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.

Definition

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

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.

Concept Ladder

Attraction $\propto$ 1/energy
$\propto$ Stability

Rack your Brain

How do atoms combined to form molecules?

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.

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.

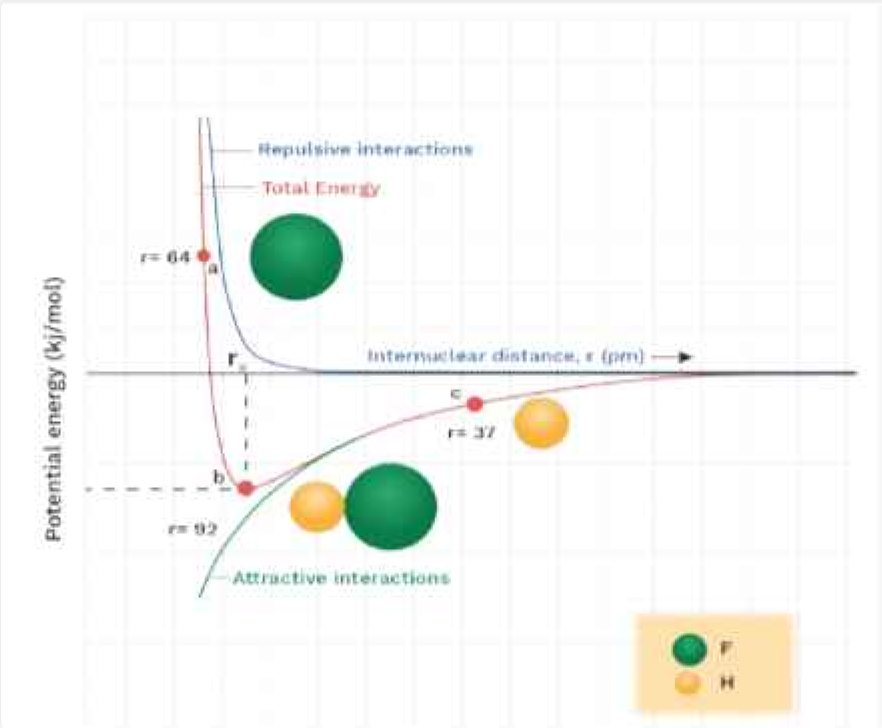
(ii) Decrease in Potential Energy — When two atoms approaches to each other then there is force of repulsion due to nucleus of two atoms & also force of attraction between nucleus of one atom & electron of another atoms.

Rack your Brain

Why inert gases are generally unreactive?

Rack your Brain

Why do atoms form bonds?



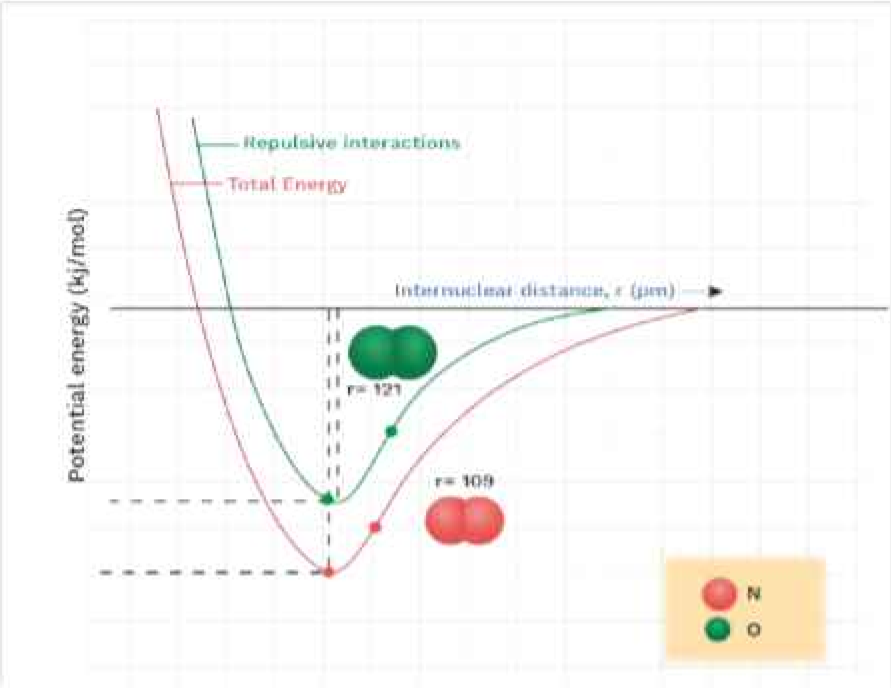
- At point (b) force of attraction is dominating so PE decreases & when PE becomes min. then bond is formed. When atom is made more closer, repulsion increases. Hence, after point (b) PE increases.
- During molecule formation attraction > repulsion PE decreases.
- ● Between two atoms, when at any particular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

Concept Ladder

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

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.



- 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	$\dot{\mathrm{H}}$
Helium (He)	2	$\ddot{\mathrm{H}}\mathrm{e}$
Lithium (Li)	2, 1	$\dot{\mathrm{L}}\mathrm{i}$
Carbon (C)	2, 4	$\cdot\underset{\cdot}{\dot{\mathrm{C}}}\cdot$
Nitrogen (N)	2, 5	$:\underset{\cdot}{\dot{\mathrm{N}}}\cdot$

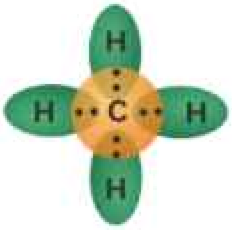
Octet Rule

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.

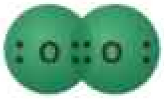
Rack your Brain

Does CO satisfy the octet rule?

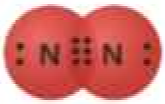
Ex.



CH_4



O_2



N_2

Exceptions of Octet Rule :

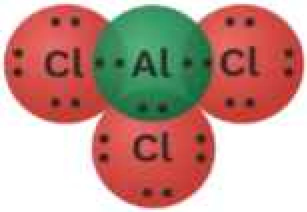
(1) **Electron Deficient Molecules:** Those molecules having less than 8 e^-.

Ex:

$BeCl_2$

Be has only 4 electrons

$AlCl_3$



Al has only 6 electrons

(2) **Odd Electron Molecules :** In molecules with odd number of electron like nitrogen dioxide, NO_2 and nitric oxide, NO, the octet rule is not satisfied for all the atoms

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

(3) Some noble gases (example Xe and Kr) also combine with O_2 and F to form a no. of compounds like XeF_2, $XeOF_2$, KrF_2 etc.,

Octet Rule does not account for the shape of molecules.

Concept Ladder

BF_3, BCl_3, BBr_3, BI_3 all are covalent compounds and not follow octet rule.

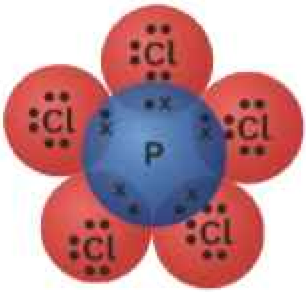
AlF_3 is ionic compound and $AlCl_3$, $AlBr_3$, AlI_3 are covalent compound.

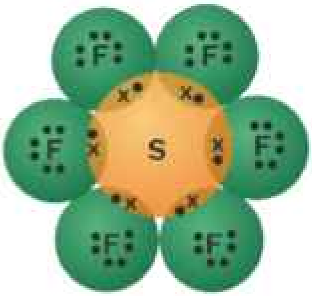
(4) It does not explain the relative stability and energy of the molecules.

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

E.g. PCl_5, SF_6, IF_7, SF_4, XeF_4

These Compounds also known as Hypervalent Compound.





Species	Valence e^-
PCl_5	10
SF_6	12
IF_7	14
SF_4	10
XeF_4	12

Concept Ladder

d-block metal ion generally contain 9 to 17 e-

They follows octet rule in their maximum oxidation state [Sc^{+3}, Ti^{+4}, V^{+5}, Ca^{+6}, Mn^{+7}]

Rack your Brain

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

Concept Ladder

Pseudo inert gas configuration

Cations which contain 18 electrons in outermost orbit

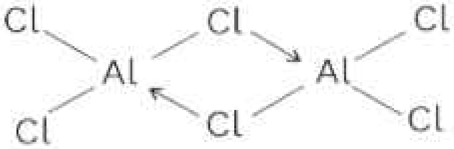
E.g. Ga^{+3}, Cu^{+}, Ag^{+}, Zn^{+2}, Cd^{+2}, Sn^{+4}, Cd^{+2} etc.

Q.1 AlF_3 is a ionic compound but rest of the members are covalent.

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

Dimer Formation

$2AlCl_3 \longrightarrow Al_2Cl_6$



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

Q.2 Octet rule is followed by :

(1) Al_2Cl_6 (2) AlF_3 (3) Both (4) None of these

A.2 (3) Al_2Cl_6 (dimer)

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

(1)Al_2Cl_6 (2) Al_2Br_6 (3) Ga_2Cl_6 (4) Al_2F_6

A.3 (4) Al_2F_6 form ionic compound

Note : $\left.\begin{array}{l}\text{Dimer of } AlCl_3 Al_2Cl_6 \\ \text{Dimer of } AlBr_3 Al_2Br_6\end{array}\right\}$ Coordinate bond

Polymer:

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

Ex : PVC, Nylon

Q.4 $BeCl_2$ follows octet rule in :

(1) Monomer (2) Dimer

(3) Polymer (4) All

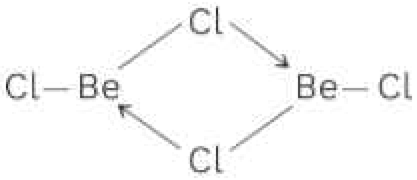
A.4 **$BeCl_2$**

Cl—Be—Cl

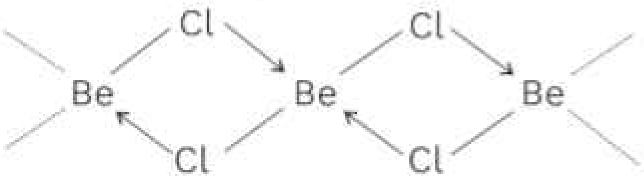
Valence electrons = 4

"Does not exist"

$(BeCl_2)_2$



$(BeCl_2)_n$



Valence electrons = 8

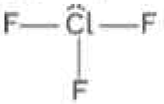
For $BeCl_{2(g)}$ octet is not completed but for $BeCl_{2(s)}$ octet is completed.

Q.5 Which is super octet.

(1) BF_3 (2) PF_3

(3) ClF_3 (4) None of these

A.5 (3) ClF_3



$F-\ddot{Cl}-F$ with F below Cl

Central atom contains 10 electrons

Duplet configuration H^-, Li^+, Be^{+2} → All are duplets

Q.6 In which compound both ions follows octet rule

(1) NaH (2) NaF

(3) MgO (4) 2 & 3

A.6 (4) NaH or Na^+H^- - does not follows octet

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

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

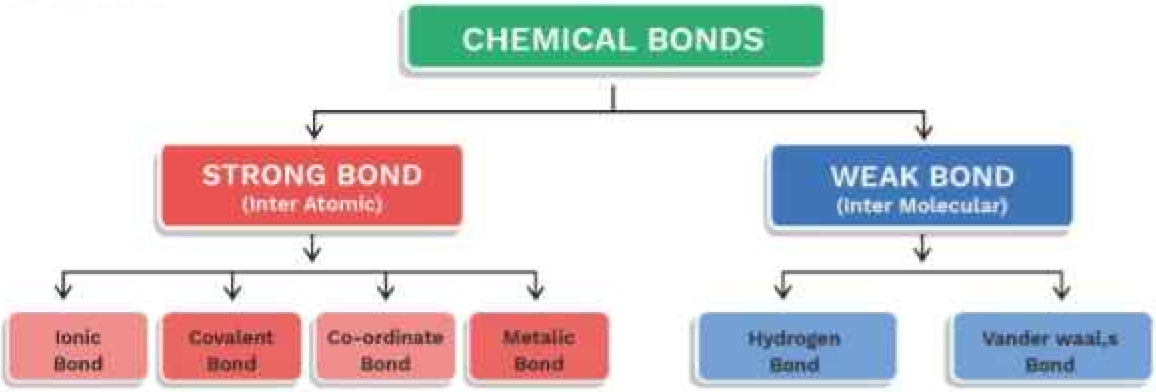
(3) NeF_2 (4) XeO_2F_2

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.

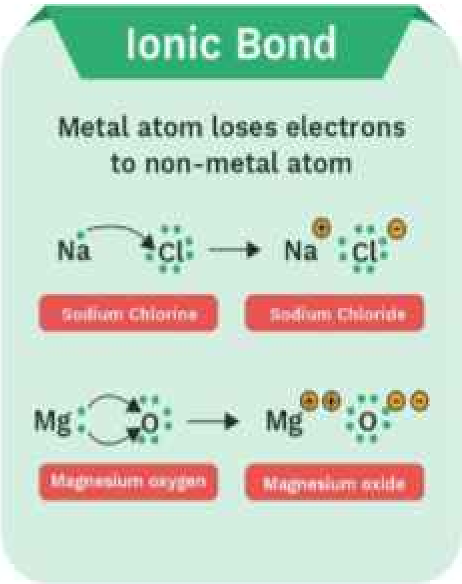
Chemical Bond



(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.



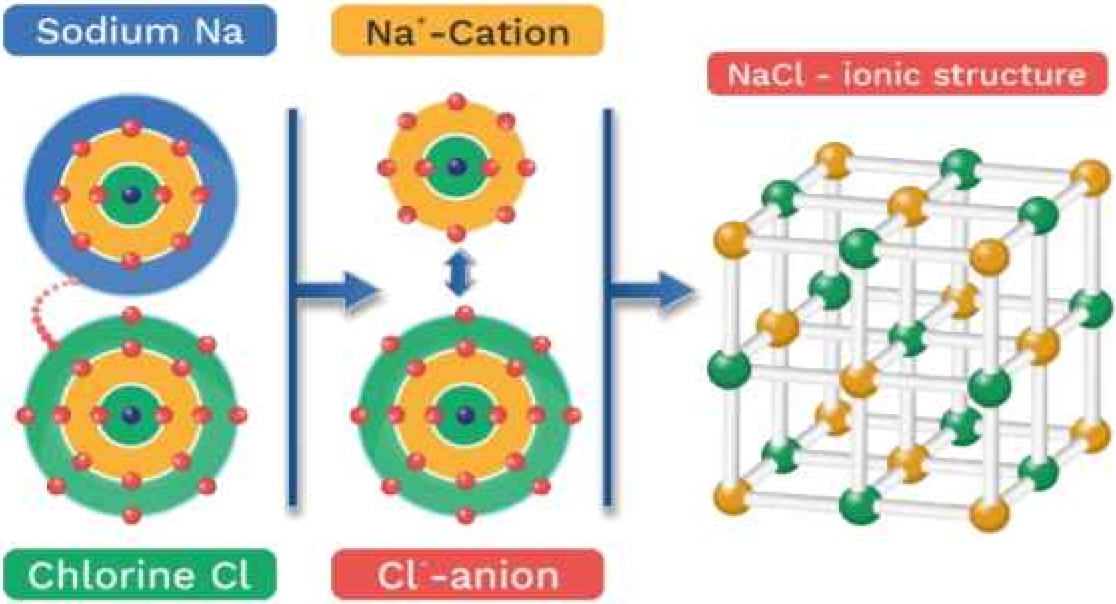
Concept Ladder

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]**

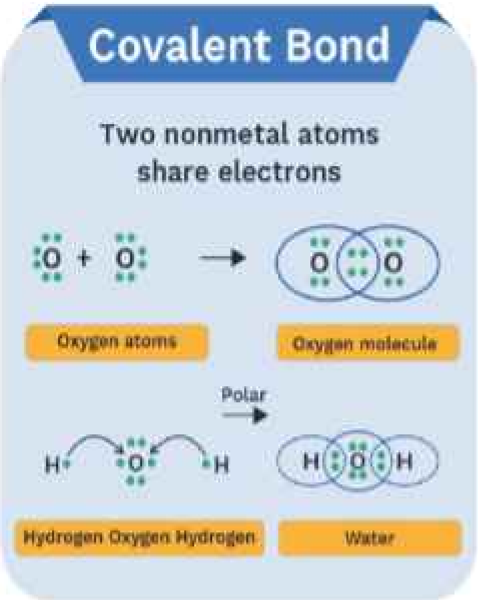
(1) Ionic	(2) Metallic
(3) Covalent	(4) Dipole



(2) Covalent bond :

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

Ex : CO_2, CCl_4, NCl_3, CS_2 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_4
(2) $CaCl_2$
(3) NH_4Cl
(4) H_2O

(3) Coordinate bond :

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

Ex:

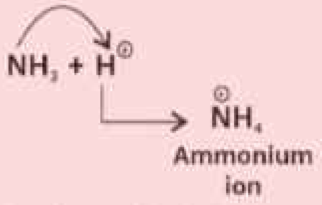
(a) $H_2\ddot{O}: + H^+ \longrightarrow H_2\ddot{O}\rightarrow H$

(b) $\ddot{N}H_3 + BH_3 \longrightarrow H_3N\rightarrow BH_3$

(c) $\ddot{N}H_3 + HCl \longrightarrow NH_3 \rightarrow Cl$

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) NH_4Cl
(2) $AlCl_3$
(3) NaCl
(4) Cl_2

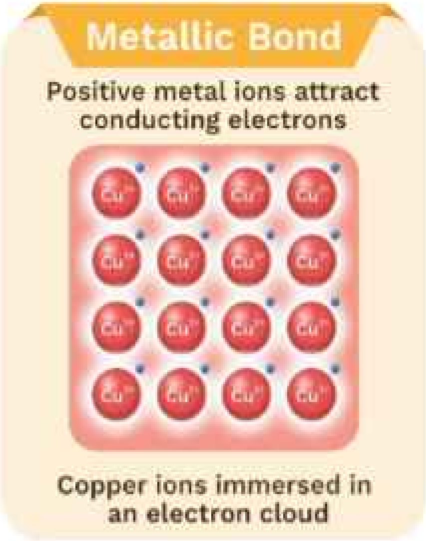
Concept Ladder

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

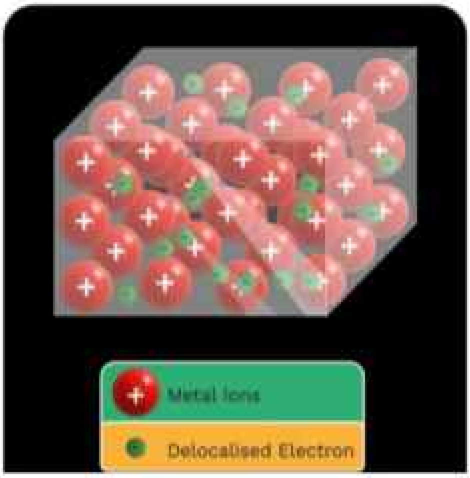
Rack your Brain

Which one stronger ionic or covalent bond?

Ex : $Na_{(s)}$, $Cu_{(s)}$ etc.



- Metals are malleable and ducticle.
- Metallic leusture 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 = Ag > Cu > Au > Al.



Concept Ladder

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

Previous Year's Question

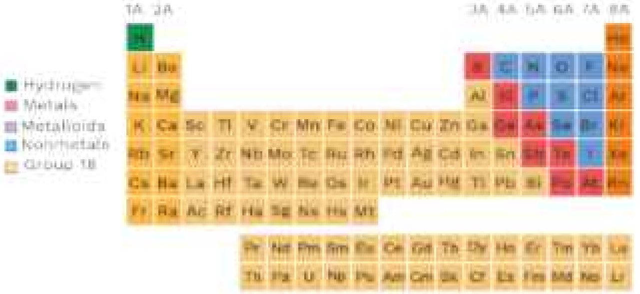
Which of the following does not apply to metallic bond **[AIPMT]**

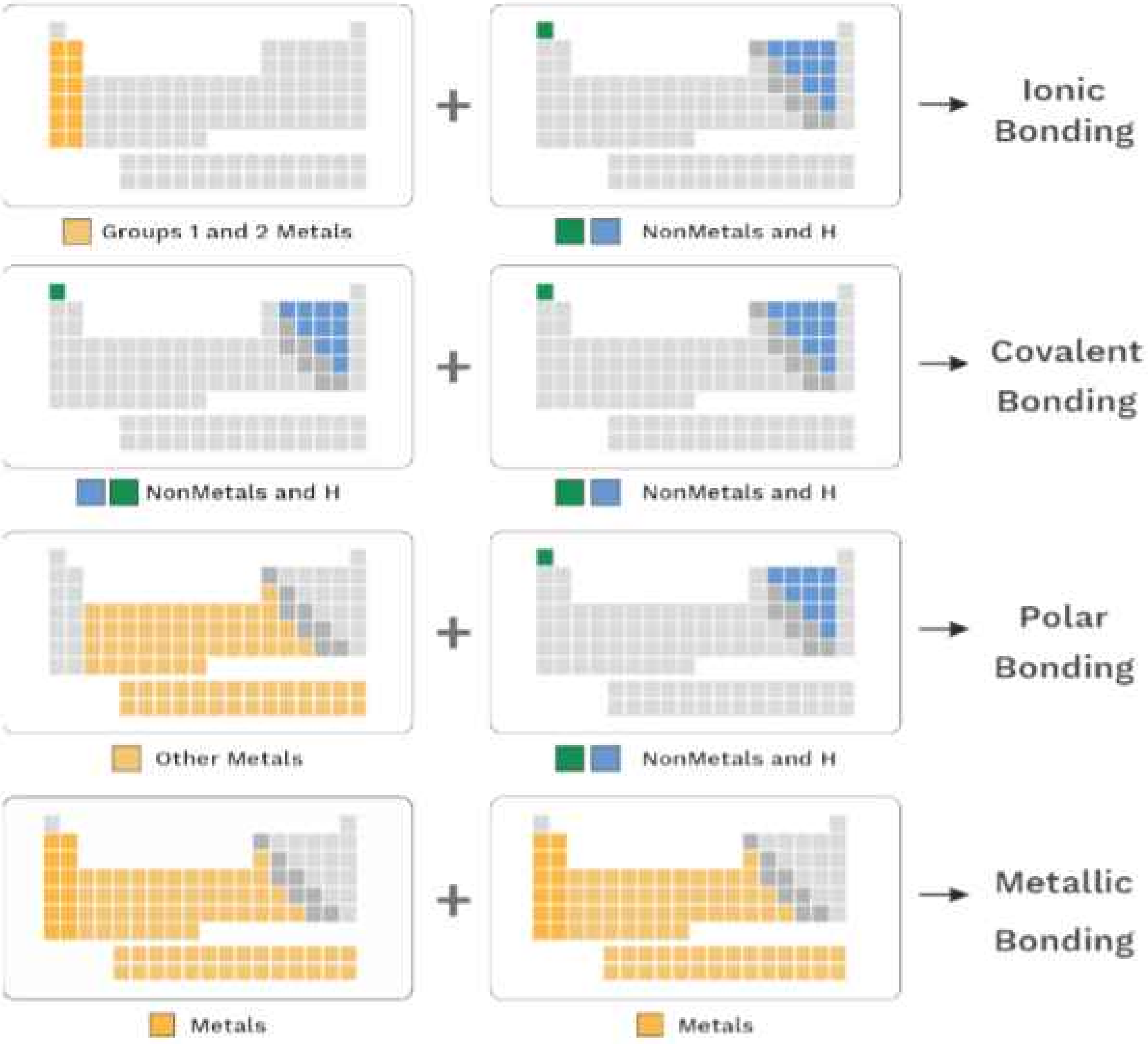
(1) Overlapping valency orbitals
(2) Mobile valency electrons
(3) Delocalized electrons
(4) Highly directed bonds

Concept Ladder

The strength of Metallic Bond is directliy related to the positively charge on the metal ion.

CHEMICAL BONDING
ROAD MAP





Groups 1 and 2 Metals + NonMetals and H → Ionic Bonding

NonMetals and H + NonMetals and H → Covalent Bonding

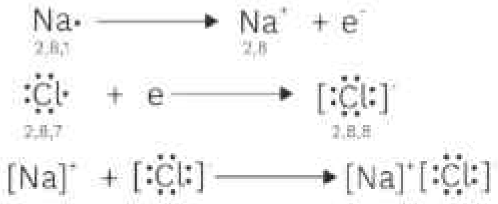
Other Metals + NonMetals and H → Polar Bonding

Metals + Metals → Metallic Bonding

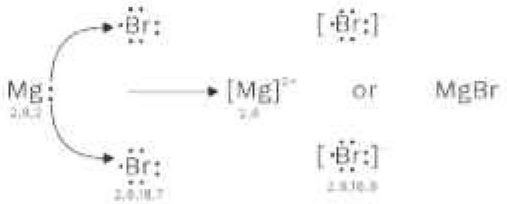
Ionic Bond or Electrovalent Bond

Number of e-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 & VIIIA group elements. Strong Ionicbond 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 Parodic Table.
- Distance between the two elements in periodic table is directly proportioanl to the ionic character of bond.
- % ionic character $16\Delta + 3.5\Delta^2$, where Δ is the electronegativity difference.

Concept Ladder

- Ionic bond is form 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^+ and Cl^- 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 compound do not have molecular formula. It has only empirical formula. eg. NaCl is the empirical formla of sodium choride.

- Compounds of Mg like MgH_2, MgF_2, MgO & Mg_2C_3 ionic in nature
- Similarly **compounds of Be has only one ionic compound (Be_2C)**
- All acids are covalent in gaseous or pure state but have ionic & conducting nature in water. Ex. – HF, HCl, HI, HNO_3 H_2SO_4 etc.

$$\underset{\text{covalent}}{HF} + aq \longrightarrow H^+_{(aq)} + F^-_{(aq)}$$

Rack your Brain

Why ionic bond is non directional?

Q.10 To find Ionic character in NaCl

A.10 EN for Na–0.9, EN for Cl–3

$\Delta EN = 3 - 0.9 = 2.1$

Percentage ionic character $= 16\Delta + 3.5\Delta^2$

$= 16 \times 2.1 + 3.5 \times (2.1)^2$

$= 49.13$

Q.11 Type of bond present in HCl

(1) Ionic (2) Electrovalent

(3) Covalent (4) Polar Covalent

A.11 (4) Polar Covalent

Note :

(a) Trend in Ionic character; LiCl < NaCl < KCl < RbCl < CsCl

(b) Ionic character NaI < NaBr < NaCl < NaF, greater the ΔEN greater will be the ionic character

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

A.12 Ionic character – $MF > MCl > MBr > MI$ and

Covalent character $MF < MCl < MBr < MI$

Covalent character is opposite of ionic character

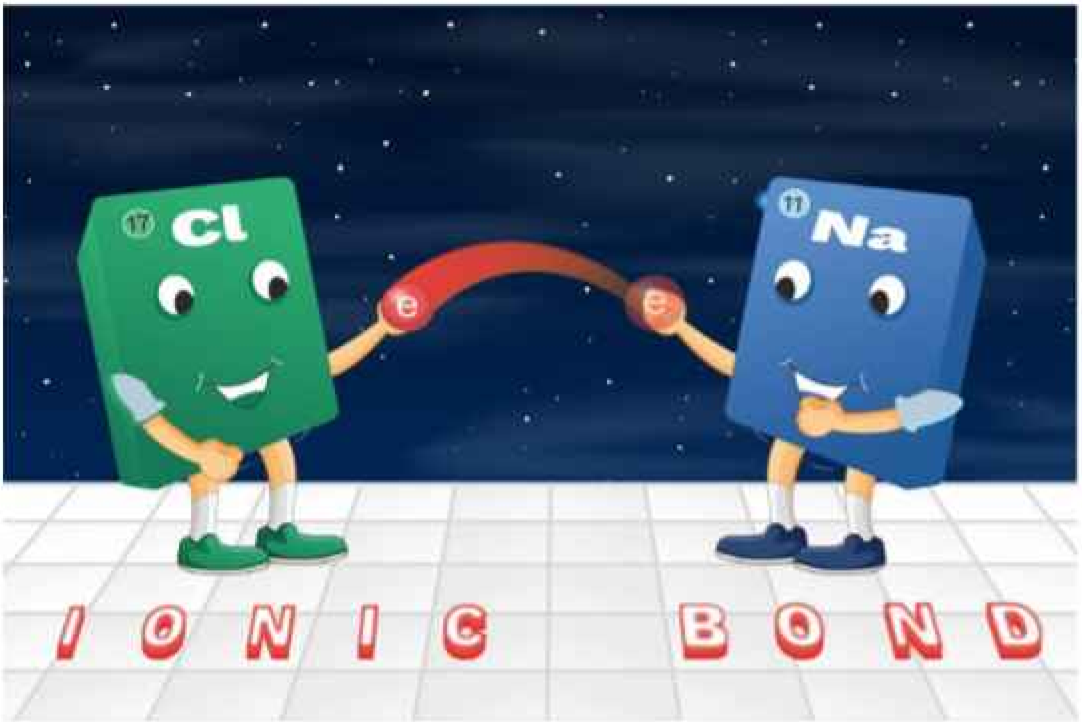
Q.13 Among NaCl, MgS & AlP which has the lowest Ionic character

A.13 Ionic character – $NaCl > MgS > AlP$, AlP has the lowest ionic character

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

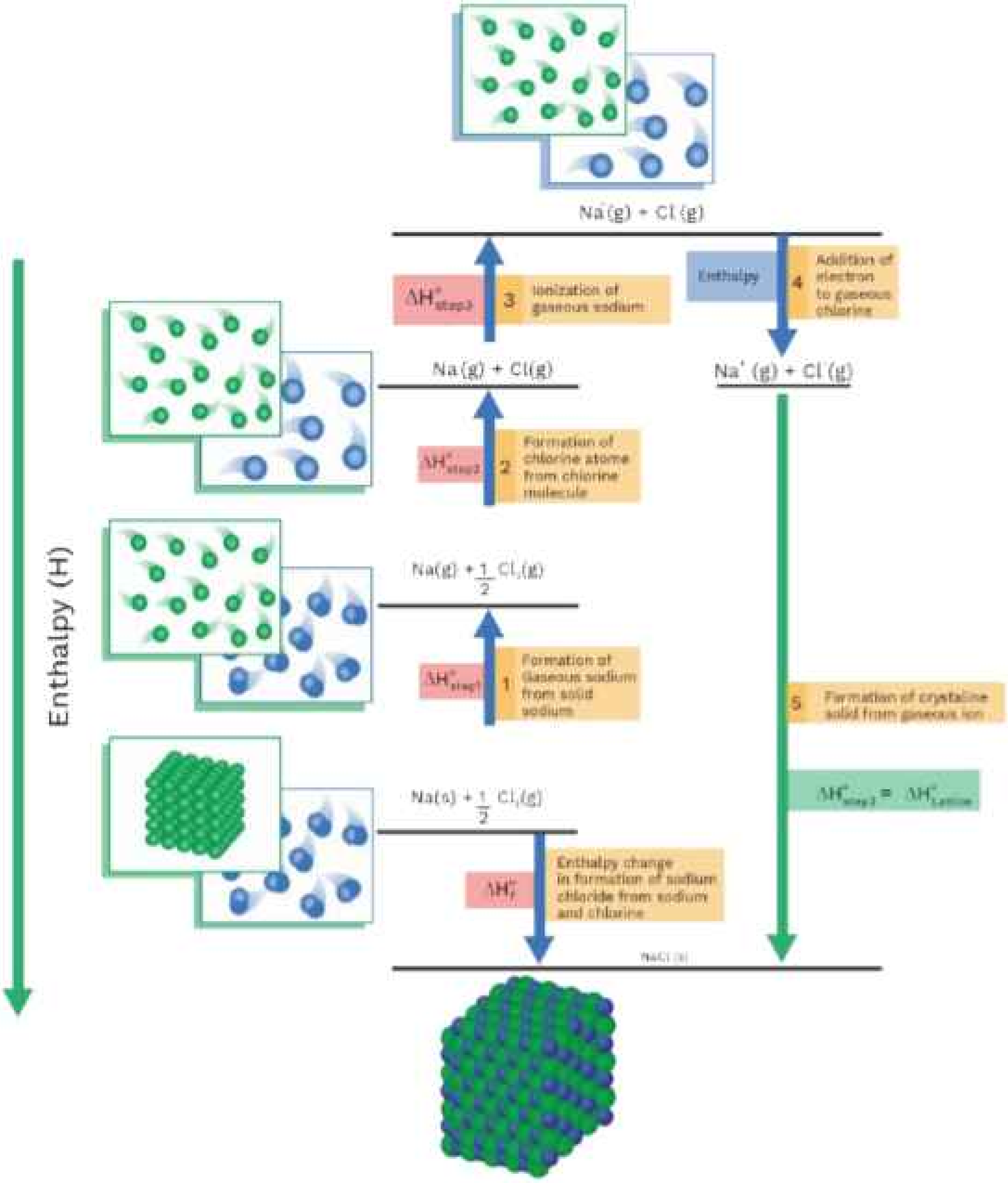
A.14 In KCl, K belongs to s-block and ΔEN of KCl > ΔEN of CuCl

($\because$ Ionic character $\propto \Delta EN$)



Born-Haber Cycle

$$\Delta H_f^0 = \Delta H_{(sub)} + \frac{1}{2}\Delta H_{(diss)} + I.E - E.A - U$$, where U 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)

$$\text{Ex.}\quad \left.\begin{array}{l} Na^{+} > Mg^{+2} > Al^{+3} \\ Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+} \end{array}\right\} \text{Cation formation tendency}$$

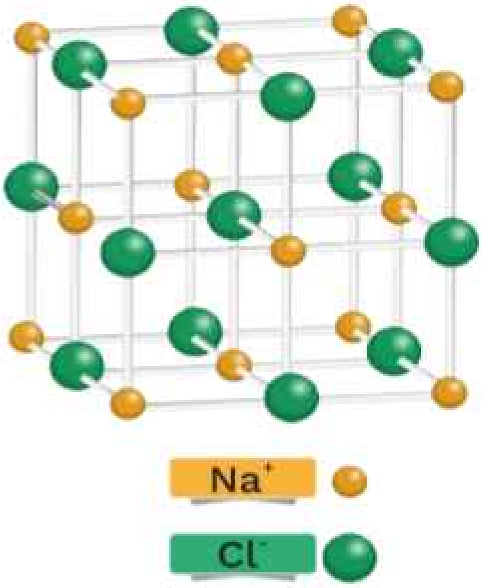
(b) Electron affinity (E.A.)

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

$$\text{Ex.}\quad \left.\begin{array}{l} Cl^{-} > F^{-} > Br^{-} > I^{-} \\ F^{-} > O^{2-} > N^{3-} \end{array}\right\} \text{Anion formation tendency}$$

(c) Lattice energy (L.E.)

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



Concept Ladder

Lesser Ionisation energy → Greater tendency to form cation.

Concept Ladder

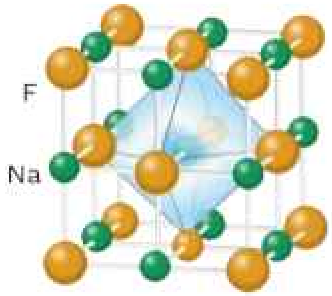
Higher electron affinity → Greater tendency to form anion.

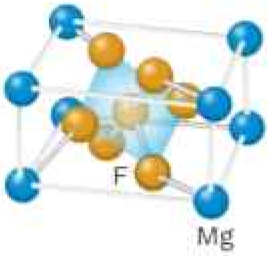
Definitions

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 µ $\frac{1}{r^+ + r^-}$

Factors affecting lattice energy

(i) Magnitude of charge :

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

$$\xrightarrow[\qquad\qquad\qquad\qquad]{\begin{matrix} NaF & MgF_2 & AlF_3 \\ Na^+ & Mg^{+2} & Al^{+3} \end{matrix}}$$

- Lattice energy increases
- Size of cation decreases

(ii) Size of Cation

Lattice energy $\propto \frac{1}{r^+ + r^-}$

$$\xrightarrow[\qquad\qquad\qquad\qquad]{LiCl \quad NaCl \quad KCl \quad RbCl \quad CsCl}$$

- 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 in not involved in 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 ($DH_f^0 = -U$)

Q.16 Which reaction represent LE for magnesium fluoride

(1) $Mg(g) + F_2(g)$ (2) $Mg(g) + 2F(g)$
(3) $Mg^{+2}(g) + F^-(g)$ (4) $Mg^{+2}(g) + 2F^-(g)$

A.16. 4), During release of LE ions will combine to form magnesium chloride 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. $LiF < MgF_2 < MgO < Al_2O_3$ (lattice energy)
$LiH > NaH > KH > CsH$ (size of cation increases lattice energy decreases)
$NaF > NaCl > NaBr > NaI$ (size of anion increases lattice energy decreases)
$NaF < MgF_2 < AlF_3$ (lattice energy)

Concept Ladder

Hardness of Ionic compound $\propto$ LE $\propto$ charge $\propto$ 1/size.

Properties of Ionic Compound

(a) Physical State

Ionic compound are hard, crystalline and brittle due to string electrostatic force of attraction. Ionic bond is non-directional in nature because the electrostatic bond is act in all directions.

Covalent and coordinates bonds are directional in nature

Q17 Why physical state of halogens vary down the group that is F_2, Cl_2 are gaseous Br_2 is liquid and 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

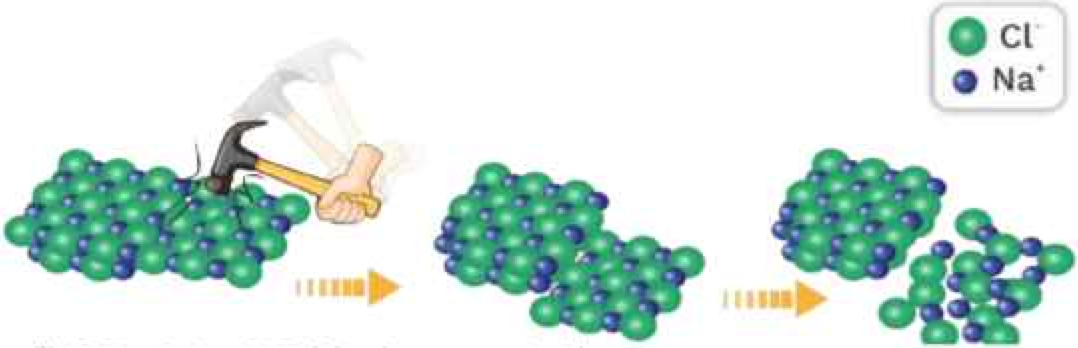
(1) NaCl(s) (2) Na(s)

(3) $CCl_4(l)$ (4) None

A.18 (3), NaCl(s) – ionic bond, Na(s) – Metallic bond, $CCl_4(l)$ – 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_2 < AlF_3 (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.

Concept Ladder

Conductivity $\propto$ Mobility

$\propto$ 1/size of atom

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.

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 compoudns

[AIPMT]

(1) AgCl (2) KCl

(3) $BaCl_2$ (4) $CaCl_2$

Example.

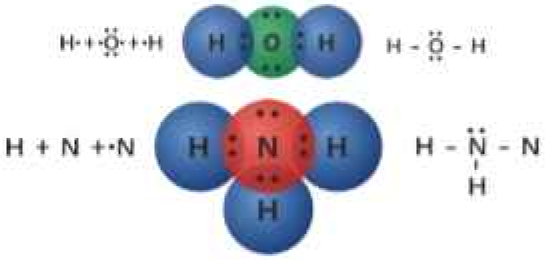
	Na^+	F^-	Mg^{2+}	O^{-2}
Valency	+1,	–1	+2,	–2
Electronic configuration	2, 8	2, 8	2, 8	2, 8
Similarly	Ca^{+2}	$2Cl^{-1}$	$2K^{+1}$	S^{-2}
	2, 8, 8	2,8,8 2,8,8	2,8,8 2,8,8	2, 8, 8

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_2, Cs_2, CCl_4 etc.)
- Less electropositive metal and non-metal ($SnCl_4$, $FeCl_3$ etc.)
- Electrons which are not participate in bond formation are known has 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

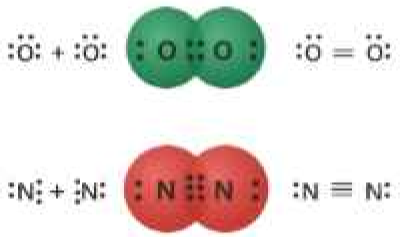
Previous Year's Question

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.

Previous Year's Question

Which one is the electron deficient compound

[AIIMS]

(1) ICl (2) NH_3
(3) BCl_3 (4) PCl_3

Rack your Brain

Is HCl is ionic or covalent?

Be B C (Absence of vacant orbital)

N O F (Presence of vacant orbital)

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

Ex. Be form BeF_2 and BeH_2 in its excited state and it has total 4 electrons in its outer most shell after formation of bond.

- For 2nd period elements promotion of electrons is not possible in excited state as the is no availability of 2d subshell.

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

Ex. N (ground state)

Previous Year's Question

Ionic and covalent bonds are present in

[AIPMT]

(1) CCl_4 (2) $CaCl_2$
(3) Na_4Cl (4) H_2O

- For the formation of ammonia (NH_3), no need of exited state as it has already 3 unpaired electron in its ground state.

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

Ex. P (ground state)

(PCl_3)

P (excited state)

(PCl_5)

Characteristics of Covalent compounds

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

Eg. Sulphur, Phosphorus, Iodine (Soft Solids). F_2 and Cl_2 (gas), 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. H_2O, liq. 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
- CsF has maximum ionic character but contain 0.1% of covalent character due to polarisation.

Concept Ladder

In case of nitrogen NH_3, NCl_3 can be formed but NH_5, 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

(a) Tendency of anion to get polarise.

(b) 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

(I) Smaller the size of cation.

(II) larger the size of anion.

(III) greater the charge on cation and anion.

(IV) ion does not have inert gas configuration, but it possesses pseudo inert gas configuration (18 electrons in the ultimate shell).

LiCl	Size of cation ↑	$BeCl_2$
NaCl	Polarization ↓	$MgCl_2$
Kcl	Covalent character ↓	$CaCl_2$
CsCl	Ionic Character ↑	$BaCl_2$

Note

(a) In s-block compounds, $BeCl_2$ has maximum covalent character & Cscl has minimum covalent character.

(b) 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_2H_6
(2) NH_4Cl
(3) HCl
(4) $AlCl_3$

(c) Polarizing power of cation is expressed in ionic potential (ϕ).

(d) Covalent character ∝ polarsation ∝ Ionic potential (ϕ) ∝ charger/size.

(e) Along the period covalent character increases, ϕ increases and polarizing power increasing.

Concept Ladder

Covalent character ∝ polarisation ∝ charge on cation ∝ size of anion

Q.21 Which has maximum covalent character?

(1) AlF_3 (2) $AlCl_3$ (3) $AlBr_3$ (4) AlI_3

A.21 (4). AlI_3 – $AlF_3 < AlCl_3 < AlBr_3 < AlI_3$ (Covalent character)

Q.22 Among $FeCl_2$ and $FeCl_3$, which one has high polarizing power.

A.22 $FeCl_2 < FeCl_3$ (polarizing power)
In $FeCl_2$, the charge on Fe is +2 where as in $FeCl_3$, Fe has +3 charge
Polarizing power $\propto$ charge

Q.23 Which cation polarizes more CN^- ion
(1) K^+ (2) Rb^+ (3) Cs^+ (4) Ag^+

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

Hydration Energy

- Amount of release energy during hydration of one mole of ionic solid.
- Polarity of solvent increases, ε_R increases (ε_R for H_2O 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) Al^{+3} (2) Li^+ (3) Be^{+2} (4) Rb^+

A.24 (4)

Solubility

(a) Solubility of metal + non metal compounds

$$M^+X^-_{(s)} + (x+y)H_2O \rightarrow M^+(H_2O)_x + X^-(H_2O)_y$$

; $\Delta s = +ve$

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

(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 ioni s highly is highly hydrated?

Concept Ladder

Generally metal hallides are water soluble except chloride, Br^-, Iodides of Pb, Hg and Ag.

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

(Mainly applicalbe for s-block elements

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

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

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

(3) Solubility in organic solvent $\propto$ polarisation or covalent character

Compare solubility order

(a) $LiF < NaF < KF < RbF < CsF$

$\longrightarrow$

Size of cation increases,
Lattice Energy Increases

(b) $BeCO_3 > MgCo_3 > CaCO_3 > SrCO_3 > BaCO_3$

$\longrightarrow$

Size of cation increases,
Hydration Energy decreases

(c) $BaF_2 < BaCl_2 < BaBr_2 < BaI_2$

$\longrightarrow$

Size of anion increases,
Lattice Energy decreases

(d) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

$\longrightarrow$

Size of Cation increases,
Hydration Energy decreases

Rack your Brain

Why Alkali metal hydroxydes and $Ba(OH)_2$ are water soluble, rest are insoluble?

Previous Year's Question

Which of the following is least soluble

[AIPMT]

(1) BaF_2
(2) SrF_2
(3) CaF_2
(4) MgF_2

Concept Ladder

All metal nitrates are water soluble.

(e) $NaF < NaCl < NaBr < NaI$ Na^{+} smaller

(f) $CsF > CsCl > CsBr > CsI$ Cs^{+} larger

(g) $Be(OH)_2 < < < Ba(OH)_2$ OH^{-} smaller

(h) $Li_2O < < < Cs_2O$ O^{-2} smaller

(i) $LiClO_4 > > > CsClO_4$ ClO^{4-} larger

(j) $BeSO_4 > > > BaSO_4$ SO_4^{-2} larger

(k) $$\underbrace{LiCl > NaCl > KCl}_{\text{Size of Cl}^{-}\text{ is larger}} \underbrace{< RbCl < CsCl}_{\text{Size of Cl}^{-}\text{ is smaller}}$$

(l) $NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$ (Due to larger size of)

(m) $LiCO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$ (Due to larger size of)

(Lattice energy increases which dominates due to crystal structure)

(n) $MgF_2 < CaF_2 < SrF_2 < BaF_2 < BeF_2$ (Size of F^{-} is smaller)

(o)

$$\left.\begin{array}{l} BeF_2 > BeCl_2 > BeBr_2 > BeI_2 \\ AgF > AgCl > AgBr > AgI \\ PbF_2 > PbCl_2 > PbBr_2 > PbI_2 \\ HgF_2 > HgCl_2 > HgBr_2 > HgI_2 \end{array}\right] \begin{array}{l} \text{Anionic size increases} \\ \text{polarisation increases} \\ \text{solubility decreases} \end{array}$$

(p) $Na_2S > ZnS > CuS$ ($Cu^{+2} < Zn^{+2}$, size increases and polarisation decreases)

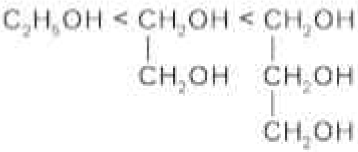
Solubility of organic compounds

Ex: Incorrect solubility order is

(a) $CH_3OH > C_2H_5OH > C_3H_7OH$

(b) $CH_3OH > CH_3OCH_3 > C_6H_6$

(c)



$$C_2H_5OH < \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} < \begin{array}{c} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{array}$$

(d) O-nitrophenol > p-nitrophenol

Concept Ladder

If common ion is smaller then solubility increases from top to bottom. If common ion is larger then solubility decreases from top to bottom.

Rack your Brain

Why all alkali metals salts are water soluble except LiF, Li_2CO_3 and Li_3PO_4?

Concept Ladder

Mostly metal sulphates are water soluble except $CaSO_4$, $SrSO_4$, $BaSO_4$ and $PbSO_4$.

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

(Melting point),	Diamond	>	NaCl	>	H_2O	>	CO_2
	Covalent Bonding		Ionic Bonding		H - bonding		V W F

(a) Melting point of metal + non metal compounds

Melting point ∝ Lattice energy (Mainly applicable for Na^+, K^+, Rb^+ or F^-, O^-, H^-)

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

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

Rack your Brain

Why NH_3 has more melting point compare to SbH_3?

Melting Point orders

(a) $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

$$\xrightarrow[\text{Size of cation increases, polarisation decreases}]{}$$

(b) $NaF < MgF_2 < AlF_3$

$$\xrightarrow[\text{Charge increases, Lattice Energy increases}]{}$$

(c) $NaCl > MgCl_2 > AlCl_3$

$$\xrightarrow[\text{Charge increases, Polarisation increases}]{}$$

(d) $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$ (anion size increases, polarisation increases)

(e) $Na_2O < MgO < Al_2O_3$ (charge increases,

Concept Ladder

For non metallic molecules if intermolecular attration 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) NaF < MgO < SCN < TiC (charge increases, Lattice energy increases)

(g) NaCl > KCl > RbCl > CaCl > LiCl (size of cation increases, lattice energy decreases)

Note : LiCl is a covalent compound due to small size of lithium.

(h) $MgF_2 > CaF_2 > SrF_2 > BaF_2 > BeF_2$ (Size of cation increases, lattice energy decreases)

Note : BeF_2 is a covalent compound

(i) $SnCl_2 > SnCl_4$ (charge increases, polarisation increases)

(j) $CaCl_2 > FeCl_2 > FeCl_3$ (charge increases, polarisation increases)

(k) Metal fluoride < Metal oxide (Charge increases, lattice energy increases)

Melting point and Boiling point of non metallic molecules

(a) $\underset{(VWF)}{CH_3-O-CH_3} < \underset{(H-bonding)}{C_2H_5OH}$ (Boiling point)

(b) $\underset{(VWF)}{(CH_3)_2SO_4} < \underset{(H-Bonding)}{H_2SO_4}$ (Boiling point)

(c) $\underbrace{\underline{H_2 < CO_2}}_{(VWF)} < \underset{(H-bonding)}{H_2O}$

(Molecular mass increases, VWF increases)

(d) $\underset{(H-Bonding)}{CH_3OH} < \underset{(H-Bonding)}{H_2O}$

Concept Ladder

Hardness = Diamond > B_4C (Artificial) > SiC > Al_2O_3 carborundum

Rack your Brain

Why SbH_3 has more boiling point compare to NH_3?

Previous Year's Question

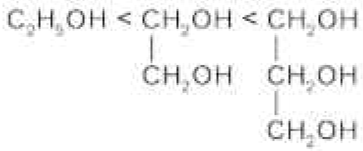
Electrovalent compounds do not have

[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.

(e) 

$C_2H_5OH < \underset{CH_2OH}{\underset{|}{CH_2OH}} < \underset{CH_2OH}{\underset{|}{\underset{CH_2OH}{\underset{|}{CH_2OH}}}}$

(f)

$\underset{(VWF)}{HCl} < \underset{(H\text{–}Bonding)}{HNO_3} < \underset{(H\text{–}Bonding)}{H_2SO_4}$

(Melting point)

(g) $H_2O < D_2O$

(Hydrogen bond strength increases, melting point increases)

(h) $CH_4 < SiH_4 < GeH_4 < SnH_4$

(Molecular mass increases, VWF increases, B.Pt increases)

(i) $PH_3 < AsH_3 < SbH_3 < NH_3$ (M.P.)

Mass ↑ VWF ↑

(j) $HCl < HBr < HI < HF$ (B.P.)

(k) $HF < NH_3 < H_2O$ (B.P.)

(l) $HCl < HBr < HF < HI$ (M.P)

(m) $PH_3 < AsH_3 < NH_3 < SbH_3$ (B.P.)

Melting point of Metals

Melting point of metals Metallic bond strength (MBS)

(a) Li > Na > K > Rb > Cs (size increases, MBS decreases, Melting point decreases)

Rack your Brain

Why HF has more boiling point compare to HI?

Concept Ladder

Giant Molecules = Diamond, Silica $(SiO_2)_x$, Borazone $(BN)_x$, Carborundum (SiC), Norbide (B_4C)

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¬eff increases)

(c) Zn > Cd > Hg (Melting point and boiling Point decreases, interelectronic repulsion increases)

(d) Be > Ca > Sr > Ba > Mg (Melting point decreases, size increases, MBS decreases)

Note:

- Maximum malting point in Boron family ⟶ B
- Minimum melting point in Boron family ⟶ Ga

Thermal Stability

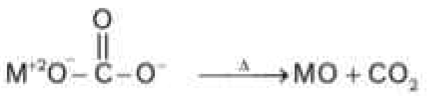
$$H_2O(l) \xrightarrow{100^\circ C} H_2O(g) \xrightarrow{2200^\circ C} H_2 + H_2O_2$$

(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

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$



$$M^{+2}O^{-}-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-} \xrightarrow{\Delta} MO + CO_2$$

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

- $LiHCO_3$ and IIA bicarbonates don't exist in solid state due to high polarising power of cation.

Concept Ladder

Maximum Melting point in all elements ⟶ C (Diamond). Minimum Melting point in elements ⟶ He.

Rack your Brain

Why $BeCO_3$ is kept in CO_2 atmosphere due to thermal stability?

Concept Ladder

Maximum Melting point in metals ⟶ W (Tungsten). Minimum Melting point in metals ⟶ Hg

Thermal stability order

$BeF_2 > BeCl_2 > BeBr_2 > BeI_2$
$AgF > AgCl > AgBr > AgI$
$PbF_2 > PbCl_2 > PbBr_2 > PbI_2$
$HgF_2 > HgCl_2 > HgBr_2 > HgI_2$

Anionic size increases
polarisation increases
solubility decreases

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 is 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

CO_3^{2-}, SO_4^{2-} and OH^- of Na, K, Rb, Cs don't decomposed (only melt) due to larges size of cation.

Rack your Brain

Why XeF_3 does not exist?

Concept Ladder

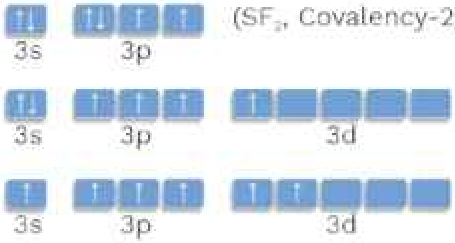
SF_3 does not exists in nature as sulphure has only valancy of 2,4,6.

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

Ex. S (ground state) (SF$_2$, Covalency-2)

S (I^{st} excited state) (SF$_4$, Covalency-4)

S (II^{nd} excited state) (SF$_6$, Covalency-6)



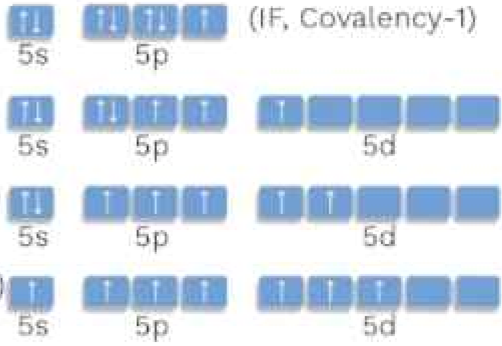
Iodine (E.C -$1s^2 2s^2 2p^6 3s^2 3p^4$)

Ex. I (ground state) (IF, Covalency-1)

I (I^{st} excited state) (IF$_3$, Covalency-3)

I (II^{nd} excited state) (IF$_5$, Covalency-5)

I (III^{rd} excited state) (IF$_7$, Covalency-7)



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$_3$ exists but FCl$_3$ does not as F belongs to IInd 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 exited state by having covalency of 2,4,6 and 8 in its I^{st}, II^{nd}, III^{rd} and IV^{th} exited state respectively. (XeF$_2$, XeF$_4$, XeF$_6$ etc.)

Q.25 PCl_5 exists but PI_5 does not similarly SF_6 exists but SCl_6 does not and also IF_7 exist but 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) NCl_5 (2) PCl_5 (3) PI_5 (4) All of these

A.26 (2), PCl_5 exists

NCl_5 – does not exists as 2d orbital is not present

PI_5 – due to steric repulsion

Q.27 From the following which compound exists.

(1) SCl_2 (2) SCl_4 (3) SCl_6 (4) (1) and (2)

A.27 (4), 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 ether a lone pair or a negative charge must be donated

$$\underset{\text{(donar)}}{F^{-}} + \underset{\text{(acceptor)}}{BF_3} \longrightarrow F^{-}\rightarrow BF_3$$

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

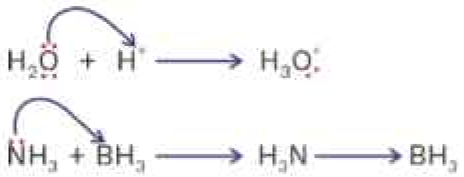
The compound containing co-ordinate bond is

[AIIMS]

(1) SO_3 (2) O_3

(3) H_2SO_4 (4) All of these

Ex:



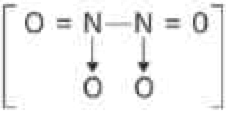
$$H_2\ddot{O} + H^+ \longrightarrow H_3O^+$$

$$\ddot{N}H_3 + BH_3 \longrightarrow H_3N \longrightarrow BH_3$$

Ex. **(a)** N_2O $(N \equiv N \rightarrow O)$

(b) O_3 $\left(O = \ddot{O} \rightarrow O\right)$

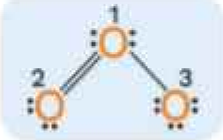
(c) N_2O_4



$$\left[\begin{array}{c} O = \underset{\substack{\downarrow \\ O}}{N} - \underset{\substack{\downarrow \\ O}}{N} = O \end{array}\right]$$

Formal charge

The Lewis structure of O_3 may be drawn as :



The atoms have been numbered as 1, 2 and 3.

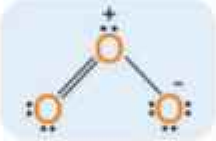
The formal charge on :

The central O atom marked (1) = 6 – 2 – ½ (6) = +1

The end O atom marked (2) = 6 – 4 – ½ (4) = 0

The end O atom marked (3) = 6 – 6 – ½ 2) = –1

Hence, we represent 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 (↔).

Concept Ladder

Formal charge = V – L – ½ 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 PO_4^{3-} ion, the formal charge on each oxygen atom and P–O bond respectively are

[AIPMT]

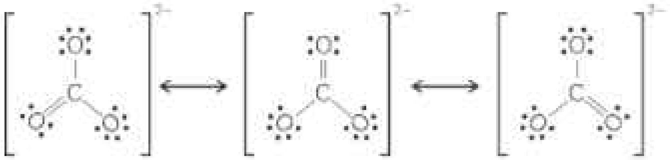
(1) -0.75, 1.75
(2) -0.75, 1.0
(3) -0.75, 0.6
(4) -3, 1.25

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 (CO_3^{2-})



$$\text{Bond order} = \frac{\begin{pmatrix}\text{total number of bond between}\\ \text{two atoms in all the structures}\end{pmatrix}}{\text{Total number of resonating structures}}$$

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

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.

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.

$$AX_pE_q$$

A = central atom

X = surrounding atom

E = nonbonding valence-electron group

p and q are integers

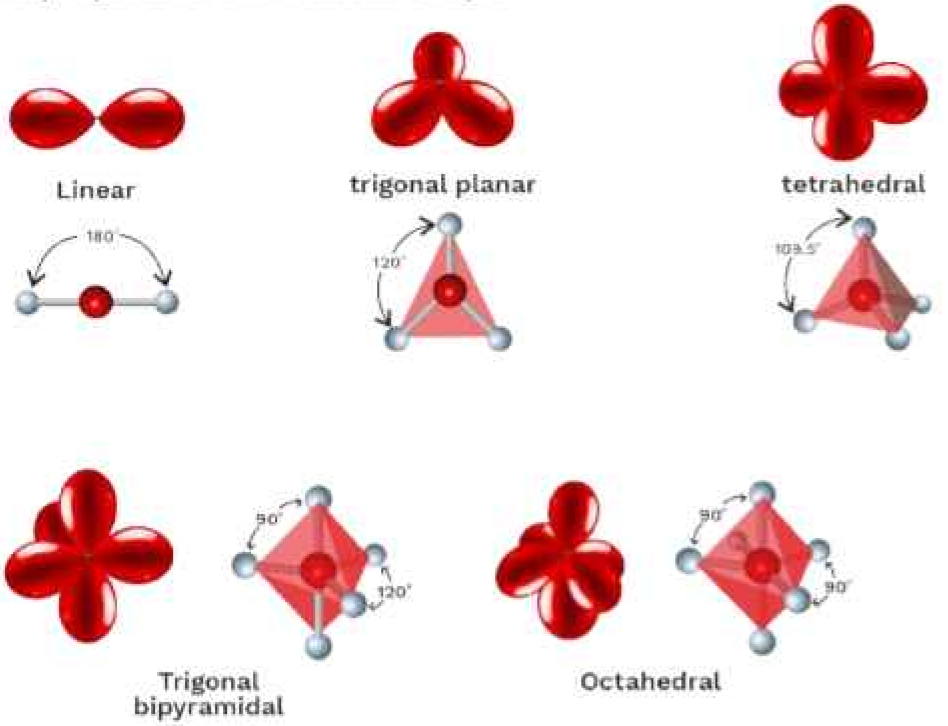
Concept Ladder

Repulsion Order

(a) Lone pair - Lone pair > Lone Pair - Bond Pair > Bond Pair - Bond Pair

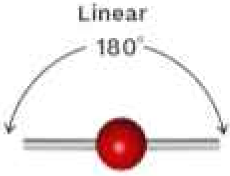
(b) Multiple Bond - Multiple bond > Multiple bond - Single bond > single bond - single bond

Electron-group repulsions and molecular shapes

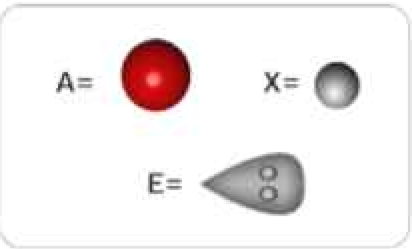


The single molecular shape of the linear electron-group arrangement.

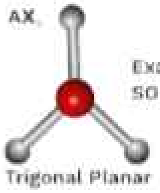
(1)



Linear
Examples:
Cs_2, HCN, BeF_2

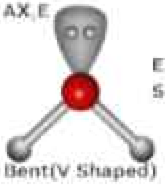


(2) (A)



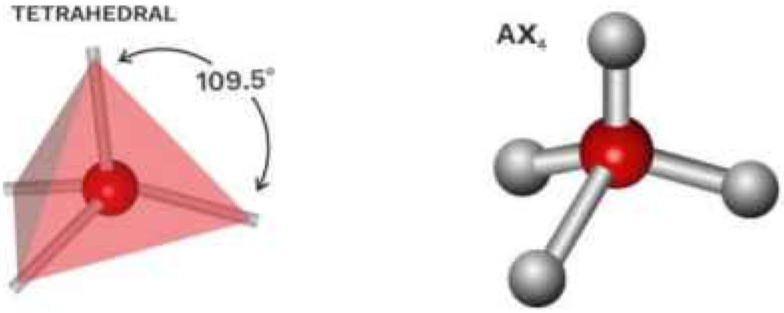
Examples
SO_3, BF_3, NO_3^-, CO_3^{2-}

(B)

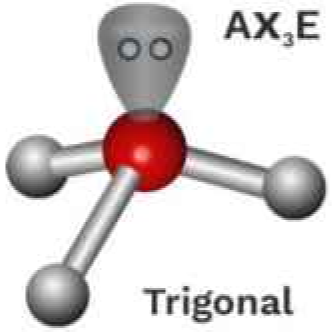


Examples
SO_2, O_3, $PbCl_2$, $SnBr_2$

(3) (a)

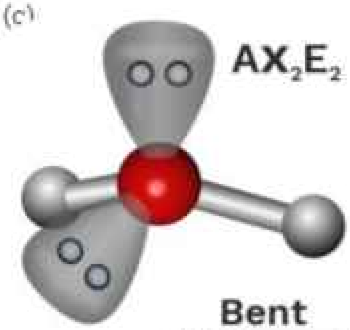


(b)



Trigonal Pyramidal

(c)



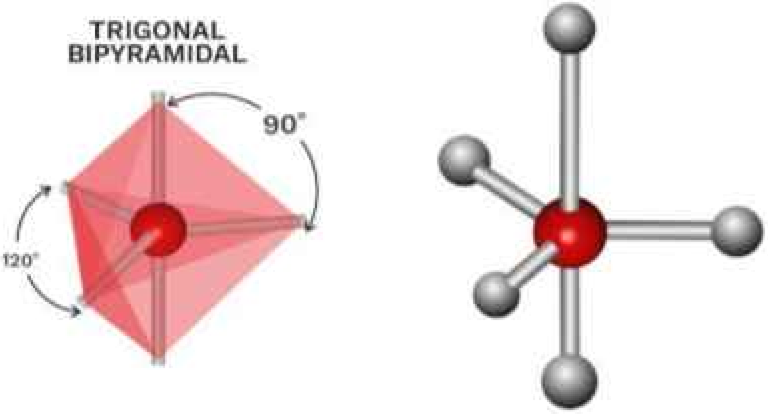
Bent (V Shaped)

Ex: AX_4 : CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-

AX_3E : NH_3, PF_3, ClO_3^-, H_3O^+

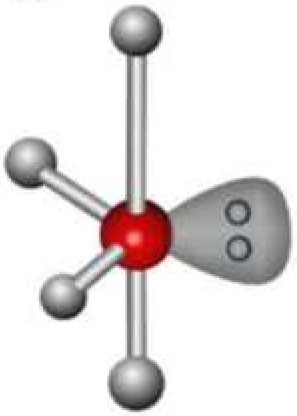
AX_2E_2 : H_2O, OF_2, SCl_{2a}

(4) **(A)**

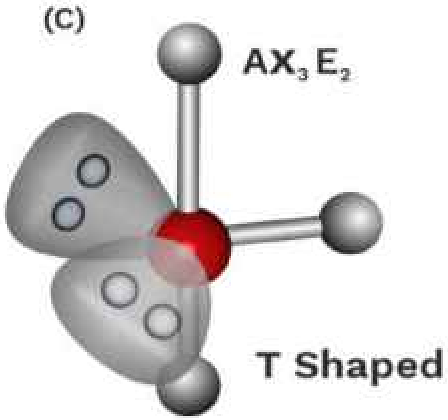


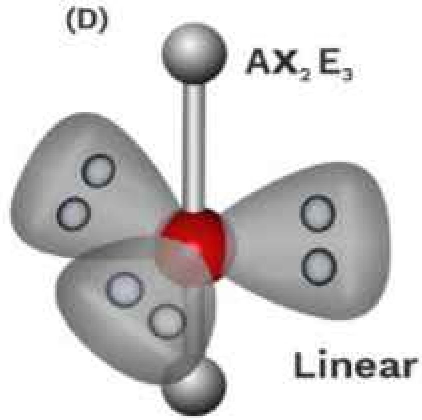
Trigonal Bipyramidal

(B)



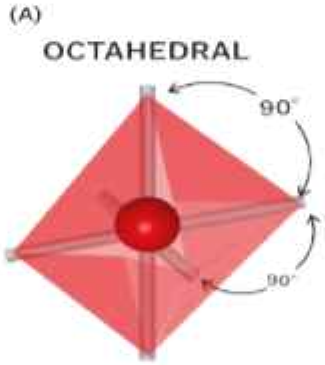
Seesaw

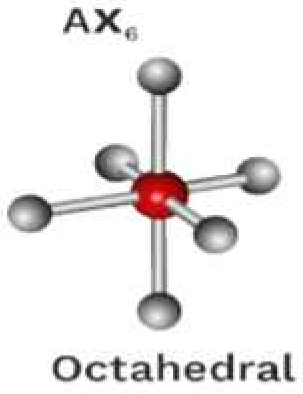


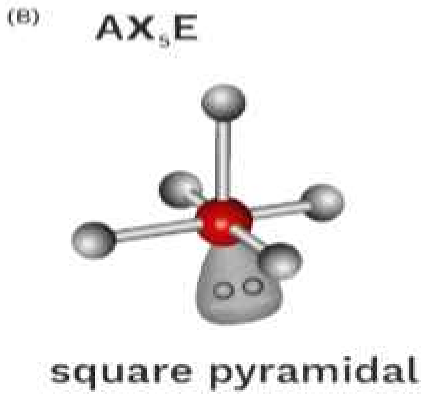


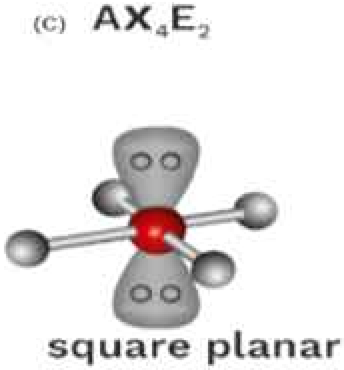
Ex: (a) AX_5 : PF_5, AsF_5, SOF_4, (b) AX_4E : SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$, (c) AX_3E_2 : ClF_3, BrF_3
(d) AX_2E_3 : XeF_2, I_3^-, IF_2^-, Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

(5)

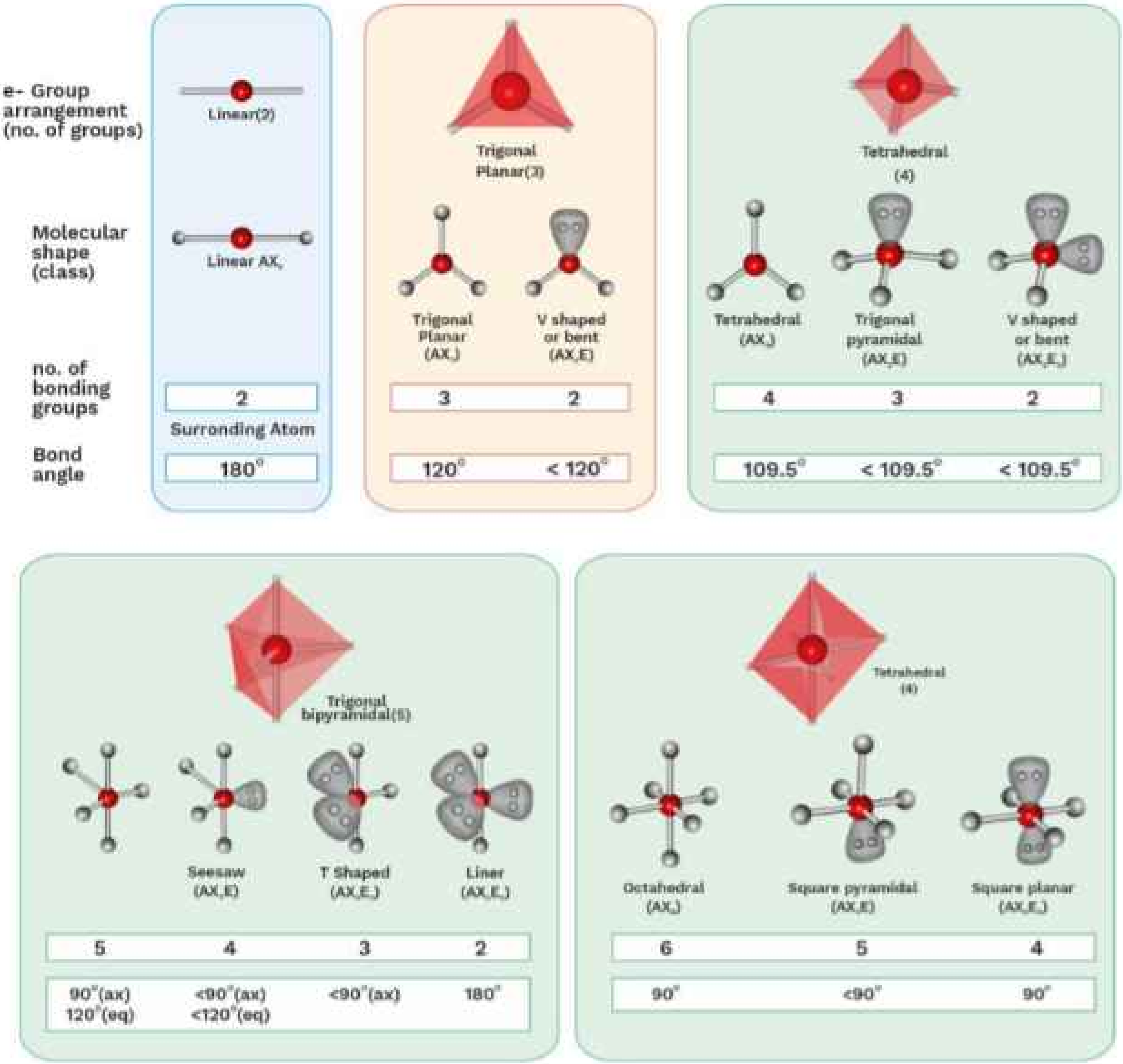








Ex: (a) AX_6 : SF_6, IOF_5 (b) AX_5E : BrF_5, TeF_5^-, $XeOF_4$ (c) AX_4E_2 : XeF_4, ICl_4^-



e- Group arrangement (no. of groups)	Molecular shape (class)	no. of bonding groups	Bond angle
Linear(2)	Linear AX_2	2 Surrounding Atom	180°
Trigonal Planar(3)	Trigonal Planar (AX_3)	3	120°
	V shaped or bent (AX_2E)	2	< 120°
Tetrahedral (4)	Tetrahedral (AX_4)	4	109.5°
	Trigonal pyramidal (AX_3E)	3	< 109.5°
	V shaped or bent (AX_2E_2)	2	< 109.5°
Trigonal bipyramidal(5)		5	90°(ax) 120°(eq)
	Seesaw (AX_4E)	4	<90°(ax) <120°(eq)
	T Shaped (AX_3E_2)	3	<90°(ax)
	Liner (AX_2E_3)	2	180°
Tetrahedral (4)	Octahedral (AX_6)	6	90°
	Square pyramidal (AX_5E)	5	<90°
	Square planar (AX_4E_2)	4	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 σ (sigma) bond takes place.

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

	Overlapping	Inter nulcear Axis	type of bond
1.	s-s	Any axis	σ
2.	$s+p_x$	x-axis	σ
	$s+p_y$	y-axis	σ
	$s+p_z$	z-axis	σ

Any other sp overlapping is not possible

3.	p_x+p_x	x-axis	σ
	p_y+p_y	y-axis	σ
	p_z+p_z	z-axis	σ
4.	p_x+p_x	y or z axis	π
	p_y+p_y	x or z axis	π
	p_z+p_z	x or y axis	π

Concept Ladder

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

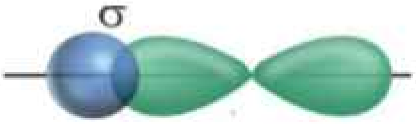
Previous Year's Questions

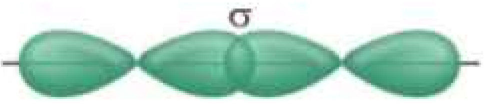
Which of the following molecules has more than one lone pair?

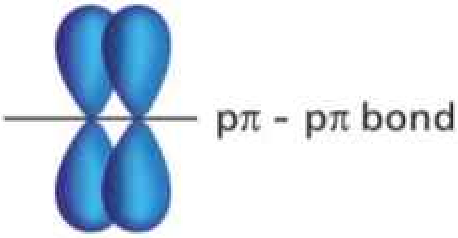
[AIIMS-2016]

(1) SO_2 (2) XeF_2

(3) SiF_4 (4) CH_4

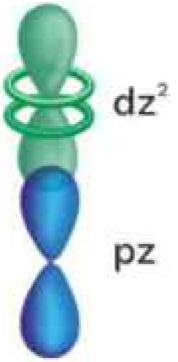






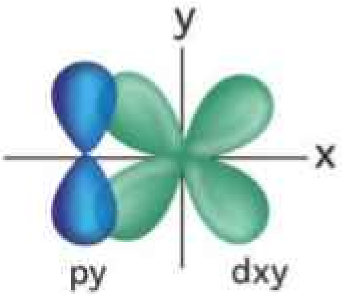
any other pp overlapping is not possible

5.	$p_z+d_{z^2}$	z-axis	σ



Any other p-d axial overlapping is not possible

6.	p_x+d_{xy}	y-axis	π
	p_y+d_{xy}	x-axis	π
7.	p_x+d_{xz}	z-axis	π
	p_z+d_{xz}	x-axis	π
8.	p_y+d_{yz}	z-axis	π
	p_z+d_{yz}	y-axis	π

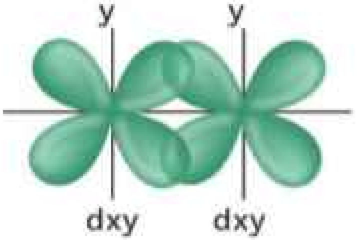


pπ - pπ bond

Any other p-d collaterol overlapping is not possible

d-d overlapping

(a)

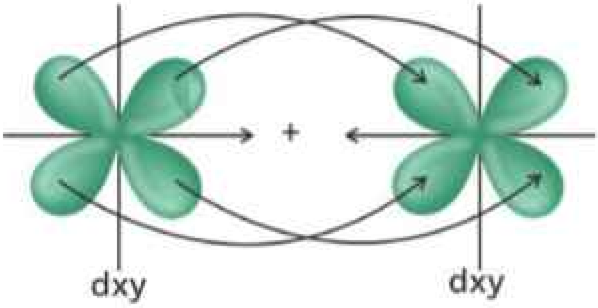


dπ - dπ bond

Rack your Brain

Is s orbital directional or non directional?

(b)



inter nuclear axis
z-axis
δ-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

B.S $\propto$ Extent of overlapping $\propto$ directional properties

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

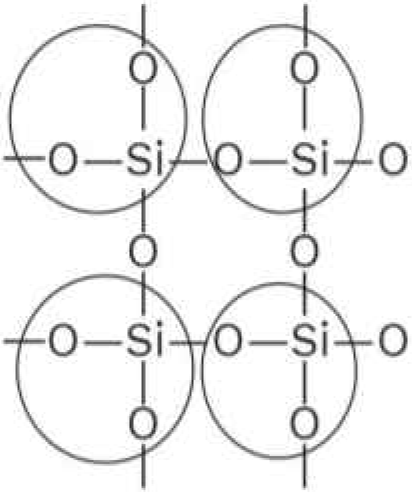
(c) **π bond strength order**

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

1. $N \equiv N$ exists but $P \equiv P$ doesn't exists.
2. O = C = O Stable molecule but O = Si = O doesn't exist

Giant molecule (covalent solid)

Ex: $(SiO_2)_n$ 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 π bond strength.

Rack your Brain

O_2 exists but S_2 does not exists 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 pouling.
- Endothermic process.
- Orbital having almost same energy but have diff. shape can participate in hybridisation.
- Hybrid orbitals always form σ bond except benzyne.
- Size or energy or directional property of hybrid orbitals $\propto \frac{1}{\text{s} - \text{character}}$

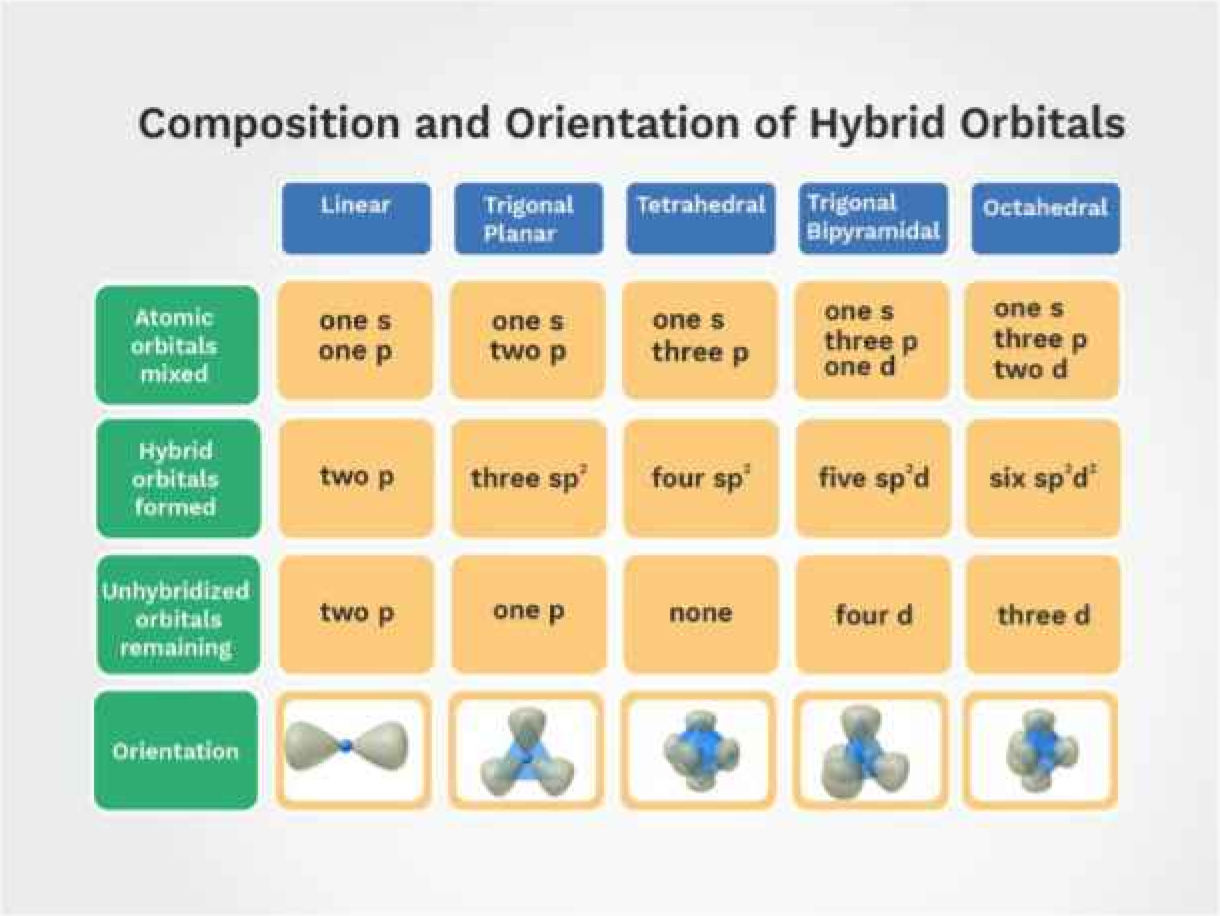
  $sp < sp^2 < sp^3$ size/energy/directional properties (s-character decreases, p-character increases)

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

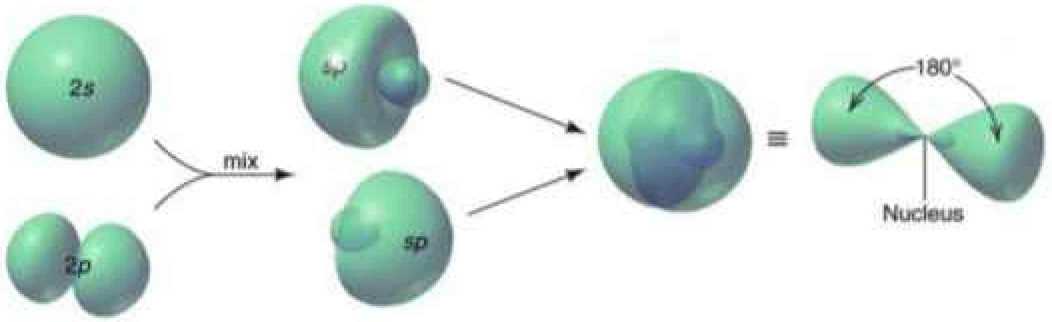


Composition and Orientation of Hybrid Orbitals

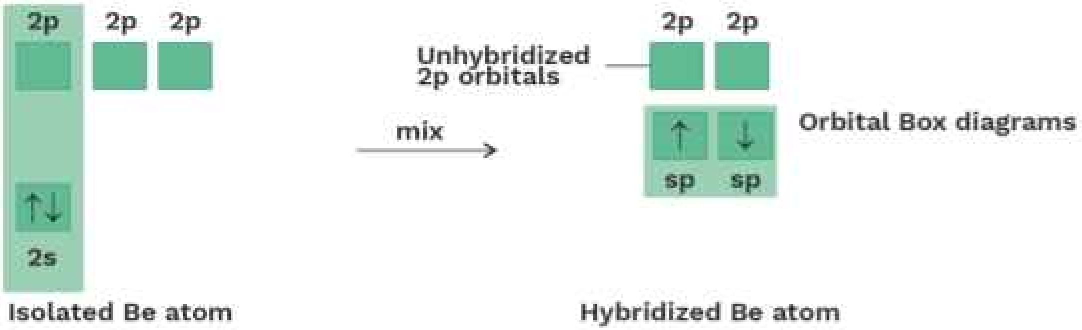
	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two p	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two p	one p	none	four d	three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

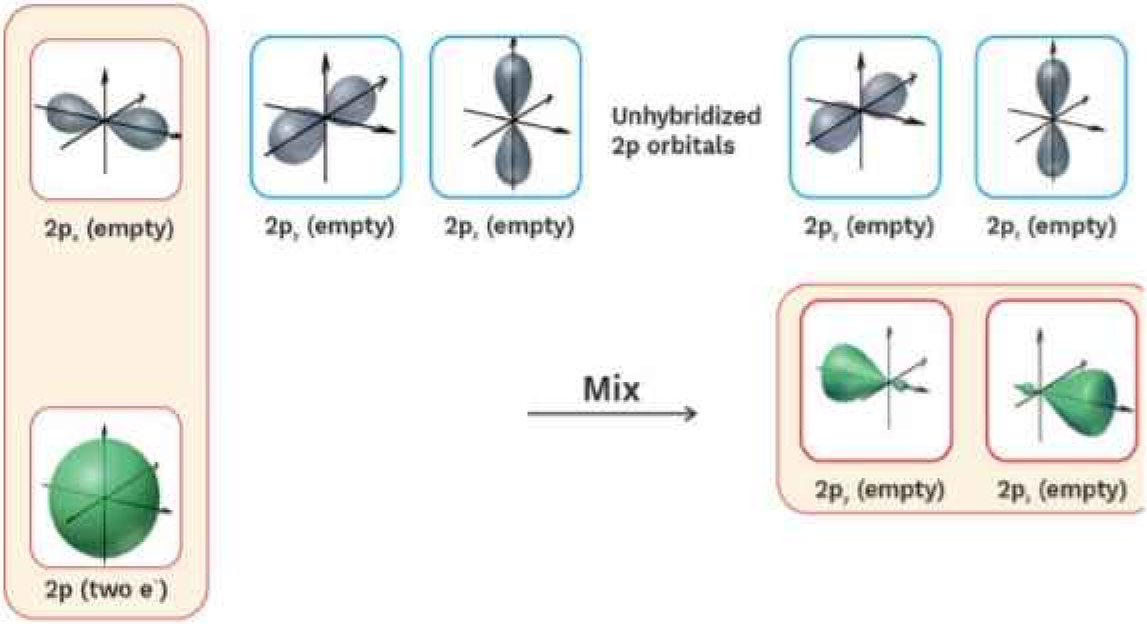
(1) sp Hybridisation

Ex: BeF_2



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

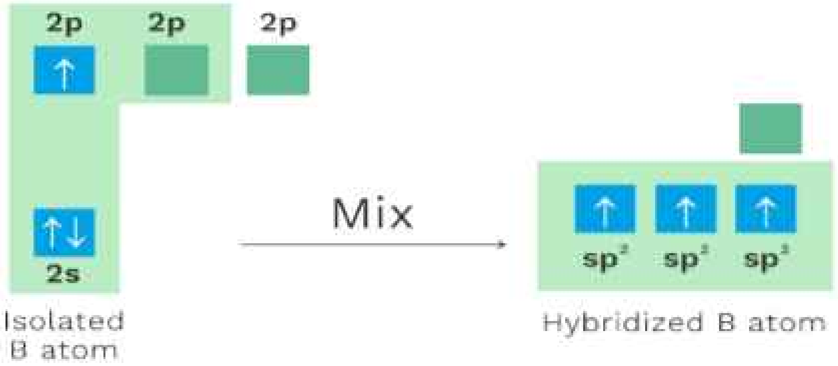




Overlap of Be and Cl orbitals to form BeCl2.

(2) sp^2 Hybridisation

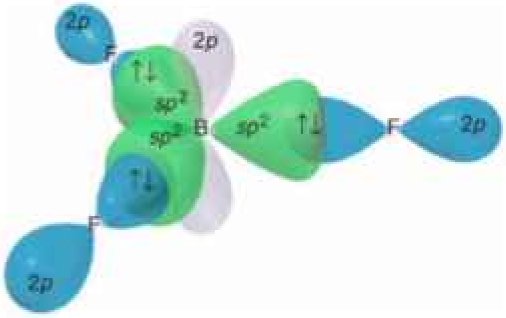
Ex: BF_3



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

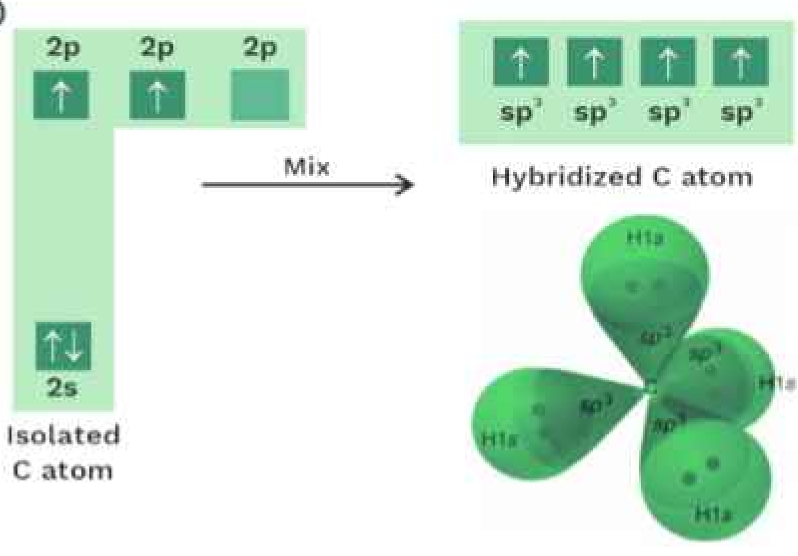
The three sp^2 orbitals to be pointed at the corners of an equilateral triangle, their axes are 120° apart.

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

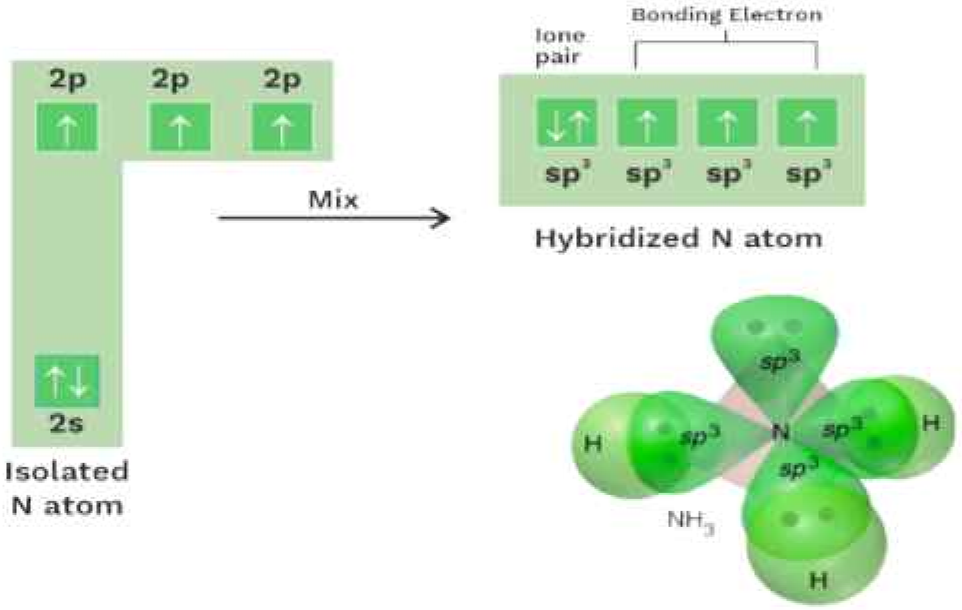


(3) sp^3 Hybridisation

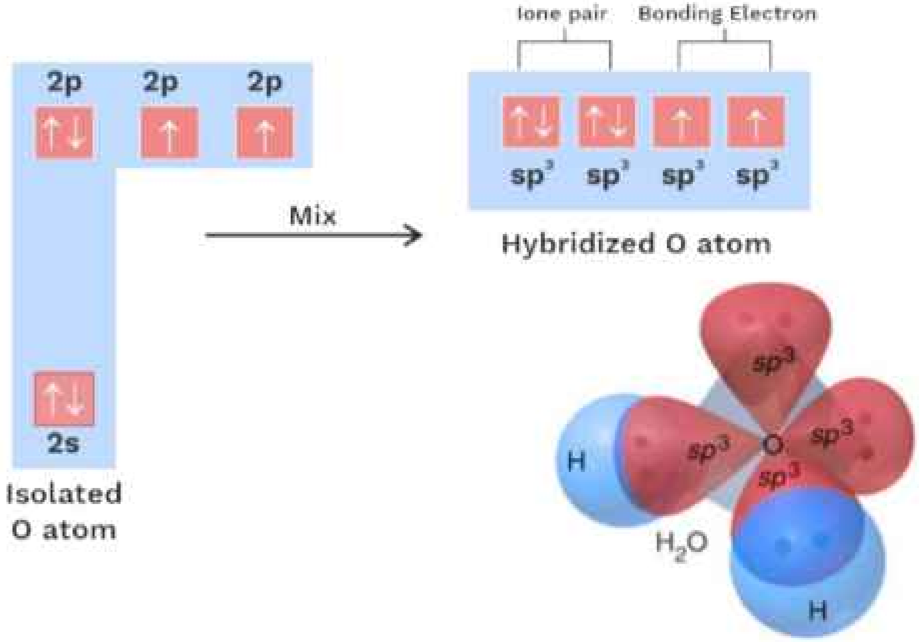
Ex: CH_4 **(Methane)**



NH_3


2p
2p
2p
↑
↑
↑
↑↓
2s
Isolated N atom
Mix
lone pair
Bonding Electron
↓↑
↑
↑
↑
sp³
sp³
sp³
sp³
Hybridized N atom
sp3
H
sp3
N
sp3
H
sp3
NH3
H

H_2O


2p
2p
2p
↑↓
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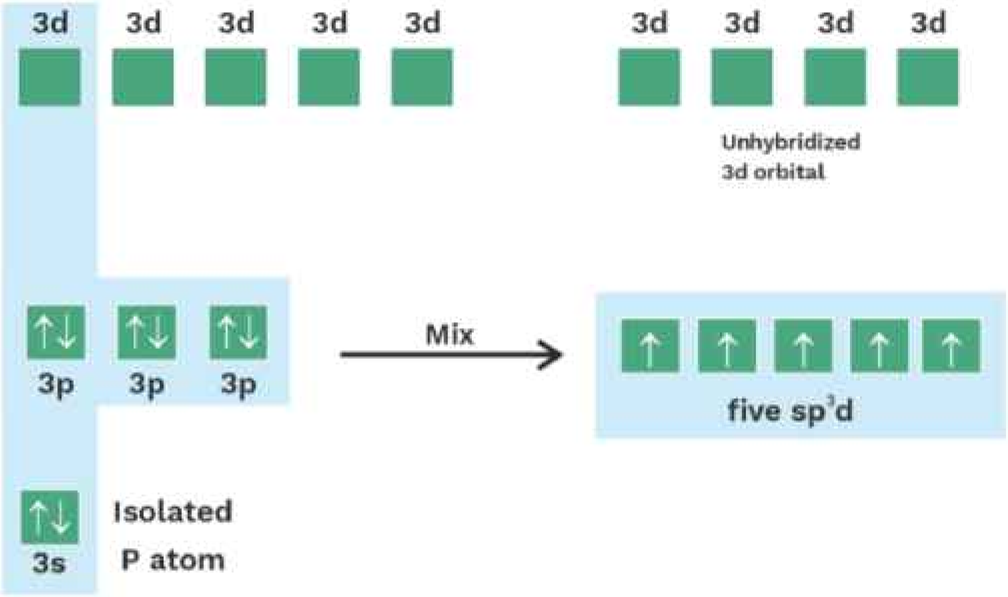
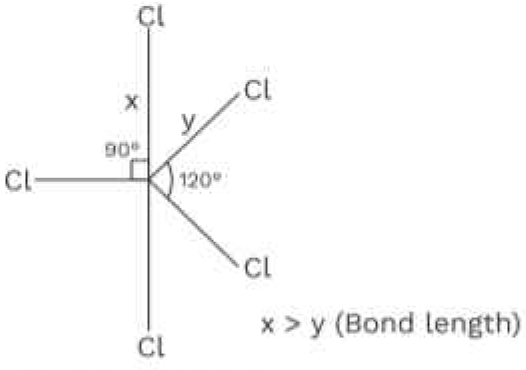
2s
Isolated O atom
Mix
lone pair
Bonding Electron
↑↓
↑↓
↑
↑
sp³
sp³
sp³
sp³
Hybridized O atom
sp3
H
sp3
O
sp3
sp3
H2O
H

(4) sp³d Hybridisation

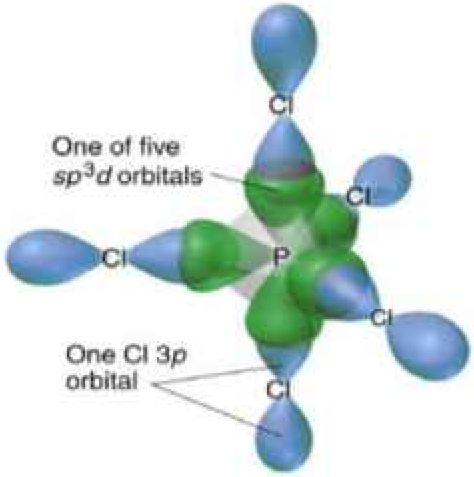
Ex: PCl_5



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

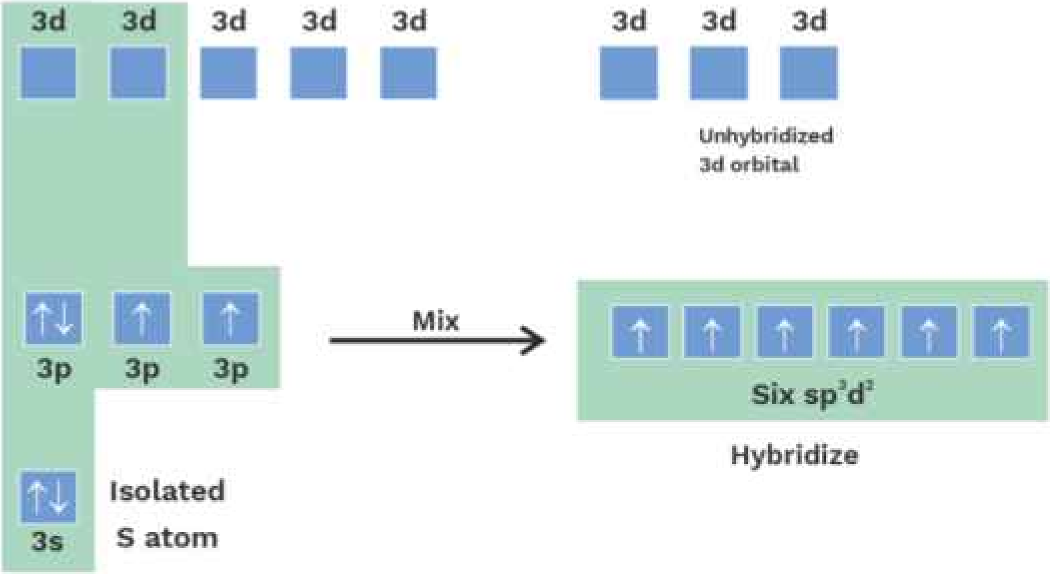


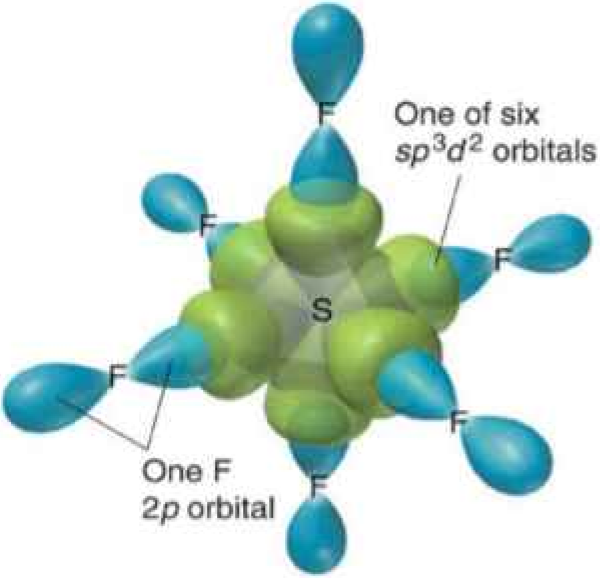
Irregular geometry



(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 = alwyas at axial position

SOME IMPORTENT EXAMPLES

(1) PCl_3F_2

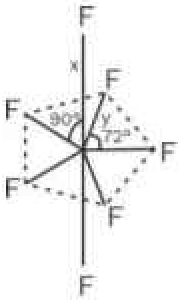
$\sigma = 7$, $lp = 0$

sp^3d^3, PBP

Non planar

$x < y$

no π bond.



(2) XeF_6

$\sigma = 6$, $lp = 1$

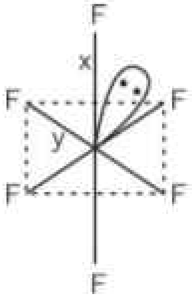
sp^3d^3, PBP

Distorted octahedral

Non planar

$x < y$

no π bond.



(3) XeF_5^-

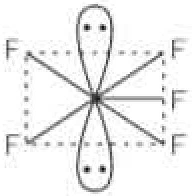
$\sigma = 5$, $lp = 2$

sp^3d^3, PBP

Pentagonal planar

no π bond

All BL are identical.



(4) IF_5

$\sigma = 5$, $lp = 1$

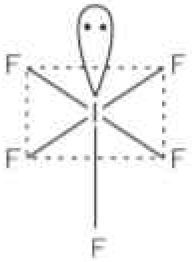
sp^3d^2, SBP

Square pyramidal

Non planar

no π bond

Not identical



(5) XeF_4

$\sigma = 4$, $lp = 2$

sp^3d^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 hybird orbitals hwich has more s-character.

Rack your Brain

What is the shape XeF_2?

Previous Year's Questions

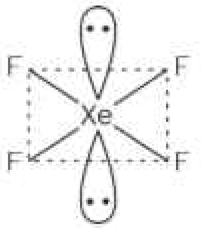
Which of the following molecules can central atom said to adopt sp^2 hybridisation

[AIPMT]

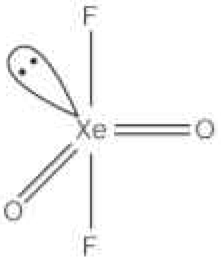
(1) BeF_2 (2) BCl_3

(3) C_2H_2 (4) NH_3

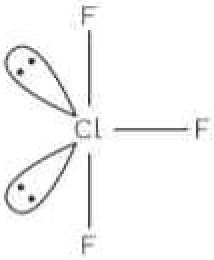
square planar
no π bond
Identical.



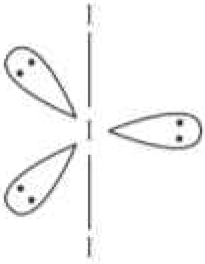
(6) XeO_2F_2
$\sigma = 4$, $lp = 1$
sp^3d, TBP
Distorted octahedral
non planar
$x < y$
no π bond



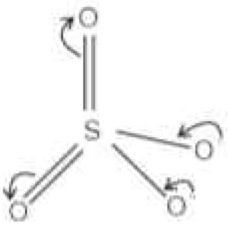
(7) ClF_3
$\sigma = 3$, $lp = 2$
sp^3d, TBP
T-shape
planar
no π bond



(8) I_3^-
$\sigma = 2$, $lp = 3$
sp^3d, TBP
Linear
Planar
no π bond
Identical



(9) SO_4^{2-}
$\sigma = 4$, $lp = 0$
sp^3, Tetrahedral



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

Previous Year's Questions

Which of the following hybridisation results in non-planar orbitals

[AIPMT]

(1) sp^3 (2) dsp^2
(3) sp^2 (4) sp

Concept Ladder

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

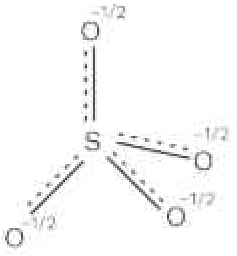
Previous Year's Questions

Which iof the following molecules has trigonal polanar geometry

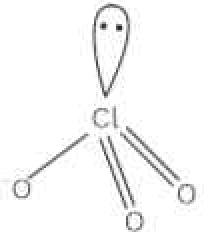
[AIPMT]

(1) IF_3 (2) PCl_3
(3) NH_3 (4) BF_3

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

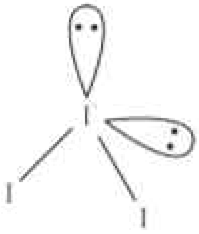


(10) ClO_3^-
$\sigma = 3,\quad lp = 1$
sp^3, Tetrahedral
Pyramidal
Non planar
$p\pi - p\pi$
Identical

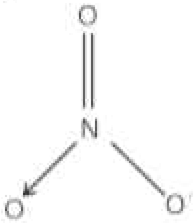


$$F.C. = -\frac{1}{3} \qquad B.O. = \frac{5}{3}$$

(11) I_3^+
$\sigma = 2,\quad lp = 2$
sp^3, Tetrahedral
v shape
Planar
no π bond
Identical



(12) NO_3^-
$\sigma = 3,\quad lp = 0$
sp^2, Trigonal planar
Trigonal planar
Planar
$p\pi - p\pi$
Identical



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

Previous Year's Questions

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

[AIPMT]

(1) AlF_3 (2) NF_3
(3) ClF_3 (4) BF_3

Concept Ladder

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

Previous Year's Questions

Whcih of the two ions from the list given below that have the geometry that is explained by the same hybridisation of orbitals, NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^-.

[AIPMT]

(1) NO_2^- and NH_2^-
(2) NO_2^- and NO_3^-
(3) NH_4^+ and NO_3^-
(4) SCN^- and NH_2^-

(13) O_3

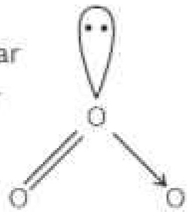
$\sigma = 2$, lp = 1

sp^2, Trigonal planar

v-shape, planar

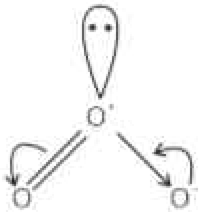
$p\pi - p\pi$

Identical



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

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



Concept Ladder

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

Do not exists

PH_5, SH_4, XeH_3 = sp_2d

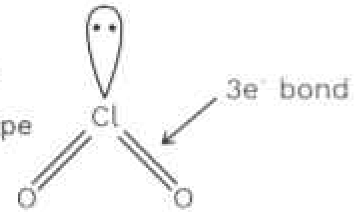
SH_6, XeH_4 = sp^3d^2

XeH_6, IH_7 = sp^3d^3

(14) ClO_2

$\sigma = 2$, lp = 1

sp^2, v-shape



Rack your Brain

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

Hybridistion state of odd e⁻ species

(1) $\dot{C}H_3$

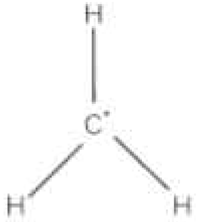
$\sigma = 3$

lp = 0.5

Steric number = $3.5 \approx 3$

(because of terminal atom is less electronegative

so we consider l.p. is ≈ 0)



(2) $\dot{C}F_3$

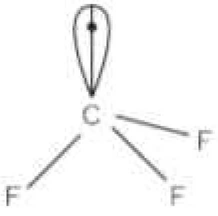
$\sigma = 3$

lp = 0.5

Steric number = $3.5 \approx 4$

(because of terminal atom is more electronegative

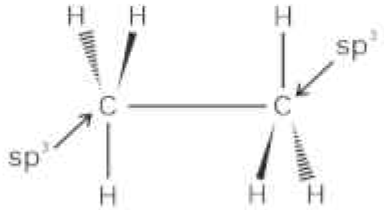
so we consider l.p. is ≈ 1)

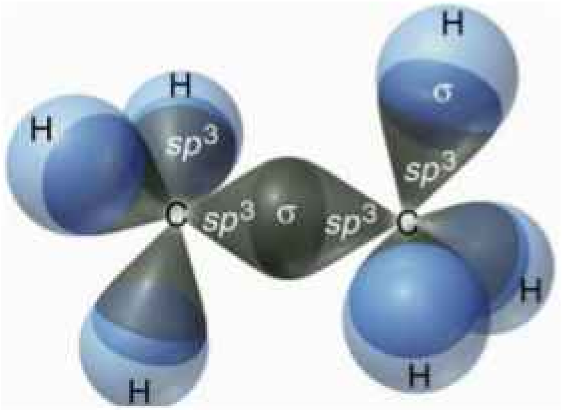


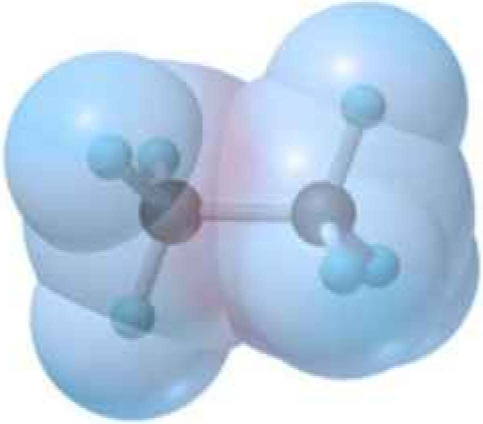
Hybridisation of Alkane, Alkene and Alkyne

(1) Ethane (C_2H_6)

$CH_3—CH_3$







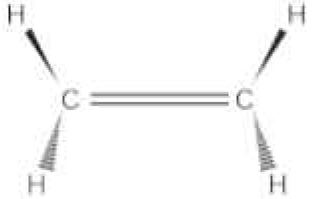
For all sigma bonds there is relatively even distribution of electron density.

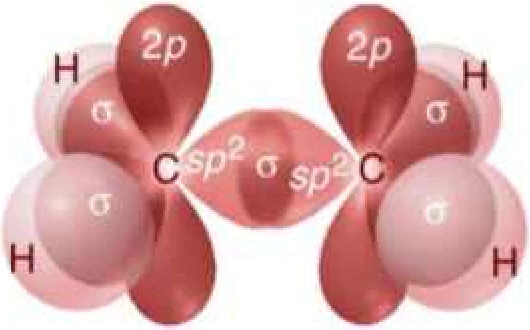
Concept Ladder

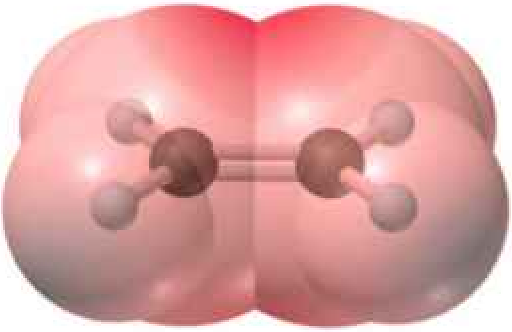
s character is the contribution of sigma type bond in a hybridization sp^3 = 25% s character, 75% = p-charatcer sp^2 = 33% s-character, 66% p-charater sp = 50% s-character, 50% p-character. The more s-charater a bond has, the stronger and shorter the bond is.

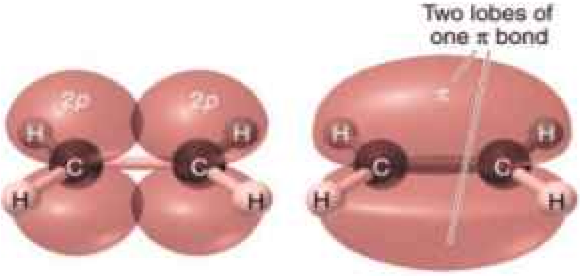
(2) Ethene (C_2H_4)

$CH_2 = CH_2$









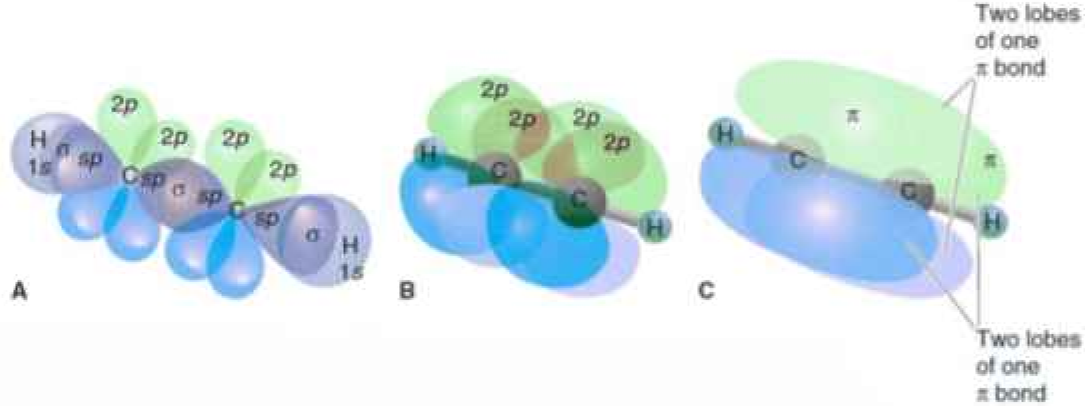
Rack your Brain

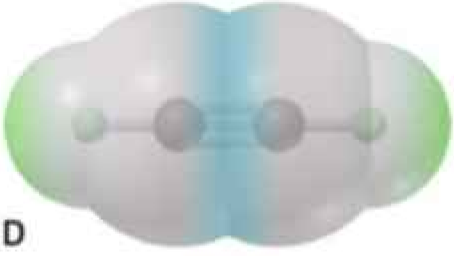
Which has stronger bond compare to alkane, alkene or alkyne?

(3) **Ethyne (C_2H_2)**

$CH \equiv CH$

$H - C \equiv C - H$





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, becuase a π bond is weaker than a σ bond.

Bond Parameter

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

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

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

Ex: (1) $Cl_2 > Br_2 > F_2 > I_2$ BE/BDE

lp-lp repulsion

(2)

$-\ddot{N}-\ddot{N}- < -\ddot{P}-\ddot{P}-$ BE/BDE

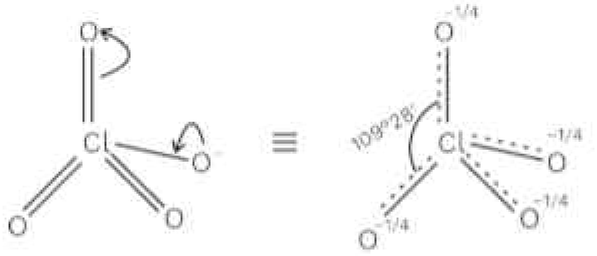
lp-lp repulsion

Catenation $\propto$ B.E.

Ex: $C-C > Si-Si \geq \underset{\text{Size}\uparrow}{Ge-Ge} > \underset{\text{B.C.}\downarrow}{Sn-Sn}$

$$\xrightarrow[\text{Catenation}]{\hspace{6cm}}$$

Ex: (1) ClO_4^-



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

Previous Year's Questions

Whcih of the following molecule has highest bond energy? **[AIIMS]**

(1) F—F (2) N—N
(3) C—C (4) O—O

Concept Ladder

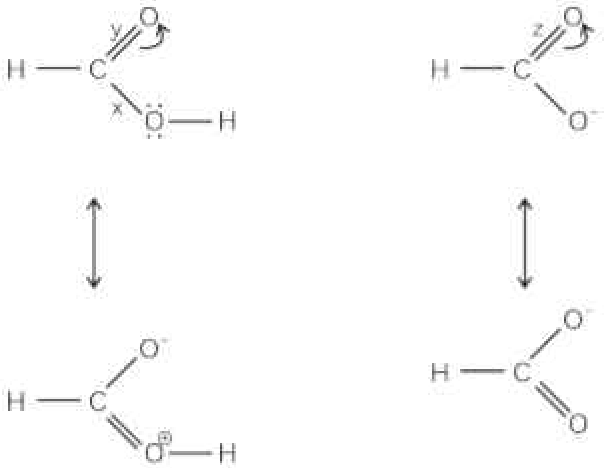
If species have equal stable resonating structure than B.L., B.S., B.D., B.A. and F.C. depends upon resonance hybrid.

Previous Year's Questions

Which of the following compounds possess the C—H bond with the lowest bond dissociation energy? **[AIIMS]**

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

(2) HCOOH



Highly unstable

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

$x > z > y$ = B.L.

1.0 1.5 2.0

Rack your Brain

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

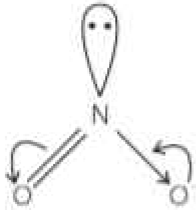
Q. Compare given properties —

(1) $H_2O_2 > O_3 > O_2$ O—O B.L.

1 1.5 2.0 B.O. ↑

(2)

$O=\overset{+}{N}=O$ <



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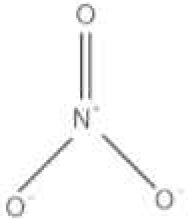


N—O B.L.

2 1.5 1.33

(3) $PO_4^{3-} > SO_4^{2-} > ClO_4^-$ F.C. on oxygen

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

Previous Year's Questions

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)

$H-O-O-H > F-O-O-F$ $O-O$ (B.L.)

size ↓ B.L. ↓

(5)

$C-H < N-H < O-H < F-H$ B.S. or B.E.

size ↓ B.L. ↓

(6) $\equiv C-H < =\overset{|}{C}-H < -\overset{|}{\underset{|}{C}}-H$ B.L.

sp sp^2 sp^3 s-character ↓

(7)

$\equiv C-C\equiv > =\overset{|}{C}-\overset{|}{C}= > -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$ B.S.

sp sp sp^2 sp^2 sp^3 sp^3 s-character ↓

(8) $\ddot{O}-\ddot{O} < S-S$ Catenation

lp-lp

repultion

Previous Year's Questions

Which of the following is correct regarding bond angles?

(i) $SO_2 < H_2O$ (ii) $H_2S < SO_2$

(iii) $SO_2 < H_2S$ (iv) $SbH_3 < NO_2^+$

[AIIMS]

(1) ii and iv (2) i, ii and iv

(3) i and iii (4) None of these

Bond Angle

(1) Hybridisation state

(a)

$\underset{sp(180^\circ)}{CO_2} > \underset{sp^2(120^\circ)}{CO_3^{-2}} > \underset{sp^3(120^\circ)}{CCl_4}$ (Order of bond angle)

(b)

$\underset{sp^3d(180^\circ)}{XeF_2} > \underset{sp^3(109^\circ)}{XeO_3} > \underset{sp^3d^2(90^\circ)}{XeF_4}$ (Order of bond angle)

Drago's Rule : -

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

$NH_3 = 107^\circ$ $H_2O = 104.5^\circ$

$PH_3 = 93^\circ$ $H_2S = 92^\circ$

$AsH_3 = 92^\circ$ $H_2Se = 91^\circ$

$SbH_3 = 91^\circ$ $H_2Te = 90^\circ$

Bond angle ≈ 90°

No hybridization

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.

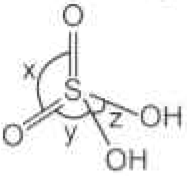
(2) $$\text{Bond angle} \propto \frac{1}{\text{number no lone pair}}$$

Ex. $\underset{sp^3 (0\ lp)}{NH_4^+} > \underset{sp^3 (1\ lp)}{NH_3} > \underset{sp^3 (2\ lp)}{NH_2^-}$ (Order of bond angle)

(3) Multi Bond — Multi Bond

or Multi Bond — Single Bond repulsion.

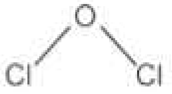
Ex. (a)



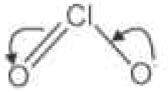
x > y > z

(b)

$\underset{sp^3 (2\ lp)}{OCl_2} < \underset{sp^3 (2\ lp)}{ClO_2^-} < \underset{sp^2}{ClO_2}$ (Order of bond angle)



SB—SB



Partial MB—MB
repulsion

(4) $$\text{Bond angle} \propto \frac{\text{EN of Central atom}}{\text{Size of Central atom}}$$

Steric repulsion increase, Bond Atom increase

Ex. $NCl_3 > PCl_3 > AsCl_3 > SbCl_3$

$$\xrightarrow{\hspace{4cm}}$$

Size of central atom increase
Bond angle decrease

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

(EN of terminal atom only for F atom)

Ex.

(a) $PF_3 < PCl_3 < PBr_3 < PI_3$

$$\xrightarrow{\hspace{4cm}}$$

Size of terminal atom increases
Bond angle increases

Previous Year's Questions

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

(1) $BeCl_2 > NO_2 > SO_2$
(2) $BeCl_2 > SO_2 > NO_2$
(3) $SO_2 > BeCl_2 > NO_2$
(4) $SO_2 > NO_2 > BeCl_2$

Rack your Brain

Why PH_3 does not show the bond angel 109°28'?

Previous Year's Questions

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

(1) $NO_2^+ < NO_2 < NO_2^-$
(2) $NO_2^+ < NO_2^- < NO_2$
(3) $NO_2^- < NO_2^+ < NO_2$
(4) $NO_2^- < NO_2 < NO_2^+$

(b) $\xrightarrow[\text{Size of terminal atom increases}]{OF_2 < H_2O < OCl_2}$
Bond angle increases

Q. Compare bond angle

(1) $\underset{sp}{NO_2^+} > \underset{sp^2}{NO_2} > \underset{sp^2}{NO_2^-}$

(2) $ClO_3^- > BrO_3^- > IO_3^-$ (EN of central atom decrease
Bond angle decrease)

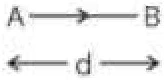
(3) $CH_4 < CF_4 < CCl_4$ (Size of terminal atom increase
Bond angle increase)

(4) $PO_4^{-3} < SO_4^{2-} < ClO_4^-$ (Number of MB increase
Bond angle increase)

Dipole Moment (D.M.)

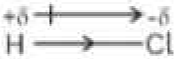
- Polarity of a bond depends upon ΔEN but polarity of a molecule depends upon DM.
- Dipole moment is a product charge and internuclear distance.

$\boxed{\mu = q \times d}$



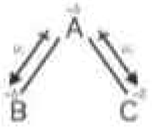
unit = debye
1 debye = 10^{-18} esu.cm
1 debye = 3.33×10^{-30} C×m

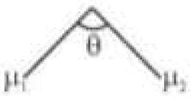
- Dipole moment is vector quantity and its direction is from positively charged atom to negatively charged atom.



$:C \equiv O:$ or $:\overset{-}{C} \overset{\leftarrow}{\equiv} \overset{+}{O}:$

- 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) CH_3Cl, CH_3Br, CH_3F
(2) CH_3Cl, CH_3F, CH_3Cl
(3) CH_3Br, CH_3Cl, CH_3F
(4) CH_3Br, CH_3F, CH_3Cl

Concept Ladder

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

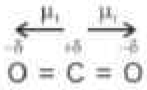
Ex: H_2S, H_2O, NH_3, PCl_3, ClF_3, BrF_3 etc.

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

$\theta = 0°$ $\mu = \mu_1 + \mu_2$ (Max. dipole moment)

$\theta = 180°$ $\mu = \mu_1 - \mu_2$ (Min. dipole moment)

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



$\overset{-\delta}{O} \overset{\xleftarrow{\mu_1}}{=} \overset{+\delta}{C} \overset{\xrightarrow{\mu_1}}{=} \overset{-\delta}{O}$

Ex: (a) O = C = O Bonds-polar but molecular is non polar.

$\mu = \mu_1 - \mu_1$

(b) 

$H-\ddot{P}(-H)-H$ Bonds-Non polar

But molecular is polar due to its lp.

Q. Which of the following molecule is non polar?

(a) $R-\ddot{\underset{\cdot\cdot}{O}}-R$

(b) 

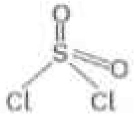
$O=S(Cl)_2=O$

(c) H_2O_2

(d) XeF_2

A. (a) $R-\ddot{\underset{\cdot\cdot}{O}}-R \longrightarrow$ V-shape

(b) 



$\mu \neq 0$

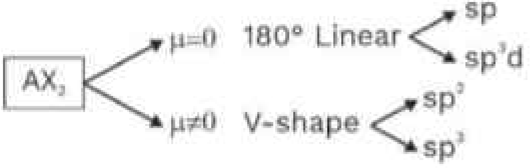
Non-polar

(c) H_2O_2 — Half open book like structure ex. O_2F_2, $S_2F_2S_2Cl_2$.

(d) $XeF_2 \longrightarrow sp^3d$

Dipole Moment and Geometry

(1)



Concept Ladder

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

Ex: CO_2, BF_3, CCl_4, PCl_5, $3F_6$, IF_7, B_2H_6, Al_2Cl_6 etc.

Previous Year's Questions

The dipole moment is minimum in

[AIIMS]

(1) NH_3 (2) NF_3

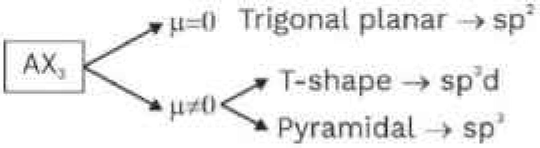
(3) SO_2 (4) BF_3

Concept Ladder

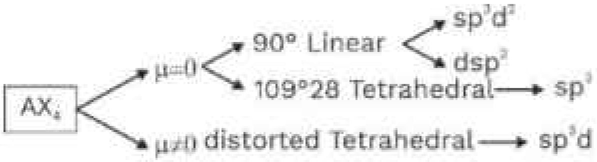
If central atom has only 1 lone pair then molecule will be polar.

Ex: XeF_6, SF_4, $TeCl_4$, SO_2, NF_3 etc.

(2)



(3)



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

$\mu_0 bs$ = given(debye)

$\mu_{Theo} = q \times (d)$

A^+B^-

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

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

Q. Compare dipole moment.

(1) HF > HCl > HBr > HI

$\mu = q \times d$

(ΔEN ⇒ dominating factor)

(2) $CH_3 - Cl > CH_3 - F > CH_3 - Br > CH_3 - I$

$\mu = q \times d$

(Size ⇒ dominating factor)

(3) $OF_2 < H_2O$

lp ↑ bp↓ lp ↑ bp ↑

(4) $H_2S < NH_3 < H_2O < HF$ (lp ↑, bp ↑)

$\xrightarrow{\hspace{1cm}} \Delta$EN ↑, ΔM ↑

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)

Molecualr 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 pouling.
- 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 molicular orbital
- According to MOT 1 atomic orbital + 1 atomic orbital = 2 molicular orbital (Antibonding molicular orbital (ABMO), Bonding molicular 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

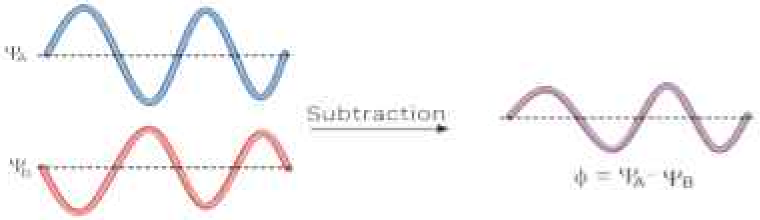
Which molecular orbital is more stable in orbital diagram?

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



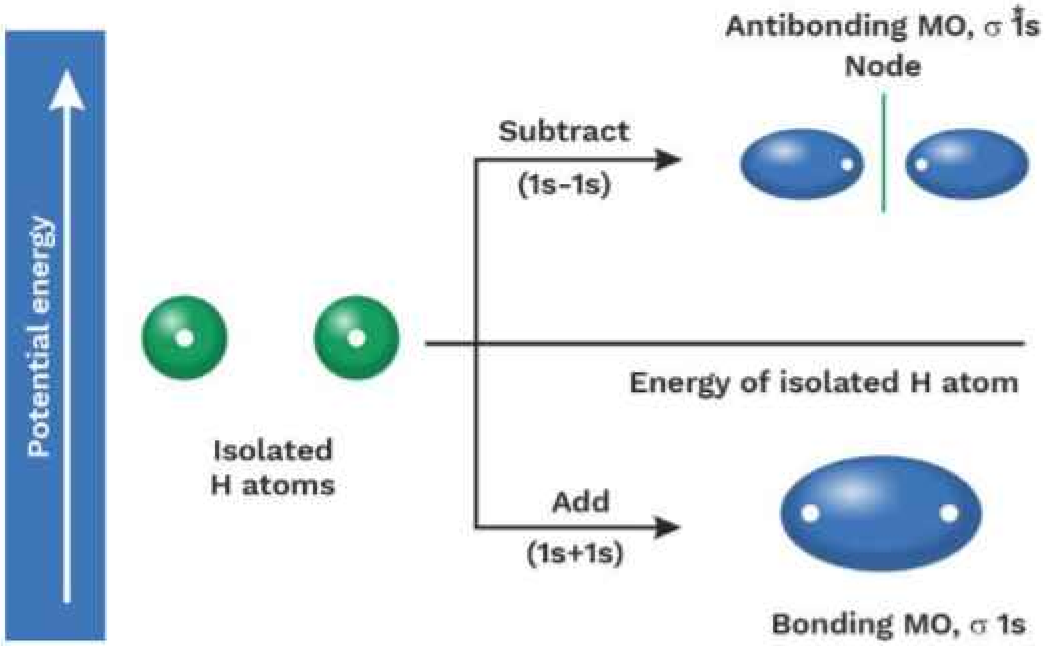
Difference between bonding and antibonding molecular orbital

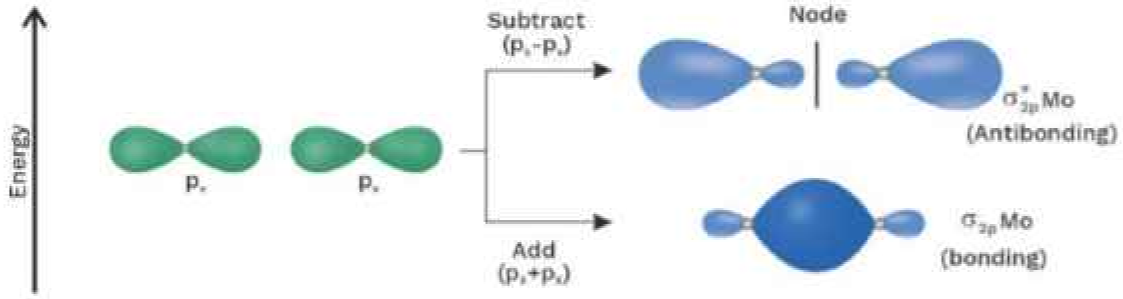
Bonding molecular orbital	Antibonding molecular orbital
$\phi_b = \Psi_A + \Psi_B$	$\phi_a = \Psi_A + \Psi_B$
Wave functions are added	Wave functions are subtracted
Electron density between the nuclei increases	Electron density between the nuclei decreases
Energy is less	Energy is more
No nodal plane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

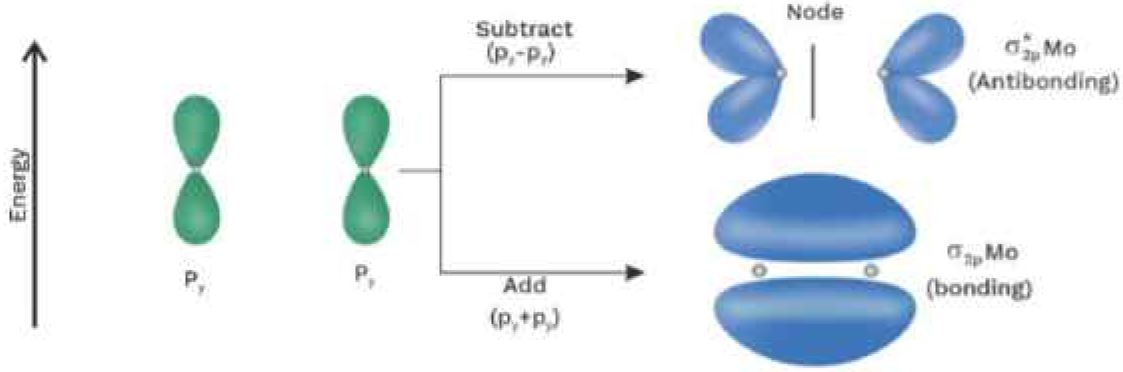
Difference between atomic and molecular orbital

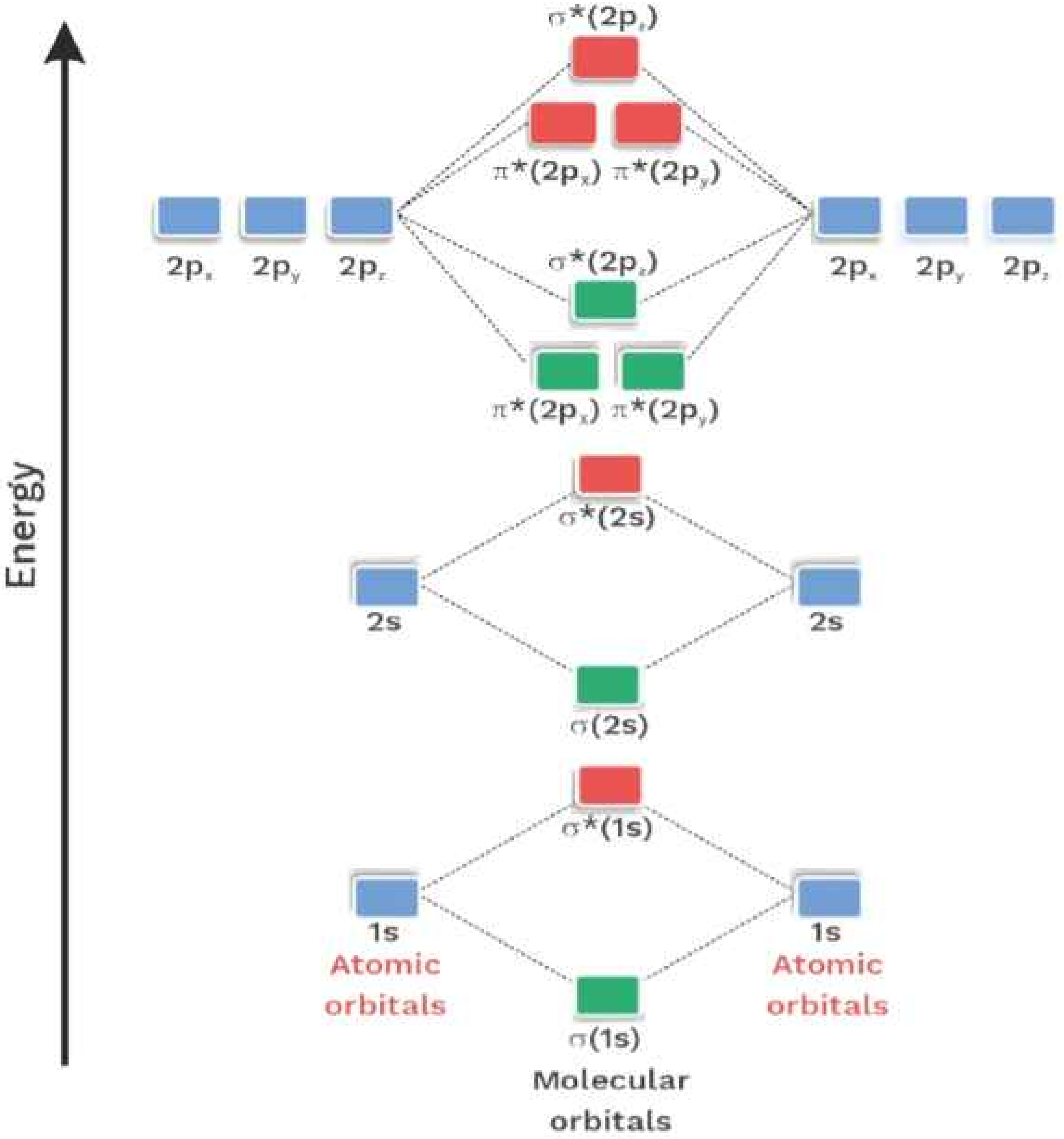
Atomic orbital	molecular orbital
Monocentric	Polycentric
Less stable	More stable

Energy Level Diagram for Molecular Orbitals



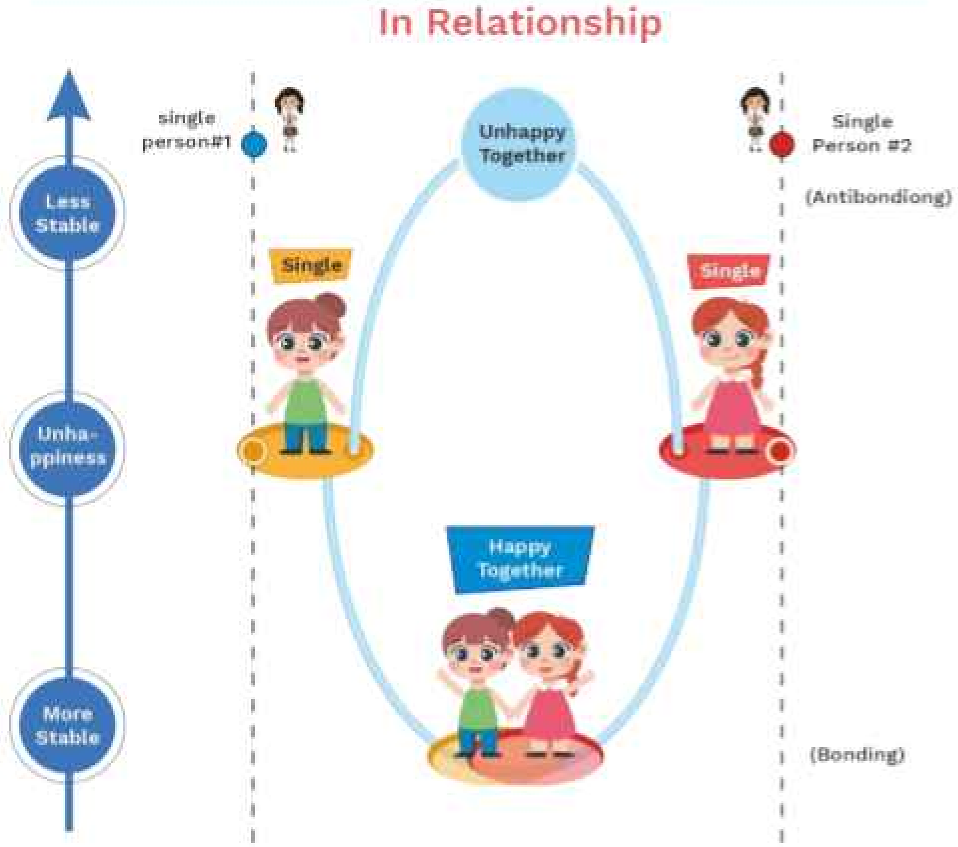






For homonuclear Diatomic Molecular (except O_2, F_2 and Ne_2)

Full Relationship Energy Diagram



Bond order

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

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

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 Li_2, Be_2, B_2, C_2, N_2

$$\underset{\text{Energy}}{\xrightarrow{\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ (\pi 2p_x = \pi 2p_y),\ \sigma 2p_z,\ (\pi^* 2p_x = \pi^* 2p_y),\ \sigma^* 2p_z}}$$

For O_2, F_2, Ne_2

$$\underset{\text{Energy increases}}{\xrightarrow{\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ \sigma 2p_z,\ (\pi 2p_x = \pi 2p_y),\ (\pi^* 2p_x = \pi^* 2p_y),\ \sigma^* 2p_z}}$$

Previous Year's Question

Which of the following is paramagnetic **[NEET]**

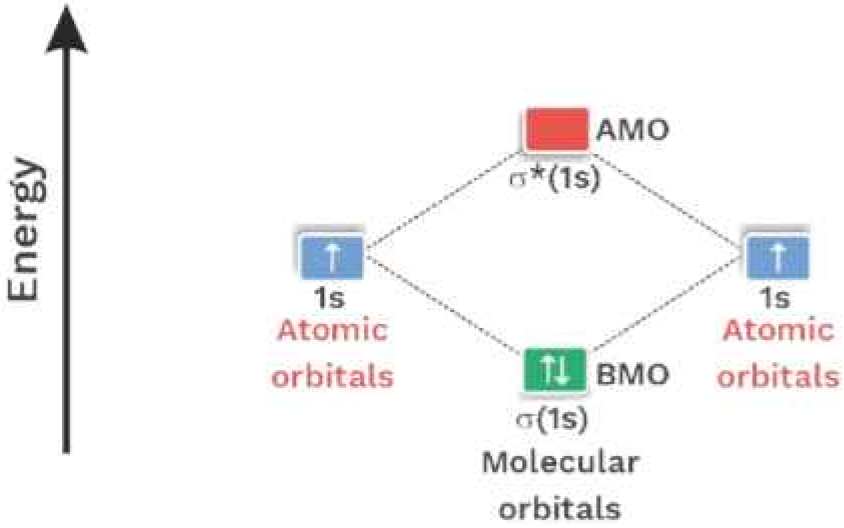
(1) CN^-

(2) NO^+

(3) CO

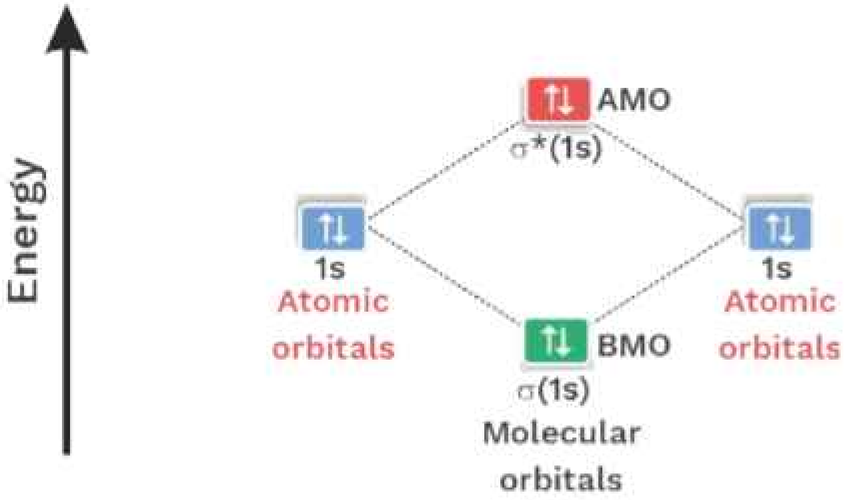
(4) O_2^-

Energy Level Diagram for H_2



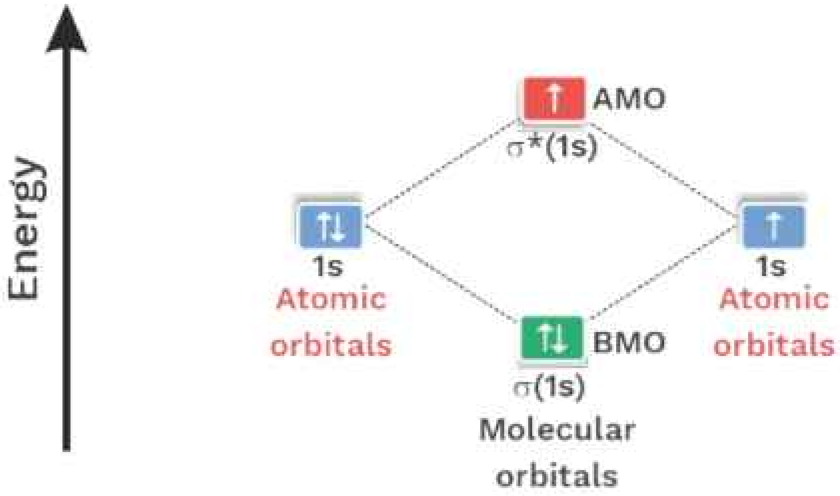
H_2 bond order = 1/2(2 − 0) = 1

Energy Level Diagram for He_2



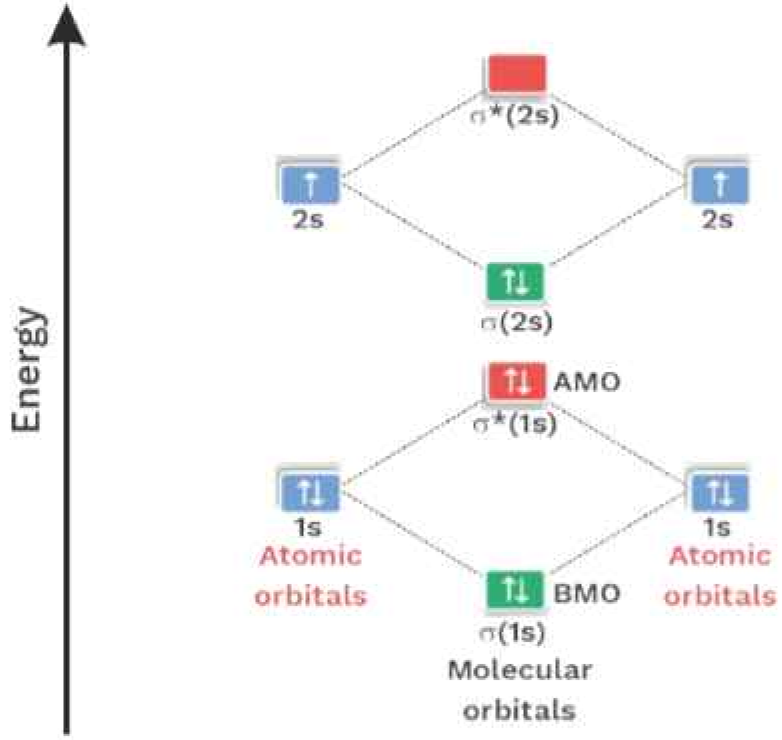
He_2 bond order = 1/2(2 − 2) = 0

Energy Level Diagram for He_2^+



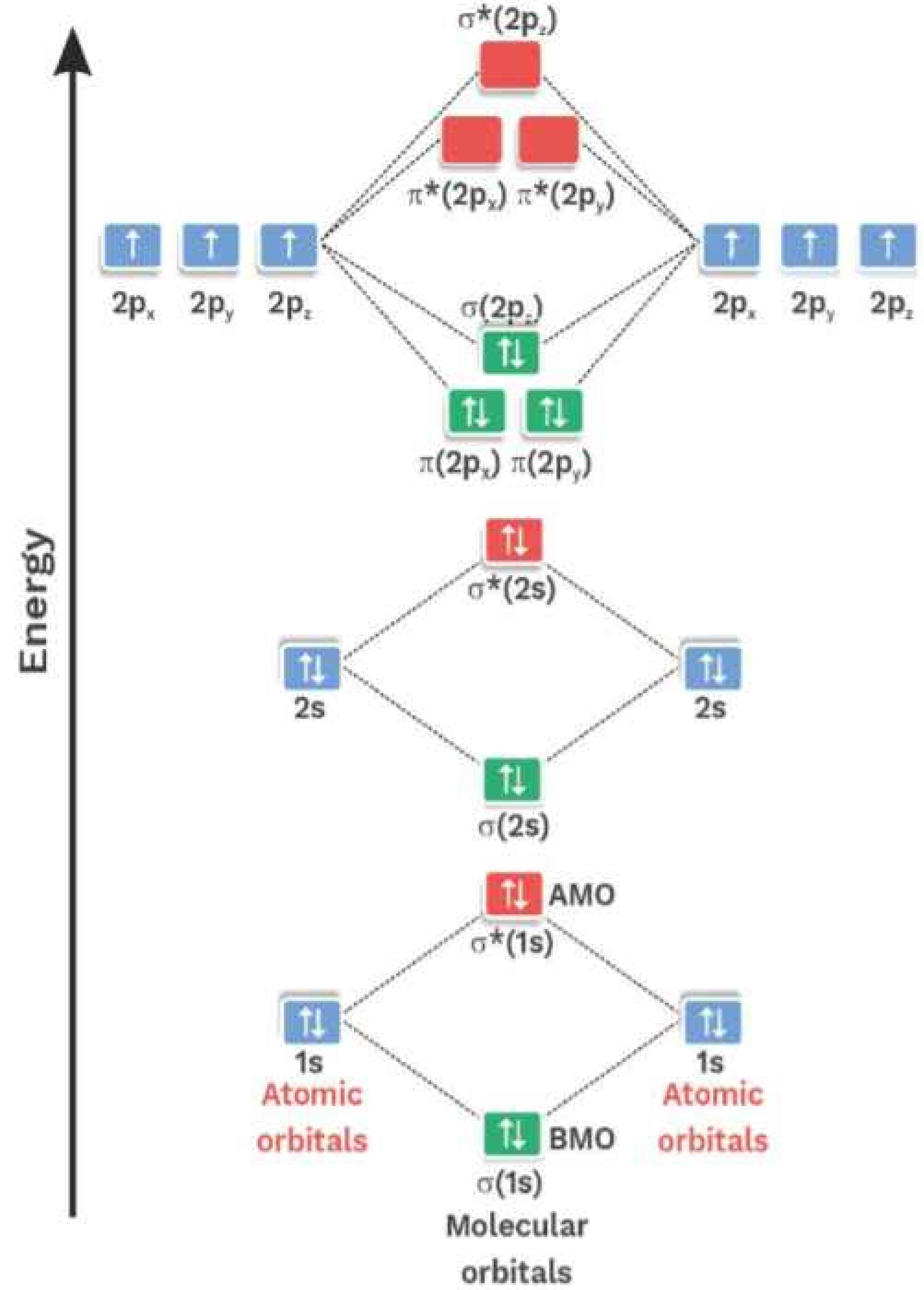
He_2^+ bond order = 1/2(2 − 1) = 1/2

Energy Level Diagram for Li_2



Li_2 bond order = 1

Energy Level Diagram for N_2



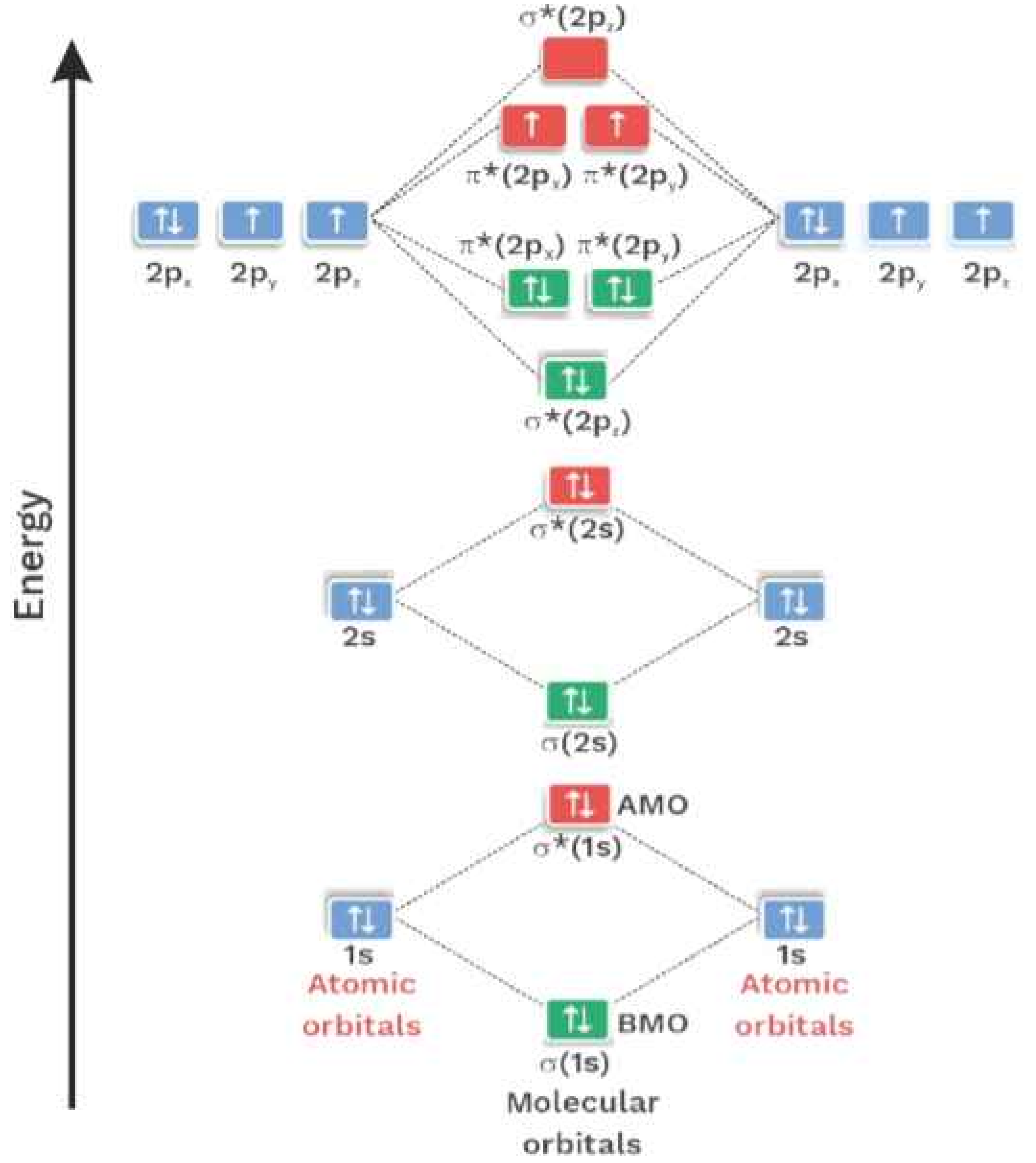
Bond order = $\frac{10-4}{2}=3$,

Magnetic character – diamagnetic

Electronic configuration –

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2, \left(\pi 2p_x^2 = \pi 2p_y^2\right), \sigma 2p_z^2$$

Energy Level Diagram for O_2



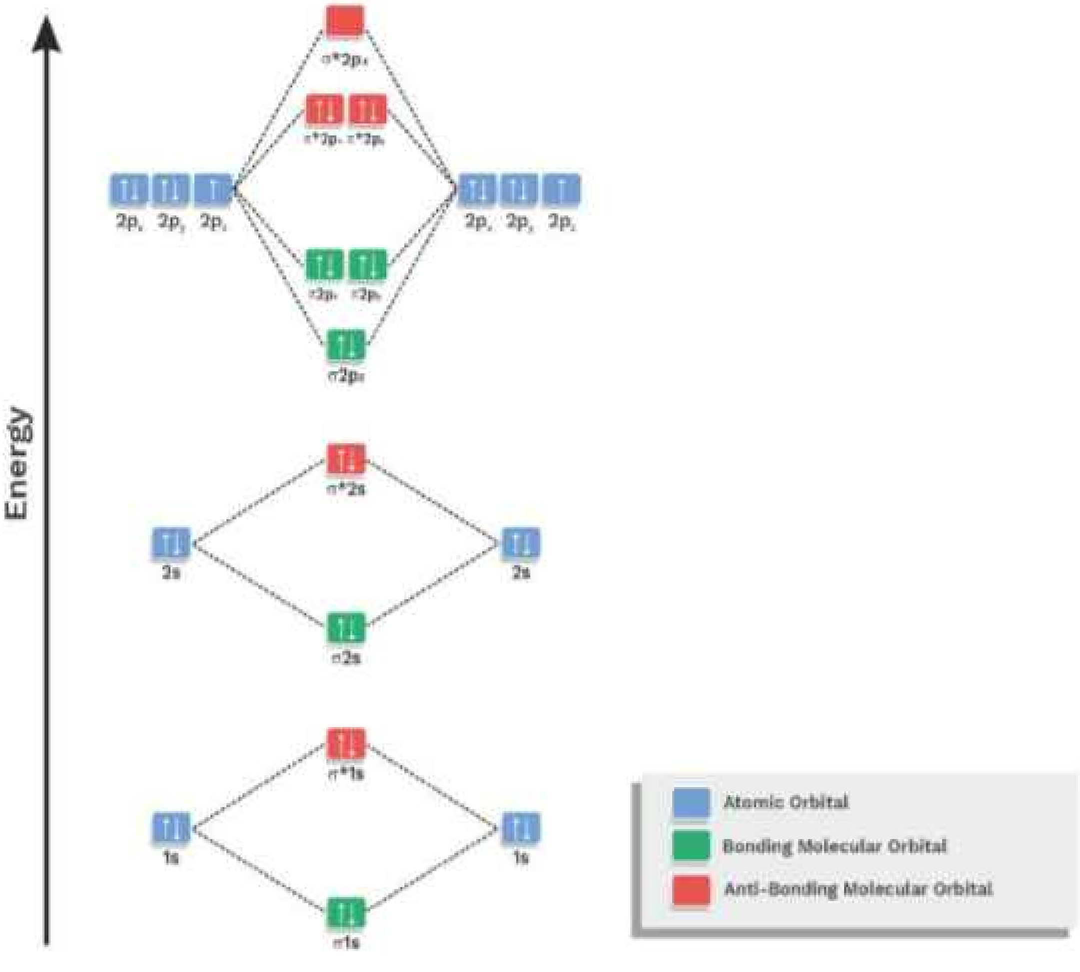
Bond order = $\frac{10-6}{2} = 2$

Magnetic character – paramagnetic (due to unpaired electron)

Electronic configuration -

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2, \sigma 2p_z^2, \left(\pi 2p_x^2 = \pi 2p_y^2\right)\left(\pi * 2p_x^1 = \pi * 2p_y^1\right)$$

Energy Level Diagram for F_2



Energy level diagram of F_2

Examples.

Species	Bond order	Stability	Magnetic Character
H_2^-	0.5	Some what stable	Paramagnetic
H_2	1	Quite stable	Diamagnetic
H_2^+	.5	Somewhat stable	Paramagnetic
N_2^{2-}	2	Least stable	Paramagnetic
N_2^-	2.5	Less stable	Paramagnetic
N_2^+	2.5	Less stable	Paramagnetic
N_2	3	Most stable	Diamagnetic
O_2^{2-}	1.0	Least stable	Diamagnetic
O_2^-	1.5	Still less stable	Paramagnetic
O_2	2.0	Less stable	Paramagnetic
O_2^+	2.5	Most stable	Paramagnetic

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

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

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

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

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

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

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

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

So, $H_2 > H_2^+ > H_2^-$
H_2^+ is more stable then H_2^- because in H_2^+ less ABMO electron present.

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

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

Two unpaired electrons present in π_b MO.

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

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

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

Bond Strength C=C < $H_2C=CH_2$

Q32 How the bond energy varies form 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 morfe stable than N_2^- as number of antibonding electrons is higher in N_2^- than N_2^+.

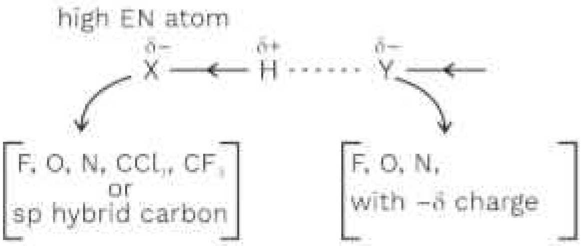
Q33 Compare the bond length of O—O in the following molecules
(a) KO_2 (b) $O_2[AsF_6]$ (c) O_2 (d) Na_2O_2

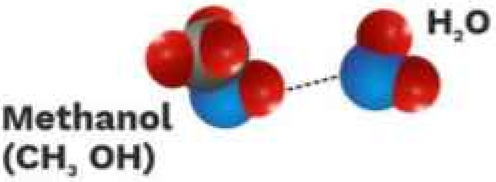
A33 (a) KO_2 has O_2^- (superoxide ion), Bond order = 1.5
(b) $O_2[AsF_6]$ has O_2^+, Bond order = 2.5
(c) O_2, Bond order = 2
(d) Na_2O_2 has O_2^{2-} (peroxide ion), Bond order = 1
Higher is the BO, smaller is the bond length. Hence, order of bond length of :
$O_2^+ < O_2 < O_2^- < O_2^{2-}$

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.

Ex. $\cdots\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\cdots\overset{+\delta}{H}-\overset{-\delta}{F}\cdots$





H bond

Bond energy = 8 – 42 KJ mol^{-1} for neutral molecules.

Conditions for hydrogen bonding

(a) Size of electronegative element should be small (F, O, N).

(b) Molecules must have highly electronegative atom link to hydrogen atom

For stronger H-bonding

(i) EN of X should be high

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

H-bond strength order

Ex: $HF > H_2O > NH_3$ (EN of X decreases)

$$\underset{X}{N}—H\cdots\cdots\underset{Y}{O} < \underset{X}{N}—H\cdots\cdots\underset{Y}{N} < \underset{X}{O}—H\cdots\cdots\underset{Y}{O} < \underset{X}{O}—H\cdots\cdots\underset{Y}{N}$$

$D_2O > H_2O$ (D is more +ve)

Extent of H-bonding

$HF < H_2O < H_2O_2$

Bonds 2 3 4

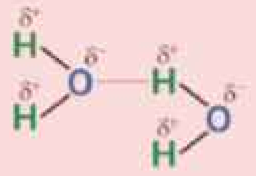
Types of hydrogen bonding

(a) Intermolecular hydrogen boding

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

Hydrogen Bond

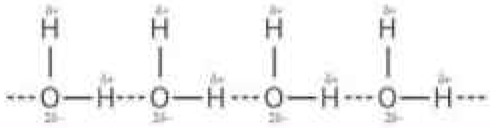
Hydrogen attracts an electronegative atom electrosatically



Two water molecules

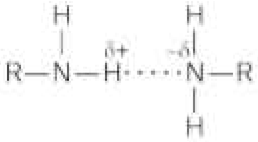
combine together to form a dimer or polymer respectively and leads to a phenomenon called association.

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

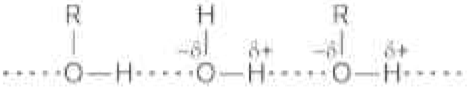


Intermolecular Hydrogen bonding in H_2O

Ex:

(1) 

$R-\overset{H}{\overset{|}{N}}-\overset{\delta+}{H}\cdots\cdots\underset{H}{\underset{|}{\overset{H}{\overset{-\delta|}{N}}}}-R$ (Homo)

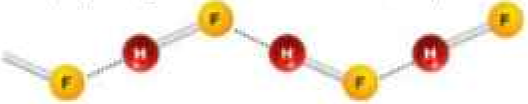
(2) 

$\cdots\cdots\overset{R}{\overset{|}{O}}-H\cdots\cdots\overset{H}{\overset{-\delta|}{O}}-\overset{\delta+}{H}\cdots\cdots\overset{R}{\overset{-\delta|}{O}}-\overset{\delta+}{H}\cdots\cdots$ (Hetro)

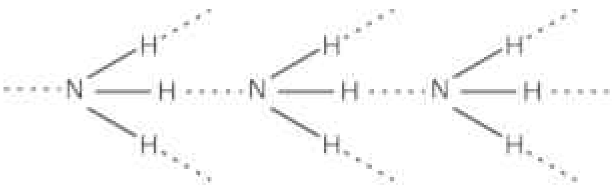
(3) 

$(CH_3)_2C=\overset{-\delta}{O}\cdots\cdots\overset{+\delta}{H}-CCl_3$

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



(5) NH_3 (linear H-bonding)



Previous Year's Questions

X — X ----Y, X and Y both are electronegative elements.Then **[NEET]**

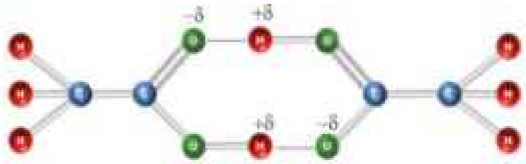
(1) Electron density on X will increase and on H will decrease

(2) In both electron density will increase

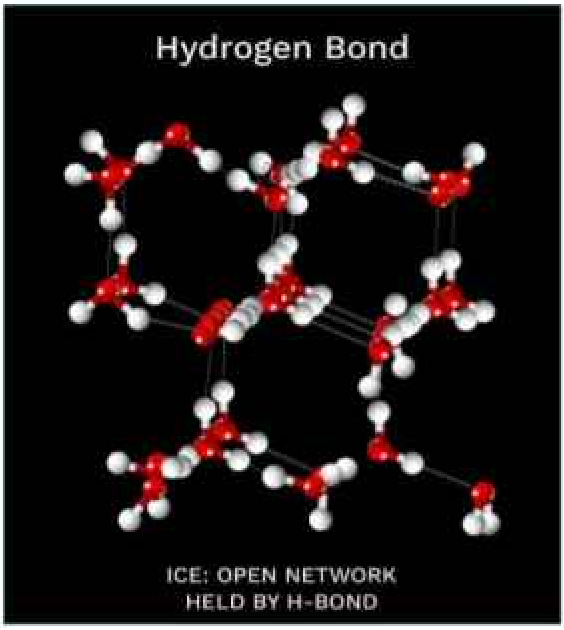
(3) In both electron density will decreases

(4) On X electron density will decrase and on H increases.

(6) CH_3COOH



(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 occure in organic compound and result 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]**

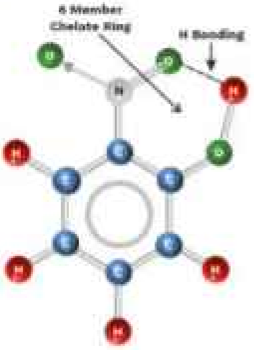
(1) H_2O_2
(2) HCN
(3) Cellulose
(4) Concentrated acetic acid

Concept Ladder

Hydrogen bonding is special type of dipole – dipole attraction

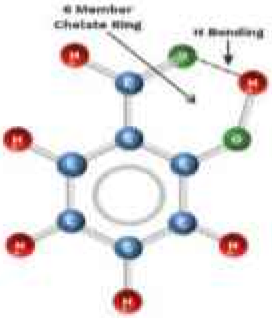
Ex:

(1) o-nitrophenol

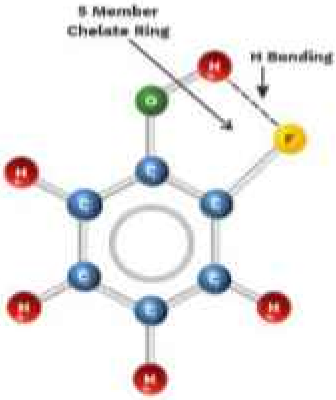


o-nitrophenol have a 6 membered ring (chelate ring), due to presence of chelate ring thermodyanmic stability increases.

(2) Salicylaldehyde



(3) o-fluorophenol



Concept Ladder

H-bond energy is only 2-10 kcal/mol, as compared tot eh covalent bond energy of 50-100 kcal/mol but it is greater than vander 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 then 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 H–F --- H > H–O ---H > H–N --- 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.

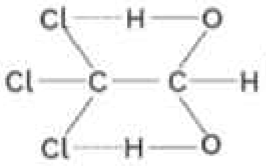
(g) O-nitrophenol is volatile but meta and para nitrophenol is not (O-nitrophenol has intra molecular hydrogen boning having law boiling point, where as para and meta nitrophenol has inter molecular hydrogen bonding having high boiling point).

EX. Intra molecular hydrogen bonding is present in

(1) Chloral (2) O-fluorophenol

(3) O-nitrophenol (4) All

Sol. (4),



In chloral H-bonding is formed between H and Cl.

Previous Year's Questions

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

(1) H_2O

(2) H_2Se

(3) H_2S

(4) HF

Rack your Brain

What is the strongest hydrogen bond?

Previous Year's Questions

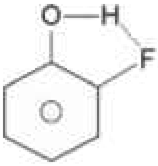
What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas? **[NEET]**

(1) Dipole-dipole interaction

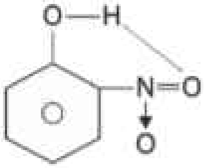
(2) Covalent bonds

(3) London disperision force

(4) Hydrogen bonding



o-flurophenol



o-nitrophenol

Applications of Hydrogen bonding

(a) **Physical state :** Due to hydrogen bonding H_2O is liquid where as H_2S, H_2Se, H_2Te are gases (absence of hydrogen bonding and presence of Vander wall forces).

(b) Melting point and boiling point of covalent bond $\propto$ vandar 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, **HF > HI > HBr > HCl** (B.P. and M.P) Similarly for $H_2O > H_2Te > H_2Se > H_2S$ (B.P. and M.P) and $NH_3 > AsH_3 > PH_3$ (B.P. and M.P) But when SbH_3 is included then $SbH_3 > NH_3 > AsH_3 > PH_3$

Previous Year's Questions

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

(1) Water
(2) Ammonia
(3) Hydrogen fluroide
(4) Hydrogen sulphide

Rack your Brain

What bonds break the easiest?

Concept Ladder

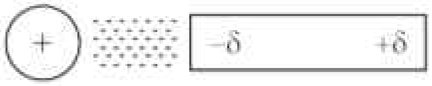
CH_3-F CH_3-Cl CH_3-Br CH_3-I	Mass ↑ VF ↑ B.P. and M.P. ↑

Weak Intermolecualr Forces

Intermolecular forces are attractive forces between molecules.

(1) **Ion Dipole Attraction**

Attractive forces between ion and polar molecule



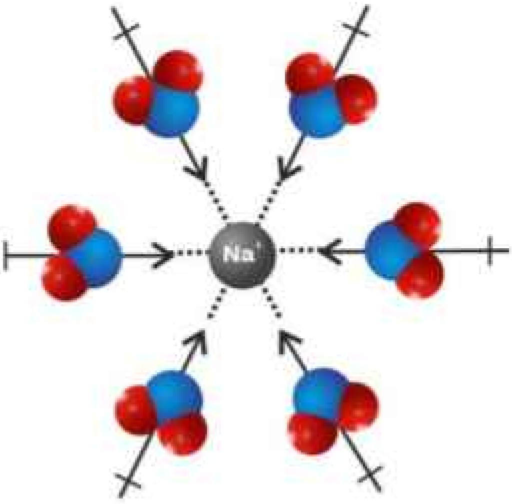
Cation

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

Ex: (i) $Li^+ + H_2O$

(ii) $Br^- + HBr$

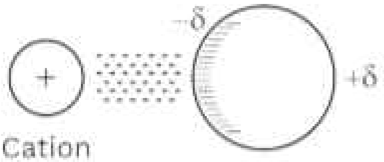
(iii) $NO_3^- + CH_3OH$



Ion-dipole

(2) **Ion Induced Dipole Attraction**

Exists between ion and non-polar molecule



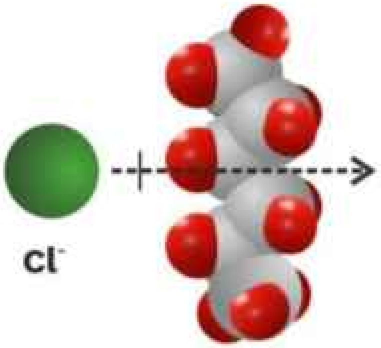
Cation

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

Ex: (i) $Cl^- + Cl_2$

(ii) $HO^- + CCl_4$

(iii) $K^+ + C_6H_6$



Hexane
(C_3H_6O)

Ion-induced dipole

(3) **Van der waal Force Attraction**

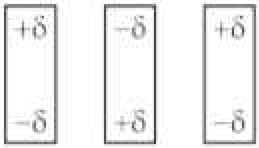
They are weaker than ionic and covalent bonds.

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.



⇒ In solid state

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

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

Ex: (i) HCl + HCl (ii) $H_2S + H_2S$

(iii)

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3-C\equiv N$

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

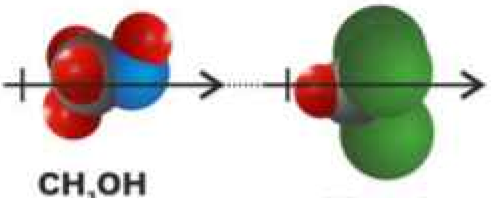
A dipole can induce a tempoary dipole to form in a non-polar molecule.

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

Ex: (i) H_2O + Xe (ii) Xe + quinol
(iii) Cl_2 + HCl (iv) $CH_3OH + C_6H_6$

Concept Ladder

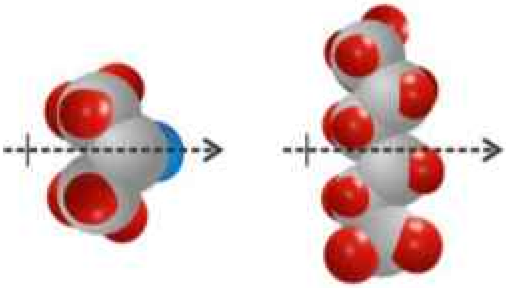
H-bond energy is only 2-10 kcal/mol, as compared tot eh covalent bond energy of 50-100 kcal/mol but it is greater than vander waals attraction which is < 1 kcal/mol.



CH_3OH

Chlorofrom ($CHCl_3$)

Dipole-dipole



Acetone (C_3H_6O)

C_6H_{14}

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) Xe + Xe (ii) $C_6H_6 + C_6H_6$

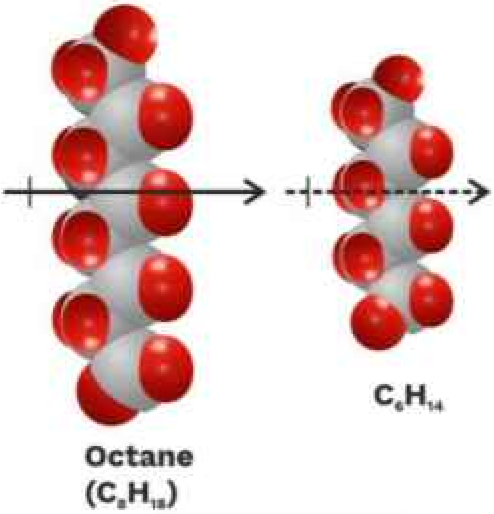
(iii) $CO_2 + CO_2$ (iv) $Cl_2 + Cl_2$

Significance

(1) In Protein folding

(2) Graphenes Bonding Forces in Graphite

(3) In Polymer Formation



Dispersion

Q34 Ethyl alcochol (C_2H_5OH) has higher boiling point than dimethyl ether (CH_3–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.

$$\cdots\cdots\overset{\overset{C_2H_5}{|}}{O}-H\cdots\cdots\overset{\overset{C_2H_5}{|}}{O}-H\cdots\cdots$$

Due to intermolecular H-bonding, ethyl alcohol remians 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 benzaldehdye while intermolecular H-bonding in p-hydroxybenzaldehyde.

o-hydroxy benzaldehyde

H-bonding is within the same molecuel, 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'se but N forms H-bonding. Why?

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

Q37 H_2O is liquid whereas H_2S is gas. Why?

A37 In H_2O, there are strong intermolecular forces due to extnesive H-bonds. No such bonding exists in H_2S 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 H_2O, as explained below. Due to H-bonding in solid ice, it forms a cage-like structure of H_2O molecules in which each H_2O molecule is linekd tetrahedrally to four H_2O molecules. The molecules of H_2O are not zso closely packed in the solid ice. When ice melts in case-like structure, H-bonds break and molecules come closer to each other. Therefore, for rthe 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 H_2O 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 ?

$$BF_3 + NH_3 \rightarrow F_3B.NH_3$$

A42 In BF_3, B is sp^2 hybridised and by accepting a lone pair of electron present on the N-atom of NH_3, one vacant p-orbital of B gets filled. Nitrogen in this adduct acts as donor atom and BF_3 acts as an acceptor. So, hybridization of B in BF_3 changes from sp^2 to sp^3 whereas there is no change in hybridization of N in 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 CH_3COOH, NH_3, HF and 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.
$HF > NH_3 > CH_3COOH$ (exist as dimer) $> CH_4$.

Q45 H_2O is a liquid whereas H_2S, H_2Se and H_2Te are all gases at ordinary temperature

A45 Due to H-bonding in H_2O, it causes association of H_2O molecules with the result that the B.P. of water is more than that of the other compound. But in H_2S, H_2Se and H_2Te 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 He < Ne < Ar < Kr < Xe
   (ii) Solubility decreases from AlF_3 to AlI_3 due to decrease in covalent character (as per Fajan's rule)
   (iii) $FeCl_3$ is more polar than $FeCl_2$
4. **Dipole moment :** Compouds 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 o > m > p.
   (ii) Order of strength of H-bonding
   H----F > H----O > H----N
   (iii) Bond length of H bond is of order 250 to 275 pm.
   (iv) Strength of H-bonding increases when structures are resonance stabilsed.
   (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) H_2O 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 H_2O is maximum at 4°C because upto 4°C intermolecular H-bonding keep on breaking thereby decreasing volume and increasing density.
6. Valence bond theory (Proposed by Heatler and London and modified by Pauling and Slator) 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) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
   (b) $N_2 > N_2^+ = N_2^- > N_2^-$

(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 ahs 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

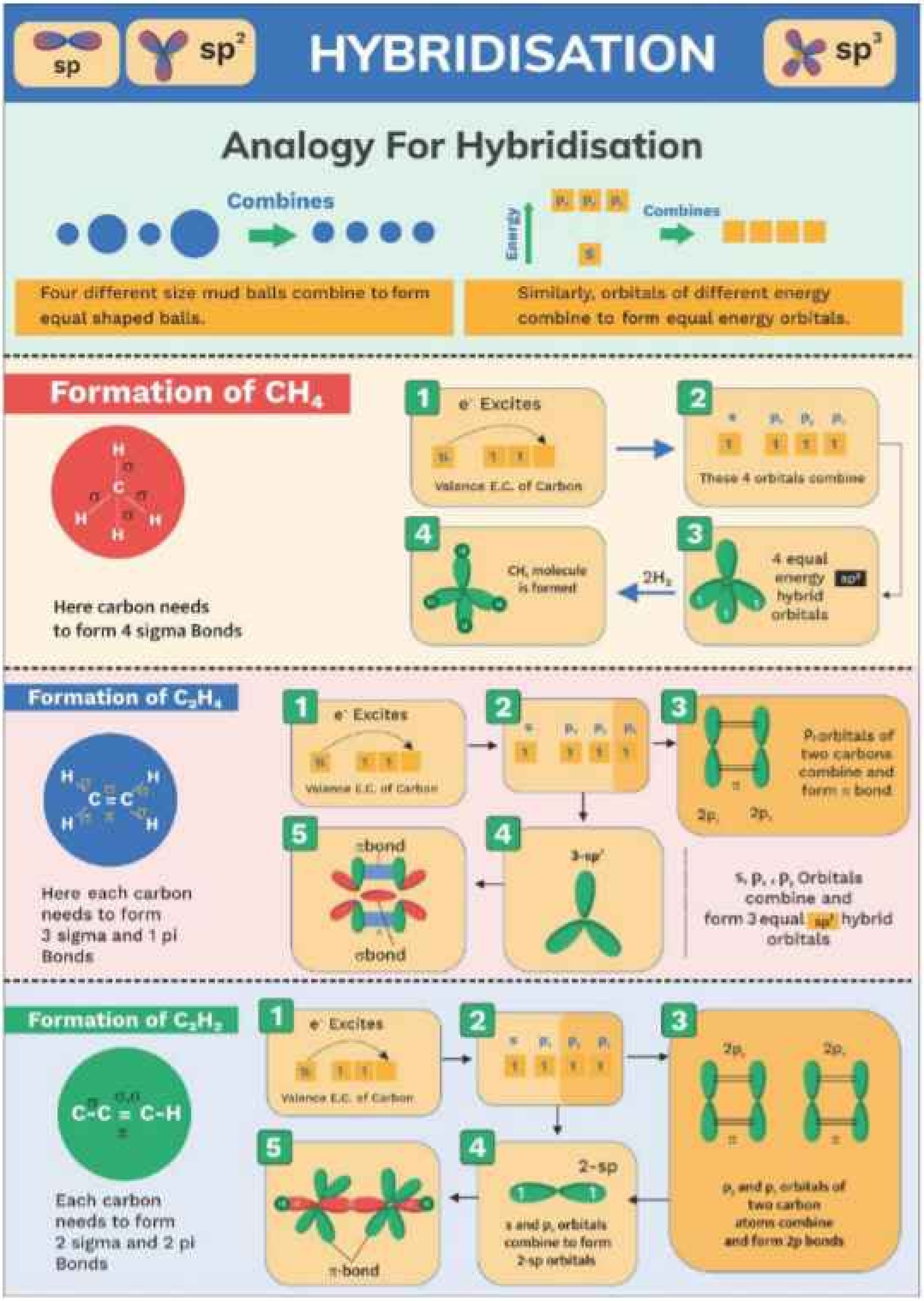
(i) In PCl_5, axial P—Cl bonds are longer than equatorial P—Cl bonds.

(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.



HYBRIDISATION

Analogy For Hybridisation

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

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

Formation of CH_4

Here carbon needs to form 4 sigma Bonds

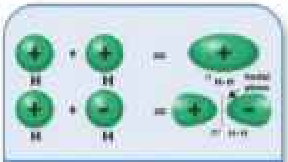
Formation of C_2H_4

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

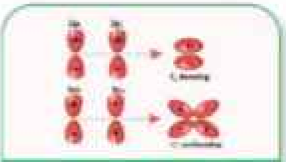
Formation of C_2H_2

Each carbon needs to form 2 sigma and 2 pi Bonds

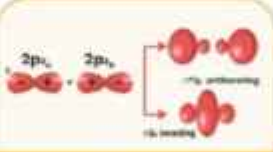
MOLECULAR ORBITAL THEORY



S-orbital of one atom combines with s-orbital of another atom constructively and destructively to form σ and σ* molecular orbitals.

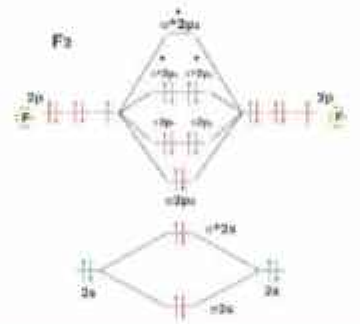


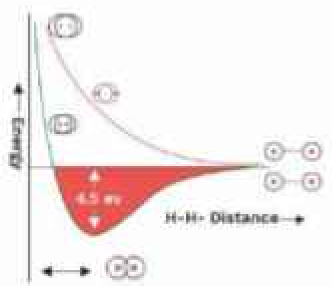
p_z orbital of one atom combines with p_z of another atom to form σ and σ* orbitals.



P_x and p_x orbitals combine and forms π and π* orbitals.

Energy Diagram of Molecular Orbitals





Hydrogen energy diagram

Bond Order

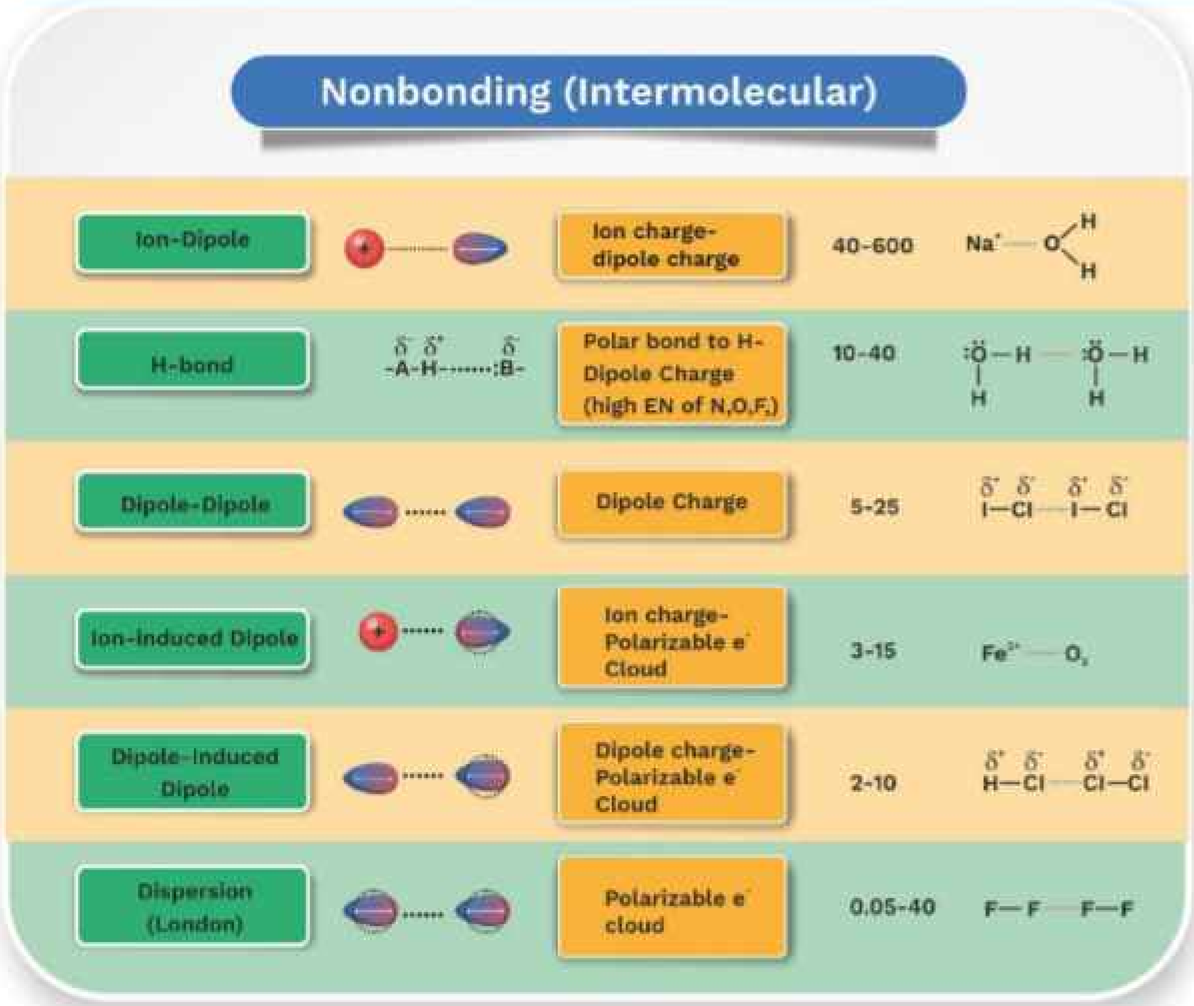
$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

N_b = Number of electrons in BMO

N_a = Number of electrons in AMO

Bond	H_2^+	H_2	He_2^+	He_2
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_2 molecule is not observed.



Nonbonding (Intermolecular)

Ion-Dipole		Ion charge-dipole charge	40-600	Na^+ — H_2O
H-bond	$-\overset{\delta^-}{A}-\overset{\delta^+}{H}\cdots\cdots:\overset{\delta^-}{B}-$	Polar bond to H-Dipole Charge (high EN of N,O,F,)	10-40	$:\ddot{O}H-H$ — $:\ddot{O}H-H$
Dipole-Dipole		Dipole Charge	5-25	$\overset{\delta^+}{I}-\overset{\delta^-}{Cl}$ — $\overset{\delta^+}{I}-\overset{\delta^-}{Cl}$
Ion-Induced Dipole		Ion charge-Polarizable e^- Cloud	3-15	Fe^{2+} — O_2
Dipole-Induced Dipole		Dipole charge-Polarizable e^- Cloud	2-10	$\overset{\delta^+}{H}-\overset{\delta^-}{Cl}$ — $\overset{\delta^+}{Cl}-\overset{\delta^-}{Cl}$
Dispersion (London)		Polarizable e^- cloud	0.05-40	F—F — F—F