Chemical Bonding & Molecular Structure

CHEMICAL BOND

(I) A force that acts between two or more atoms to hold them together as a stable molecule.

(II) This process accompanied by decrease in energy.

Solved Examples

Ex.1 When two atoms combine to form a molecule -

(A) Energy is released

(B) Energy is absorbed

(C) Energy is neither released nor absorbed

(D) Energy may either released or absorbed

Sol. (A) To attain stability energy is released.

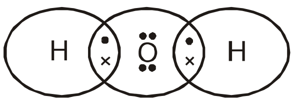
LEWIS OCTET RULE

(I) Every atom has a tendency to complete its octet outermost.

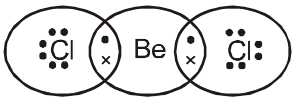
(II) H has the tendency to complete its duplet.

(III) To acquire inert gas configuration atoms loose or gain electron or share electron.

(IV) The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obeys octet rule



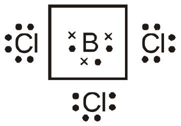
Doesn't obeys octet rule

Exception of Octet Rule :

(a) Incomplete octet molecules : - or (electron defficient molecules)

Compound in which octet is not complete in outer most orbit of central atom.

Examples - Halides of IIIA groups, BF_3, $AlCl_3$, BCl_3, hydride of III A/13th group etc.

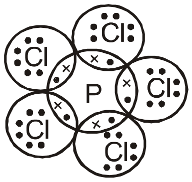


In BCl_3
Boron has only 6 electrons

Other examples - $BeCl_2$ ($4e^-$), $ZnCl_2$($4e^-$), $Ga(CH_3)_3$ ($6e^-$)

(b) Expansion of octet or (electron efficient molecules)

Compound in which central atom has more than 8e$^-$ in outermost orbits.



Electron dot formula of PCl_5

Example - In PCl_5, SF_6, IF_7, the central atom P, S and I contain 10, 12, and 14 electrons respectively.

(c) I-Pseudo inert gas configuration : -

(I) **Cations of transition metals, which contains 18 electrons in outermost orbit**

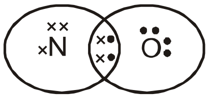
Examples : Ga^{+3}, Cu^+, Ag^+, Zn^{+2}, Cd^{+2}, Sn^{+4}, Pb^{+4} etc.

Electronic configuration of Ga - $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^1$

Electronic configuration of Ga^{+3} - $1s^2, 2s^2 2p^6, \underbrace{3s^23p^63d^{10}}_{18e^-}$

(d) Odd electron molecules : -

Central atom have an unpaired electron or odd no (7e$^-$, 11e$^-$ etc) of electrons in their outer most shell.



Examples : NO, NO_2 ClO_2 etc.

Solved Examples

Ex.2 Which follows octet rule -

(A) $FeCl_2$ (B) AgCl

(C) $CaCl_2$ (D) CuCl

Sol. (C) Because in other compounds there is more than 8 e$^-$ in outermost shell of central atom.

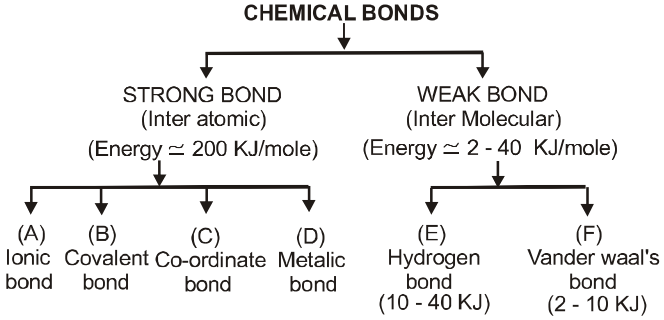
Ex.3 The octet rule is not obeyed in -

(A) CO_2 (B) BCl_3

(C) PCl_5 (D) SiF_4

Sol. (B) & (C) As B is electron dificient, P undergoes octet expansion.

Classification of bonds : -



ELECTROVALENT OR IONIC BOND

(I) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called **Ionic or electrovalent bond.**

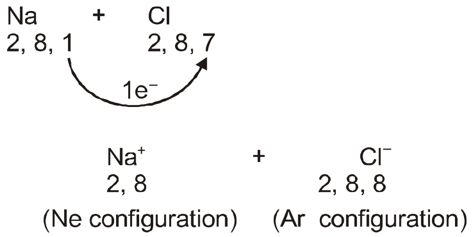
(II) Electro +ve atom loses electron (group IA to IIIA)

(III) Electro –ve atom gains electron (group VA to VIIA)

(IV) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Electronegativity difference ∝ nature of ionic bond.

Example IA and VIIA group elements form maximum ionic compound.

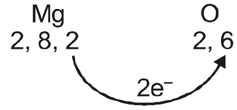


(V) More the distance between two elements in periodic table more will be ionic character of bond.

(VI) Total number of electron lose or gained is called electrovalency.

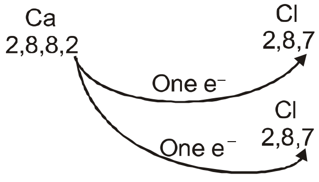
Example –

(a)



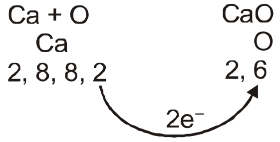
electrovalency of Mg = 2
electrovalency of O = 2

(b)



electrovalency of Ca = 2
electrovalency of Cl = 1

(c)



electrovalency of Ca = 2
electrovalency of O = 2

(VII) The **force of attraction is equal in all direction so ionic bond is non-directional.**

(VIII) Ionic compound do not have molecular formula. It has only empirical formula. eg. NaCl is empirical formula of sodium chloride.

Conditions for Forming Ionic Bonds :

Formation of Ionic bond depends upon these three factors –

(a) Ionisation energy :

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

Lesser Ionisation energy → Greater tendency to form cation.

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

Cation formation tendency

(b) Electron affinity

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

Higher electron affinity → Greater tendency to form anion

e.g. $Cl^{-} > F^{-} > Br^{-} > I^{-}$

$F^{-} > O^{-2} > N^{-3}$

(c) Lattice energy - (Energy released) Amount of energy released when one mole of crystal lattice is formed Higher lattice energy → Greater will be the stability or strength of ionic compound.

Factors affecting lattice energy :

(i) Magnitude of charge → $U \propto z^{+} z^{-}$ (Ionic charge)

Lattice energy ∝ Magnitude of charge

NaCl	$MgCl_2$	$AlCl_3$
Na^{+}	Mg^{+2}	Al^{+}

$$\xrightarrow{\hspace{12em}}$$

– Lattice energy increases

– Size of cation decreases.

(ii) Size of Cation : – Lattice energy $\propto \dfrac{1}{r^{+} + r^{-}}$

LiCl NaCl KCl RbCl CsCl

$$\xrightarrow{\hspace{12em}}$$

– Size of cation increasing

– Size of anion is constant

– Lattice energy decreases

(d) Overall lowering of energy :

Energy must be released during bond formation.

Energy changes are involved in the following steps –

$A + IE = A^{+} + e^{-}$

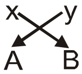
and $B + e^{-} = B^{-} + EA$

This concludes that for lower value of IE and higher value of EA there is more ease of formation of the cation & anion respectively and consequently more chances of electrovalent bond formation.

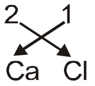
Representation of formula of compounds :

(a) Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as $A^{+}B^{-}$

(b) Write their electrovalencies in figure at the top of each symbol as A^xB^y

(c) Now apply criss cross rule as 

, i.e formula AyBx.

Examples : Calcium chloride 

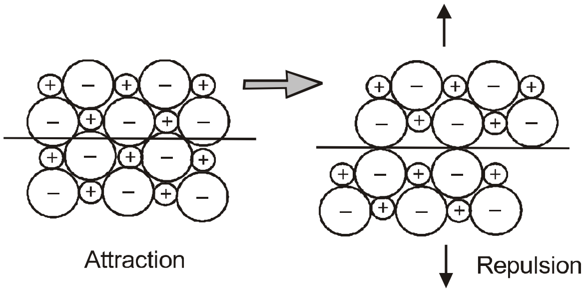
$= CaCl_2$

Properties of ionic compounds :

(a) Physical state –

Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction.

Brittleness →



(Same charged ions comes nearer.
So they repell each other)

(b) Isomorphism –

(I) Two compounds are said to be isomorphous if they have similar no. of electrons i.e.similar configuration of their cation and anion.

(II) They have similar crystal structure.

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

(c) Boiling point and melting point –

Ionic compounds have high boiling point and melting point due to strong electrostatics force of attraction among oppositely charged ions.

(d) Conductivity –

It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity.

In fused state or aqueous solution Due to free ions - Good conductor of eletricity.

conductivity order : Solid state > Fused state < Aqueous solution

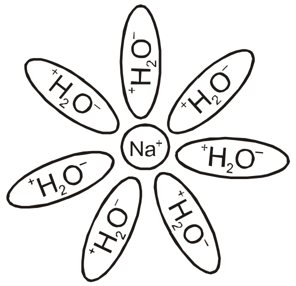
(e) Solubility –

Highly soluble in water (Polar solvents)

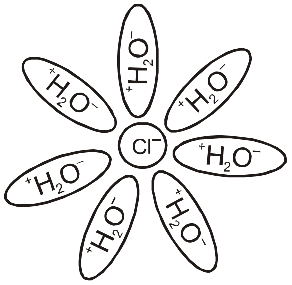
Example : NaCl in water

(I) The Na^+ ions get associates with– vely charged 'O' of water

(II) And Cl^- ions associates with +vely charged 'H' of water.



Oxygen atom of H_2O give its electron to Na^+



H atom of H_2O gain electron from Cl^-

(III) Thus charge on Na^+ and Cl^- decreases and electrostatics force of attraction also decreases which leads to free ion.

(IV) The energy released due to interaction between solvent and solute is called solvation energy.If water is used as solvent it is called hydration energy.

(V) For an ionic compound to be soluble in water – Hydration energy > Lattice energy

$$\text{Lattice energy} \propto \frac{1}{\text{Solubility}}$$

Hydration energy $\propto$ Solubility.

$$\text{Hydration energy (H)} \propto \frac{1}{r^+} + \frac{1}{r^-}$$

{r^+ & r^- are radius of cation and anion}

(VI) Hydration energy mainly depends on the cation radius because the value $\frac{1}{r^-}$ is negligible in comparison to $\frac{1}{r^+}$.

(VII) Down the group both the lattice energy & hydration energy decreases, if decreases in lattice is greater than hydration energy, solubility increases down the group and vice versa.

Solved Examples

Ex.4 Out of following which has maximum value of lattice energy -

(A) NaF (B) NaCl
(C) NaBr (D) NaI

Sol. (A) Due to small size of anion.

Ex.5 The crystal lattice of electrovalent compound is composed of -

(A) Atoms
(B) Molecules
(C) Oppositely charged ions
(D) Both molecules and ions

Sol. (C) It is the fact that electovalent compounds are made of ions.

Ex.6 Ions are formed from neutral atoms by -

(A) Loss of electron
(B) Gain of electrons
(C) Sharing of electrons
(D) Loss and gain of electrons

Sol. (D) Cation and anion are formed by losing and sharing of electrons respectively.

Factor affecting solubility :

(I) Dielectric constant –

The **capacity of solvent to neutralise the charge of ionic compounds** is called Dielectric constant. It is represented by "ε"

(a) Water has maximum dielectric constant ($\varepsilon = 80$)
(CH_3OH $\varepsilon = 35$) ,
(Acetone $\varepsilon = 21$)
(C_2H_5OH $\varepsilon = 27$) ,
(Ether = 4.1)
(Benzene $\varepsilon = 2.3$)
$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

(b) Ionic compounds are more soluble in the solvents, having high dielectric constant.

(c) H_2SO_4 and H_2O_2 have high dieletric constant but these are not a good solvent due to oxidising nature

(II) Size of ion :

(a) Keeping size of cation constant, the lattice energy decreases with the increases of anionic radius. Hence order of solubility of LiX in water is LiF < LiCl < LiBr < LiI

$$\text{As solubility} \propto \frac{1}{\text{lattice energy}}$$

(b) in LiI covalent nature is more according to Fajan's rule but HE > LE therefore Li is more soluble in water.

(c) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. hence order of solubility of MSO_4 will be –
$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
(Exception of Fajan's rule)

(d) If size of cation and anion is very large, solubility decreases from top to bottom.

(e) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)
$NaCl > MgCl_2 > AlCl_3$

(III) Polarisation of anion :

Polarisation capacity is maximum in pseudo inert gas configuration.

$$\text{solubility} \propto \frac{1}{\text{polarisation}}$$

$$\underrightarrow{\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}}$$

– Polarisation increases.

– Covalent character increases.

– Solubility decreases.

(IV) 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.

e.g. When NaCl is added in $AgNO_3$ solution, white ppt of AgCl is formed at once.

$$Ag^+NO_3^- + Na^+NO^- \rightleftarrows Na^+ NO_3^- + \underset{\text{white ppt.}}{AgCl\downarrow}$$

POLARISATION

(Fajan's Rule) (Covalent nature in ionic bond)

(I) When a cation approaches an anion closely the positive charge of a cation attract the electron cloud of the anion towards itself, due to the electrostatic force of attraction between them.

(II) At the same time cation also repel the positively charge nucleus of anion.

(III) Due to this combined effect, cloud of anion is bulged or elongated towards the cation. This is called distortion, deformation or Polarisation of the anion by the cation and anion is called Polarised.

Polarisation Power :

The ability of cation to polarise a nearby anion is called Polarisation power of cation.

Polarizability :

(I) ability of anion to get polarised by the cation.

(II) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.

(III) Polarisation $\propto$ Covalent character

(IV) Magnitude of polarisation depends upon a no. of factors, suggested by Fajan and are known as ajan's rule.

Fajan's rule : (Factors Affecting Polarisation)

(a) Size of cation : - Polarisation of the anion increases as the size of cation decreases.

$$\text{Polarisation} \propto \frac{1}{\text{size of cation}}$$

In a group –

$BeCl_2$
$MgCl_2$
$CaCl_2$
$SrCl_2$
$BaCl_2$ ↓

- Size of cation increases
- Covalent character decreases
- Ionic character increases

● Greatest polarising power of Be^{2+}, shows its maximum covalent character

In a period –

$$\underrightarrow{Na^+,\ Mg^{+2},\ Al^{+3},\ Si^{+4}}$$

- Size of cation decreases
- Covalent charater increases

(b) Size of anion : - If the size of the anion increases for a given cation, the covalent character increases/ Nature Polarisation $\propto$ size of anion.

CaF_2
$CaCl_2$
$CaBr_2$
CaI_2 ↓

- Size of anion increases
- Covalent character increases
- Ionic character decreases

(c) Charge on cation and anion : -

- Polarisation ∝ charge on cation anion

(I) Charge on cation ∝ Polarisation (covalent character)

eg. NaCl MgCl$_2$ AlCl$_3$ SiCl$_4$

Na^+ Mg^{++} Al^{+++} Si^{++++}

$\longrightarrow$

- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)

Charge on anion ∝ polarisation ∝ covalent nature $\propto \frac{1}{\text{M.P.}}$

(d) Electronic configuration of cation : -

Polarisation capacity of cation having pseudo inert gas configuration is high. If the size of cations is same than that of cation having inert gas configuration.

CuCl (M.P. 442°C) $\longrightarrow Cu^+$ 2, 8, 18 (Covalent)

NaCl (M.P. 800°C) $\longrightarrow Na^+$ 2, 8 (Ionic)

Cu^+ and Na^+ both the cation (Pseudo & inert) have same charge and size but polarising power of Cu^+ is more than Na^+ because –

zeff of ns^2p^6 (inert) < zeff. of $ns^2p^6d^{10}$ (pseudo)

Na^+ < Cu^+

(Ionic) (Covalent)

So CuCl has more covalent character than NaCl.

Solved Examples

Ex.7 Compound with maximum ionic character is formed from -

(A) Na and Cl (B) Cs and F

(C) Cs and I (D) Na and F

Sol. (B) Using fajan's rule, larger cation and smaller anion will have max. Ionic character.

Ex.8 Out of the following which one has the highest values of covalent character -

(A) ZnCl$_2$ (B) CaCl$_2$ (C) CdCl$_2$ (D) CuCl

Sol. (A) Because Zn^{+2} has smallest size among the all.

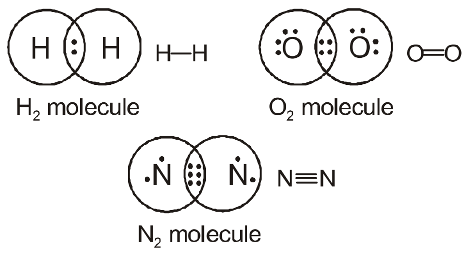
Ex.9 Compound having highest M.Pt. –

(A) BeCl$_2$ (B) MgCl$_2$ (C) CaCl$_2$ (D) SrCl$_2$

Sol. (D) As the size of cation increases polarisizing power decreases hence ionic character increases

COVALENT BOND

(I) A covalent bond is formed by the mutual sharing of electrons between two atoms of electro negative elements to complete their octet. (Except H which completes its duplet).

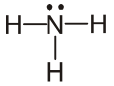


H$_2$ molecule O$_2$ molecule N$_2$ molecule

(II) The shared pair of electrons should have opposite spins, and are localised between two atoms concerned.

(III) Shairing of electrons may occurs in three ways –

No. of electrons shared between two atoms	Electron pair	Bond
2	1	Single bond (—)
4	2	Double bond (=)
6	3	Triple bond (≡)

Examples –  Three single bonds

(not triplet bond)

N≡N Triple bond. (not three bond) O=O Double bond (Not two single bond) H—O—H (Two single bonds.)

Lewis structure and covalent bond :

(I) Electron dot structures, also known as Lewis structures of covalent molecules, are written in accordance with octet rule.

(II) All atoms in a formula will have a total of eight electrons by sharing in the valence shell except the H-atom which forms the largest number of bonds with other atoms placed in the centre of skeleton structure. Other atoms surrounds it to complete the octet.

(III) Structure in which valence electrons are represented by dots are called lewis structures.

(IV) Structure represented by line (–) or dashes are known as couper structrue.

(V) Lewis dot formulae show only the number of valency electron, the number and kinds of bonds, but do not depict the three dimensional shapes molecules and polyatomic ions.

Orbital concept of covalent bond :

(I) One orbital can accomodate at the most 2 electrons with opposite spins $\boxed{\uparrow\downarrow}$

(II) Half filled orbital or unpaired electron orbital accepts one electron from another atom, to complete its orbitals.

(III) Tendency to complete orbital or to pair the electron is an essential condition of covalent bond. Completion of octet is not the essential condition of covalent bond.

(IV) **Covalency :** It is defined as the number of electrons contributed by an atom of the element for shairing with other atoms to achieve noble gas configuration.

(V) If the outermost orbit has empty orbitals then covalent bonds are formed in exicted state.

Variable valency in covalent bonds :

(I) Variable valencies are shown by those elements which have empty orbitals in outermost shell.

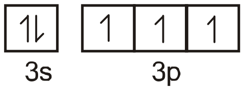
(II) Lone pair electrons gets excited in the subshell of the same to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

(III) The energy required for excitation of electrons is called promotion energy.

(IV) Promotion rule – Excitation of electrons in the ame orbit.

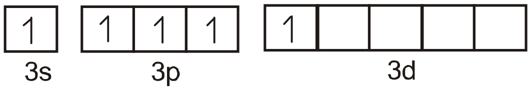
Example –

(a) Phosphorus → Ground state



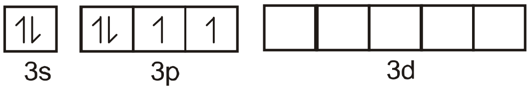
Covalency 3 (PCl_3)

Phosphorus → Excited state



Covalency – 5 (PCl_5)

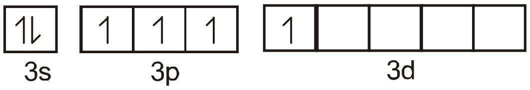
(b) Sulphur → Ground state.



Covalency – 2 (SF_2)

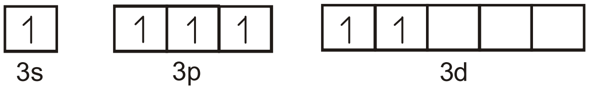
Sulphur → Excited state

1st excited state



Covalency – 4 (SF_4)

2st excited state

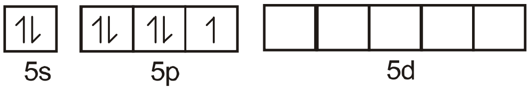


Covalency – 6 (SF_6)

So variable covalency of S is 2, 4 & 6.

(c) Iodine has three lone pair of electrons

(Ground state)



So it shows three excited states – Maximum number unpaired electrons = 7

Variable Valencies are 1, 3, 5, 7

Applications of Variable Valency :

(I) To explain existence of molecules –

NCl_3 – exists

NCl_5 – doesn't exists (due to absence of d-orbitals in Nitrogen.) While PCl_3 and PCl_5 both exist because 3d orbitals are present in phosphorus.

OF_2 — exists, but OF_4 and OF_6 doesn't exists due to absence of d-orbitals While SF_4 and SF_6 exists due to presence of d-orbital, present in its valence shell.

(II) Hydrolysis of compounds –

$CCl_4 + H_2O \rightarrow$ No reaction occurs

$SiCl_4 + H_2O \rightarrow$ Reaction occurs

In C-atom there are no empty d-orbitals to accept the lone pair of electrons from water. While $SiCl_4$ has

empty 3d-orbitals.

$$SiCl_4 + 4H_2O \xrightarrow[-4HCl]{} \underset{\text{Unstable}}{Si(OH)_4} \longrightarrow SiO_2$$

Solved Examples

Ex.10 A covalent bond is possible between -

(A) Similar atom
(B) Dissimilar atoms
(C) Similar and dissimilar atoms
(D) Similar molecules

Sol. (C) It is related to electronegativity.

Ex.11 Which of the following is most covalent -

(A) AlF_3 (B) $AlCl_3$
(C) $AlBr_3$ (D) AlI_3

Sol. (D) As the size of anion increases covalent character increases.

Ex.12 Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order -

(A) $LiCl < BeCl_2 > BCl_3 > CCl_4$
(B) $LiCl > BeCl_2 < BCl_3 < CCl_4$
(C) $LiCl < BeCl_2 < BCl_3 < CCl_4$
(D) $LiCl > BeCl_2 > BCl_3 > CCl_4$

Sol (C) The covalent character increases according to charge on cation.

Wave mechanical concept of chemical bonding – (Overlapping)

To explain the nature of covalent bond two theories based on quantum mechanics have been proposed.

(1) Valence bond theory (VBT)
(2) Molecular orbital theory (MOT)

VALENCE BOND THEORY

(I) It was presented by Heitler & London to explain how a covalent bond is formed.
It was extended by Pauling & Slater.

(II) The main points of theory are –

(a) To form a covalent bond overlapping occurs between half filled valence shell orbitals of the two atoms.

(b) Resulting bond acquires a pair of electrons with opposite spins to get stability.

(c) Orbitals come closer to each other from the direction in which there is maximum overlapping

(d) So covalent bond has directional character.

(e) Extent of overlapping $\propto$ strength of chemical bond.

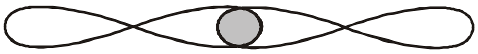
(f) Extent of overlapping depends on two factors.

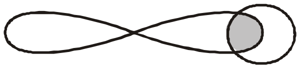
(i) Nature of orbitals – p, d and f are directional orbitals → more overlapping
s-orbitals → non directional – less overlapping

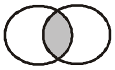
(ii) Nature of overlapping – Co-axial overlapping - extent o overlapping more.
Collateral overlapping - extent of overlapping less

Order of strength of Co - axial overlapping

– p - p > s - p > s - s


p - p


p - s


s - s

(g) As the value of n increases, bond strength decreases.

1 - 1 > 1 - 2 > 2 - 2 > 2 - 3 > 3 - 3

(h) If n is same 2p - 2p > 2s - 2p > 2s - 2s
1s - 2p > 2s - 2p > 3s - 3p

(i) Electron which is already paired in valency shell can enter into bond formation, it they can be unpaired first and shifted to vacant orbitrals of slightly higher energy of the same energy shell.

(j) This point can explain the trivalency of boron, tetravalency of carbon, penta valency of phosphorus etc.

(k) Two types of bonds are formed on acount of overlapping.

(A) Sigma (σ) bond
(B) Pi (π) bond

(A) Sigma (σ) bond :

(I) Bond formed between two atoms by the overlapping of half filled orbitals along their axis (end to end overlap) is called sigma bond.

(II) σ bond is directional.

(III) σ bond do not take part in resonance.

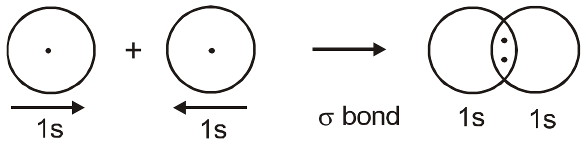
(IV) Free rotation is possible about a single σ bond.

(V) Maximum overlapping is possible between electron clouds and hence it is strong bond.

(VI) There can be only σ bond between two atoms.

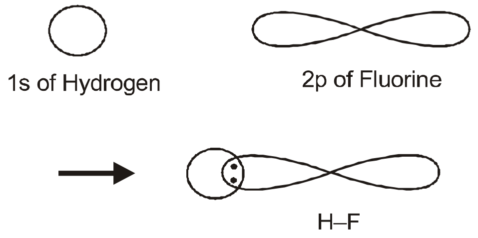
Sigma bond are formed by four types of overlapping

(a) s - s overlapping (H_2) - Two half filled S-orbitals overlap along the internuclear axis.



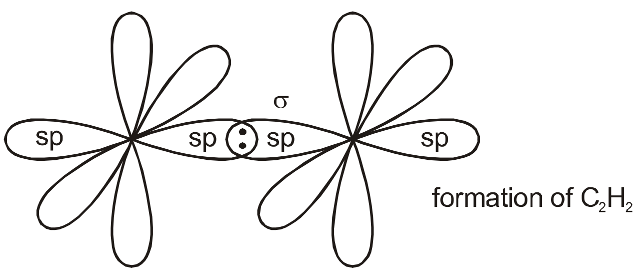
(Formation of H_2 molecule)

(b) s - p overlapping (Formation of HF) – When half fill s-orbital of one atom overlap with half filled p-orbital of other atom.



(c) Bond between two hybrid orbitals –

sp^3 - sp^3, sp^2 - sp^2, sp^3 - sp^2, sp^3 - sp etc.

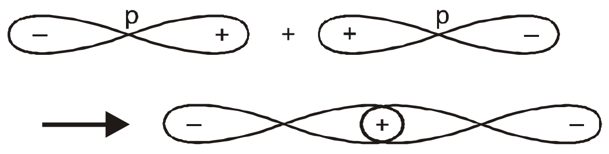


sp-sp hybrid orbital

overlapping of orbitals form σ bond.

(d) p - p overlapping – (Coaxial) – It involves the coaxial overlapping between half filled p-orbitals of two different atoms.

eg. Formation of Cl_2, F_2, Br_2



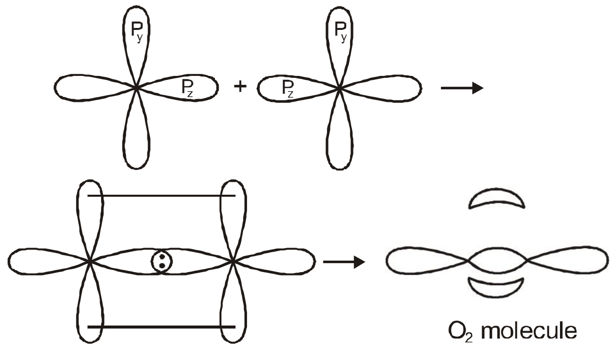
p-p overlapping

(B) Pi (π) bond

(I) The bond formed by sidewise (lateral) overlapping are known as π bonds.

(II) Lateral overlapping is only partial, so bonds formed are weaker and hence more reactive than σ bonds (Repulsion between nucleus is more as orbitals have to come much close to each other for π bonds formation)

Example – Formation of O_2 molecule –



Only p_y and p_z of oxygen atom have unpaired e^- in each orbital for bonding.

Electron configuration of oxygen is – $1s^2 2s^2 2p_x^2$ $2p_y^1 2p_z^1$

(III) Free rotation about a π bond is not possible.

(IV) π bond is weaker than σ bond (Bond energy difference is 63.5 KJ or 15 K cal/mole)

(V) π bonds are non-directional, so do not determine the shape of a molecule.

(VI) π bond takes part in resonance.

(VII) π bond formed by pure or unhybrid orbitals.

HYBRIDISATION

Consider an example of Be compound :-

If it is formed without hybridisation then -

$$Cl\overset{s-p}{—}Be\overset{p-p}{—}Cl$$

both the Be–Cl bonds should have different parameters and p-p bond strength >s-p bond strength.

Practically bond strength and distance of both the Be-Cl bonds are same.

This problem may overcome if hybridisation of s and p-orbital occurs.

Hybridisation :

(I) It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.

(II) **Definition :** Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals. and the phenomenon is called hybridisation.

Now after considering s-p hybridisation in $BeCl_2$

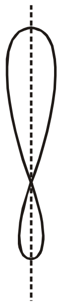
$$Cl\overset{sp-sp}{—}Be\overset{sp-p}{—}Cl$$

bond strength of both the bonds will be equal.

Characteristic of Hybridisation :

(I) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.

(II) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.



Structure of hybrid orbital

(III) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.

(IV) The number of hybrid orbitals on central atom of a molecule or ion = number of σ bonds + lone pair of electron.

(i) The 1st bond between two atoms will be sigma.

(ii) The other bond between same two atoms will be pi bond.

(iii) Maximum two pi bonds may be present on a single atom.

(iv) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.

(V) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp, sp^2 and sp^3 hybridisation in its compounds.

(VI) Hybrid orbitals are differentiated as **sp, sp^2, sp^3** etc.

(VII) The order of repulsion between Ip & bp is :

Ip - Ip > Ip - bp > bp - bp

(VIII) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.

$$sp < sp^2 < sp^3 < sp^3d < sp^2d^2 < sp^3d^3$$

Difference between hybridisation & overlapping

Overlapping	Hybridisation
● It occurs between orbitals of two atoms	● It occurs among orbitals of the same atom
● Only half filled orbitals takes part in overlapping	● Any type of orbital can participates
● It occurs during bond formation bond formed after hybridisation	● Process, just before overlapping.
● Orbital of different energies may participates in excited states.	● It may takes place in ground or in excited state Inground state– NH_3, NCl_3, PH_3, PCl_3,
● Molecular orbitals are formed	● Hybridised orbitals are formed

Determination of hybridisation state –

Method (I) :

Count the following pair of e^- arround the central atom :

(a) Count all pure σ bonded electron pairs (or σ bonds)

(b) Count all lone pair of electron

(c) Count Co ordinate bond

(d) Count negative charge

Method (II) :

To predict hybridisation following formula may be used :

No. of hybrid orbital = $\frac{1}{2}$

[Total number of valence e^- in the central atom + total number of monovalent atoms – charge on cation + charge on anion]

eg. NH_4^+ $\frac{1}{2}[5+4-1]=4$ sp^3 hybridisation.

SF_4 $\frac{1}{2}[6+4]=5$ sp^3d hybridisation.

SO_4^{2-} $\frac{1}{2}[6+2]=4$ sp^3 hybridisation.

('O' is divalent so add only charge on anion)

NO_3^- $\frac{1}{2}[5+1]=3$ sp^2 hybridisation.

If such type of e^- pairs are –

two	–	sp	hybridisation
three	–	sp^2	hybridisation
four	–	sp^3	hybridisation
five	–	sp^3d	hybridisation
six	–	sp^3d^2	hybridisation
seven	–	sp^3d^3	hybridisation

Types of Hybridisation :

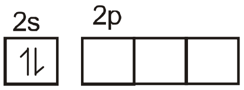
sp hybridisation :

(I) In this hybridisation one s– & one P–orbital of an atom are mixed to give two new hybrid orbitals which are equivalent in shape & energy known as sp hybrid orbitals.

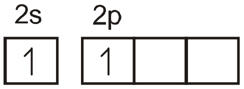
(II) These two sp hybrid orbitals are arrange in straight line & at bond angle 180°.

(III) s-character 50%

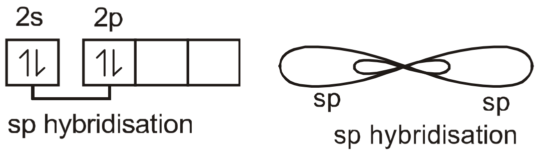
Be (ground state)



Be (excited state)

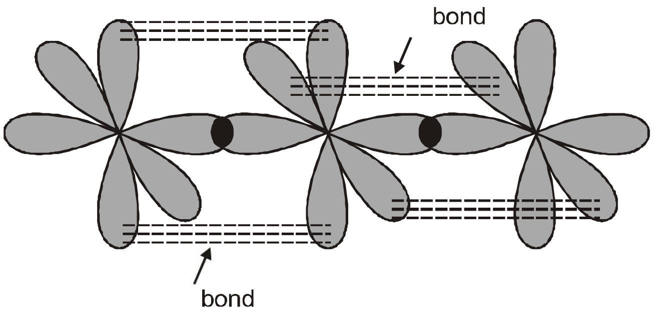


Be atom accepts two electrons from F in BeF_2,



CO_2 Molecule (O = C = O) :

In CO_2 molecule, C has two sp hybrid orbitals & two unhybridised p orbitals.



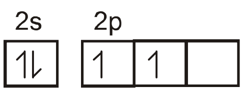
Molecular orbital picture of CO_2

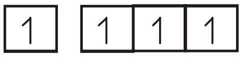
- Thus, CO_2 molecule is a linear in shape & having 180° bond angle.
- The bond length between C–O bond is reduced due to the presence of π bond.

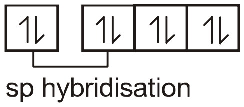
$CH\equiv CH$ [$H—C_A\equiv C_B—H$]

In $CH\equiv CH$ molecules, each C atom contains two sp hybrid orbitals & two unhybridised p orbitals

C(ground state)



C(excited state) 

C atom accepts four electrons 

from H & C, In C_2H_2

- sp hybrid orbital of each C overlaps to give sigma bond between C – C.
- The remaining one sp hybrid orbital of each C atom overlaps with s orbital of H, forming sigma bond between C – H.
- The two unhybridised p orbitals of each C atom (p_y and p_x) overlap laterally to form two pi(π) bonds.
- Therefore in $H{-}XC_A \equiv C_B{-}H$
  sigma bond between $C_A - C_B$ is formed sp – sp overlapping
  sigma bond between C_A – H is formed sp – s overlapping
  sigma bond between C_B – H is formed sp – s overlapping
  pi bond between $C_A - C_B$ is formed : $p_y - p_y$, $p_x - p_x$ overlapping
- Each C atom forms two sigma bonds but in C_2H_2, total sigma bonds are 3
- Each C atom forms two π bonds. Total π bonds in C_2H_2 are two
- Total number of bonds in acetylene are :
  $3\sigma + 2\pi$ bond = 5 bonds

Examples on sp hybridisation

Example	s bond	I.p.e.	Hybridisation	Bond angle	Shape
BeH_2	2	-	sp	180°	Linear
BeF_2	2	-	sp	180°	Linear
$BeCl_2$	2	-	sp	180°	Linear
$BeBr_2$	2	-	sp	180°	Linear
BeI_2	2	-	sp	180°	Linear
CO_2	2	-	sp	180°	Linear
CO	1	1	sp	180°	Linear
NO_2^+	2	-	sp	180°	Linear
C_2H_2	2	-	sp	180°	Linear
HCN	2	-	sp	180°	Linear
$ZnCl_2$	2	-	sp	180°	Linear
$HgCl_2$	2	-	sp	180°	Linear
$CdCl_2$	2	-	sp	180°	Linear
N_2O	2	-	sp	180°	Linear
N_3^-	2	-	sp	180°	Linear

sp^2 Hybridisation :

(I) In this hybridisation one & two p orbitals are mixed to give three new sp^2 hybrid orbitals which all are in the same shape & equivalent energies.

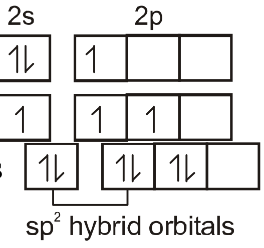
(II) These three sp^2 hybrid orbitals are at angle of 120° & giving **trigonal planar shape.**

B (ground state)

B (excited state)

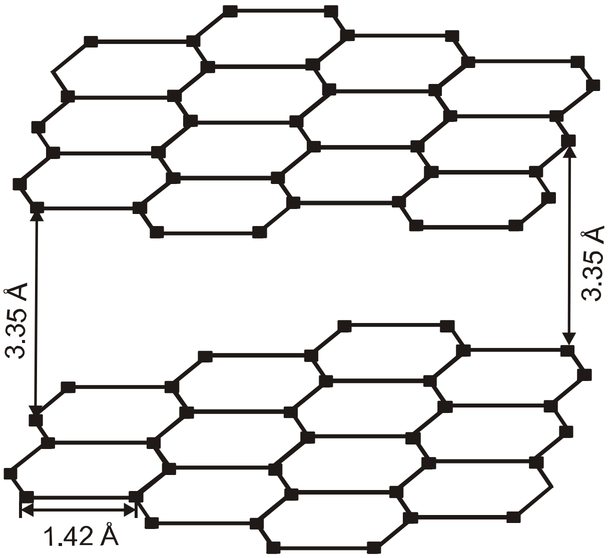
B atom accepts 3 electrons

From 3 F atom ∴ in BF_3



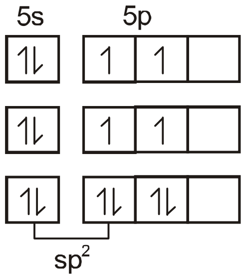
(III) s - character 33.3%

Graphite :



- The hybridisation on each carbon atom of graphite is sp^2
- Three sp^2 hybrid orbital are present on each carbon atom at 120° & they overlap to sp^2 hybrid orbitals of adjacent C atoms forming layers of hexagons.
- On each carbon atom, one unhybridised. p orbital is also present, which is perpendicular to the plane of sp^2 hybrid orbitals.
- The distance between two layer in graphite is 3.35 Å.

SnX_2 (X = F, Cl, Br, I)



Sn (ground state)

Sn (excited state)

Sn after hybridisation

shares $2e^-$ with 2 atom.

- SnX_2 having two σ bonds & one LP electron therefore hybridisation is sp^2
- The bond angle is SnX_2 will be less than 120° (due to presence of one LPe.)
- The shape of SnX_2 molecule is bent.

Examples on sp^2 hybridisation

Example	s bond	I.p.e.	Hybridisation	Bond angle	Shape
BH_3	3	-	sp^2	120°	Trigonal planar
BF_3	3	-	sp^2	120°	Trigonal planar
BCl_3	3	-	sp^2	120°	Trigonal planar
CH_3	3	-	sp^2	120°	Trigonal planar
$CH_2= CH_23$,	3	-	sp^2	120°	Trigonal planar
Graphite	3	-	sp^2	120°	Trigonal planar
HNO_3	3	-	sp^2	120°	Trigonal planar
NO_3^-	3	-	sp^2	120°	Trigonal planar
HNO_2	2	-	sp^2	< 120°	Angular (V)
SO_2	2	-	sp^2	< 120°	Angular (V)
SO_3	3	-	sp^2	120°	Trigonal planar
HCO_3^-	3	-	sp^2	120°	Trigonal planar
CO_3^{-2}	3	-	sp^2	120°	Trigonal planar
$SnCl_2$	2	1	sp^2	< 120°	Angular (V)
$SnBr_2$	2	1	sp^2	< 120°	Angular (V)
SnI_2	2	1	sp^2	< 120°	Trigonal planar
$AlCl_3$	3	-	sp^2	120°	Trigonal planar
$GaCl_3$	3	-	sp^2	120°	Trigonal planar
$PbCl_2$	2	1	sp^2	< 120°	Angular (V)

sp^3 Hybridisation :

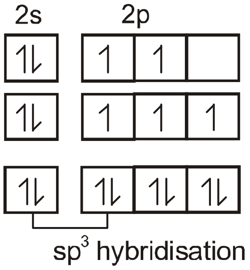
(I) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

(II) The angle between these four hybrid orbitals will be 109°28’

C (ground state)

C (excited state)

C atom share four electrons with 4 hydrogen atoms



(III) The shape obtained from these hybrid orbitals would be tetrahedron.

Three following examples represent this condition.

(a) Four sigma bonds with zero lone pair electron :

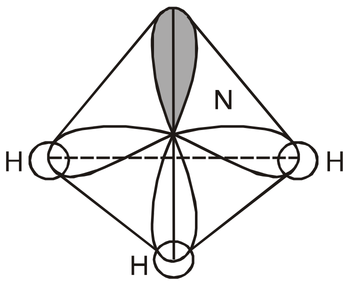
The following examples represent this condition.

CH_4, CF_4, CCl_4, CBr_4, Cl_4, NH_4^+, BF_4^-, AlF_4^-, BeF_4^{-2},

In above compounds, bond angle is 109°28’ & tetrahedron shape.

(b) Three sigma bonds & one lone pair of electron

(I) This condition is shown by following compounds & ions.



Molecular pyramidal orbital of NH_3

NH_3,PH_3,AsH_3,SbH_3,BiH_3,NF_3,PF_3,NCl_3,PCl_3 : CH_3,H_3O^+ ClO_3^-

(II) sp^3 hybridisation, pyramidal shape & bond angle will be less than due to the presence of the lone pair electron on nirtogen repels bond pair electron more therefore bond angle is reduced from 109°28’ to 107°.

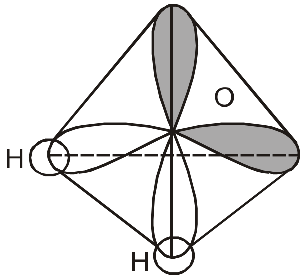
The repulsion between IP – b.p > bp – bp.

(c) Two sigma bonds & two lone pair lone pair electrons :

(I) This condition is shown by following compounds and ions.

H_2O, H_2S, H_2Se, H_2Te, OCl_2, OBr_2, OF_2, OI_2 etc.

(II) In all above examples, the central atom showing sp^3 hybridisation, angular shape and bond angle will be either less then 109°28’ or more than 109°28’.



Molecular angular orbital of H_2O

In H_2O the hybridisation on O atom is sp^3, but due to presence of two lone pair electrons they repell each other and then repell their adjacent bond pair electron. These repulsion will be in following order.

I.p. – I.p. > I.p. – b.p. > b.p. – b.p.

l.p. = lone pair electron

b.p. = bond pair electron

Examples on sp^3 Hybridisation

Example	σ bond	l.p.e.	Hybridisation	Shape
CH_4	4	-	sp^3	Tetrahedron
CCl_4	4	-	sp^3	Tetrahedron
CBr_4	4	-	sp^3	Tetrahedron
PCl_4^+	4	-	sp^3	Tetrahedron
NH_4^+	4	-	sp^3	Tetrahedron
BF_4^-	4	-	sp^3	Tetrahedron
AlF_4^-	4	-	sp^3	Tetrahedron
BeF_4^{-2}	4	-	sp^3	Tetrahedron
MgF_4^{-2}	4	-	sp^3	Tetrahedron
$Ni(CO)_4$	4	-	sp^3	Tetrahedron
NF_3	3	-	sp^3	Pyramidal
NCl_3	3	1	sp^3	Pyramidal
$N(CH_3)_3$	3	1	sp^3	Pyramidal
PF_3	3	1	sp^3	Pyramidal
PCl_3	3	1	sp^3	Pyramidal
$AsCl_3$	3	1	sp^3	Pyramidal
$SbCl_3$	3	1	sp^3	Pyramidal
$BiCl_3$	3	1	sp^3	Pyramidal
NH_3	3	1	sp^3	Pyramidal
$:^{-}CH_3$	3	1	sp^3	Pyramidal
H_3O^+	3	1	sp^3	Pyramidal
SO_3^{2-}	3	1	sp^3	Pyramidal
ClO_3	3	1	sp^3	Pyramidal
XeO_3	3	1	sp^3	Pyramidal
H_2O	2	2	sp^3	Angular (V)
H_2S	2	2	sp^3	Angular (V)
NH_2^-	2	2	sp^3	Angular (V)
OF_2	2	2	sp^3	Angular (V)
Cl_2O	2	2	sp^3	Angular (V)
SCl_2	2	2	sp^3	Angular (V)
Diamond	4	-	sp^3	Tetrahedron
SiO_2	4	-	sp^3	Tetrahedron
SiC	4	-	sp^3	Tetrahedron

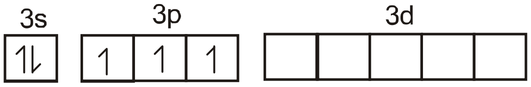
sp^3d Hybridisation :

(I) In this hybridisation one s orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

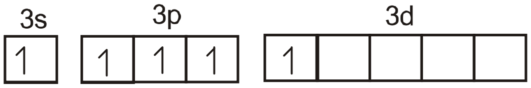
(II) Out of these five orbitals, three hybrid orbitals are at 120° angle and two hybrid orbitals are perpendicular to the plane of three hybrid orbitals that is trigonal planar, the shape of molecule becomes is trigonal bipyrmaidal.

For example, PF_5 showing sp^3d hybridisation

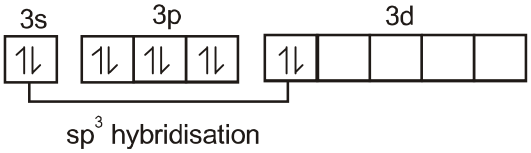
P (ground state)



P* (excited state)



P atom share with five e of F



(III) In this hybridisation dz^2 orbital is hybridised with s and p orbitals.

In this way five sp^3d hybrid orbitals form five sigma bond with five F atoms and give a molecule of PF_5, shape of this molecule is trigonal bipyramidal.

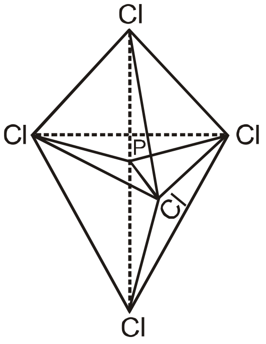
Axial two P–Cl bonds are longer than equatorial three P–Cl bond due to repulsion between 3 equatorial bp of e^- and 2 axial b.p. of e^-

In above hybridisation there are four conditions

(a) Five sigma bonds and zero lone pair electron :

The following examples represent this conditions.

PF_5, PCl_5, PBr_5, PI_5, AsF_5, $AsCl_5$, $SbCl_5$, SbF_5 etc.



Structure of PCl_5

The shape of all above molecules is trigonal bipyramidal.

(b) Four sigma bonds and one lone pair of electron

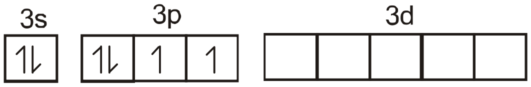
The following examples represent this condition.

SF_4, SeF_4, TeF_4, PoF_4, PF_4^-, SbF_4^-, SCl_4, $SeCl_4$, $TeCl_4$ etc.

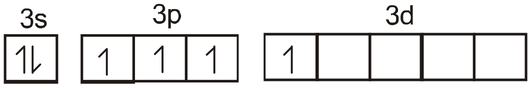
The shape of all above examples will be irregular tetrahedron.

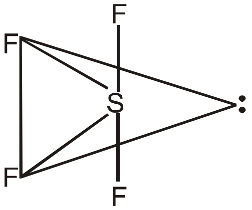
Examples SF_4

S ground state



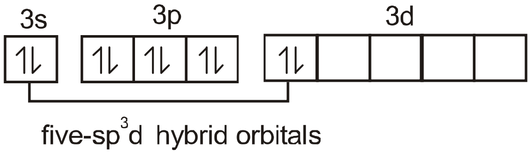
S excited state





Structure of SF_4

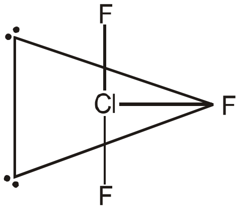
S atom share with four e^- of F



(c) Three sigma bonds & two lone pair of electrons :

The following examples represent this condition.

ClF_3, BrF_3, IF_3, $BrCl_3$, ICl_3 etc.



Structure of ClF_3

The shape of all above compounds is 'T' shape.

(d) Two sigma bonds & three lone pair of electrons :

The following examples represent this condition.

ICl_2^-, IBr_2^-, ClF_2^-, IF_2^-, BrF_2^-, XeF_2^-, I_3^-, Br_3^-

The geometry of above examples will be linear

sp^3d^2 Hybridisation :

(I) In this hybridisation, one s-orbitals, three p-orbitals & two d-orbitals are mixed to give six new hybrid orbitals known as sp^3d^2 hybrid orbitals.

(II) The shape of molecule obtained from above six hybrid orbitals will be symmetrical octahedral.

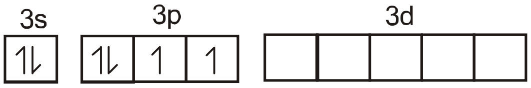
(III) The angle between all hybrid orbitals will be 90°.

Example : SF_6, AlF_6^{-2}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,

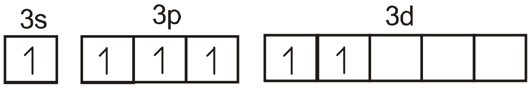
(IV) Two 'd' orbital participates in the hybridisation are $d_{x^2-y^2}$ and d_{z^2}.

SF_6 :

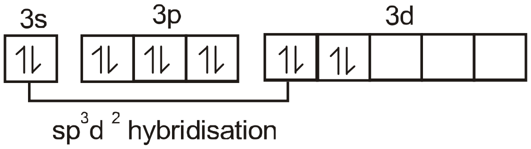
S (ground state)



S (excited state)



S (after hybridisation)



sp^3d^3 Hybridisation :

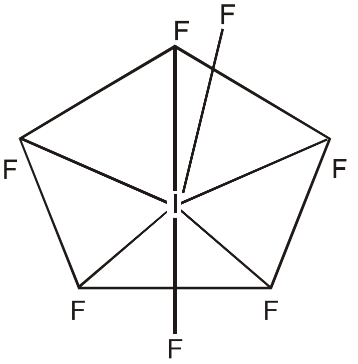
(I) In this hybridisation, one s-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.

(II) In this hybridisation d-orbitals used are d_{xy} d_{xz} & d_{yz} orbitals.

(III) These seven sp^3d^3 orbitals are configurated in pentagonal bipyramidal shape.

(IV) Five bond angles are of 72° & two bond angles of 90°.

(V) The following examples showing sp^3d^3 hybridisation –IF_7 & XeF_6.



Structure of IF_7

Shape of covalent molecules :

- It was given by Sidgwick & Powel.
- According to this concept the shape of covalent compound depends on total pairs of electron (bonded or non bonded) present on the central atom. Which is given as below –

S.No.	Total pair of e^-	Shape	Hybridisation
1.	Two	Linear	sp
2.	Three	Coplaner trigonal (Triangular)	sp^2
3.	Four	Tetrahedral	sp^3
4.	Five	Trigonal bipyramidal	sp^3d
5.	Six	Octahedral (Square bipyramidal)	sp^3d^2
6.	Seven	Pentagonal bipyramidal	sp^3d^3

Solved Examples

Ex.13 The hybridization of carbon atoms ion C – C single bond of $H - C \equiv C - CH = CH_2$ is -

(A) sp^3-sp^3 (B) sp^2-sp

(C) sp-sp^2 (D) sp^3-sp

Sol. (C) As the first carbon has triple bond and second one has double bond with other two carbon atom.

Ex.14 C – C bond in C_2H_6 undergoes heterolytic fission, the hybridisation of carbon is/are -

(A) sp^2 (B) sp^3

(C) sp^2, sp^3 (D) sp, sp^2

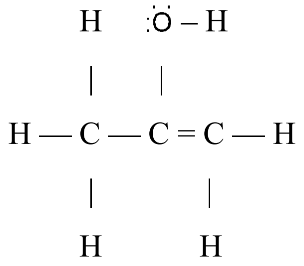
Sol. (C) During heterolytic fission there will be formation of CH_3^+ and CH_3^- which has sp^2 and sp^3 hybridization respectively.

Ex.15 The enolic form of actone contain σ bond (a), π bond (b) lone pair (c) -

(A) 9a, 1b, 2c (B) 8a, 2b, 2c

(C) 10a, 1b, 1c (D) 9a, 2b, 1c

Sol. (A) This is clear from its structure as shown below.



Ex.16 The hybridization and geometry of BrF_3 molecule are -

(A) sp^3d and distorted trigonal bipyramidal

(B) sp^3d^2 and Tetragonal

(C) sp^3d and bent

(D) None

Sol. (A) There is one s, three p and one d orbital while hybridization

Glesspie and Nyhom theory or VSEPR theory :

(Valence shell electron pair repulsion theory)

(I) If the cenral atom possess only bonded pairs of electrons along with identical atoms then shape of the compound is symmetrical and according to Sidgwick & Powl.

eg. BF_3 – 120° – triangular

CH_4 – 109°28' – tetrahedral

CO_2 – 180° – linear

(II) If the central atom possess bonded pair of electrons as well as lone pair of electron, then shape of the molecule will be unsymmetrical ie. the original bond angle will disturbed due to repulsion between lone pair of electrons.

similarly on having different type of side atoms, molecule becomes unsymmetrical due to unequal force of repulsion between e^-. Order of repulsion is –

$$\ell.p. - \ell.p > \ell.p - b.p. > b.p. - b.p.$$

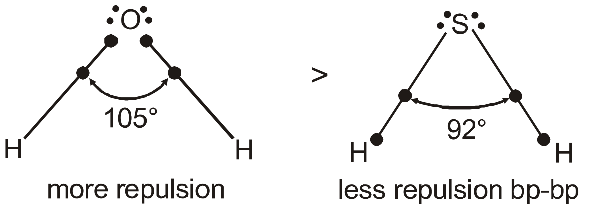
$$\text{Bond angle} \propto \frac{1}{\text{No. of lone pair of electron}}$$

(III) By increasing one lone pair of electron, bond angle is decreased approx by 2.5°.

$$\text{e.g.} \quad \underset{109°}{CH_4} \quad \underset{107°}{NH_3} \quad \underset{105°}{H_2O} \longrightarrow \underset{\text{hybridisation}}{sp^3}$$

(IV) In the different molecules if central atom have same number of lone pair of electron then bond angle will depend on electronegativities of A & B.

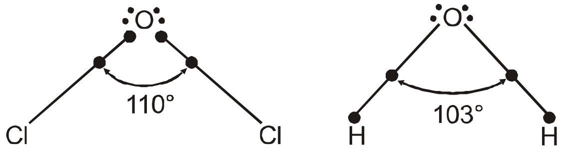
In AB_x type of molecules if side atoms are same **EN of central atom increases** the **bond angle increases**



Electronegativity of 'O' > Electronegativity of 'S'

Bond angle of – $NH_3 > PH_3 > AsH_3$

In AB_x type molecules, if central atoms are same and the EN of side atoms increases then bond angle decreases.



Electronegativity of Fluorine is greater than chlorine

$PF_3 < PCl_3 < PBr_3 < PI_3$

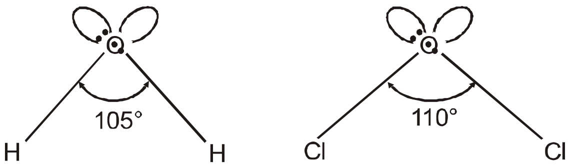
(EN of side atom decrease)

$OF_2 < Cl_2O < Br_2O$

$SF_2 < SCl_2 < SBr_2$

Bond angle depends on size of side atom, On increasing size of atom bond angle increases.

$Cl_2O > H_2O$



Solved Examples

Ex.17 In following which central atom has different hybridisation than other –

(A) Cl_2O (B) OF_2

(C) H_2O (D) SO_2

Sol. (D) Because it has sp^2 hybridisation other three have sp^3 hybridisation.

Ex.18 In following hydrocarbon which one has 75% p character and 25% s charater -

(A) C_2H_4 (B) C_2H_2

(C) CH_4 (D) $:CH_2$

Sol. (C) CH_4 because it has sp^3 hybridisation.

Ex.19 Which of the following statement in incorrect -

(A) Non-bonding pairs occupy more space than bonding pairs

(B) The bonding orbitals in a trigonal bipyramidal molecule are described as sp^3d hybrid

(C) $SnCl_2$ has linear shape

(D) PCl_4^+ and $AlCl_4^-$ are isoelectronic

Sol. (C) $SnCl_2$ is a bent shape molecule due to presence of lonepair of electron other choices are correct.

Ex.20 Shape of NH_3 is very similar to -

(A) CH_4 (B) CH_3^-

(C) BH_3 (D) CH_3^+

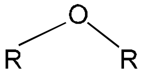
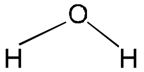
Sol. (B) Both have the same state of hybridization with one lone pair of e^- each.

Ex.21 Which of the following has pyramidal shape-

(A) XeO_3 (B) XeF_4

(C) XeF_2 (D) XeF_6

Sol. (A) Due to presence of lone pair of electron.

Ex.22 Ether  and water  have same hybridization at oxygen. What angle would you expect for them -

Sol. In H_2O bond angle is less than 109º28' due to lone pair and bond pair repulsion. But in ether, due to strong mutual repulsion between two alkyl groups bond angle becomes greater then 109º28'

Characteristic of Covalent Compound

(I) Physical state :- Covalent compounds are found in all the three states - Gas, Solid & Liquid.

Separate molecules – In gaseous state

Associate molecules – In liquid & solid state

(Due to strong vander waal's force and hydrogen bonding among the molecules.)

As the molecule weight increases physical state changes -

eg.	F_2 and Cl_2	Br_2	I_2, At_2
	gas	liquid	solid

$\xrightarrow{\hspace{6cm}}$

Top to bottom in a group. Vander waal's force increases between the molecules.

(II) Covalent solid : - Those solids in which atoms are linked together by covalent bonds, forms inifinite three dimensional giant structure.

e.g. Diamond, Graphite, AlN, SiC, SiO_2 etc.

Molecular solid : - Discrete (separate) molecules are formed by covalent bonds and then the molecules associated due to intermolecular force of attraction. (Vanderwaal force)

eg. Solid I_2, dry ice (Solid CO_2) etc.

(III) Conductivity : - Mostly covalent compounds are bad conductor of electricity. But few polar covalent compounds due to self ionisation can conduct electricity.e.g. H_2O, liq. NH_3 etc.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

Free ions are formed which can conduct electricity.

Exceptions : - Graphite, HCl in water.

(IV) Solubility : - Non polar compound are soluble in non polar solvents. Non polar compounds forms Vander waal bond with non polar solvent molecules.

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

eg. Organic compounds.

(VI) Reaction : - Reaction between covalent compounds are slow. Because it involves breaking of odl bonds and formation of new bonds.

DIPOLE MOMENT

(Ionic Nature in Covalent Bond)

(I) Polarity of any polar covalent bond or moleucule is measured in terms of dipole moment.

(II) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ).

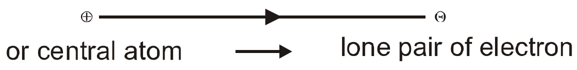
The product of positive or negative charge (q) and the distance (d) between two poles is called dipole moment.

Here **- $\mu = q \times d$**

(magnitude of charge × distance)

(III) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.

(IV) Direction of dipole moment is represented by an arrow pointing from electro +ve to electro -ve element and from central atom to lone pair of electrons.



(V) Unit of dipole moment is Debye

1 Debye $= 1 \times 10^{-18}$ esu cm.

$= 1.6 \times 10^{-29}$ coulomb metre

(VI) In the diatomic molecule μ depends upon difference of EN i.e. $\mu \propto \Delta EN$

order of μ : H–F > H–Cl > H–Br > H–I

$\mu = 0$ for H–H, F–F, Cl–Cl, Br–Br, O–O

(VII) For polyatomic molecules μ depends on the vector sum of dipole moments of all the covalent bonds.

(VIII) For PCl_5 and SF_6, etc. $\mu = 0$ due to their regular geometry.

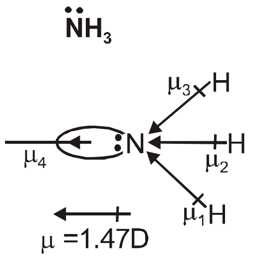
(IX) Benzene, naphthalene, diphenyl have $\mu = 0$ due to planar structure.

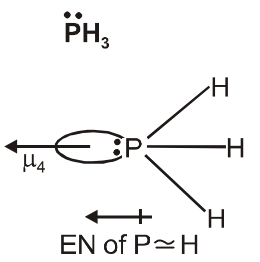
(X) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual μ of every bond should be zero).

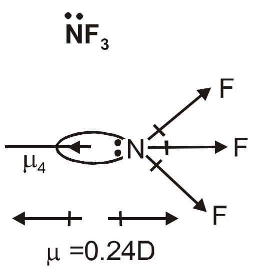
Example : (A) BX_3, CCl_4, $SiCl_4$, CH_4, CO_2CS_2, PCl_5, SiH_4 etc.

In these examples the bond B–F, C–Cl, C–H, C–O, P–Cl etc. are polar even though compounds are non-polar.

(B)

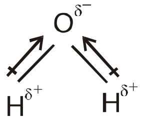






Total $\mu = \mu_1 + \mu_2 + \mu_3 + \mu_4 = 1.47D$

(XI) Dipole moment of H_2O is 1.85 D which is resultant μ of two O–H bonds.



μ of H_2O μ of H_2S because electronegativity of oxygen is higher than sulphur.

(XII) Angular structure of molecule have greater dipole moment.

Application of dipole moment :

(I) To determine polarity and geometry of molecule -

If $\mu = 0$ compound is non polar and symmetrical

eg. CO_2, BF_3, CCl_4, CH_4. BeF_2 etc.

If $\mu \neq 0$ compound will be polar and unsymmetrical.

H_2O, SO_2, NH_3, Cl_2O, CH_3Cl, $CHCl_3$ etc.

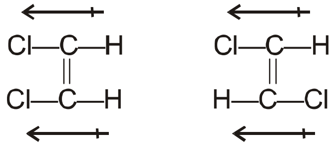
(II) To calculate % ionic character :-

$$\boxed{\% \text{ Ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoritical value of } \mu} \times 100}$$

(III) To distinguish cis form or trans form:-

(a) Dipole moment of cis isomers is normally higher than trans isomers.

eg. –

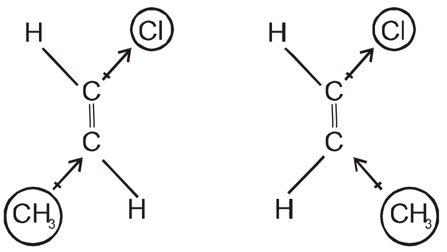


$\mu \neq 0$ cis-form Polar ($\mu \neq 0$)

$\mu = 0$ Trans-form Non Polar ($\mu \neq 0$)

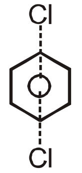
(b) If two groups have opposite inductive effect than trans-isomer will have greater dipole moment \-

eg.



(IV) To locate position of substituents in aromatic compounds. $\mu \propto \frac{1}{\text{Bond angle}}$

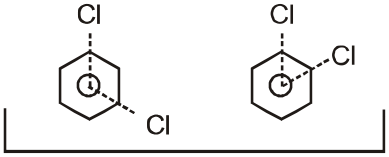
(a) If same substituents are preset in the symmetrical position μ of benzene ring compounds will be zero



$\mu = 0$

Angle 180°

p-dichloro benzene



$\mu \neq 0$

Angle 120° m-dichloro benzene

Angle 60° o-dichloro benzene

(b) As angle between subtituents decrease value of μ increase

Some important orders of diple moments-

$HF > H_2O > NH_3 > NF_3$ $H_2O > H_2S$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

$BF_3 < NF_3 < NH_3$

$HF > H_2O > SO_2 > NH_3$ $PH_3 < PCl_3$

$NO_2^- > NO_2 > NO_2^+$ $H_2O < H_2O_2$

Solved Examples

Ex.23 Which of the following bonds is most polar -

(A) O – H (B) P – H

(C) C – F (D) S – Cl

Sol. (C) Due to maximum electronegativity difference.

Ex.24 Bond length of HCl is 1.275 Å (Charge = 4.8×10^{-10} e.s.u.) if $\mu = 1.02$ D, then HCl is -

(A) 100% ionic (B) 83% covalent

(C) 50% covalent (D) 40% ionic

Sol. (B) % ionic character

$$= \frac{\text{observed } \mu}{\text{theoritical } \mu} \times 100 = \frac{1.02}{1.275 \times 4.8} \times 100$$

= 17% ionic = 83% covalent

Ex.25 The dipole moment of the ammonia molecule is 1.48D. The length of the dipole is -

(A) 3.08×10^{-11} m (B) 5×10^{2} m

(C) 308 m (D) None

Sol. (A) $M = 1.48 \times 3.33 \times 10^{-30}$ cm

$= 4.93 \times 10^{-30}$ cm.

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

$$l = \frac{\mu}{q} = \frac{4.93 \times 10^{-30}}{1.6 \times 10^{-19}} = 3.08 \times 10^{-11} \text{ m}$$

$= 0.0308$ nm

The NH_3 molecule can not have the shape of an equilateral triangle because in the case its dipole moment would equal zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

COORDINATE BOND

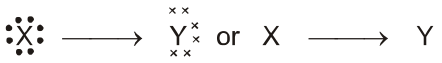
(I) It is a covalent bond in which the shared e⁻ pair come from one atom is called coordinate bond.

(II) Necessary conditions for the formation of co-ordinate bond are-

(a) Octet of donor atom should be complete and should have atleast one lone pair of electron.

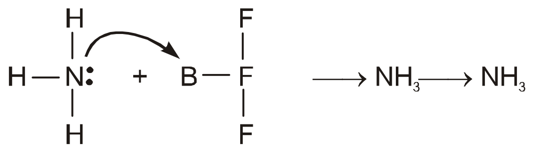
(b) Acceptor atom should have a defficiency of at least one pair of electron.

eg.



(III) Atom which provide electron pair for shairing is called donor.

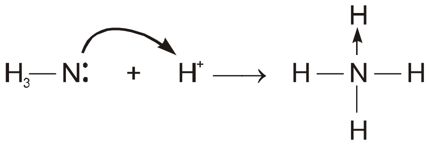
(IV) Other atom which accepts electron pair is called acceptor. That is why it is called donor-acceptor or dative bond



BF_3 is electron defficient compound.

Example:

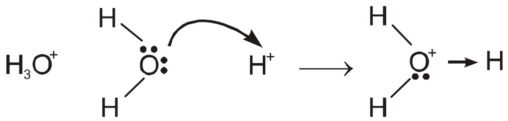
NH_4^+



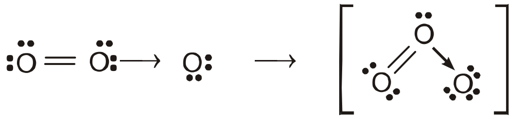
(Lowry - Bronsted acid)

(e⁻ acceptor)

H_3O^+



O_3



N_2O

Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows-

NH_4Cl, $CuSO_4$, $K_4[Fe(CN)_6]$, KNC, Na_3PO_4, KNO_3, etc

Solved Examples

Ex.26 The compound which contains both covalent and co-ordinate bond is -

(A) C_2H_5NC (B) C_2H_5CN

(C) HCN (D) None

Sol. (A) Though all compounds have covalent bond but there is coordination bond also between N and C in C_2H_5 NC

Ex.27 The type of bond present in N_2O_5 are -

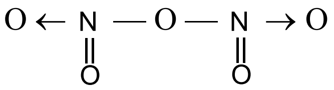
(A) Only covalent

(B) Only ionic

(C) Ionic and covalent

(D) Covalent and coordinate

Sol. (D) The structure of N_2O_5 clears about it



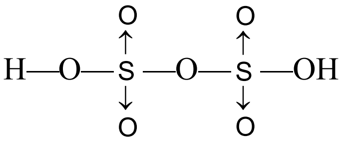
$$O \leftarrow \underset{\overset{\|}{O}}{N} - O - \underset{\overset{\|}{O}}{N} \rightarrow O$$

Ex.28 No. of covalent and co-ordinate bond in pyrosulphuric acid are -

(A) 6, 4 (B) 6, 6

(C) 4, 4 (D) 4, 6

Sol. (A) Structure of $H_2S_2O_7$ is as follows



$$H—O—\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}—O—\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}—OH$$

Ex.29 Which is not true according to VBT -

(A) A covalent bond is formed by the overlapping of orbitals with unpaired electrons of opposite spins

(B) A covalent bond is formed by the over lapping of orbitals with unpaired electrons of same spin

(C) The greater the extent of overlapping the stronger is the bond

(D) Overlapping takes place only in the direction of maximum electron density of the orbital

Sol. (B) Electrons of same spin never combine to form a bond. Other facts are true for VBT.

Ex.30 Why covalent bonds are always directional -

Sol. As the covalent bonds are formed due to overlapping of orbitals which are directional

Ex.31 Allyl cyanide has -

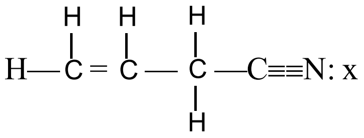
(A) 9 sigma bonds and 4 Pi bonds

(B) 9 sigma bonds, 3 pi bonds and 1 lonepairs

(C) 8 sigma bonds and 5 pi bonds

(D) 8 sigma bonds, 3 pi bonds an 4 non-bonding electrons

Sol. (B) This is clear from structure of allylcyanide



$$H—\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}—\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}—C\equiv N:\ x$$

HYDROGEN BOND

Definintion :

(I) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electonegative atom (F, O, N)

(II) It is not formed in ionic compounds

(III) H–bond forms in polar covalent compouds, (not in non-polar)

(IV) It is also known as dipole-dipole attraction

$H^{\delta+} — F^{\delta-}$ .... $H^{\delta+} — F^{\delta-}$...... $H^{\delta+} — F^{\delta-}$

Main condition for H-bonding : -

(I) H— should be covalently bonded with high electro–ve element like F, O, N

(II) Atomic size of electro–ve element should be small.

Decreasing order of atomic size is–

N > O > F

Decreasing order of atomic size is–

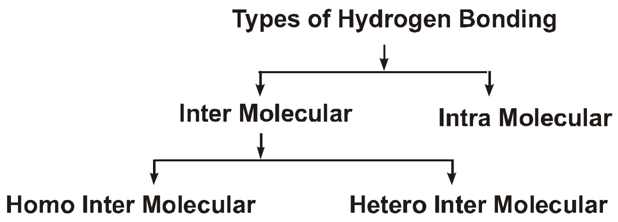
F > O > N

(4.0) (3.5) (3.0)

(III) Strength of H–bond $\propto$ Electronegativity of Z (element) $\propto \dfrac{1}{\text{atomic size of Z}}$

(IV) Hydrogen bonding occurs in HCN, due to ($-C\equiv N$) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

$H—C\equiv N$.........$H—C\equiv N$..........$H—C\equiv N$

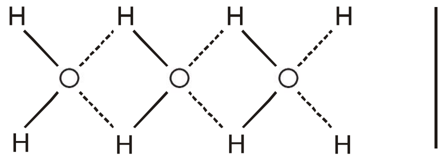


(A) Intermolecular H–bond

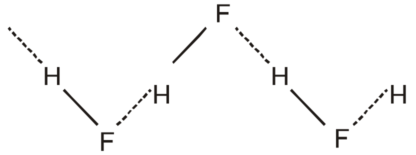
H–bond formation berween two or more molecules of eithe the same or different compounds known as **Inter molecular H–bonding**

These are two types.

(i) **Homointermolecular :-** H–bond between molecules of same compounds.

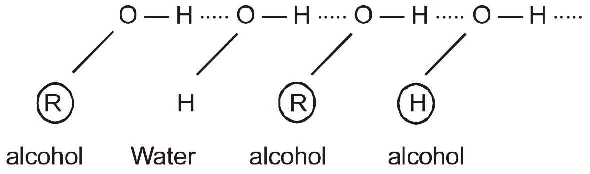


eg.



(ii) **Hentro intermolecular :-** H–bond between molecules of different compounds.

eg. alcohol, water



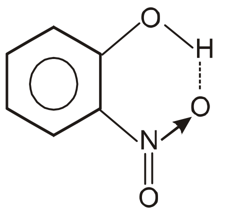
(B) Intra molecula H–bond :- It takes place within the molecule.

(i) H–bonded with electronegative elements of a functional group, form H–bond with another electronegative element present on nearest position on the same molecule.

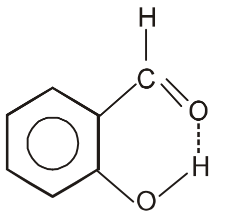
(ii) This type of H–bond is mostly occured in organic compounds.

(iii) It result in ring formation (Chelation).

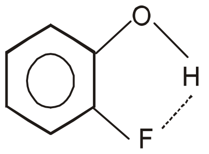
eg.



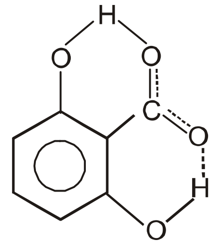
O–nitrophenol



Salicylaldehyde



O–fluorophenol



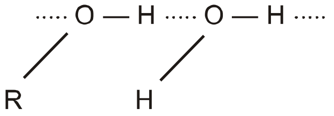
2-6 dihydroxyl benzoate

Effect of H–bond on physical properties :

(I) Solubility

(A) Inter molecular H–bonding

(a) Few organic compounds (Non-polar) are soluble in water (Polar solvent) due to H–bonding



Other examples–Glucose, Fructose etc, dissolve in water.

(b) Ketone, ether, alkane etc. are insoluble (no H–bond). Dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H–bonding interupts

(c) Solubility order– $CH_3OCH_3 < CH_3OH$

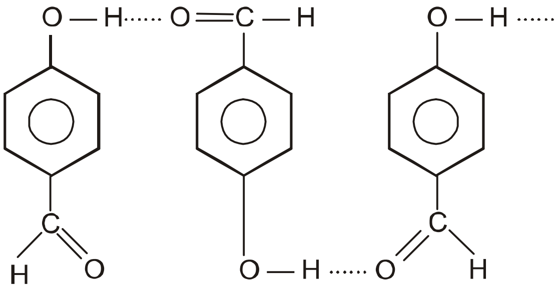
Primary amine > secondary amine > tertiary amine

(B) Intra molecular H–bonding:

(a) It decreases solubility as it form chelate by H–bonding, so H–is not free for other molecule.

(b) It can not form H–bond with water molecule so can not dissolves.

(C) Inter molecular H–bond

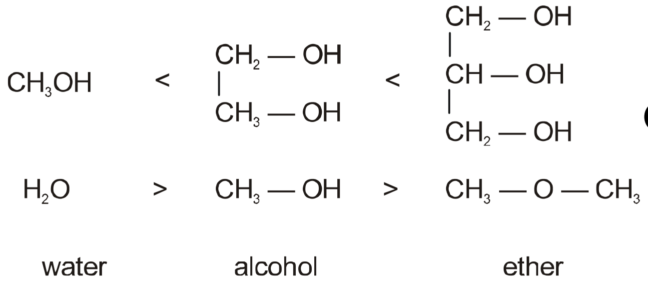


p–hydroxy benzaldehyde

It can form H–bond with water molecule so it can dissolvel

(II) Viscosity:

H – bond associates molecules together so viscosity increases



$$CH_3OH < \begin{matrix} CH_2-OH \\ | \\ CH_3-OH \end{matrix} < \begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix}$$

$$\underset{\text{water}}{H_2O} > \underset{\text{alcohol}}{CH_3-OH} > \underset{\text{ether}}{CH_3-O-CH_3}$$

(III) Melting point and boilling point

(a) Due to intermolecular H–bond M.P. & B.P. of compounds increases.

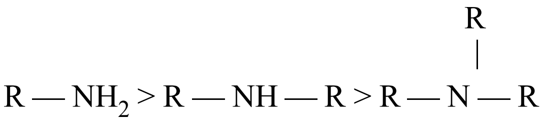
$H_2O > CH_3OH > CH_3—O—CH_3$

(b) Trihydric alcohol > dihydric alcohol > monohydic alcohol

Monocarboxylic acid form stronger H–bond than alcohol of comparable molecular weight. Therefore B.P. of carboxylich acid is higher than alcohol.

(c) Decreasing order of M.P. & B.P. isomer amines-

1°–amine > 2°–amine > 3°–amine



$$R—NH_2 > R—NH—R > R—\overset{\overset{R}{|}}{N}—R$$

(no hydrogen with nitrogen atom)

(d) Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.

VA	VIA	VIIA	
NH_3	H_2O	HF	b.p. $HF > HI > HBr > HCl$
PH_3	H_2S	HCl	$H_2O > TeH_2 > SeH_2 > H_2S$
AsH_3	SeH_2	HBr	$NH_3 > SbH_3 > AsH_3 > PH_3$
SbH3	TeH_2	HI	

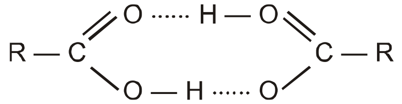
(e) But sudden increase in boiling point of NH_3, H_2O and HF is due to H–bonding

$H_2O > HF > NH_3$ $PH_3 < H_2S < HCl$

Intramolecular H–bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal force. So M.P. and B.P are low.

(IV) Molecular weight :

Molecular wt. CH_3COOH is double of its molecular formula, due to dimer formation occur by H–bonding



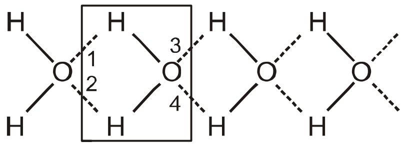
(V) Physical state:

H_2O is liquid while H_2S is gas.

Water and Ice:- Both have H–bonding even then density of ice is less than water.

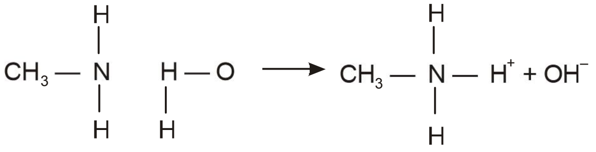
Volume of ice is more because of open cage like crystal structure, from by association of water molecules with the help of H–bond.

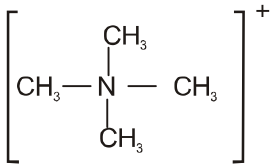
H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.



(VI) Base strength

CH_3NH_2, $(CH_3)_2$ NH, $(CH_3)_3$ N form H–bond with water. So less hydrolysis i.e. it gives OH^- ions. While $(CH_3)_4N^+OH^-$ (ammonium compound) will give OH^- ion in large amount due to no H–bonding.



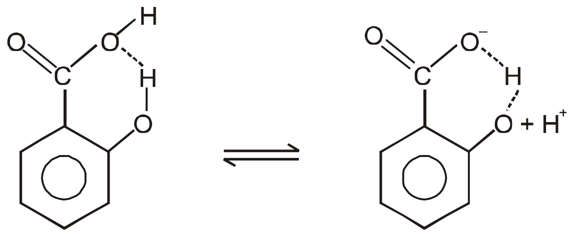


(Ammonium compound.) NO H–atom bonded directly with N–atom so no hydrogen bonding occurs.

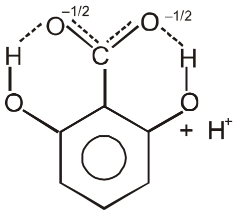
Effect of intramolecular H–bonding

(I) Strength of acid

(a) The formation of intramolecular H–bonding in the conjugate base of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid and 2, 6 – dihydroxy benzoic acid > salicylic acid.



Conjugate base



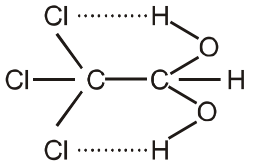
2, 6 dihydroxy benzoate ion

(b) C_2H_2SH is more acidic than C_2H_5OH. In C_2H_5OH, H–bond forms so H^+ is not free

(c) HF is weaker acid than HI, due to H–bond in H – F, H^+ is not free

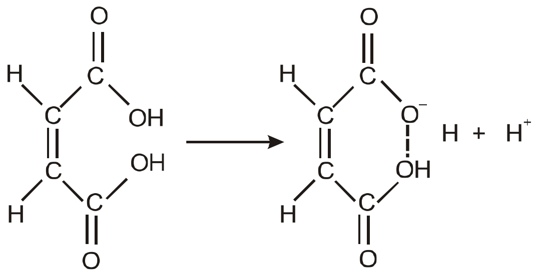
(II) Stability of chloral hydrate:-

If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to H–bonding).

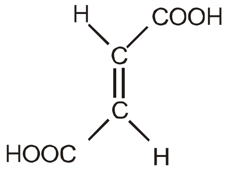


Chloral hydrate

(III) Maleic acid (cis) is stronger acid than fumaric acid (trans).



Stable conjugate base of maleic acid



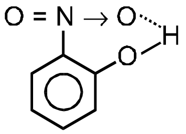
Fumaric acid (No-intramolecular H-bonding)

Solved Examples

Ex.32 Which one of the following does not have intermolecular H-bonding -

(A) H_2O (B) o-Nitrophenol
(C) HF (D) CH_3

Sol. Nitrophenol has intermolecular H bonding as shown below



Hence (2)

Ex.33 Arrange in incresing order of their boiling point- HF, HCl, HBr, HI

Which order is correct –

(A) HCl < HBr < HI < HF
(B) HCl > HBr > HI > HF
(C) HCl < HBr > HI < HF
(D) None

Sol. (A) HCl < HBr < HI < HF

due to strong hydrogen bonding in HF

VANDER WAAL'S FORCES

(a) This type of attractive forces occurs in case of non polar molecules such as H_2, O_2, Cl_2, CH_4, CO_2 etc.

(b) The existence of weak attractive forces among the nonpolar molecule was first proposed by dutch scientist J.D. Vander Waal

(c) Vander waal force $\propto$ molecular weight

$\propto$ Atomic weight

$\propto$ Boiling point

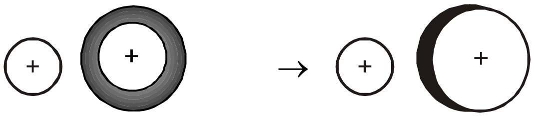
Types of Vander Waal's force : -

(i) Ion dipole attraction - This force is between an ion such as Na+ and a polar molecule such as HCl

(ii) Dipole Dipole attraction - It is again in between two polar molecules such as HF and HCl

HF HCl(g)

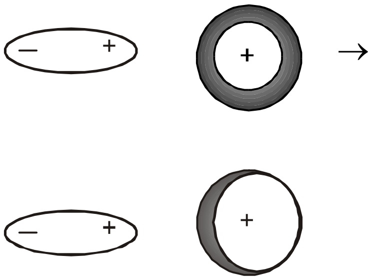
(iii) Ion induced dipole attraction - In this case a neutral molecule is induced by an ion as a dipole as shown in fig



Na^+ Cl_2

Before induction after induction

(iv) Dipole - Induced dipole attraction : In this case a neutral molecule is induced as a dipole by another dipole as shown in fig.



e.g. HCl Cl_2

(v) Induced dipole - induced dipole attraction or London dispersion force between two non polar molecules as in Cl_2, He etc.

Cl_2 Cl_2

Note: The relative strength of various bonds is as follows

Ionic bond > Covalent bond > Metallic bond > H-bond > Vander waal bond

POINTS TO REMEMBER

(a) Bond energy of a diatomic molecule is enthalpy change to dissociate one mole of the diatomic gaseous molecule to form the respective gaseous atoms.

(b) Strong metallic bonding is favoured by smaller size of kernel.

(c) Band theory is related with metallic nature

(d) The resonance structure do not have independent existence.

(e) The hydration of ionic compounds involves evolution of heat, weakening of attractive forces and dissociation into ions

(f) The maximum covalency is equal to the actual number of s-and p-electrons in the outermost shell

(g) Many ionic crystals dissolve in water because water decreases the interionic attraction in the crystal lattice due to solvation.

(h) Hydrogen bond stabilizes the secondary structure of proteins.

(i) Isoelectronic molecular species have similar molecular orbitals and similar structure according to iso electric principle

(j) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as bond dissociation energy

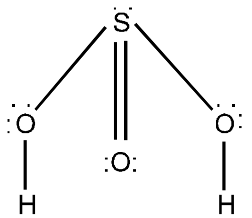
(k) The average angle between the bonded orbitals is known as bond angle θ.

(l) Bond length may be defined as the average distance between the centres of nuclei of two bond atoms.

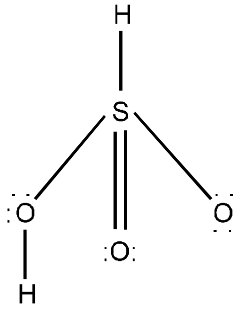
(m) Polymorphism (Allotropy) is a term used when one and the same substance can crystallise in more than one forms.

(n) In SO_2 there is $p\pi - p\pi$ bonding as well as $p\pi - d\pi$ bonding due to overlap of filled $p\pi$ orbitals of oxygen with the vacant 3d orbitals of sulphur.

(o) H_2SO_3 exists in two forms which are always in equilibrium with one another



(Symmetrical sulphurous acid)

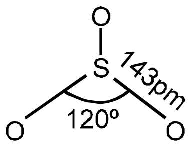


(Unsymmetrical sulphurous acid)

The unsymmetrical form containing S – H bond explains the reducing character of H_2SO_3.

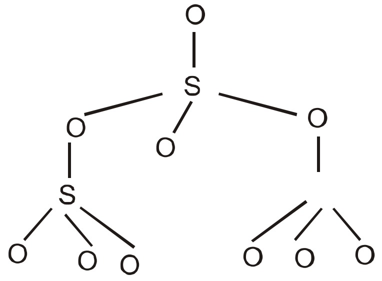
(p) The anion of H_2SO_3 i.e. SO_3^{2-} has a pyramidal structure with S atom in sp^3 hybridization and all the S – O bonds are of equal bond length (134 pm)

(q) In the gas phase, SO_3 is a planar triangular molecule with sulphur atom in sp^2 hybridization state

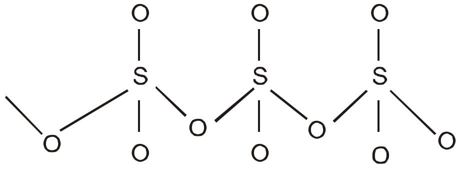


In order to account for the equivalency of all the S – O bonds and short S – O distance of 143 pm, SO_3 may be considered as a resonanchybrid involving pπ-pπ S – O bonding along with additional pπ-pπ bonding.

(r) In the solid phase, SO_3 polymerizes to puckered rings or the more stable layer structure as shown.



Ring Structure



Layer Structure

Molecular Orbital theory (MOT):

MOT put forward by Hund & Mulliken, which can be applied to explain the properties, which the old VBT (Valence bond theory) was unable to explain eg. Paramagniic nature Of O_2 molecule, as per VBT (**:O: :O:**) it should be diamagnetic.

Definition:

The atomic orbital lose their identity during molecule formation (overlapping) and form new orbitals termed as molecular orbitals.

Characteristic of molecular orbitals:

(I) Molecular orbital formed by overlapping of atomic orbital of same energy

(II) Number of melecular orbital formed = number of atomic orbital involved in overlapping

(III) Half of the molecular orbital have lower energy are called Bonding molecular orbital.

(IV) Half are of higher energy - termed as Antibonding molecular orbital

(V) Electronic configuration in various molecular orbital are governed by same three rules.

(a) Aufbau's rule

(b) Hund's rule

(c) Pauli's exclusion principle

Comparision of Bonding molecular orbital & Antibonding molecular orbital :

Bonding molecular orbital (BMO)	**Antibonding Molecular orbital (ABMO)**
Bonding MOis the result fo the linear combination of AO when their wave function are added $Y_b = Y_A + Y_B$	ABMO is result of linear combination of AO when their wave function are substracted $Y_b = Y_A + Y_B$
It does not have node.	It always have a node between two nuclei of bonded atom.
Charge density increase between two nuclei resulting attraction between two atoms	Charge density decrease in between two nuclei, leads to repulsion between two atoms.
Energy of BMO is less, hense stable	Energy of ABMO is high, hence unstable

Notation of molecular orbitals:

As atomic orbitals are known by letters s, p, d and f depending on their shapes. Similarly for molecular orbital.

For bonding molecular orbital- σ, π, δ etc.

For antibonding molecular orbital- $\sigma*, \pi*, \delta*$ etc.

are used for different shapes of electron cloud.

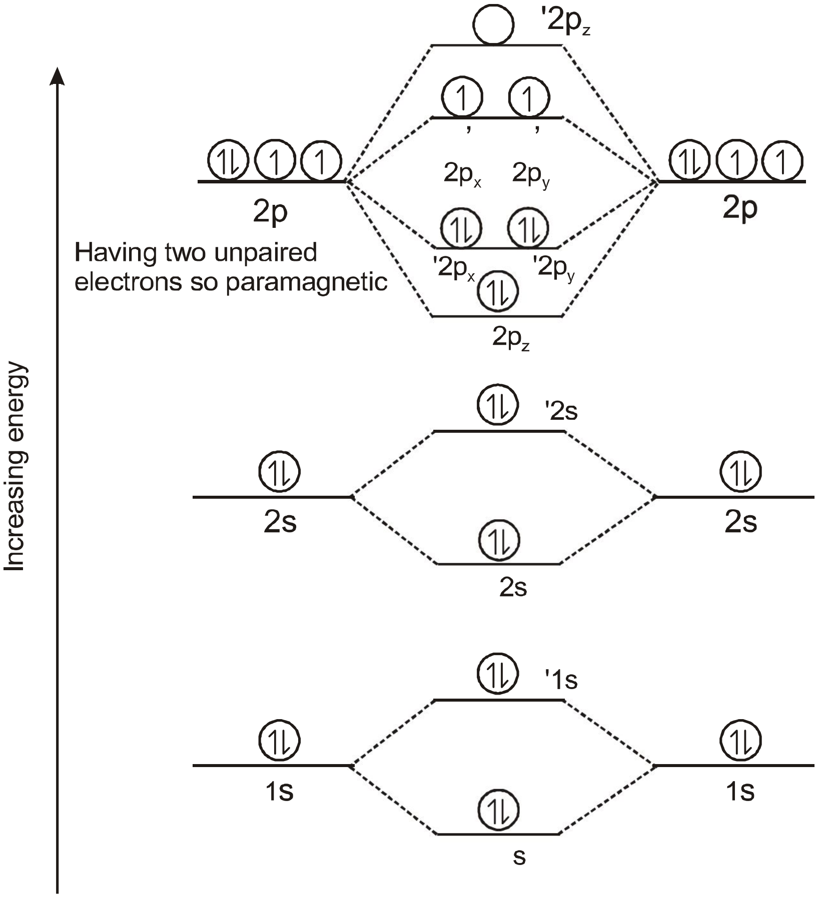
Energy Level Diagram of molecular orbital :

On the basis of Aufbau's rule - increasing order of energies of various molecular orbitals is-

$\sigma\ 1s < \sigma*\ 1s < \sigma\ 2s < \sigma*\ 2s < \sigma\ 2p_z < \pi\ 2p_x \equiv \pi 2p_y < \pi*\ 2p_x \equiv \pi*\ 2p_y < \sigma*\ 2p_z$

Energy level diagram for homonuclear diatomic molecules like, O_2, F_2, Ne_2

For O_2 molecule-



Bond order $= \frac{1}{2}(8 - 4) = 2$

Bond order $O_2 = 1/2\,[8 - 4] = 2$

$O_2^{+} = 1/2\,[8 - 4] = 2.5$

$O_2^{-} = 1/2\,[8 - 5] = 1.5$

$O_2^{2-} = 1/2\,[8 - 5] = 1.5$

$O_2^{+2} = 3$

Stability order –

$O_2^{+2} > O_2^{+} > O_2 > O_2^{-} > O_2^{2-}$

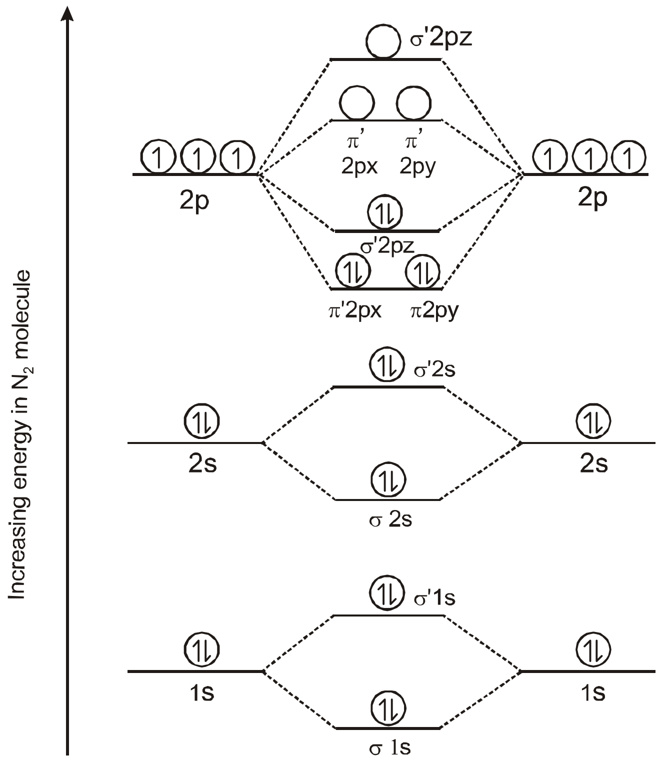
Bond length –

$O_2^{2-} > O_2^{-} > O_2 > O_2^{+} > O_2^{+2}$

Energy level diagram for B_2, C_2 and N_2 molecules –

σ 1s < σ* 1s < σ 2s < σ* 2s < $\pi 2p_x \equiv \pi 2p_y < \sigma 2p_z < \pi^* 2p_x \equiv \pi^* 2p_y < \sigma^* 2p_z$

For N_2 molecule



Cause of exceptional behavior of molecular orbital in B_2, C_2 and N_2:

- Energy of 2s and 2p atomic orbitals lie fairly close
- Due to small energy difference between 2s and $2p_z$ orbitals, the interaction between them is quite large.
- This results in loss of energy by σ 2s and σ* 2s and thus σ 2s and σ* 2s becomes more stable at the cost of σ 2px and σ* 2px which gets unstablised (Higher energy).

Electronic configuration of molecules and their related properties :-

for writing electronic configuration of diatomic molecules following two rules to be followed-

- Count the number of electrons present in two atoms and then fill in the appropiate energy level diagram according to Aufbau rule.
- The pairing in π 2px and π 2py or π* 2px and π* 2py will take place only when each molecular orbital of indenticle energy has one electron.
- After writing the molecular orbital diagram following parameter about molecules/ion may be predicted.

(i) Bond order :-

Bond order = ½ [No. of electron in bonding molecular orbital ie. Nb – No. of electron in antibonding molecular orbital ie. Na] = ½[Nb–Na]

B.O. = ½ [Nb–Na]

(ii) Bond length :- (distance between two nuclei)

$$\text{Bond length} \propto \frac{1}{\text{Bond order}}$$

If Nb > Na Molecule exists

$$\left.\begin{matrix} Nb < Na \\ Nb = Na \end{matrix}\right\} \text{Molecule do not exists}$$

(iii) Stability of molecules - stability ∝ Bond order of molecule

(iv) Dissociation energy - Bond disssociation energy ∝ Bond order

(v) Magnetic property -

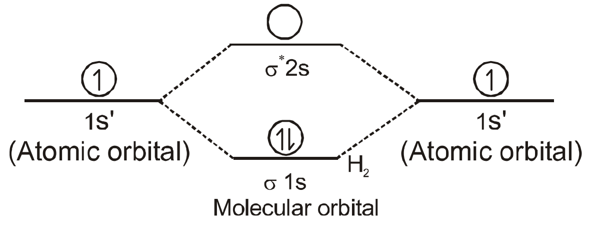
(a) When electron in MO are paired – diamagnetic

(b) When electron in MO are unpaired – paramagnetic

Bonding in molecules :-

(I) Hydrogen molecule-

Having two H atoms with one electron each (1s')



M.O. configuration of $H_2 = (\sigma\ 1s)^2\ (\sigma * 1s)^0$

Bond order = ½ $[N_b - N_a]$

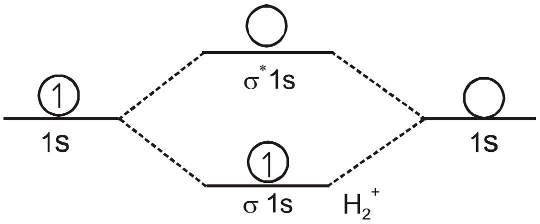
= ½ [2 – 0] = 1 i.e. single bond

Having paired electron so diamagnetic.

Stability → quite stable (having single bond)

(II) H_2^+ ion –

Configuration of $H_2^+ = (\sigma \text{ is})\ 1\ (\sigma * \text{is})^0$
One electron in bonding molecular orbital.



So paramagnetic

Bond order = ½ [1– 0] = ½

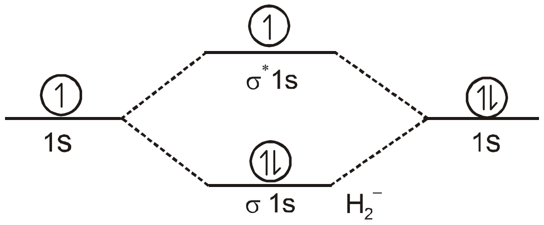
Less stable

(III) H_2^- anion -

M.O. configuration - $(\sigma\ 1s)^2\ (\sigma*\ 1s)^1$

Paramagnetic

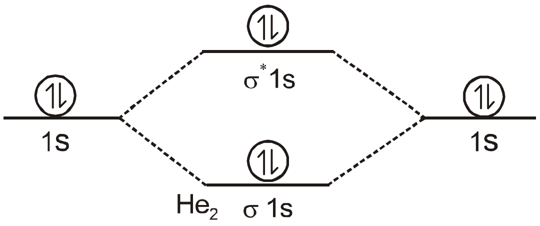
Bond order = ½ [2 – 1] = ½



Stability is less than $[H_2^+]$ because H_2^-
Contain ab ABMO electron

(IV) Helium molecule (He_2) :

- M.O. configuration $(\sigma\ 1s)^2\ (\sigma*\ 1s)^2$
- Diamagnetic
- Bond order = ½ [2 – 2] = 0 (zero)
- Bond order zero indicates no linkage



between He atoms. Hence He_2 molecule does not exist

- Stability (He_2) Highly unstable molecule

Solved Examples

Ex.34 The bond order of N_2^- anion is -

(A) 1 (B) 2
(C) 2.5 (D) 3

Sol. (C) Out of 15 e^- in N_2^-, 10 are in bonding MO's and $5e^-$ are in the anti bonding MO's Hence

bond order = $\frac{1}{2}$ (10 - 5) = 2.5

Ex.35 Which of the following has maximum bond strength

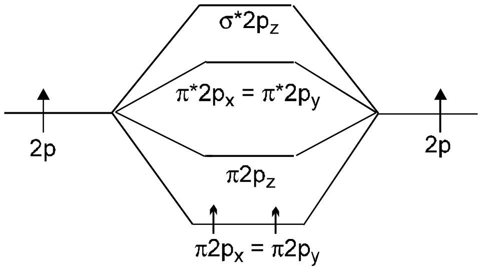
(A) O_2 (B) O_2^+
(C) O_2^- (D) O_2^{2-}

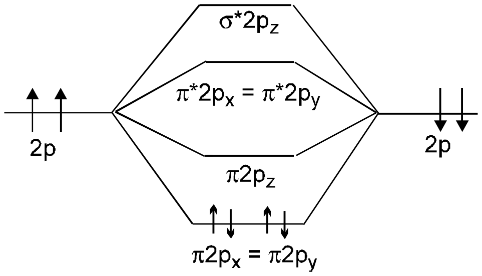
Sol. (B) Bond order of O_2^+ is 2.5 which is maximum among all the species hence its bond strength will also be the maximum.

Ex.36 Which of the molecules B_2 and C_2 has a higher energy of dissociation into atoms? compare the magnetic properties of these molecules.

Sol. We draw energy level diagrams showing the formation of B_2 and C_2 molecules

AO's	MO's	AO's
B	B_2	B
AO's	MO's	AO's
C	C_2	C





Energy level diagrams showing the formation of B_2 and C_2 molecules.

The difference between the number of bonding and the number of antibonding electrons in the B_2 molecule can be seen to be two, and in the C_2 molecule, four. This corresponds to a bond multiplicity of 1 and 2, respectively. Consequently, the C_2 molecule having a higher multiplicity of the bond between the atoms must be more stable. This conchosion corresponds to the experimentally established values of the energy of dissociation into atoms of the molecules B_2 (276 KJ/mol) and C_2(605 KJ/mol)

In the B_2 molecule, two electrons are arranged, according to Hund's rule, in two πp_x $\pi 2p_y$ orbitals. The presence of two unpaired electrons imparts paramagnetic properties to this molecule. In the C_2 molecule, all the electrons are paired, consequently, this molecule is diamagnatic

BOND PARAMETERS

(I) Bond Lengthe (Bond distance)

(II) Bond Angle

(III) Bond Energy

(I) Bond Lenght :- The average distance between the nucleus of two atoms is known as bond lenght, normally it is represented in Å. eg. A———B

- It depends mainly on electronegativilties of constituent atoms

Case - I Electronegativity difference is zero then-

Bond length = $r_A + r_B$

Or $d_{A-B} = r_A + r_B$

where$_A$ is covalent radius of A

r_B is covalent radius of A

X_A is electronegativity of A

X_B is electronegativity of B

If $r_A = r_B$ then Bond length = $2r_A$ or $2r_B$

Case II Electronegative difference is not equal to zero then-

Bond length is given by shomaker & Stevenson formula is Bond length = $r_A + r_B - 0.09\ (X_A - X_B)$ Difference in electronegativities

Factors affecting Bond Length :-

(a) Δ electronegativity :- Bond lengh $\propto \frac{1}{\Delta EN}$ (While B.E. $\propto \Delta$EN)

H–F < H–Cl < H–Br < H–I

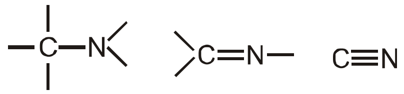
(b) bond order or number of bonds :- Bond length

$$\propto \frac{1}{\text{Number of bond or bond order}}$$

Bond energy ∝ Number of bond

e.g.	C–C,	C = C,	C ≡ C
Bond length	1.54 Å	1.34 Å	1.20 Å
			$\xleftarrow{\text{increasing}}$
Bond energy	80	140	180–200K.Cal.
			$\xrightarrow{\text{increasing}}$

C—0	C=O	C≡O
1.43 Å	120 Å	1.13Å



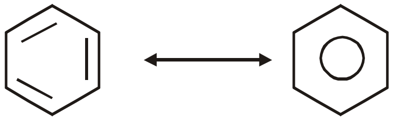
1.47 Å 1.28 Å 1.15 Å

(c) Resonance :- (due to resonance bond length affected)

eg.1. Benzene

C—C bond length 1.54Å

C—C bond length 1.34 Å



but bond length is between

single & double bond is = 1.39 Å

eg. 2. Bond length of C—O in CO_2 is 1.15 Å

Resonance occurs in CO_2 a follows-

$$O{=}C{=}O \longleftrightarrow O^{-}{-}C{\equiv}O^{+} \longleftrightarrow O^{+}{\equiv}C{-}O^{-}$$

Bond length = 1.15 Å

(Between double & triple bond)

(d) Hybridisation :-

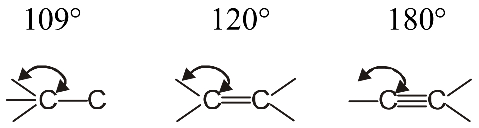
Bond length $\propto \frac{1}{\text{s character}}$

Example :-	Compound	Hybridisation	Bond length
S-character increases ↓	Ethane	sp^3— sp^3	1.54 Å
	$>$C—C=	sp^3— sp^2	1.51 Å
	$>$C—C≡C	sp^3— sp	1.47 Å
	C=C—C=C	sp^2— sp^2	1.46 Å
	C=C—C≡C	sp^2— sp	1.42 Å
	C≡C—C≡C	sp sp	1.37 Å

(II) Bond Angle :- The angle between any two adjacent bond is known as bond angle. It is represented in degree (°), min (') and second ('')

Factors affecting the bond angle-

(a) Number of bond : Bond angle $\propto$ Number of bonds (Bond order)



(b) Hybridisation :-

Case 1

When hybridisation is same, bonded atoms are same, central atom and lone pair are different.

Then bond angle $\propto \frac{1}{\text{No.of lone pair}}$

Example :-

	CH_4	$\ddot{N}H_3$	$H_2\ddot{\underset{\cdot\cdot}{O}}$
Hybridisation	sp^3	sp^3	sp^3
Bond angle	109 >	107 >	105
	No 1.p.	one 1.p.	two 1.p.

Case-II

When hybridisation is same, bonded atoms are same lone pair is same but central atom is different. Then bond angle $\propto$ electrongativity of central atom

Example:-	$\ddot{N}H_3$	$\ddot{P}H_3$	$\ddot{As}H_3$
Bond angle	107°	93°	91°

$\longrightarrow$

– Eletronegativity decreasing

– Bond angle will decrease

Case-III

When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

sp_3 OF_2 103 – 105°

sp_3 Cl_2O 109 – 111°

sp_3 Br_2O 116 – 118° ↓ Electronegativity of bonded atom is decreasing

Here bond angle

$\propto \frac{1}{\text{electrongativity of bonded atom}}$

$\propto$ size of side atom

(III) Bond Energy (BE) :- Bond energy may be difined as-

(a) Bond formation energy:- Energy released when any bond is formed is known as bond formation energy or bond energy.

(b) Bond dissociation energy :- Energy required to dissociate any bond is known as bond dissociation energy.

Calculation of released energy is more diffcult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

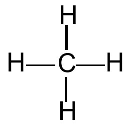
Case-I In diatomic molecule :

Bond energy = bond dissociation energy

eg :- $N_2 > O_2 > H_2 > F_2$

Case-II For polyatomic molecule :-

Bond energy ι Bond dissociation energy (D)

eg;-  Bond energy

$$H-\underset{H}{\overset{H}{C}}-H$$

= per C—H bond is 99.5 K. Cal/mole

Theoritical values of bond dissociation energy (D) of individual C—H bonds CH_4 are given below-

$D(CH_3—H)$ = 102 K Cal/mole

$D(CH_2—H)$ = 105 K Cal/mole

$D(CH—H)$ = 108 K Cal/mole

$D(C—H)$ = 83 K Cal/mole

Hence bond energy E per C—H bond in methane

$= \frac{398}{4} = 99.5$ K Cal/mole.

- Bond dissociation energy (D) is related to the state of hybirdisation.

Factors affecting the bond energy : -

(a) ΔElectronegativity	(b) Bond order
(c) Atomic size	(d) Bond polarity
(e) Resonance	(f) Hybridisation
(g) Lone pair electron	

(a) Δ Electronegativity :- Bond energy $\propto \Delta EN$

eg. HF > HCl > HBr > HI

(b) Bond order :- Bond energy ∝ Bond order

eg. C—C < C = C < C ≡ C

79 K. Cal, 143.3 K. Cal., 199.0 K. Cal.

(c) Atomic size :- Bond energy $\propto \frac{1}{\text{Atomic size}}$

eg. C≡C < C≡N < N≡N

Exception :- In case of ha $\ddot{A}sH_3$ logen group, order of bond energy is-

Cl — Cl > Br — Br > F — F > I — I

Because of higher electron densityb and small size of F atoms, repulsion between of two F atom, weakens the bond energy.

Other ex. S – S > O – O

C – C > Si – Si > Ge – Ge

(d) Bond Polarity :- Bond energy ∝ polarity

eg. H—F > H—Cl > H—Br > H—I

(e) Resonance :- Bond energy increases due to resonance

eg. In benzene bond energy of C—C increases due to π electrons of C = C.

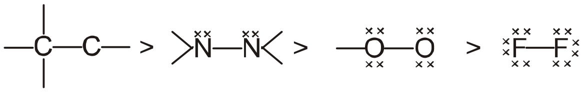
(f) Hybridisation :- Bond energy ∝ s-character in hybrid orbitals.

eg. sp—sp > sp^2—sp^2 > sp^3—sp^3

s. character- 50% 33.3% 25%

(g) Lone pair of electrons :-

Bond energy $\propto \frac{1}{\text{lone pair of electrons}}$



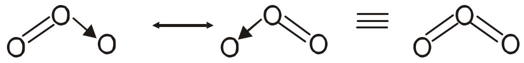
Size of F and O atoms small so their bond energy should be high (small atomic radius) but it is actually less due to lone pair of electrons present on F and O atoms, which repells each other in F—F and —O—O— type of bonds.

RESONANCE

(I) The concept of resonance was introduced by heisen berg (1920) , and later developed by pauling and ingold, to explain the properties of certain molecules,

(II) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonane hybrid and the different individual structures are called resonating structures or canonical forms. This phenomeni is called resonance.

(III) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O—O = 1.48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.

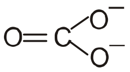


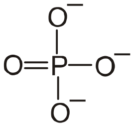
Resonance hybrid

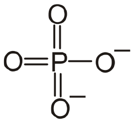
To calculate bond order in the polyatomic molecule or ion use following formula :

Bond order

$$= \frac{\text{Totalnumber of bonds in a molecule}}{\text{Resonating Structures}}$$

eg.  C—O Bond order $= \frac{4}{3} = 1.33$

 P—O Bond order $= \frac{5}{4} = 1.25$

 Cl—O Bond order $= \frac{7}{4} = 1.75$

METALLIC BOND

(a) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.

(b) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.

(c) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.

(d) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.

(e) Due to small ionisation energy the valence electrons of metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.

(f) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

1. Properties of metals and their explanation by electron sea model :

1. Metallic lusture :

(a) It is due to presence of delocalised mobile electrons

(b) These loosely bond electrons vibrate due to energy photon of incident light and radiates energy immediately

2. Electrical conductivity :

(a) It is due to mobile electrons.

(b) These electrons flow equaly in all direction.

(c) While applying a potential difference across a metal, there will be a directed flow of electrons towards the positive electrode.

(d) The directed flow of electrons carries the electric current from one point to another and therefore, the metals are known to be good conductors.

3. Thermal conductivity :

(a) It can also be explained on the basis of electron gas model.

(b) While heating a metal kinetic energy of electron increases and propagates through collisons.

4. Malleability and ductility :

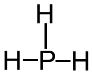
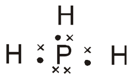
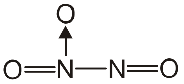
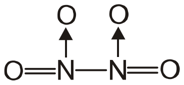
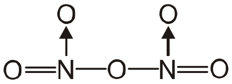
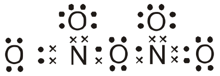
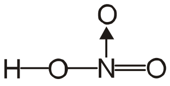
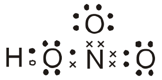
(a) This property is due to non directional nature of metallic bond.

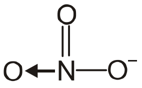
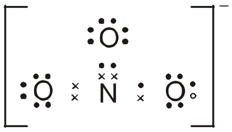
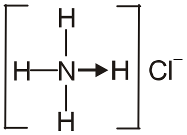
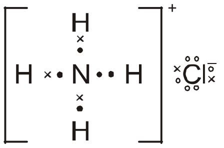
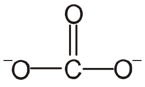
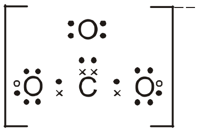
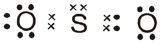
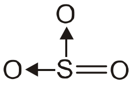
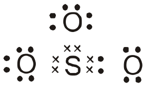
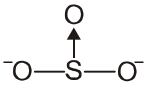
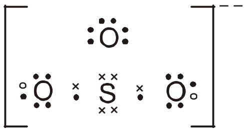
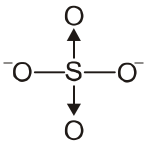
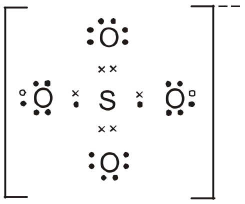
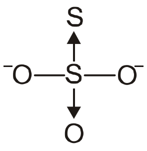
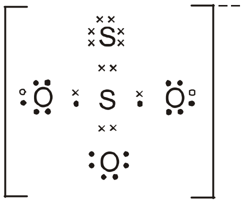
(b) Basically the kernels can slip over each other when a deforming force is applied.

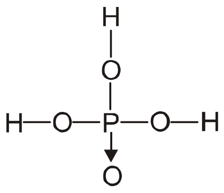
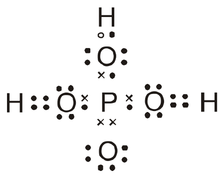
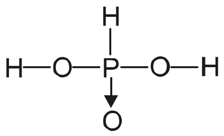
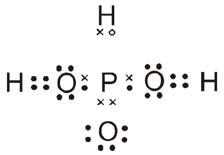
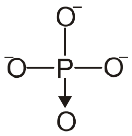
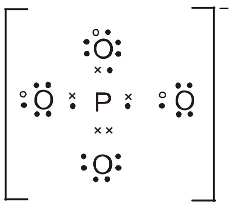
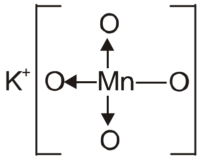
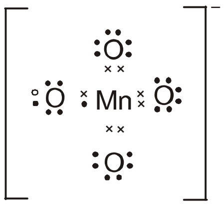
5. High tensile strength :

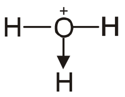
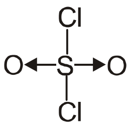
It is due to positively charged kernels and the mobile valence electrons.

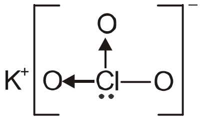
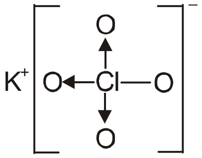
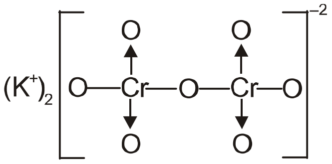
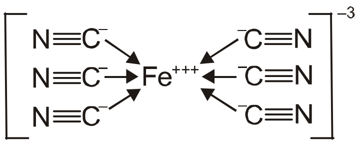
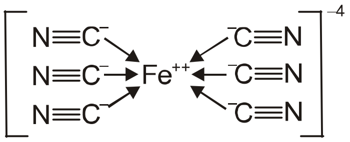
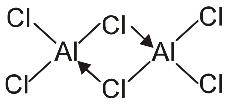
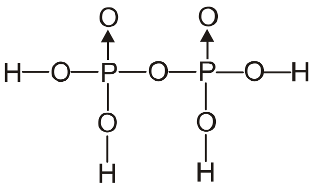
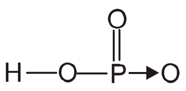
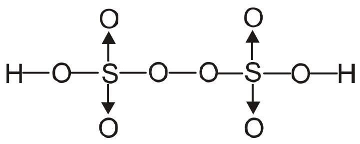
STRUCTURES / FORMULAE OF IMPORTANT COMPOUNDS

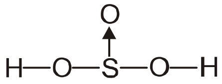
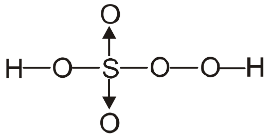
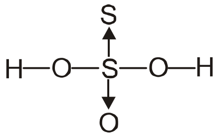
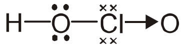
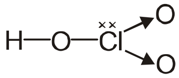
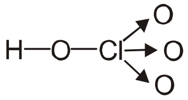
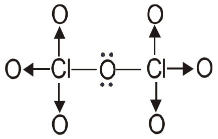
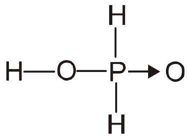
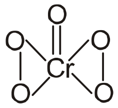
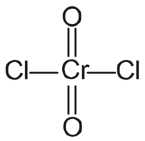
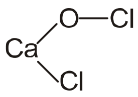
Compound	Structure	Electron dot/Cross formula
1. Sodium Sulphide (Na_2S)	$(Na^+)_2S^{--}$	
2. Calcium Hydride (CaH_2)	$Ca^{++}(H^-)_2$	
3. Hydrogen Peroxide (H_2O_2)	H–O–O–H	
4. Phosphene (PH_3)	 $H-\overset{\overset{H}{\vert}}{P}-H$	
5. Carbon mono-oxide(CO)	$C \equiv O$	
6. Carbon di-oxide (CO_2)	$O=C=O$	
7. Hydrogen Cyanide (HCN)	$H-C\equiv N$	
8. Potassium Isocyanide (KNC)	$K^+\,{}^-N\equiv C$	
9. Sodium Hydroxide (NaOH)	$Na^+\,{}^-O-H$	
10. Nitrous oxide (N_2O)	$N\equiv N\rightarrow O$	
11. Nitric oxide (NO or N_2O_2)	$O=N-N=O$	
12. Dinitrogen tri oxide (N_2O_3)	 $O=\overset{\overset{O}{\uparrow}}{N}-N=O$	
13. Dinitrogen tetraoxide (N_2O_4)	 $O=\overset{\overset{O}{\uparrow}}{N}-\overset{\overset{O}{\uparrow}}{N}=O$	
14. Nitrogen Penta oxide (N_2O_5)	 $O=\overset{\overset{O}{\uparrow}}{N}-O-\overset{\overset{O}{\uparrow}}{N}=O$	
15. Nitrous acid (HNO_2)	$H-O-N=O$	
16. Nitric acid (HNO_3)	 $H-O-\overset{\overset{O}{\uparrow}}{N}=O$	

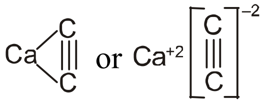
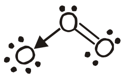
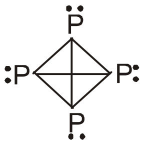
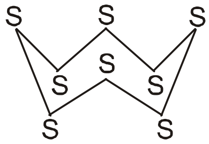
17. Nitrate Ion (NO_3^-)		
18. Ammonium Chloride (NH_4Cl)		
19. Carbonate Ion (CO_3^{--})		
20. Sulphur di-oxide (SO_2)	$O \leftarrow S = O$	
21. Sulphur Tri-oxide (SO_3)		
22. Sulphite Ion (SO_3^{--})		
23. Sulphate Ion (SO_4^{--})		
24. Thio-sulphate Ion ($S_2O_3^{--}$)		

25. Phosphoric Acid (H_3PO_4)		
26. Phosphorous acid (H_3PO_3)		
27. Phosphate Ion (PO_4^{---})		
28. Potassium Permagnate ($KMnO_4$)		

Compound	Structure
29. Carbon di-sulphide (CS_2)	$S{=}C{=}S$
30. Nitronium Ion (NO_2^+)	$O{=}\overset{+}{N}{=}O$
31. Nitrite Ion (NO_2^-)	$O{=}N{-}O^-$
32. Hydronium Ion (H_3O^+)	 $H-\underset{\underset{H}{\downarrow}}{\overset{+}{O}}-H$
33. Sulphuryl chloride (SO_2Cl_2)	 $O\leftarrow\underset{\underset{Cl}{\mid}}{\overset{\overset{Cl}{\mid}}{S}}\rightarrow O$

34. Potassium chlorate ($KClO_3$)	
35. Potassium per-chlorate ($KClO_4$)	
36. Potassium dichromate ($K_2Cr_2O_7$)	
37. Ferry-cyanide Ion $[Fe(CN)_6]^{-3}$	
38. Fero-cyanide Ion $[Fe(CN)_6]^{-4}$	
39. Aluminium chloride (Al_2Cl_6)	
40. Pyro phosphoric acid ($H_4P_2O_7$)	
41. Hypophosphate acid (HPO_3)	
42. Per-di-sulphuric acid ($H_2S_2O_8$)	

Compound	Formula	Structure
43. Sulphurous acid	H_2SO_3	
44. Persulphuric acid Peroxo monosulphuric acid (caro's acid)	H_2SO_5	
45. Thiosulphuric acid	$H_2S_2O_3$	
46. Chlorous acid	$HClO_2$	
47. Chloric acid	$HClO_3$	
48. Perchloric acid	$HClO_4$	
49. Perchloric anhydride	Cl_2O_7	
50. Hypophosphorous acid	H_3PO_2	
51. Perchromate	CrO_5	
52. Chromyl Chloride	CrO_2Cl_2	
53. Carbon suboxide	C_3O_2	$O=C=C=C=O$
54. Bleaching Powder	$CaOCl_2$	

55. Calcium carbide	CaC_2	
56. Ozone	O_3	
57. Ground state of phosphorous	P_4	
58. Ground state of sulphur	S_8	
59. Nitrosyl chloride (Tilden reagent)	NOCl	$\text{Cl}-\text{N}=\text{O}$
60. Sodium thiosulphate	$Na_2S_2O_3$