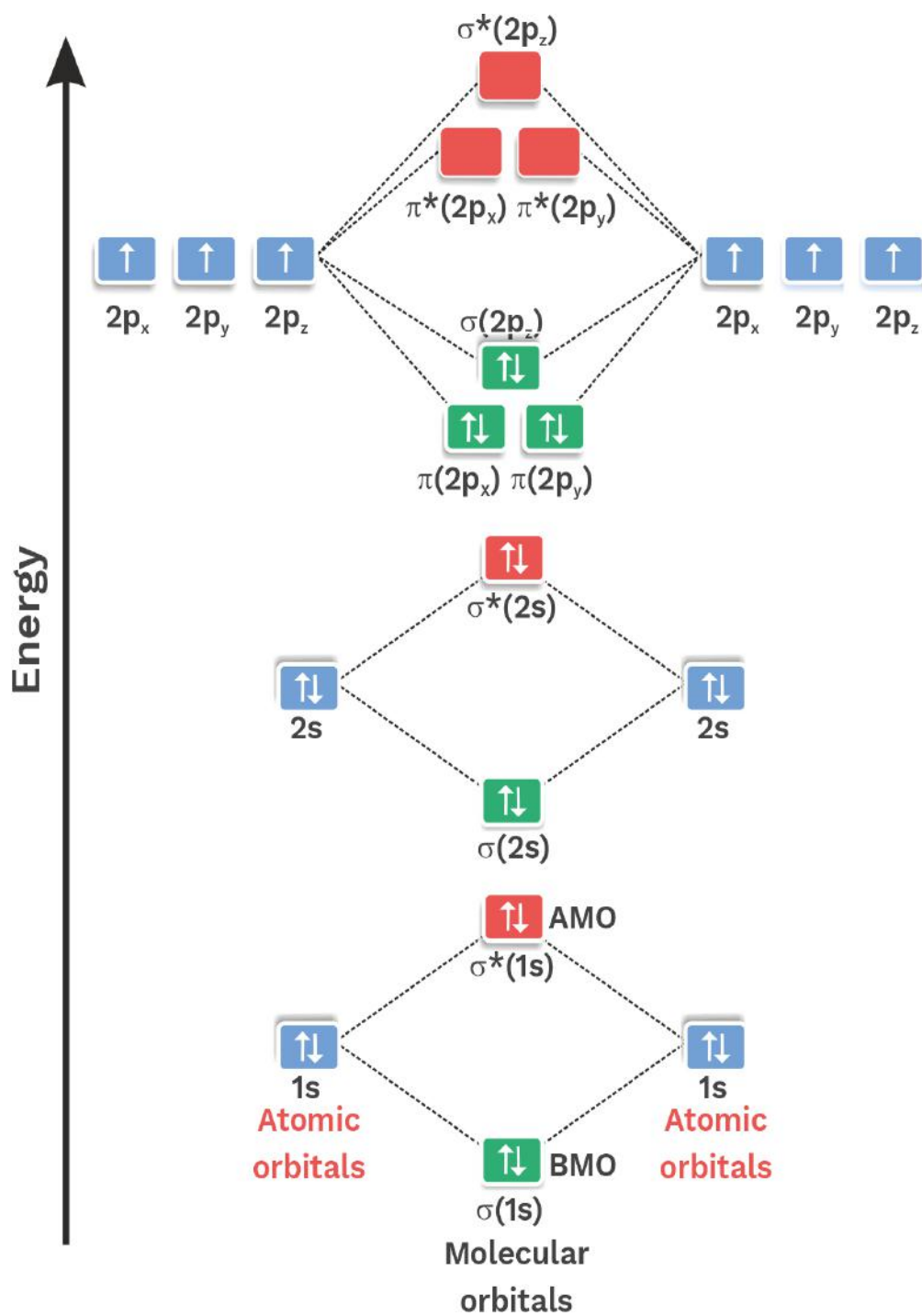


$$\text{Li}_2 \text{ bond order} = 1$$





### Energy Level Diagram for $N_2$



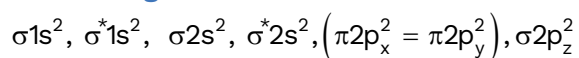




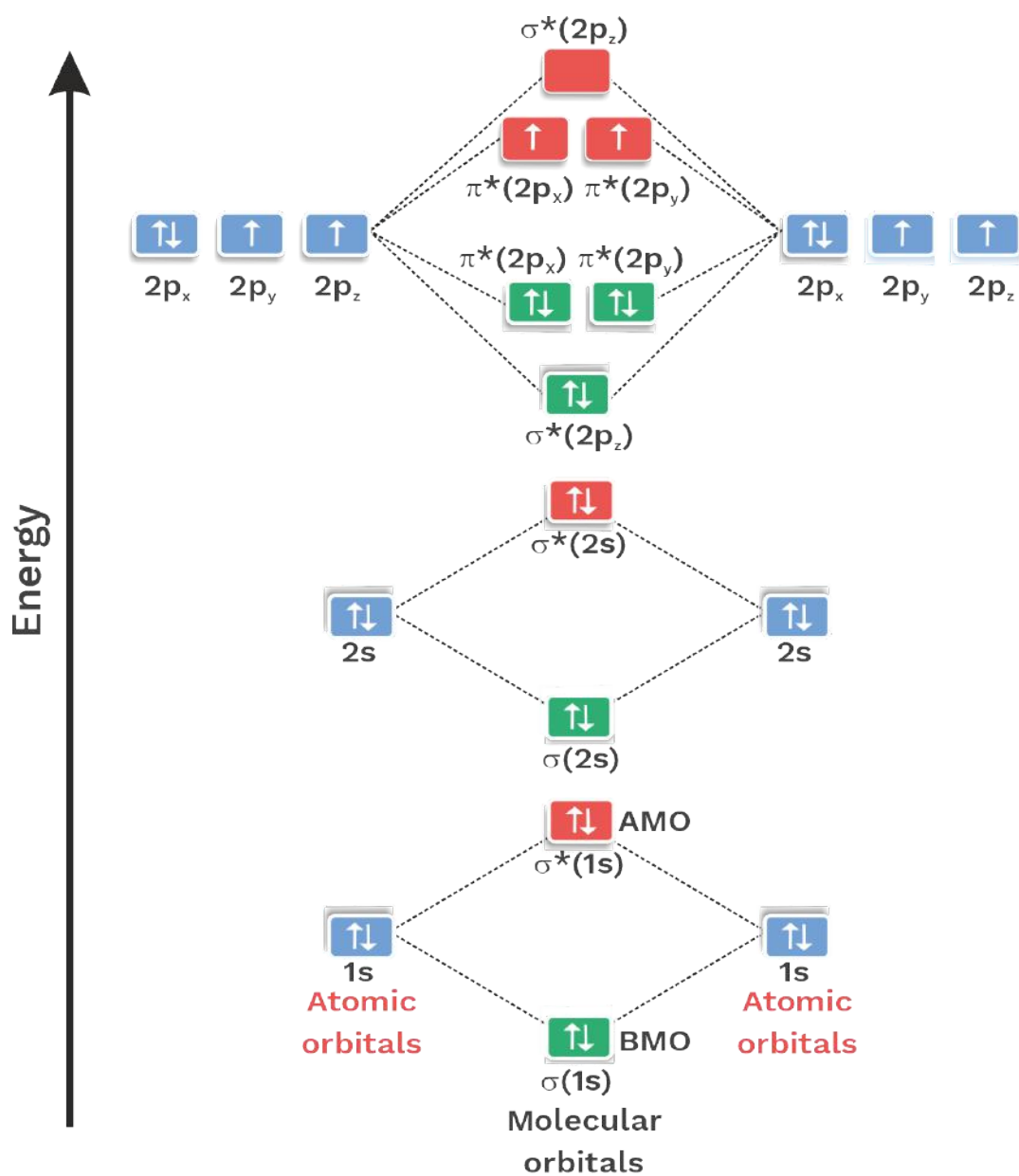
**Bond order** =  $\frac{10 - 4}{2} = 3$ ,

**Magnetic character** – diamagnetic

**Electronic configuration** -



**Energy Level Diagram for O<sub>2</sub>**



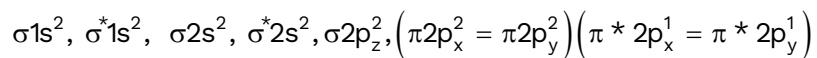




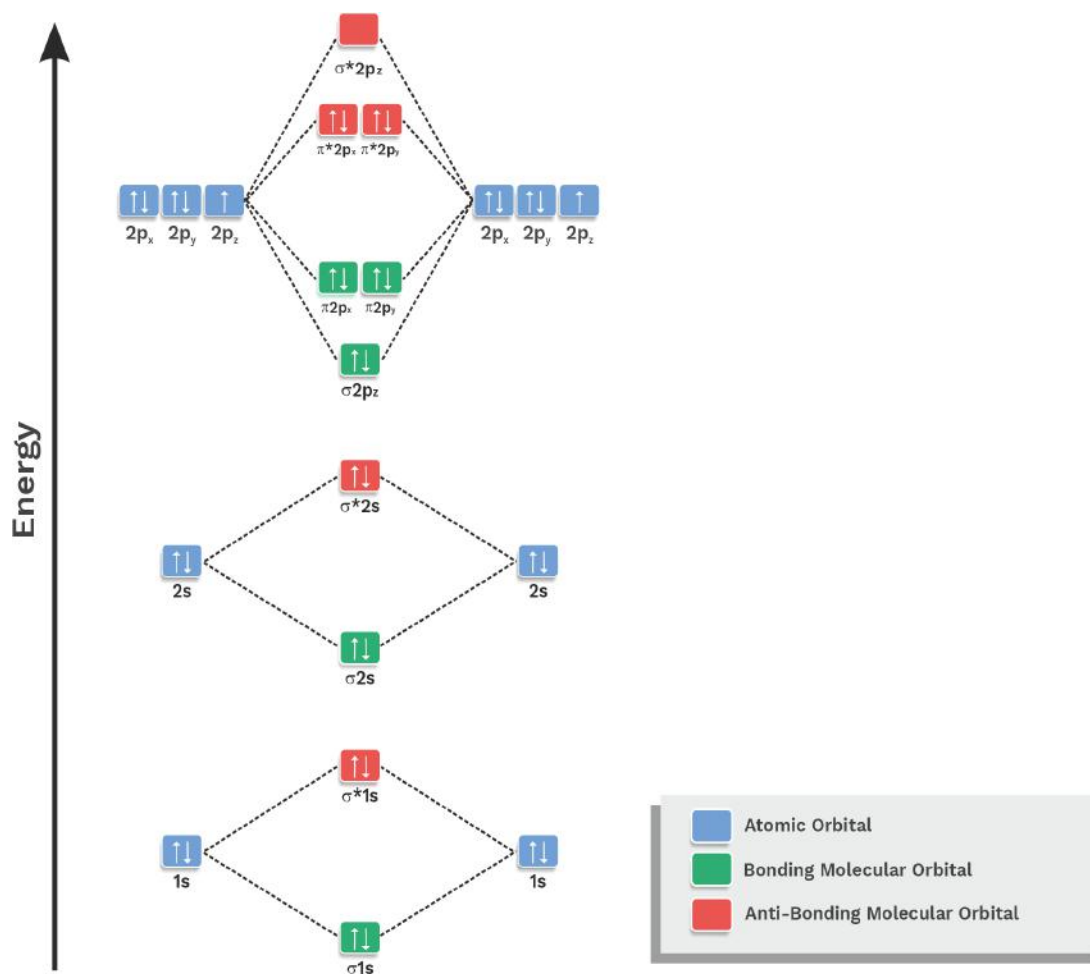
$$\text{Bond order} = \frac{10 - 6}{2} = 2$$

**Magnetic character** – paramagnetic (due to unpaired electron)

**Electronic configuration** -



**Energy Level Diagram for  $F_2$**



Energy level diagram of  $F_2$





### Examples.

Species	Bond order	Stability	Magnetic Character
$\text{H}_2^-$	0.5	Some what stable	Paramagnetic
$\text{H}_2$	1	Quite stable	Diamagnetic
$\text{H}_2^+$	.5	Somewhat stable	Paramagnetic
$\text{N}_2^{2-}$	2	Least stable	Paramagnetic
$\text{N}_2^-$	2.5	Less stable	Paramagnetic
$\text{N}_2^+$	2.5	Less stable	Paramagnetic
$\text{N}_2$	3	Most stable	Diamagnetic
$\text{O}_2^{2-}$	1.0	Least stable	Diamagnetic
$\text{O}_2^-$	1.5	Still less stable	Paramagnetic
$\text{O}_2$	2.0	Less stable	Paramagnetic
$\text{O}_2^+$	2.5	Most stable	Paramagnetic





**Q28** Write electronic configuration, B.O. of  $O_2$  and explain its paramagnetic nature?

**A28**  $O_2 (16e^-) = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1, \sigma^* 2p_z^2$

$$B.O. = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

$O_2$  has two unpaired electrons  $\pi^* 2p_x^1 = \pi^* 2p_y^1$ .

**Q29** Compare stability of  $H_2$ ,  $H_2^+$ ,  $H_2^-$ .

**A29** stability  $\propto$  Bond order

$$B.O. = \frac{N_b - N_a}{2}$$

$$H_2 - \sigma 1s^2 \quad B.O. = \frac{2 - 0}{2} = 1$$

$$H_2^+ - \sigma 1s^1 \quad B.O. = \frac{1 - 0}{2} = 0.5$$

$$H_2^- - \sigma 1s^2 \sigma^* 1s^1 \quad B.O. = \frac{2 - 1}{1} = 0.5$$

So,  $H_2 > H_2^+ > H_2^-$ .

$H_2^+$  is more stable than  $H_2^-$  because in  $H_2^+$  less antibonding MO electron present.

**Q30** The paramagnetic behaviour of  $B_2$  is due to presence of :

**A30**  $B_2 (10e^-) = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \pi 2p_x^1 = \pi 2p_y^1, \sigma 2p_z^0$

Two unpaired electrons present in  $\pi_b$  MO.





**Q31** Compare C—C bond strength of  $C_2$  and  $C_2H_4$ .

**A31**  $C_2 (12 e^-) = \sigma 1s^2 \sigma^* 1s^2, \sigma 2s^2 \sigma^* 2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^0$

$$B.O. = \frac{8 - 4}{2} = 2 \text{ for } C_2 [C=C] \text{ both are } \pi\text{-bonds}$$

Bond Strength  $C=C < H_2C=CH_2$

**Q32** How the bond energy varies from  $N_2^-$ ,  $N_2^+$  and why?

**A32** Bond energy of  $N_2^+$  equal to Bond energy of  $N_2^-$  because the bond order is same in both the species. However,  $N_2^+$  is slightly more stable than  $N_2^-$  as number of antibonding electrons is higher in  $N_2^-$  than  $N_2^+$ .

**Q33** Compare the bond length of O—O in the following molecules  
(a)  $KO_2$       (b)  $O_2 [As F_6]$       (c)  $O_2$       (d)  $Na_2O_2$

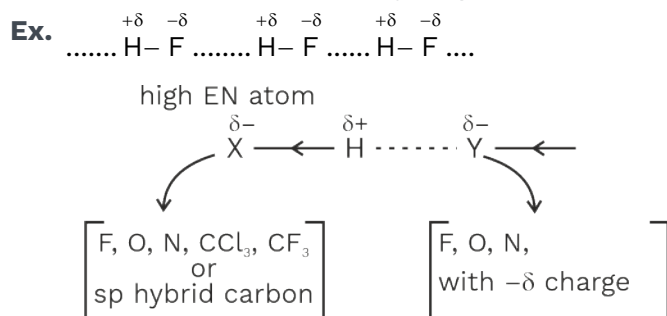
**A33** (a)  $KO_2$  has  $O_2^-$  (superoxide ion), Bond order = 1.5  
(b)  $O_2 [As F_6]$  has  $O_2^+$ , Bond order = 2.5  
(c)  $O_2$ , Bond order = 2  
(d)  $Na_2O_2$  has  $O_2^{2-}$  (peroxide ion), Bond order = 1  
Higher is the BO, smaller is the bond length. Hence, order of bond length of :  
 $O_2^+ < O_2 < O_2^- < O_2^{2-}$





## Hydrogen Bonding

When H atom is directly bonded with highly electro negative element (F,O,N) then the bond formed is termed as hydrogen bond.



Bond energy = 8 – 42 KJ mol<sup>-1</sup> for neutral molecules.

### Conditions for hydrogen bonding

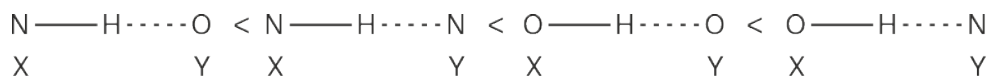
- Size of electronegative element should be small (F, O, N).
- Molecules must have highly electronegative atom link to hydrogen atom

### For stronger H-bonding

- EN of X should be high
- EN of Y should be less (if X is same)

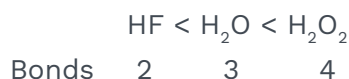
### H-bond strength order

**Ex:** HF > H<sub>2</sub>O > NH<sub>3</sub> (EN of X decreases)



D<sub>2</sub>O > H<sub>2</sub>O (D is more +ve)

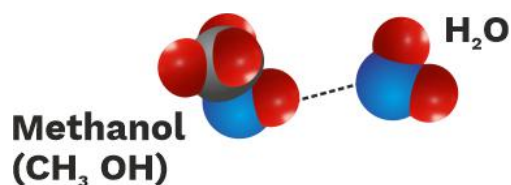
### Extent of H-bonding



### Types of hydrogen bonding

#### (a) Intermolecular hydrogen bonding

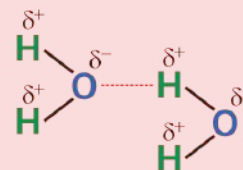
This type of bonding is between two or more same or different molecules when



**H bond**

### Hydrogen Bond

Hydrogen attracts an electronegative atom electrostatically



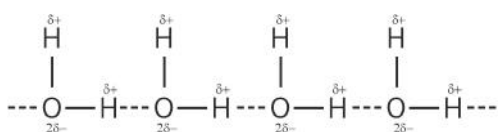
**Two water molecules**





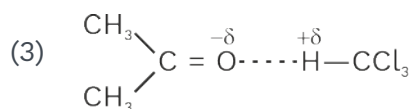
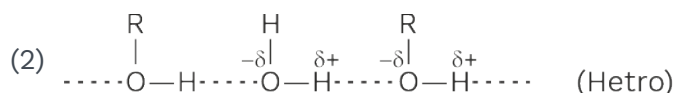
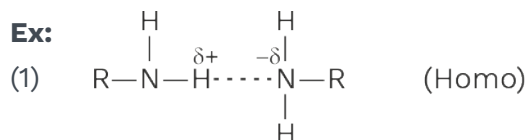
combine together to form a dimer or polymer respectively and leads to a phenomenon called association.

Intermolecular H-bonding increase the boiling points of the compound and also its solubility in water.

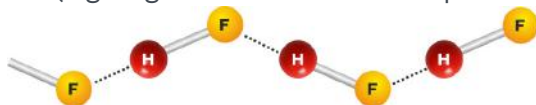


### Intermolecular Hydrogen bonding in H<sub>2</sub>O

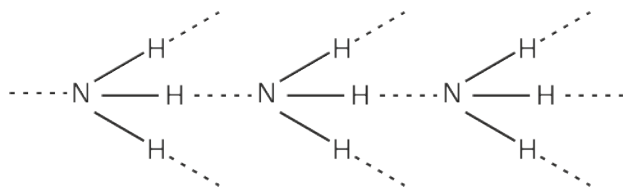
**Ex:**



(4) HF (zig-zag structure in solid/liq. state)



(5) NH<sub>3</sub> (linear H-bonding)



### Previous Year's Questions



$\text{X}-\text{X} \cdots \text{Y}$ , X and Y both are electronegative elements. Then

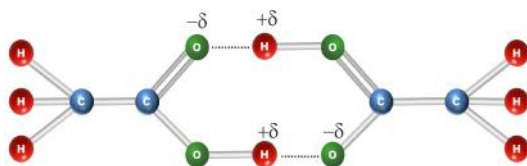
**[NEET]**

- (1) Electron density on X will increase and on H will decrease
- (2) In both electron density will increase
- (3) In both electron density will decrease
- (4) On X electron density will decrease and on H increases.

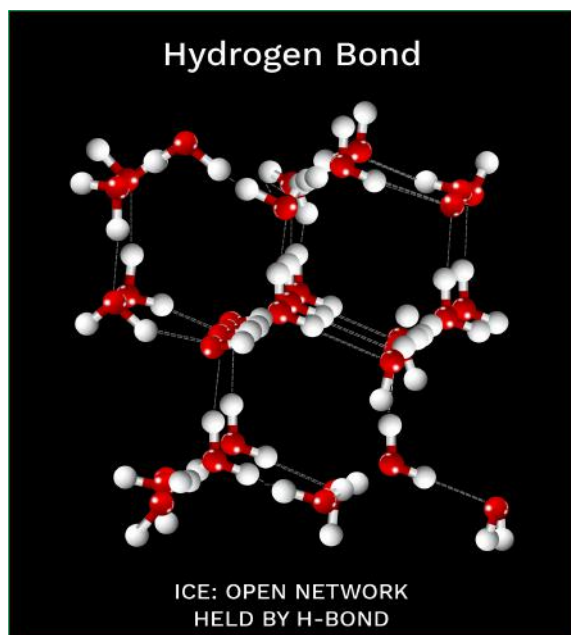




(6)  $\text{CH}_3\text{COOH}$



(7) Ice : Each oxygen atom is bonded with 4H atom in tetrahedral geometry and form open cage like structure.



**(b) Intramolecular hydrogen bonding**

Intramolecular hydrogen bond formed between two different atoms in the same molecules and leads to a phenomenon called Chelation.

This type of H-bonding occurs in organic compound and results in the cyclisation (six or five member ring) of the molecule.

This type of H-bonding decreases the boiling point of the compound and also its solubility in water.

**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.

**Previous Year's Questions**



Which one of the following compounds shows the presence of intramolecular hydrogen bond ?  
[NEET]

- (1)  $\text{H}_2\text{O}_2$
- (2) HCN
- (3) Cellulose
- (4) Concentrated acetic acid

**Concept Ladder**



Hydrogen bonding is special type of dipole – dipole attraction

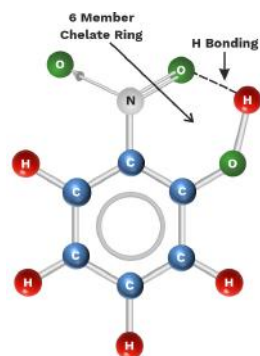






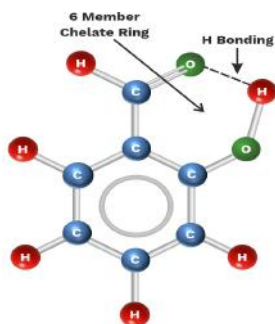
Ex:

(1) **o-nitrophenol**

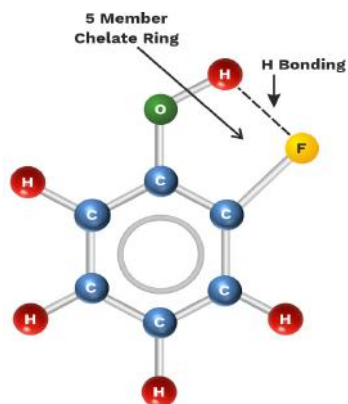


o-nitrophenol have a 6 membered ring (chelate ring), due to presence of chelate ring thermodynamic stability increases.

(2) **Salicylaldehyde**



(3) **o-fluorophenol**



**Concept Ladder**



H-bond energy is only 2-10 kcal/mol, as compared to the covalent bond energy of 50-100 kcal/mol but it is greater than van der Waals attraction which is < 1 kcal/mol.

**Rack your Brain**



Why acetic acid exist in dimer form?





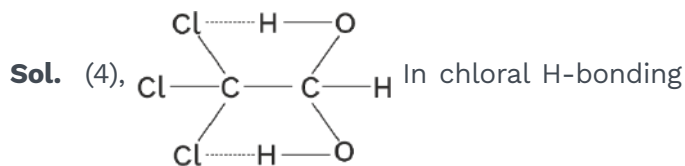
Urea, oxyacids, carbohydrates, protein etc. have intermolecular H-bonding.

**Note :**

- (a) Hydrogen bonding never involves more than two atom.
- (b) It is a electrostatic force instead of chemical bond.
- (c) Intra molecular hydrogen bonding is weaker than intermolecular H-bonding.
- (d) Hydrogen bond strength  $\text{H-F} \cdots \text{H} > \text{H-O} \cdots \text{H} > \text{H-N} \cdots \text{H}$
- (e) In wate each O-atoms is linked with four H-atoms, two by covalent bond and two by hydrogen bonds.
- (f) Due to intermolecular hydrogen bonding water has maximum density at 4°C.
- (g) O-nitrophenol is volatile but meta and para nitrophenol is not (O-nitrophenol has intra molecular hydrogen boning having low boiling point, where as para and meta nitrophenol has inter molecular hydrogen bonding having high boiling point).

**EX.** Intra molecular hydrogen bonding is present in

- (1) Chloral                      (2) O-fluorophenol
- (3) O-nitrophenol            (4) All



is formed between H and Cl.

**Previous Year's Questions**

Which one shows maximum hydrogen bodning? **[NEET]**

- (1)  $\text{H}_2\text{O}$
- (2)  $\text{H}_2\text{Se}$
- (3)  $\text{H}_2\text{S}$
- (4) HF

**Rack your Brain**

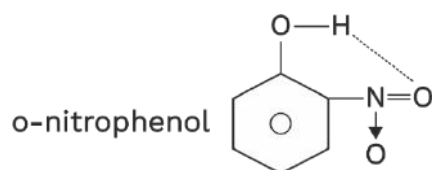
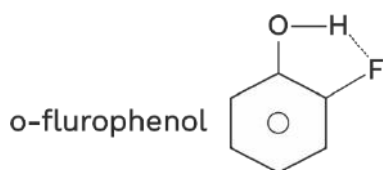
What is the strongest hydrogen bond?

**Previous Year's Questions**

What is the dominant intermolecular force or bond that must be overcome in converting liquid  $\text{CH}_3\text{OH}$  to a gas? **[NEET]**

- (1) Dipole-dipole interaction
- (2) Covalent bonds
- (3) London disperision force
- (4) Hydrogen bonding





### Applications of Hydrogen bonding

- (a) **Physical state** : Due to hydrogen bonding  $\text{H}_2\text{O}$  is liquid where as  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$  are gases (absence of hydrogen bonding and presence of Vander wall forces).
- (b) Melting point and boiling point of covalent bond  $\propto$  vander wall forces  $\propto$  Mass
- On moving down in a group mass increases, forces of attraction increases, melting and boiling point increases
- Due to presence of hydrogen bonding B.P. and M.P. of HF is maximum in hydride of halogens,  **$\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$**  (B.P. and M.P) Similarly for  $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$  (B.P. and M.P) and  $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3$  (B.P. and M.P) But when  $\text{SbH}_3$  is included then  $\text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$

### Previous Year's Questions



Strongest hydrogen bond is shown by **[NEET]**

- (1) Water
- (2) Ammonia
- (3) Hydrogen fluoride
- (4) Hydrogen sulphide

### Rack your Brain



What bonds break the easiest?

### Concept Ladder



$\text{CH}_3\text{—F}$		Mass $\uparrow$
$\text{CH}_3\text{—Cl}$		VF $\uparrow$
$\text{CH}_3\text{—Br}$		B.P. and M.P. $\uparrow$
$\text{CH}_3\text{—I}$		



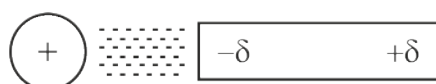


### Weak Intermolecular Forces

Intermolecular forces are attractive forces between molecules.

#### (1) Ion Dipole Attraction

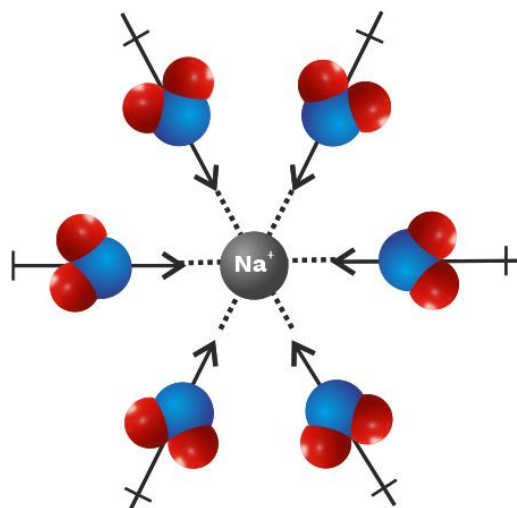
Attractive forces between ion and polar molecule



Cation

$$\text{interaction energy} \propto \frac{1}{r^2}$$

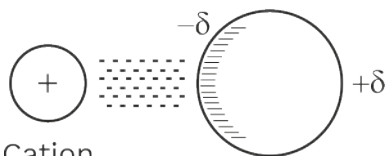
- Ex:** (i)  $\text{Li}^+ + \text{H}_2\text{O}$   
(ii)  $\text{Br}^- + \text{HBr}$   
(iii)  $\text{NO}_3^- + \text{CH}_3\text{OH}$



**Ion-dipole**

#### (2) Ion Induced Dipole Attraction

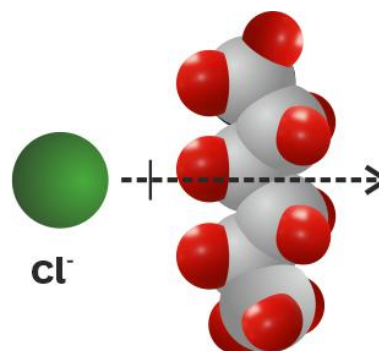
Exists between ion and non-polar molecule



Cation

$$\text{Interactive energy} \propto \frac{1}{r^4}$$

- Ex:** (i)  $\text{Cl}^- + \text{Cl}_2$   
(ii)  $\text{HO}^- + \text{CCl}_4$   
(iii)  $\text{K}^+ + \text{C}_6\text{H}_6$



**Hexane  
( $\text{C}_6\text{H}_{14}$ )**

**Ion-induced dipole**





### (3) Van der waal Force Attraction

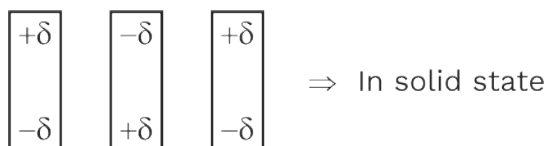
They are weaker than ionic and covalent bonds.

They have no directional characteristic.

Van der Waal's forces are independent of temperature except dipole-dipole interactions.

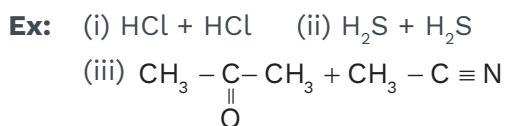
#### (a) Dipole-dipole Attraction (Keesom)

Two polar molecules align so that  $\delta+$  and  $\delta-$  are matched (electrostatic attraction). Attractive forces between polar molecules.



Interaction energy in solid state  $\propto \frac{1}{r^3}$

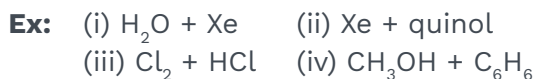
Interaction energy in liquid/gaseous state  $\propto \frac{1}{r^6}$



#### (b) Dipole-induced dipole attraction (Debye force)

A dipole can induce a temporary dipole to form in a non-polar molecule.

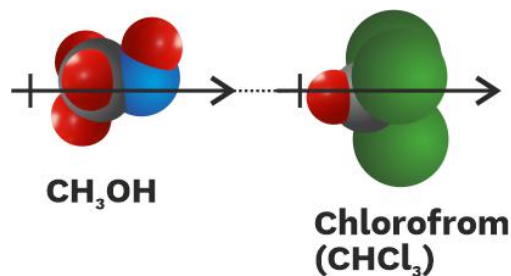
$$\text{I.E.} \propto \frac{1}{r^6}$$



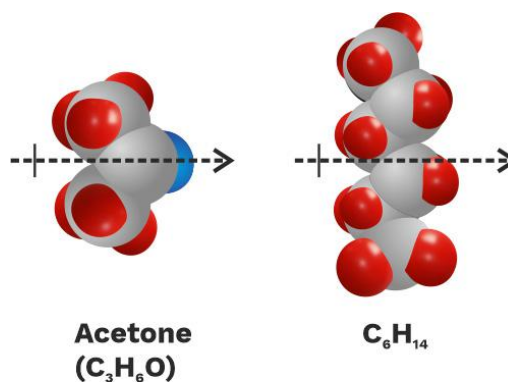
#### Concept Ladder



H-bond energy is only 2-10 kcal/mol, as compared to the covalent bond energy of 50-100 kcal/mol but it is greater than van der Waals attraction which is  $< 1$  kcal/mol.



#### Dipole-dipole



#### Dipole-Induced dipole





**(c) Instantaneous dipole + induced dipole attraction (Dispers ion force/london force)**

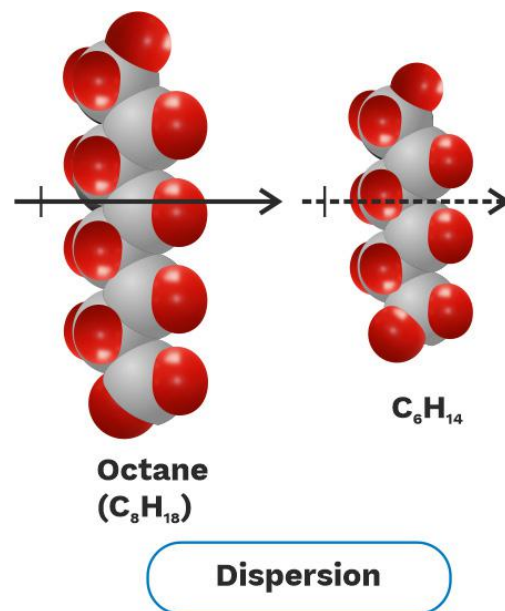
Formation of temporary dipole from a non-polar molecule which leads to a temporary dipole to form in another non-polar molecule (exists between non polar - non polar).

$$\boxed{\text{I.E.} \propto \frac{1}{r^6}}$$

**Ex:** (i)  $\text{Xe} + \text{Xe}$  (ii)  $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_6$   
(iii)  $\text{CO}_2 + \text{CO}_2$  (iv)  $\text{Cl}_2 + \text{Cl}_2$

**Significance**

- (1) In Protein folding
- (2) Graphenes Bonding Forces in Graphite
- (3) In Polymer Formation

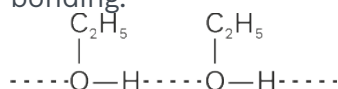






**Q34** Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) has higher boiling point than dimethyl ether ( $\text{CH}_3\text{--O--CH}_3$ ) although the molecular weight of both are same.

**A34** Though ethyl alcohol and dimethyl ether have the same molecular weight but in ethyl alcohol the hydrogen of the O–H groups forms intermolecular hydrogen bonding with the OH group in another molecule. But in case of ether the hydrogen is linked to C is not so electronegativity to encourage the hydrogen to form hydrogen bonding.



Due to intermolecular H-bonding, ethyl alcohol remains in the associated form and therefore boils at a higher temperature compared to dimethyl ether.

**Q35** o-Hydroxy benzaldehyde is liquid at room temperature while p-hydroxy benzaldehyde is high melting solid.

**A35** These are intermolecular H-bonding in o-hydroxy benzaldehyde while intermolecular H-bonding in p-hydroxy benzaldehyde.

**o-hydroxy benzaldehyde**

H-bonding is within the same molecule, thus less interaction in comparison to p-hydroxy benzaldehyde, thus is liquid.

**p-hydroxy benzaldehyde**

In this case interaction increases close packing, thus becomes solid, so obviously high melting point.

**Q36** Nitrogen and chlorine have almost same EN's but N forms H-bonding. Why?

**A36** Due to the large size of Cl, interacting with neighbouring molecules is not so strong.

**Q37**  $\text{H}_2\text{O}$  is liquid whereas  $\text{H}_2\text{S}$  is gas. Why?

**A37** In  $\text{H}_2\text{O}$ , there are strong intermolecular forces due to extensive H-bonds. No such bonding exists in  $\text{H}_2\text{S}$  since EN of O > EN of S.



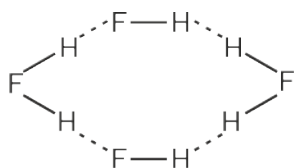


**Q38** Density of ice is less than that of water or ice floats over water. Why?

**A38** ICE has lower density than  $\text{H}_2\text{O}$ , as explained below. Due to H-bonding in solid ice, it forms a cage-like structure of  $\text{H}_2\text{O}$  molecules in which each  $\text{H}_2\text{O}$  molecule is linked tetrahedrally to four  $\text{H}_2\text{O}$  molecules. The molecules of  $\text{H}_2\text{O}$  are not so closely packed in the solid ice. When ice melts in cage-like structure, H-bonds break and molecules come closer to each other. Therefore, for the same mass of water, the volume decreases and hence density increases. Thus ice floats on water.

**Q39** Water forms four H-bonds are compared to two in HF. Explain?

**A39** Each HF molecule forms two H-bonding with two other HF molecules. This is due to the fact that size of F atom is so small that it cannot accommodate four HF molecules around it unlike  $\text{H}_2\text{O}$  which forms 4 H-bonds.



However in the gaseous state, several polymeric forms of the HF molecules exist in which the monomers are held together through H-bonding to form a pentagonal arrangement.

**Q40** Why a molecule is more stable in terms of energy than the uncombined atoms?

**A40** In the formation of molecule there is always release of energy. Thus, P.E. of a molecule is less than that of uncombined atoms and therefore, the molecule is more stable.

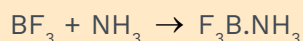




**Q41** Define electronegativity. How does it differ from electron gain enthalpy ?

**A41** The relative tendency of a bonded atom to attract the shared electron pair towards itself is called electronegativity while electron gain enthalpy is the energy change that occurs for the process of adding an electron to a gaseous isolated atom to convert it into a negative ion i.e. to form a monovalent anion. Electron gain enthalpy and electronegativity both measure the power of attracting electrons, but electron gain enthalpy is concerned with an isolated gaseous atom while electronegativity is concerned with the atom in combination.

**Q42** Is there any change in the hybridization of B and N atoms as a result of the following reaction ?



**A42** In  $\text{BF}_3$ , B is  $\text{sp}^2$  hybridised and by accepting a lone pair of electron present on the N-atom of  $\text{NH}_3$ , one vacant p-orbital of B gets filled. Nitrogen in this adduct acts as donor atom and  $\text{BF}_3$  acts as an acceptor. So, hybridization of B in  $\text{BF}_3$  changes from  $\text{sp}^2$  to  $\text{sp}^3$  whereas there is no change in hybridization of N in  $\text{NH}_3$  and in the adduct.

**Q43** Covalent bonds are directional bonds while ionic bonds are non-directional.

**A43** Since the covalent bond depends on the overlapping of orbitals between different orbitals, the geometry of the molecule is different. The orientation of overlap is the factor responsible for their directional nature.

**Q44** Among the compounds  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_3$ ,  $\text{HF}$  and  $\text{CH}_4$  in which the strongest H-bonding is present.

**A44** HF due to maximum EN of F. Decreasing order of strength of H-bonding.  
 $\text{HF} > \text{NH}_3 > \text{CH}_3\text{COOH}$  (exist as dimer)  $> \text{CH}_4$ .

**Q45**  $\text{H}_2\text{O}$  is a liquid whereas  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  are all gases at ordinary temperature

**A45** Due to H-bonding in  $\text{H}_2\text{O}$ , it causes association of  $\text{H}_2\text{O}$  molecules with the result that the B.P. of water is more than that of the other compound. But in  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  there is no such H-bonding.





## Chapter Summary



- 1. Lattice energy (U)** is amount of energy released when one mole of ion crystal is formed from its constituent ions in vapour state.
  - (i) Ionic bond is formed when lattice energy + electron affinity > ionisation energy
  - (ii) Solubility of ionic compounds is determined by ionic nature.
- 2.**
  - (i) Fajan's rule determines % of covalent character in ionic acid.
  - (ii) Dipole moment determines % of covalent character in ionic acid.
- 3. Fajan's rule**
  - (i) Order of polarisability of noble gases  $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$
  - (ii) Solubility decreases from  $\text{AlF}_3$  to  $\text{AlI}_3$  due to decrease in covalent character (as per Fajan's rule)
  - (iii)  $\text{FeCl}_3$  is more polar than  $\text{FeCl}_2$
- 4. Dipole moment :** Compounds of transition metals in lower oxidation state are ionic with partial covalent character.
- 5. Hydrogen bonding**
  - (i) Decreasing order of dipole moment in o, p, and m isomers is  $\text{o} > \text{m} > \text{p}$ .
  - (ii) Order of strength of H-bonding  
 $\text{H} \cdots \text{F} > \text{H} \cdots \text{O} > \text{H} \cdots \text{N}$
  - (iii) Bond length of H bond is of order 250 to 275 pm.
  - (iv) Strength of H-bonding increases when structures are resonance stabilised.
  - (v) Intramolecular H-bonding increases boiling and melting points, solubility, viscosity and surface tension and intermolecular H-bonding has opposite effects.
  - (vi) Chlorine has same electronegativity as of nitrogen, yet it does not form H-bond due to its larger size.
  - (vii)  $\text{H}_2\text{O}$  forms - 4 H bonds two through H-atoms and two through lone pairs at oxygen atom.
  - (viii) Ice has open cage like structure due to H-bonding.
  - (ix) Density of  $\text{H}_2\text{O}$  is maximum at  $4^\circ\text{C}$  because upto  $4^\circ\text{C}$  intermolecular H-bonding keep on breaking thereby decreasing volume and increasing density.
- 6. Valence bond theory** (Proposed by Heitler and London and modified by Pauling and Slater) fail to explain paramagnetic behavior of substance and geometry of non linear molecule.
- 7. Molecular orbital theory and bond order**
  - (i) Order of stability and bond dissociation energies
    - (a)  $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$
    - (b)  $\text{N}_2 > \text{N}_2^+ = \text{N}_2^- > \text{N}_2^{2-}$





(ii) Among  $O_2^+$ ,  $O_2$ ,  $O_2^-$ ,  $O_2^{2-}$  is diamagnetic.

(iii) Bond order of  $H_2^+$  and  $H_2^-$  both is same (e.g. 1/2) but  $H_2^-$  is less stable than  $H_2^+$  because it has one  $e^-$  in antibonding molecular orbital which decreases repulsion and decreases stability.

(iv) Bond order of  $CO$ ,  $CN^-$ ,  $NO^+$  = 3 and that of  $CO^+$ ,  $CN$  and  $NO$  = 2.5

#### 8. Shapes of molecules

(i) In  $PCl_5$ , axial P—Cl bonds are longer than equatorial P—Cl bonds.

(ii) T-shaped molecules —  $ClF_3$ ,  $ICl_3$ ,  $XeOF_2$ .

#### 9. Resonance

(i) Resonating structures differ only in arrangement of electrons.

(ii) Resonance hybrid has lower energy than contributing structures.





**sp**

**sp<sup>2</sup>**

# HYBRIDISATION

**sp<sup>3</sup>**

## Analogy For Hybridisation

**Combines**

Four different size mud balls combine to form equal shaped balls.

**Combines**

Similarly, orbitals of different energy combine to form equal energy orbitals.

---

### Formation of CH<sub>4</sub>

Here carbon needs to form 4 sigma Bonds

**1** e<sup>-</sup> Excites  
  
Valence E.C. of Carbon

**2**  
  
These 4 orbitals combine

**3**  
  
4 equal energy hybrid orbitals **sp<sup>3</sup>**

**4**  
  
CH<sub>4</sub> molecule is formed

### Formation of C<sub>2</sub>H<sub>4</sub>

Here each carbon needs to form 3 sigma and 1 pi Bonds

**1** e<sup>-</sup> Excites  
  
Valence E.C. of Carbon

**2**  
  
s, p<sub>x</sub>, p<sub>y</sub> Orbitals combine and form 3 equal **sp<sup>2</sup>** hybrid orbitals

**3**  
  
p<sub>z</sub> orbitals of two carbons combine and form  $\pi$  bond

**4**  
  
3-sp<sup>2</sup>

**5**  
  
 $\pi$  bond and  $\sigma$  bond

### Formation of C<sub>2</sub>H<sub>2</sub>

Each carbon needs to form 2 sigma and 2 pi Bonds

**1** e<sup>-</sup> Excites  
  
Valence E.C. of Carbon

**2**  
  
s and p<sub>x</sub> orbitals combine to form 2-sp orbitals

**3**  
  
p<sub>y</sub> and p<sub>z</sub> orbitals of two carbon atoms combine and form 2p bonds

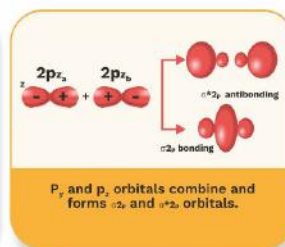
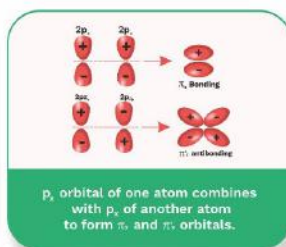
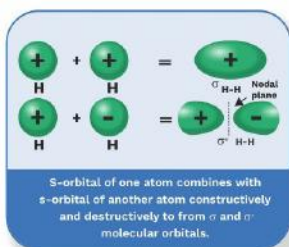
**4**  
  
2-sp

**5**  
  
 $\pi$ -bond

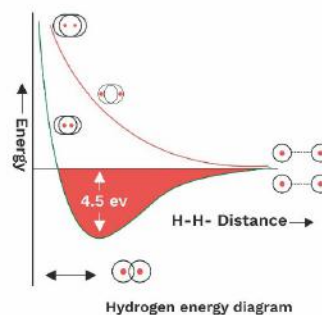
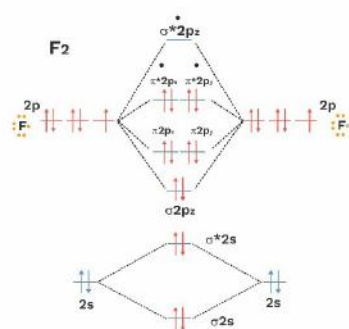




## MOLECULAR ORBITAL THEORY



### Energy Diagram of Molecular Orbitals



### Bond Order

$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

$N_b$  = Number of electrons in BMO

$N_a$  = Number of electrons in AMO

Bond	H <sub>2</sub> <sup>+</sup>	H <sub>2</sub>	He <sub>2</sub> <sup>+</sup>	He <sub>2</sub>
Bond Order	$\frac{1}{2}$	1	$\frac{1}{2}$	0

The bond order must be positive non-zero for a bond to be stable Helium has a bond order of zero and that is why the He<sub>2</sub> molecule is not observed.





## Nonbonding (Intermolecular)

Ion-Dipole		Ion charge-dipole charge	40-600	$\text{Na}^+ \cdots \text{O} \begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array}$
H-bond	$\delta^- \delta^+ \delta^-$ $\text{-A-H} \cdots \text{:B-}$	Polar bond to H-Dipole Charge (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 Charge	5-25	$\begin{array}{c} \delta^+ \delta^- \delta^+ \delta^- \\ \text{I-Cl} \cdots \text{I-Cl} \end{array}$
Ion-induced Dipole		Ion charge-Polarizable $e^-$ Cloud	3-15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-Induced Dipole		Dipole charge-Polarizable $e^-$ Cloud	2-10	$\begin{array}{c} \delta^+ \delta^- \delta^+ \delta^- \\ \text{H-Cl} \cdots \text{Cl-Cl} \end{array}$
Dispersion (London)		Polarizable $e^-$ cloud	0.05-40	$\text{F-F} \cdots \text{F-F}$