CHEMICAL BONDING

INTRODUCTION

(a) It is well known fact that except for inert gases, no other element exists as independent atoms under ordinary condition.

(b) Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.

(c) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.

Chemical Bond

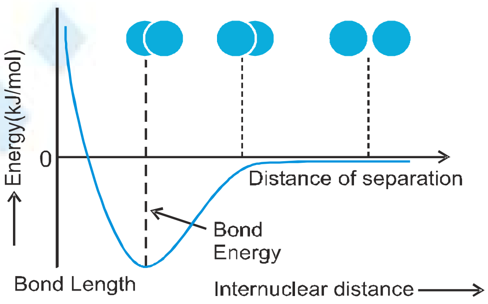
(a) A force that acts between two or more atoms to hold them together as a stable molecule.

(b) It is union of two or more atoms involving redistribution of e^- among them.

(c) This process accompanied by decrease in energy.

(d) Decrease in energy α Strength of the bond.

(e) Therefore molecules are more stable than atoms.



Potential Energy diagram

CAUSE OF CHEMICAL COMBINATION

1. Tendency to Acquire Minimum Energy :

(a) When two atoms approaches to each other-

Nucleus of one atom attracts the electron of another atom.

(b) Two nuclei and electron of both the atoms repells each other.

(c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.

(d) So Attraction α 1/energy α Stability.

(e) Bond formation is an exothermic process

2. Octet Rule

Octet rule was given by Lewis & Kossel

Atoms Combines to complete an octet of electrons in their outer most orbit. Complete orbital represents to get most stable state. Hence all atoms have a tendency to acquire octet (s^2p^6) configuration in their outermost orbit.

The octet may be complete in following manner:

Complete transfer of electrons from one atom to another.

Ex. NaCl, $CaCl_2$ & MgO etc. (Ionic Bond)

Sharing of electrons between atoms.

(a) Sharing of equal number of electron between two atoms.

Ex. Cl_2, N_2, O_2 etc., (Covalent bond)

(b) Sharing of electron pair given by only one atom

Ex. [$NH_3 \rightarrow H^+$] & $NH_3 \rightarrow BF_3$ (Co-ordinate Bond)

Exceptions of Octet Rule

1. Transition Metal Ions

Cr^{3+}	Mn^{2+}	Fe^{2+}
$[Ar]3d^3$	$[Ar]3d^5$	$[Ar]3d^6$
[2, 8, 11]	[2, 8, 13]	[2, 8, 14]

2. Pseudo Inert Gas Configuration $[s^2p^6d^{10}]$

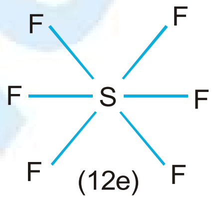
Zn^{2+}	Cd^{2+}
$[Ar]3d^{10}$	$[Kr]4d^{10}$

3. Contraction of Octet (Incomplete Octet)

$\underline{Be}F_2$	$\underline{B}F_3$	$\underline{Al}Cl_3$	$\underline{B}\,Cl_3$
(4e)	(6e)	(6e)	(6e)

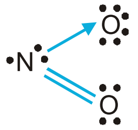
4. Expansion of Octet (Due to Empty d-Orbitals)

PCl_5	SF_6	ClF_3	ICl_5	IF_7
↓	↓	↓	↓	↓
(10e)	(12e)	(10e)	(12e)	(14e)



5. Odd Electron Species

Ex. NO, NO_2, ClO_2 etc.



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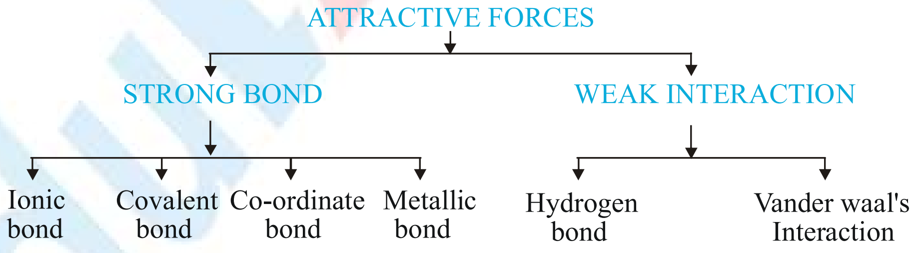
6. Compounds of Noble Gases

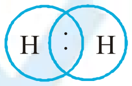
Noble gases which have already completed their octets (or douplet in case of He.) should not form compounds. However, their compounds like XeF_2, XeF_6 & KrF_2 etc., have been actually prepared.

CLASSIFICATION OF BONDS



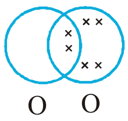
Covalent Bond

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

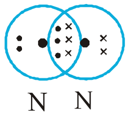


H – H

H_2 molecule



O = O

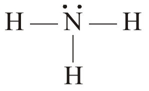


$\ddot{N} \equiv \ddot{N}$

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

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

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

Ex. 
$H-\ddot{N}-H$ with H below N {Three single bonds (not triple bond}

$N\equiv N$ Triple bond. (not three single bond) $O=O$ (Double bond) $H-O-H$ (Two single bonds.)

Co-ordinate Bond

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

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

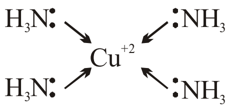
(i) Octet of donor atom should be complete and should have atleast one lone pair of electron.

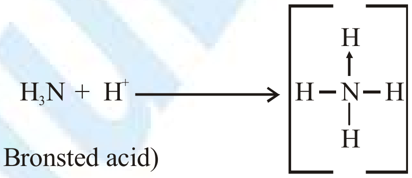
(ii) Acceptor atom should have a deficiency of at least one pair of electron.

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

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

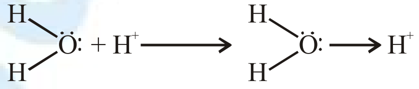
BF_3 is electron deficient compound.

Metal co-ordinate compounds - $[Cu(NH_3)_4]^{+2}$ ⇒ 

Ex. NH_4^+; 

(Lowry - Bronsted acid)

(e^- acceptor)

H_3O^+; 

N_2O ; $N\equiv N\!:\rightarrow O$

EDUBULL KEY POINTS

Compounds in which Ionic, covalent and co-ordinate bonds are present, are as follows -
NH_4Cl, $CuSO_4.5H_2O$, $K_4[Fe(CN)_6]$, KNC, KNO_3, etc.

WAVE MECHANICAL CONCEPT OF CO-VALENT BONDING –

(a) One orbital can accommodate at the most 2 electrons with opposite spins

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

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

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

Variable Valency in Covalent Bonds

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

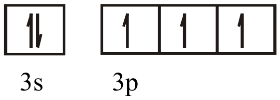
(ii) Lone pair electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

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

(iv) Promotion rule – Excitation of electrons in the same orbit.

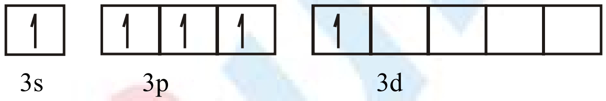
Ex.

(I) Phosphorus → Ground state



Covalency 3 (PCl_3)

Phosphorus → Excited state



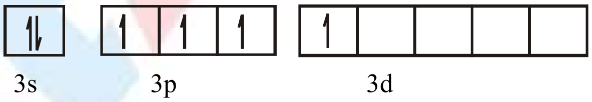
Covalency – 5 (PCl_5)

(II) Sulphur → Ground state.

Covalency - 2 (SF_2)

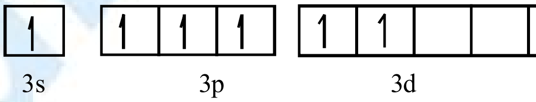
Sulphur → Excited state

Ist excited state



Covalency - 4 (SF_4)

2nd excited state

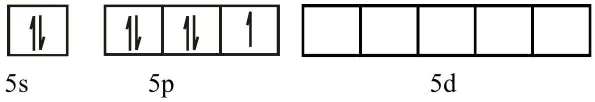


Covalency - 6 (SF_6)

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

(III) Iodine has three lone pair of electrons

(Ground state)



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

Variable Valencies are 1, 3, 5, 7

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

- Valence bond theory (VBT)
- Molecular orbital theory (MOT)

VALENCE BOND THEORY (VBT)

(A) Overlapping theory **(B)** Hybridisation theory

(A) OVERLAPPING THEORY

(1) It was presented by Heitler & London to explain how a covalent bond is formed.

(2) 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

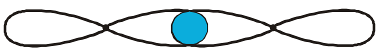
s-orbital → non directional – less overlapping

(ii) Nature of overlapping –

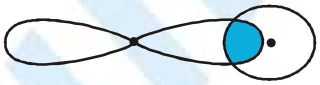
Co-axial overlapping - extent of overlapping more.

Collateral overlapping - extent of overlapping less

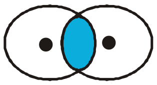
Order of strength of Co - axial overlapping – p - p > s - p > s - s



p - p



p–s



s–s

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

1s - 2p > 2s - 2p > 3s - 3p

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

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

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

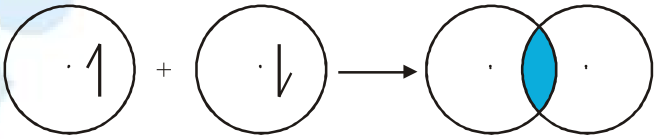
(k) Three types of bonds are formed on account of overlapping.

(1) Sigma (σ) bond (2) Pi (π) bond (3) delta (δ) bond

1. Sigma (σ) Bond

When orbitals overlaps along their inter nuclear axis, σ-bond is formed **Ex.** The bond formed by overlapping of s - s, s - p, p - p (axial), sp^3 – s, sp^2 – s, sp^3 – sp^3, sp^3 – sp^2 & sp – sp atomic orbitals.

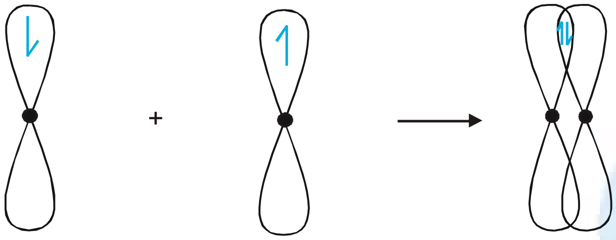
Sigma bond



S – S overlapping

p-p co-axial overlapping

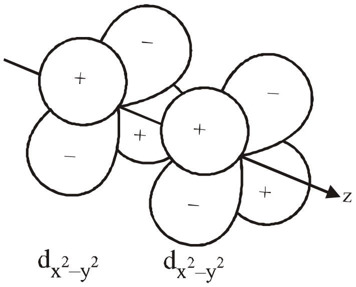
2. **Pi (π) Bond :** When two p-orbitals along the lateral axis (side way), π-bond is formed.



DIFFERENCE BETWEEN SIGMA AND PI-BOND

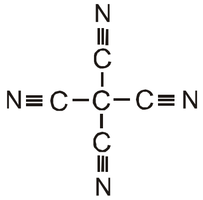
S.No.	Sigma-bond	Pi-bond
1.	A σ-bond is formed by the axial overlapping of atomic orbitals.	A π-bond is formed by the side ways overlapping of orbitals.
2.	σ-bond formation involves overlapping of s-s, s-p and p-p orbitals.	It involves overlapping of p-p orbitals.
3.	σ-bond is stronger because of larger extent of overlapping	π-bond is relatively weaker because of smaller extent of overlapping.
4.	The molecular orbital is symmetrical about internuclear axis and electron cloud is present on this axis	The molecular orbital is discontinuous and consists two electron clouds below and above the internuclear axis
5.	Free rotation exists around a σ-bond.	Free rotation does not exist around π-bonds.
6..	A sigma bond may exist either alone or or along with π-bonds.	A π-bond is always present along with a sigma-bond
7.	Hybridised orbitals or unhybridised orbitals are involved in σ-bond.	Hybridised orbitals are never involved in π-bond.

3. **Dalta(δ)-Bond:** It is special type of lateral overlapping in which all four lobs of d-orbital are overlap laterally with other smilar d-orbital produce delta(δ)-bond.



Ex. What are the total number of σ & π bonds in tetracyanomethane.

Sol.



(in triple bond $\equiv \begin{smallmatrix}\pi\\ \sigma\\ \pi\end{smallmatrix}$)

From the structure it is clear that it has 8 σ and 8 π bonds.

(B) HYBRIDISATION THEORY

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

Consider an example of Be compound :-

If it is formed without hybridisation then -

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

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.

(b) **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 $BeCl_2$

$$\text{Cl}\overset{\text{p–sp}}{\text{————}}\text{Be}\overset{\text{sp–p}}{\text{————}}\text{Cl}$$

bond strength of both the bonds will be equal.

Characteristic of Hybridisation

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

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

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

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

(e) One element can represent many hybridisation state depending on experimental conditions

Ex. C showing sp, sp^2 and sp^3 hybridisation in its compounds.

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

(g) 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.

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

(h) Hybridize orbitals show axial overlapping & form σ bond

TYPES OF HYBRIDISATION

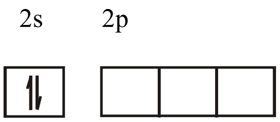
1. sp Hybridisation

(a) 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.

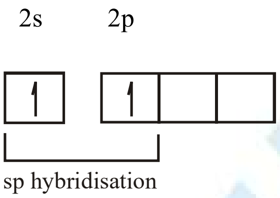
(b) These two sp hybrid orbitals are arrange in straight line & at bond angle 180°.

(c) s-character 50%

Be (ground state)

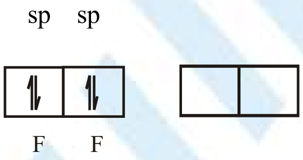


Be (excited state)



Be atom share two electrons

with F in BeF_2,



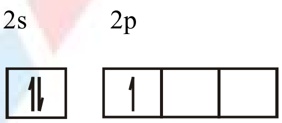
2. sp^2 Hybridisation

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

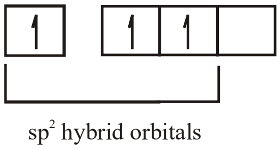
(b) These three sp^2 hybrid orbitals are at angle of 120° & giving trigonal planar shape.

(c) s-character 33.33% in each orbital.

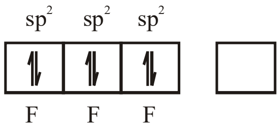
B (ground state)



B (excited state)



B atom share 3 electrons



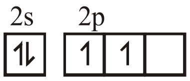
with 3 F atoms in BF_3

3. sp^3 Hybridisation

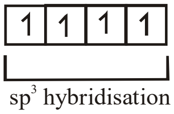
(a) In this hybridisation one s orbital & three p orbitals of an atom of a molecule or ion, are mixed to give four new hybrid orbitals called as sp^3 hybrid orbitals.

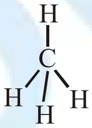
(b) The angle between these four hybrid orbitals will be 109° 28'

C (ground state)

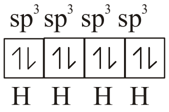


C (excited state)





C atom share



four electrons with

4 hydrogen atoms

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

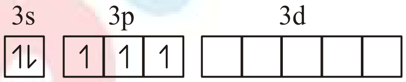
4. sp^3d Hybridisation

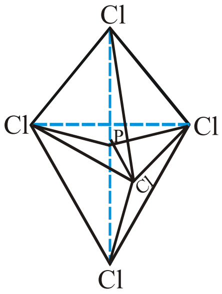
(a) In this hybridisation one s orbital, three p orbitals and one d orbital are mixed to give five new hybrid orbitals which are equivalent in shape and energy called as sp^3d hybrid orbitals.

(b) Out of these five hybrid 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 bipyramidal.

For example, PCl_5 showing sp^3d hybridisation

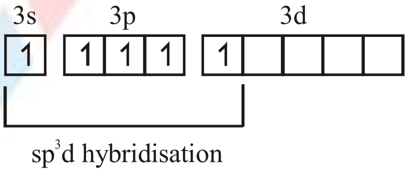
P (ground state)



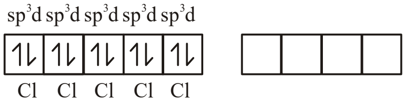


Structure of PCl_5

P* (excited state)



P atom share five e with Cl



(c) 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 Cl atoms and give a molecule of PCl_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 equitorial b.p. of e^- and 2 axial b.p. of e^-

5. sp^3d^2 Hybridisation

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

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

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

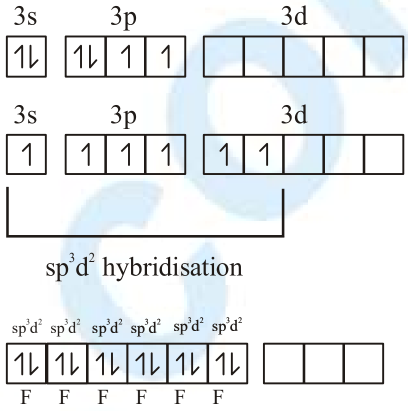
Ex. SF_6, AlF_6^{-3}, PF_6^-, ICl_5, XeF_4, $XeOF_4$, ICl_4^-,

(d) Two 'd' orbital participates in the hybridisation are $dx^2–y^2$ and dz^2.

SF_6 S (ground state)

S (II^{nd} excited state)

S (after hybridisation) share $6e^-$ with 6 F atoms



6. sp^3d^3 Hybridisation

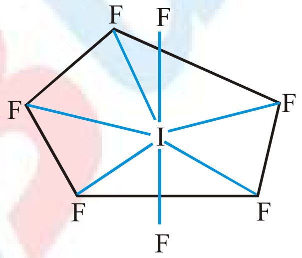
(a) In this hybridisation, one s-orbital, three p-orbitals & three d-orbitals are mixed to give seven new hybrid orbitals known as sp^3d^3 hybrid orbitals.

(b) In this hybridisation d-orbitals used are d_{xy}, $d_{x^2-y^2}$ & d_{z^2} orbitals.

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

(d) Five bond angles are of 72° & ten bond angles of 90°.

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



VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

(a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.

(b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states

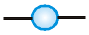
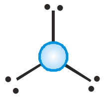
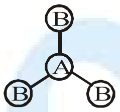
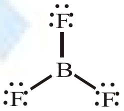
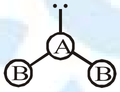
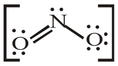
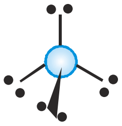
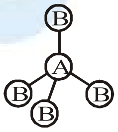
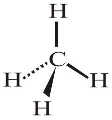
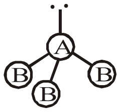
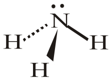
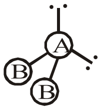
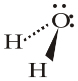
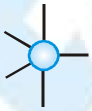
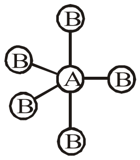
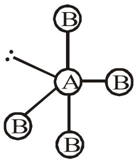
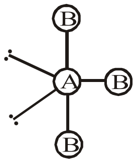
(i) Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localised orbitals. These orbitals arrange themselves in so as to minimize the mutual electronic repulsions.

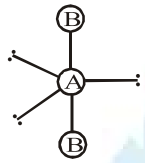
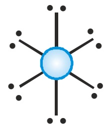
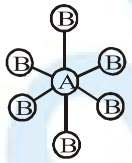
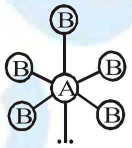
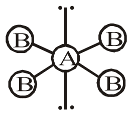
(ii) The magnitude of the different types of electronic repulsions follows the order given below:

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

(iii) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.

(iv) The actual shape of the molecules containing lone pairs is a little distorted from the basic shape as in the NH_3 and H_2O molecules, the bond angles are not 109°28' but 107° and 104.5° respectively due to presence of one lone pair in NH_3 and two lone pairs in H_2O.

Number of Electron pairs	Molecule Type	Electronic Geometry	Bonding Pair	Non-bonding Pair (E)	Molecular Geometry	Example
2	AB_2		2	0	 Linear	$BeF_2, BeCl_2$ Linear $\ddot{O}=C=\ddot{O}$ etc
3	AB_3	 Trigonal planar	3	0	 Trigonal planar	
	AB_2	Trigonal planar	2	1	 Bent	 $, SO_2, O_3$
4	AB_4	 Tetrahedral	4	0	 Tetrahedral	
	AB_3E	Tetrahedral	3	1	 Trigonal pyramidal	
	AB_2E_2	Tetrahedral	2	2	 Bent	
5	AB_5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
	AB_4E	Trigonal bipyramidal	4	1	 See saw	SF_4
	AB_3E_2	Trigonal bipyramidal	3	2	 T-shaped	ClF_3

	AB_2E_3	Trigonal bipyramidal	2	3	 Linear	XeF_2
6	AB_6	 Octahedral	6	0	 Octahedral	SF_6
	AB_5E	Octahedral	5	1	 Square pyramidal	BrF_5
	AB_4E_2	Octahedral	4	2	 Square planar	XeF_4

DETERMINATION OF HYBRIDISATION STATE

METHOD (I)

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

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

(b) Count all lone pair of electron

(c) Count all coordinate bond.

(d) Count all negative charge.

METHOD (II)

To predict hybridisation following formulae 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]

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

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

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

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

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

BOND LENGTH

(i) The internuclear distance between the two single covalently bonded atoms is called bond length or bond distance.

(ii) If the electronegativities of both the atoms are equal, then the bond length is equal to the sum of the covalent radii of two bonded atoms. $d_{A-A} = r_A + r_A$

(ii) If the electronegativities of two bonded atoms differ, then the bond length is smaller than the sum of their covalent radii. $d_{A-B} < r_A + r_B$

Factors Affecting Bond Length

(i) Size of Atoms

HI > HBr > HCl > HF

$H_2Te > H_2Se > H_2S > H_2O$

(ii) Hybridization State of The Bonded Atoms: If the s-character in hybridization state of the bonded atoms increases, the C–H bond distance decreases.

Ex. In C – C single bond.

$sp^3 - sp^3$ single bond length = 1.54 Å

$sp^3 - sp^2$ single bond length = 1.52 Å

$sp^2 - sp^2$ single bond length = 1.51 Å

$sp^3 - sp$ single bond length = 1.46 Å

$sp^2 - sp$ single bond length = 1.45 Å

sp – sp single bond length = 1.37 Å

Bond length decreases in the order $sp^3 - sp^3 > sp^2 - sp^2 > sp - sp$

(iii) Resonance or Delocalisation of Electrons of The Bond: Bond length between atoms are changed if a molecule shows resonance.

BOND ANGLE

The angle between two bonds is known as bond angle.

Factors Affecting Bond Angle

(i) Hybridisation State of Central Atom: Compounds having different hybridisation have different bond angle.

Ex.	BeH_2	BH_3	CH_4
Hybridisation	sp	sp^2	sp^3
Bond angle	180°	120°	109°28'

(ii) Lone Pair of Electron: If compounds have same hybridisation states then bond angle depends on lone pair of electron.

Ex.

	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
Lone pair e^-	zero	one	two
Bond angle	109°28'	107°	105°

The different in bond angle is explained on the basis of following repulsion sequence

The repulsion between

lone pair-lone pair > lone pair - bonded pair > bonded pair - bonded pair

(iii) Electronegativity: When compounds having same hybridisation state of central atom and some number of lone pair of electrons, then bond angle depends on electronegativity.

Bond angle $\propto$ electronegativity

Ex. $H_2O > H_2S$

$NH_3 > PH_3$

E.N. of oxygen is more than sulphur therefore the bond angle in H_2O will be more than H_2S.

(iv) Size of Terminal Atoms: When size of terminal atoms increases, bond angle increases.

Ex. $OF_2 < Cl_2O < Br_2O$

$PF_3 < PCl_3 < PBr_3$

BOND ENERGY

(i) The amount of energy required to break one mole of the bond and separate the bonded atoms in the gaseous state is known as the bond energy of that particular bond.

(ii) B.E. is expressed in KJ mol^{-1} (in SI units) or in Kcal mol^{-1}.

Factors Affecting Bond Energy

(a) Electronegativity Difference of The Bonded Atoms : As the EN difference of the bonded atoms increases the bond energy increases because the ionic nature of the bond increases.

Ex. Bond strength of hydrogen halides decreases in the order

$H-F > H-Cl > H-Br > H-I$

(b) Bond Order Bond energy $\propto$ Bond order, therefore the increasing order of bond energy is

$C-C < C=C < C\equiv C$

(c) Hybridisation State of The Bonded Atoms : Bond energy $\propto$ s-character

Ex. $\underset{sp^3}{-C-H} < \underset{sp^2}{-C=H} < \underset{sp}{-C\equiv H}$

(d) Atomic Size of Bonded Atoms : Atoms with small atomic radii form stronger bonds because the extent of overlapping of atomic orbitals is more

Ex. B.E. of halogens is of the order

$Cl-Cl > Br-Br > I-I$

because their atomic sizes are in the order $Cl < Br < I$.

(e) **Extent of Overlapping of Atomic Orbitals:** A larger extent of overlapping of component atomic orbitals imparts great strength to the bond.

(f) **Repulsion Between the Lone Pairs of Electrons of Bonded Atoms:**

$$\boxed{\text{Bond energy} \propto \frac{1}{\text{No. of lone pair of electron on the bonded atoms}}}$$

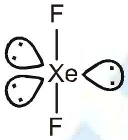
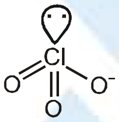
Ex. the bond energies of the following single bonds having zero, one, two and three lone pair of electrons are in the order.

$$C-C > \ddot{N}-\ddot{N} > :\ddot{O}-\ddot{O}: > :\underset{\cdot\cdot}{\ddot{F}}-\underset{\cdot\cdot}{\ddot{F}}:$$

Ex. Use the VSEPR model to predict the geometry of the following :

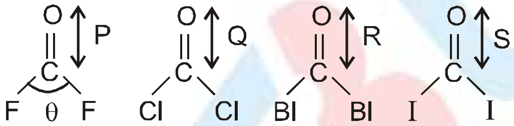
(a) XeF_2 (b) ClO_3^-

Sol.

	Species	Structure	
(a)	XeF_2		lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.
(b)	ClO_3^-		To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Ex. Discuss the bond angle in carbonyl halides COF_2 , $COCl_2$, $COBr_2$, COI_2

Sol.

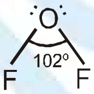


Bond angle $\theta \Rightarrow COF_2 < COCl_2 < COBr_2 < COI_2$

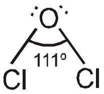
Double bonds require more room than single bonds. Hence C = O group compresses the molecule and bond angle decrease maximum in COF_2 as bond pairs of electrons are more closer to the fluorine atoms because of high electronegativity of fluorine. As size of halogen atoms increase and their electronegativity decreases repulsion between bond pairs increases and therefore θ increase.

Ex. Compare bond angle of OF_2 , Cl_2O and Br_2O.

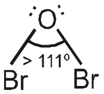
Sol. OF_2



Cl_2O



Br_2O



Bond pairs of electrons are more closer to the fluorine atoms (because of high electronegativity of fluorine). So the lp - lp repulsion is more than bp - bp. Thus the F—O—F bond angle decreases to 102° from 109.5°. In Cl_2O, the bond pair are more closer to the oxygen atom because of the high electronegativity of oxygen. So the bp - bp repulsion is more than lp - lp. Thus the bond angle Cl—O—Cl increases to ≈111° due to bp - bp repulsion and repulsion between larger Cl atoms.

Note : The steric crowding of the larger halogen atoms also contributes in the increasing bond angles.

Ex. Which is linear PH_4^+, H_3S^+ or NO_2^+ ?

(A) Phosphonium ion (PH_4^+) **(B)** Sulphonium (H_3S^+)

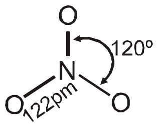
(C) Nitronium ion (NO_2^+) . **(D)** None of these

Sol. Phosphonium ion (PH_4^+) is tetrahedral, sulphonium (H_3S^+) is pyramidal, but nitronium ion (NO_2^+) is linear ; $O = \overset{\oplus}{N} = O$ (sp hybridisation). **Ans. (C)**

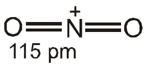
Ex. The ONO angle is maximum in :

(A) NO_3^- **(B)** NO_2^+ **(C)** N_2O_4 **(D)** NO_2

Sol. (A)

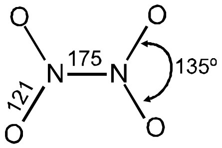


(B)

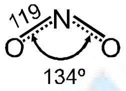


Bond angle is 180° because of sp hybridisation of nitrogen.

(C)



(D)



Ans. (B)

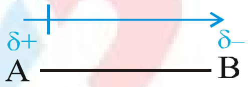
Ex. The triiodide ion (I_3^-) in which the I atoms are arranged in a straight line is stable, but the corresponding F_3^- ion does not exist.

Sol. F_3^- and I_3^- are of same group. Iodine can expand its octet but F cannot and thus, in I_3^- octet rule is not violated, but in F_3^- octet rule is violated.

DIPOLE MOMENTS & MOLECULAR POLARITY

(a) The degree of polarity of covalent bond is given by the dipole moment (μ), which is the product of either charge (e) and the distance (d) between them. $\mu = d \times e$. 'e' is the order of magnitude of the electronic charge, i.e., about 10^{-10} esu and d is the distance between the atomic centres, i.e., about 10^{-8} cm.

(b) Hence dipole moments may be expected to have value around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm. It is however, general particle to express dipole moments in **Debye units** (D), $1\ D = 10^{-18}$ esu-cm.



Electronegativity of A < Electronegativity of B

If the charge is in SI units (Coulombs) and d in metre, μ will be coulomb-metre (cm) unit.

$1D = 3.336 \times 10^{-30}$ cm

(c) Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compound containing such bonds will have dipole moment,for the polarity of the molecule as a hole is the vector sum of the individual bond moment.

$$\boxed{\mu_{resultant} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}}$$

(i) For example, CO_2 is a linear molecule, $O = C = O$, so that the dipole moments of the two $C = O$ bonds cancel out.

(ii) The $C \rightarrow Cl$ bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4C – Cl bond moments is zero.

(iii) On the contrary CH_3Cl, CH_2Cl_2 and $CHCl_3$ have definite dipole moments.

(Order of dipole moment $CH_3Cl > CHCl_3 > CH_2Cl_2 > CCl_4 = CH_4$)

Application of Dipole Moment Measurements

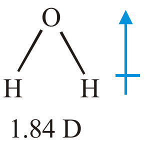
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shape of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated fairly.

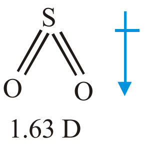
1. INORGANIC SUBSTANCES

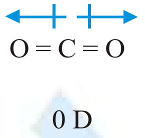
(a) Monoatomic molecules such as He, Ne, etc., have zero dipole moment becaue they are symmetrical.

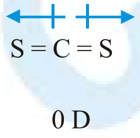
(b) Diatomic molecules such as H_2, Cl_2 and N_2 have no dipole moment; so these molecules are symmetrical.

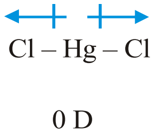
(c) Triatomic molecules some of these molecules possess zero dipole moment so they have a symmetrical linear structure, **Ex.** CO_2, CS_2, $HgCl_2$. Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structures. (V-shaped)



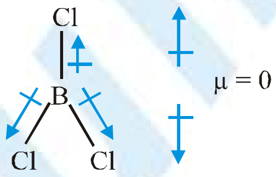




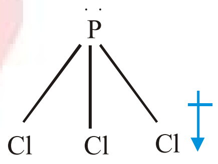




(d) Tetratomic molecules some molecules like BCl_3 have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other example are BF_3, BBr_3, CO_3^{2-}, and NO_3^-

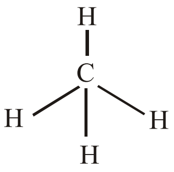


(e) PCl_3, $AsCl_3$, NH_3, PH_3, AsH_3, H_3O^+ have appreciable dipole moment. They possess trigonal pyramidal structure.



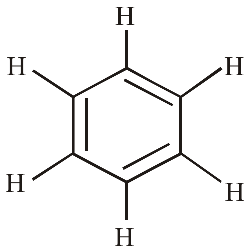
2. ORGANIC SUBSTANCES

(a) Methane and CCl_4 have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.



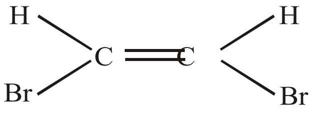
Methane

(b) Benzene has zero dipole moment. All the 6C and 6H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

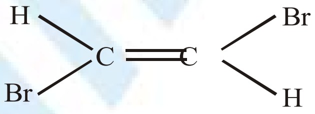


(c) Measurement of dipole moments will enable us to detect cis-and trans isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.

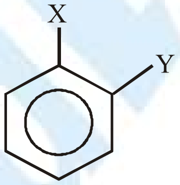


cis-dibromoethylene (μ = 1.4D)

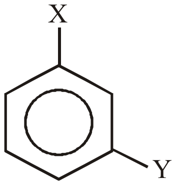


trans-dibromoethylene (μ = 0)

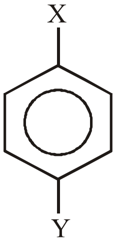
(d) The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers. o-nitrophenol, m-nitrophenol and p-nitrophenol. We also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



Ortho



Meta



Para

In those cases where X = Y, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other (NO_2) is electron withdrawing while in aminophenols, both the groups (OH and NH_2) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment. Then calculation of dipole moment follows as:

Case (i) : When X and Y both are electron pushing or electron withdrawing.

Let the bond dipole of C–X bond is represented by μ_1 and that of C–Y bond by μ_2. Now let us assume that the electron pushing groups have +ve bond moment and the electron withdrawing groups have –ve bond moment. The net dipole moment is the resultant of two bond dipoles at different orientations.

$$\mu_{ortho} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cdot \frac{1}{2}}$$

$$\therefore \quad \mu_o = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$\mu_{meta} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos 120^\circ}$$

$$\therefore \quad \mu_m = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$\mu_{para} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2}$$

$$\therefore \quad \mu_p = \mu_1 - \mu_2$$

From the above expressions of μ_o, μ_m and μ_p, it is clear that when both X and Y are of the same nature i.e., both are electron withdrawing or both are electron pushing the para product has the least dipole moment and ortho product has the highest dipole moment. When X = Y, $\mu_1 = \mu_2$, thus μ_p would be zero.

Case (ii) : When X is electron pushing and Y is electron withdrawing or vice versa.

Let the bond moment of C–X dipole is μ_1 and that of C–Y dipole is μ_2.

$$\mu_o = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$= \sqrt{(\mu_1 + \mu_2)^2 - 3\mu_1\mu_2}$$

$$\mu_{meta} = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 120^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$= \sqrt{(\mu_1 + \mu_2)^2 - \mu_1\mu_2}$$

$$\mu_{para} = \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} = \mu_1 + \mu_2$$

Looking at the expressions of μ_o, μ_m and μ_p, it is clear that the para isomer has the highest dipole moment and ortho has the least.

3. DIPOLE MOMENT AND PERCENTAGE IONIC CHARACTER

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge = 4.8×10^{-10} e.s.u.

1 D = 1×10^{-18} e.s.u × cm.

$$\therefore \quad \%\ \text{ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoritical dipole moment}} \times 100$$

Theoretical dipole moment is confined when we assume that the bond is 100% ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

Ex. The resultant dipole moment of water is 1.85 D ignoring the effects of lone pair. Calculate, the dipole moment of each OH bond (given that bond angle in H_2O = 104°, cos 104° = – 0.25).

Sol. $R^2 = P^2 + Q^2 + 2PQ\cos\theta$

$$(1.85)^2 = x^2 + x^2 + 2x^2\left(-\frac{1}{4}\right)$$

$$(1.85)^2 = 2x^2 - \frac{x^2}{2} \Rightarrow \frac{3x^2}{2}$$

$$\therefore \quad x = 1.51\ \text{D}$$

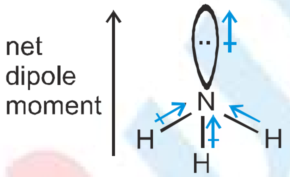
Ex. For HCl molecule observed dipole moment is 1.03 D and bond length is 1.275 Å. Calculate % ionic character.

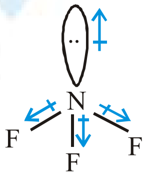
Sol. Dipole moment = $4.8 \times 10^{-18} \times 1.275 \times 10^{-8} = 4.8 \times 1.275$

$$\%\ \text{ionic character} = \frac{1.03 \times 100}{1.275 \times 4.8} \approx 17\%$$

Ex. Why NH_3 is having more dipole moment than NF_3.

Sol. In $\ddot{N}H_3$ molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards. Nitrogen atom but in NF_3 molecule. Fluorine is more electronegative than. Nitrogen so the net dipole moment is towards fluorine atoms. In NH_3 the bond pair moments and lone pair moments are in the same direction while in NF_3 the lone pair moment and bond pair moments are in opposite direction.



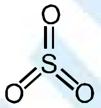


Ex. The geometry of SO_3 and its dipole moment are :

(A) pyramidal and non-zero.
(B) trigonal planar and non-zero.
(C) trigonal planar and zero.
(D) T-shaped and zero.

Ans. (C)

Sol.



The steric number of sulphur = 3; so hybridisation is sp^2. There is no lone pair on sulphur atom, therefore, according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence the molecule will be symmetrical (trigonal planar) with zero dipole moment.

ELECTROVALENT OR IONIC BOND

(a) 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.

(b) Electro positive atom loses electron (group IA to IIIA)

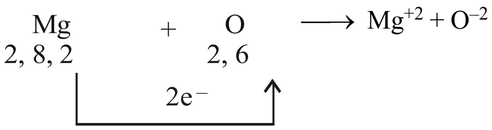
(c) Electro negative atom gains electron (group VA to VIIA)

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

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

Ex.

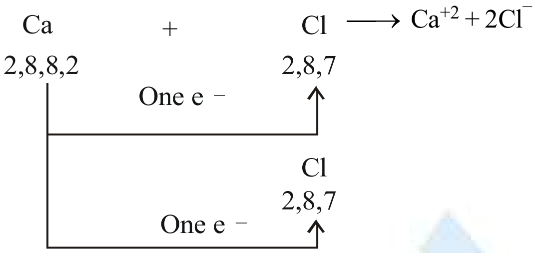
(i)



electrovalency of Mg = 2

electrovalency of O = 2

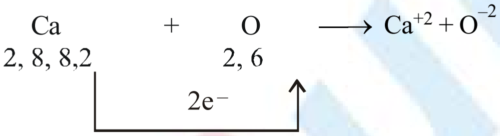
(ii)



electrovalency of Ca = 2

electrovalency of Cl = 1

(iii)



electrovalency of Ca = 2

electrovalency of O = 2

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

(g) A definite three dimensional structure is formed called crystal lattice.

(h) Ionic compound do not have molecular formula. It has only empirical formula.

Ex. NaCl is empirical formula of sodium chloride

FORMATION OF IONIC COMPOUND - BORN HABER CYCLE

(a) When elements react to form compounds, ΔG (the free energy of formation) is negative. For a reaction to proceed spontaneously, the free energy of the products must to lower than that of the reactants.

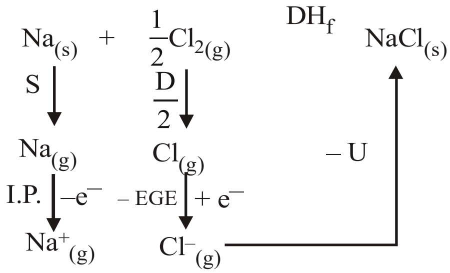
(b) Usually the energy changes are measured as enthalpy values ΔH, and ΔG is related to ΔH by the equation

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

In many cases enthalpy values are used instead of free energy values, and the two are almost the same if the term $T\Delta S$ is small. At room temperature T is almost 300 K, so ΔG and ΔH are similar when the change in entropy ΔS is very small. Entropy changes are large when three is a change in physical state, **Ex.** solid to liquid, or liquid to gas, but otherwise entropy changes are usually small.

(c) A whole series of energy changes is involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.

Formation of NaCl (s) involves



thus $$S + I.P. + \frac{D}{2} - EGE - U = \Delta H_f$$

here S = heat of sublimation of Na(s)

I.P. = ionisation potential of Na(g)

D = bond dissociation energy of Cl_2

EGE = electron gain enthalpy of Cl(g)

U = lattice energy

ΔH_f = enthalpy heat of formation of NaCl(s)

If lattice is MgX_2(s) then

$$S + (IP_1 + IP_2) + D - 2EGE - U = \Delta H_f$$

where $(IP_1 + IP_2)$ = total ionisation energy to form $Mg^{2+}_{(g)}$ from $Mg_{(g)}$.

FACTORS FAVOURING IONIC BONDING

(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 Ionization energy → Greater tendency to form cation.

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

(b) Electron Affinity

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

Higher electron affinity → Greater tendency to form anion

Ex. $Cl^- > F^- > Br^- > I^-$

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

(c) Lattice Energy - (Energy released)

The energy released in the formation of 1g mole electrovalent compound from isolated gaseous ions is called lattice energy (U) of that compound.

Higher lattice energy → Greater will be the stability or strength of ionic compound.

FACTORS AFFECTING LATTICE ENERGY

(i) Magnitude of charge → $U \alpha z^+ z^-$ (Ionic charge)

Lattice energy α Magnitude of charge

NaCl	$MaCl_2$	$AlCl_3$
Na^+	Mg^{+2}	Al^{+3}

$\longrightarrow$

– Lattice energy increases

– Size of cation decreases.

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

LiCl NaCl KCl RbCl CsCl

$\longrightarrow$

– Size of cation increasing

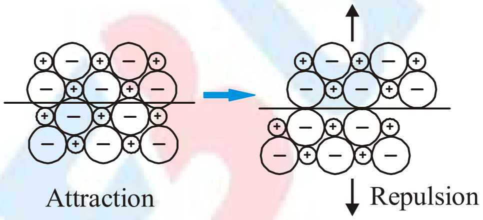
– Size of anion is constant

– Lattice energy decreases.

Properties of Ionic Compound

(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 :** Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism

Ex. NaF, MgO, $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$. All alums $M_2'SO \cdot M_2''(SO_4)_3 \cdot 24H_2O$.

(c) **Boiling Point and Melting Point** –

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

(d) **Conductivity** – It depends on ionic mobility.

(i) In solid state - No free ions - Bad conductor of electricity.

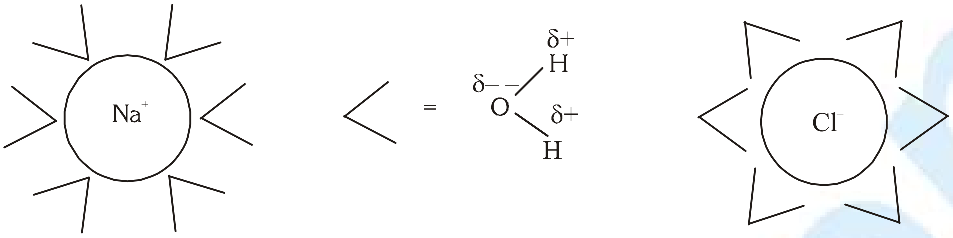
(ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity Order Solid state < fused state < Aqueous solution

(e) **Solubility –** Highly soluble in water (Polar solvents) **Ex.** 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.



(iii) Thus charge on Na^+ and Cl^- decreases and electrostatic force of attraction also decreases which leads to produce 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

$$\boxed{\text{Lattice energy } \alpha \ \frac{1}{\text{Solubility}}}$$

$$\boxed{\text{Hydration energy } \alpha \text{ Solubility.}}$$

$$\boxed{\text{Hydration energy (H) } \alpha \ \frac{1}{r^+} + \frac{1}{r^-} \ \{ r^+ \ \& \ r^- \text{ are radius of cation and anion} \}}$$

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

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

FACTOR AFFECTING SOLUBILITY

(a) Dielectric Constant of Solvent

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

(i) Water has maximum dielectric constant ($\varepsilon = 80$)

(CH_3OH $\varepsilon = 35$) , (Acetone $\varepsilon = 21$)

(C_2H_5OH $\varepsilon = 27$) , (Ether $\varepsilon = 4.1$)

(Benzene $\varepsilon = 2.3$)

$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

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

(iii) H_2SO_4 and H_2O_2 have high dielectric constant but these are not a good solvent due to oxidising nature.

(b) Size of Ion

(i) Keeping size of cation constant, the lattice energy decreases with the increase of anionic radius.

Hence order of solubility of LiX in water is LiF < LiCl < LiBr < LiI

As $\boxed{\text{solubility } \alpha \ \frac{1}{\text{lattice energy}}}$

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

(iii) 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)

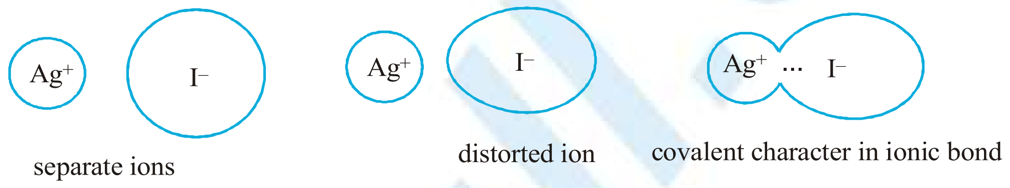
(iv) If size of cation and anion is very large, solubility decreases from top to bottom.

(v) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)

$NaCl > MgCl_2 > AlCl_3$

TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

(a) Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of Agl.



separate ions distorted ion covalent character in ionic bond

(b) **Factors Influencing Ion – Deformation or Increasing Covalent Character**

(i) **Large Charge on the Ions**

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl, AlF_3, AgF are ionic.

(ii) **Small Cation and Large Anion**

For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalent charcter with a small cation and a large anion, as in AgI.

(iii) **Cation with a Pseudo-Inert Gas Type of Electronic Configuration**

A cation with a 18 electron in outermost shell such as Ag^+ ([Kr] $4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+. The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+. Thus AgI is more covalent than KI, although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors, which influence covalent character, are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

Polarisation power of a cation is usually called ionic potential or charge density.

$$\boxed{\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}}$$

Application of Concept of Polarisation

(a) To Determine Covalent and Ionic Character of Molecule

$$\boxed{\phi \propto \frac{\text{Covalent character}}{\text{Ionic character}}}$$

From left (larger size) to right (smaller size) in a period ϕ increases so covalent character increases.

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

$\longrightarrow$

- charge increases
- size decreases ϕ increases
- Covalent character increases with particular anion

From top to bottom in a group ϕ decreases so covalent, character decreases.

Li^+

Na^+ - Size increases (charge is fix)

K^+ - ϕ decreases

Rb^+ - Hence covalent character decreases with particular anion

Cs^+

(b) To Determine Nature of Oxide

$\sqrt{\phi} < 2.2$ (Basic oxides)

$\sqrt{\phi} = 2.2$ to 3.2 (Amphoteric oxides)

Neutral oxides doesn't react with acid & base eg. H_2O, CO etc.

Amphoteric oxides (Al_2O_3 etc.) reacts with acid & base

$\sqrt{\phi} > 3.2$ (Acidic oxide)

Ex. $Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O$

$\longrightarrow$

– $\sqrt{\phi}$ decreases

– Basic character increases

(c) To Determine Conductivity of Metal Halides (MX)

If $\sqrt{\phi} < 2.2$ MX - ionic nature

If $\sqrt{\phi} > 2.2$ MX - covalent nature

(d) Formation of Complex Compounds

Smaller the cation, more will be the tendency of forming complex compounds.

High value of ϕ shows tendency of forming complex compounds.

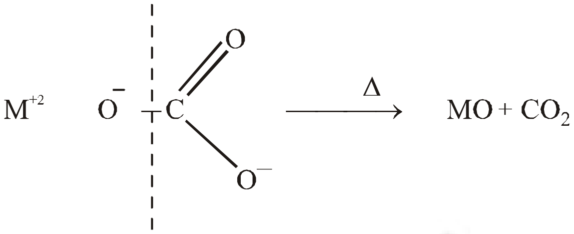
If ϕ is low → No or less tendency of forming complex compounds.

s-block metals (larger size) doesn't have the tendency to form complex compounds.

Exceptions - Li, Be, Mg (small size)

d-block metals have the tendency to form complex compounds (small in size, high charge).

(e) To Determine Thermal Stability of Metal Carbonates : stability $\alpha \frac{1}{\phi}$ (Covalent nature)



More smaller the size of metal cation, its polarisation capacity increases - strength of M—O bond increases and C—O bond decreases. So thermal stability of carbonates decreases.

$$CO_3^{-2} \xrightarrow{\Delta} O^{-2} + CO_2$$

From top to bottom thermal stability of carbonates increases (as size of cation increases)

(Ionic character increases or covalent character decreases)

$BeCO_3$
$MgCO_3$ – size of cation increases
$CaCO_3$ – ϕ decreases (covalent character decreases)
$SrCO_3$ – Thermal stability increases
$BaCO_3$

(f) To Explain Colour of Compounds

More the covalent character, more will be the colour intensity.

Colour density $\propto \phi$ (Covalent character)

Ex.

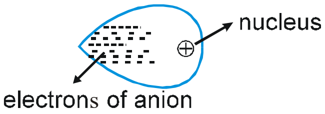
AgCl	AgBr	AgI
(White)	(Light yellow	(Dark yellow)
SnO_2	SnS_2	
(White)	(Yellow)	

(g) To Explain Diagonal Relationship

Since the value of ϕ for Be^{2+} is almost of the same order as that of diagonally situated Al^{3+}. Hence have many similar properties. Similarly value of ϕ for Li^+ is equal to Mg^{+2}, so have diagonal relationship.

Ex. AgCl is colourless whereas AgI is yellow, because of :
(A) Ag^+ have 18 electron shell to screen the nuclear charge.
(B) Ag^+ shows pseudo inert gas configuration.
(C) distortion of I^- is more pronounced than Cl^- ion.
(D) existence of d – d transition.

Sol. (C), the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



MOLECULAR ORBITAL THEORY (MOT)

Given by hund & Mulican

(a) Two atomic orbital come nearer & then overlap each other to form two molecular orbitals (MO)

(b) Combination of two atomic orbital (AO) forms two molecular, orbital (MO):

$$\text{AO} + \text{AO} \begin{array}{l} \nearrow \text{ ABMO (antibonding molecular orbital)} \\ \searrow \text{ BMO (bonding molecular orbital)} \end{array}$$

(c) Both orbitals can be filled by electrons according to Auffbau principle.

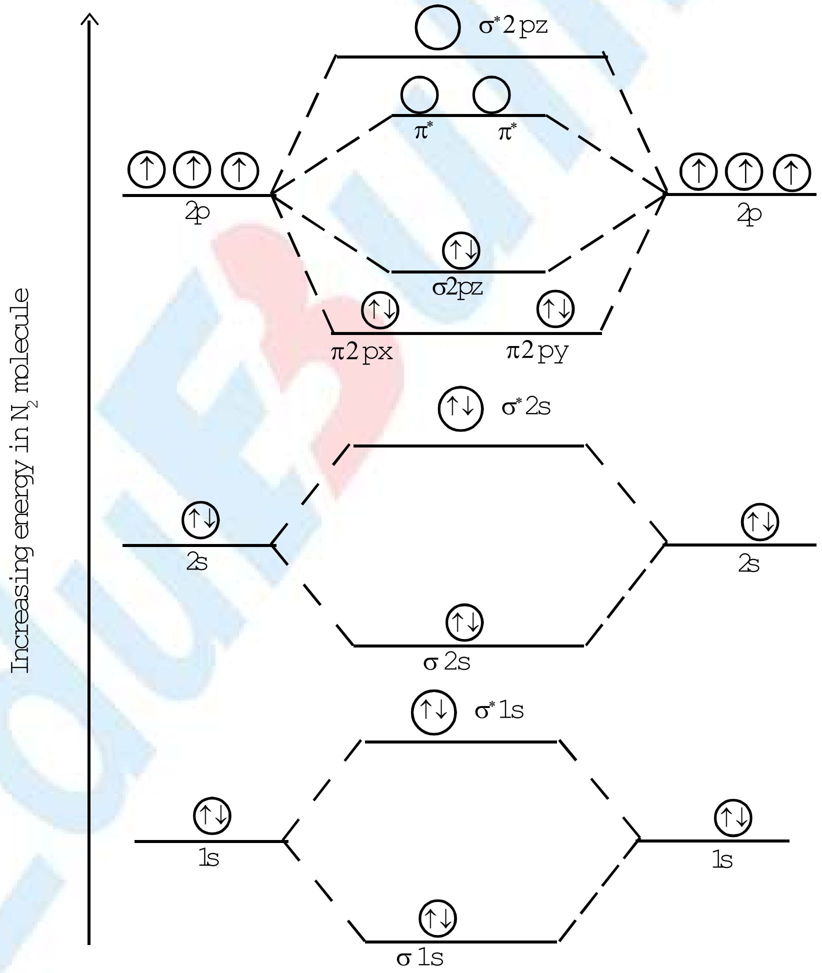
(d) Energy of BMO < Energy of ABMO.

(e) Order of energy in molecular orbitals of di-atomic molecules.

(i) From H_2 to N_2:

$$\sigma\, 1s < \sigma\, {}^*1s < \sigma\, 2s < \sigma\, {}^*2s < \pi\, 2p_z = \pi\, 2p_y < \sigma\, 2p_x < \pi\, {}^*2p_z = \pi\, {}^*2p_y < \sigma\, {}^*2p_x$$

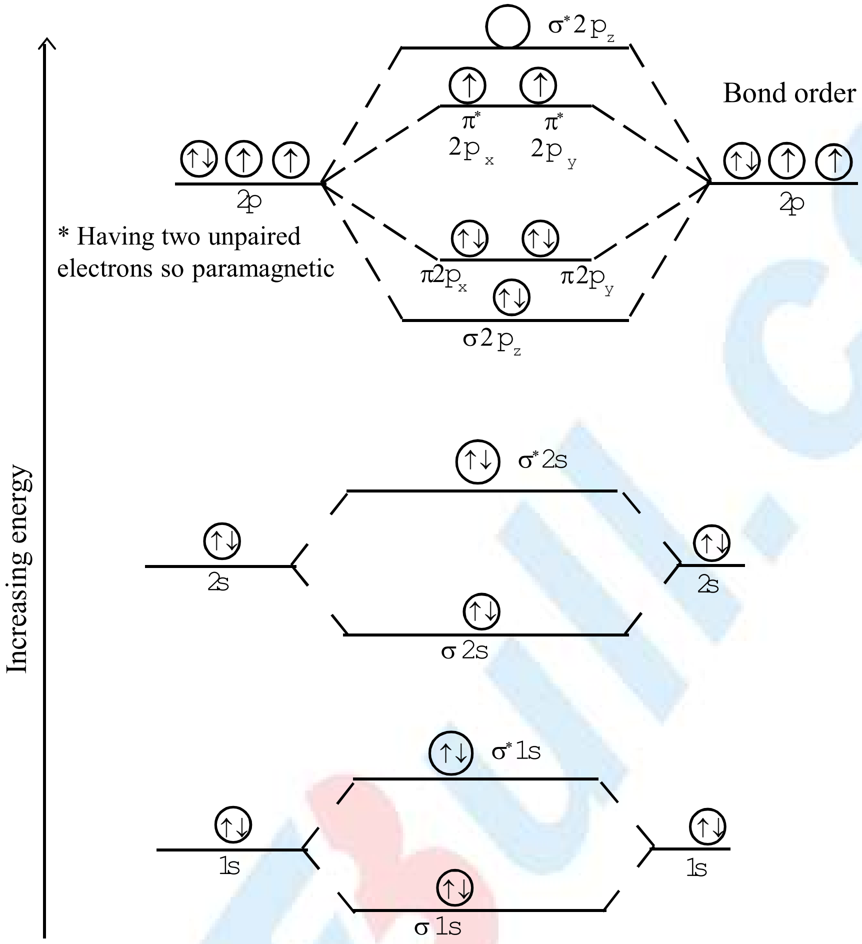
For N_2 Molecule



(ii) For O_2 & F_2:

$\sigma 1s < \sigma^*1s\,; < \sigma 2s < \sigma^*2s < \sigma 2p_x < \pi 2p_z = \pi 2p_y < \pi^*2p_z = \pi^*2p_y < \sigma^*2p_x$

For O_2 Molecule



Bond order = ½ (8–4) = 2

* Having two unpaired electrons so paramagnetic

σ^*, π^* = antibonding molecular orbital

σ, π = bonding molecular orbital

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

N_b = No. of electron in bonding MO's

N_a = No. of electron in antibonding MO's

(g) If bond order = 0, it means species does not exist.

(h) Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.

(i) Bond order ↑ stability of molecule ↑ bond length ↓

(j) If the molecule has one or more unpaired electron, it will be paramagnetic, while if all the electrons are paired it will be diamagnetic.

Ex. H_2 = Configuration : $\sigma(1s)^2\,\sigma^*(1s)^0$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1, \quad \text{Hence H – H (diamagnetic)}$$

MO Electronic Configuration of Some Molecules

Molecule or Ion	Total No. of Electrons	MO Configuration	Bond Order	Magnetic Behaviour
H_2	2	$(\sigma\,1\,s)^2$	1	Diamagnetic
H_2^+	1	$(\sigma\,1s)^1$	0.5	Paramagnetic
H_2	3	$(\sigma\,1s)^2, (\sigma * 1s)^1$	0.5	Paramagnetic
He_2	4	$(\sigma\,1s)^2, (\sigma * 1s)^2$	0	Diamagnetic
N_2	14	$KK\,(\sigma\,2s)^2, (\sigma * 2s)^2,$ $(\pi\,2p_y)^2{=}(\pi\,2p_z)^2, (\sigma\,2p_x)^2$	3	Diamagnetic
O_2	16	$KK\,(\sigma\,2s)^2, (\sigma * 2s)^2\,(\sigma\,2p_x)^2,$ $(\pi\,2p_y)^2{=}(\pi\,2p_z)^2\,(\pi * 2p_y)^1\,(\pi * 2p_z)^1$	2	Diamagnetic
O_2^+	15	Remove one electron from $\pi * 2p_z$ from O_2	2.5	Paramagnetic
O_2^{2+}	14	Same as that of N_2	3	Diamagnetic
O_2	17	$KK\,(\sigma\,2s)^2, (\sigma * 2s)^2\,(\sigma\,2p_x)^2,$ $(\pi\,2p_y)^2,(\pi\,2p_z)^2$ $(\pi\,{*}2p_y)^2,(\pi\,{*}2p_z)^1$	1.5	Paramagnetic
O_2^{2-}	18	$KK\,(\sigma\,2s)^2, (\sigma * 2s)^2\,(\sigma\,2p_x)^2$ $(\pi\,2p_y)^2,(\pi\,2p_z)^2$ $(\pi\,{*}2p_y)^2,(\pi\,{*}2p_z)^2$	1	Diamagnetic
F_2	18	Same as above	1	Diamagnetic
Ne_2	20	18 as above and $(\sigma * 2p_x)^2$	0	Diamagnetic
CO	14	Same as in N_2	3	Diamagnetic
NO	15	Same as in O_2^+	2.5	Paramagnetic
NO^+	14	Same as in N_2	3	Diamagnetic
NO^{2+}	13	$KK(\sigma\,2s)^2\,(\sigma * 2s)^2\,(\sigma\,2p_x)^2$ $(\pi\,2p_y)^1,(\pi\,2p_z)^1$	2.5	Paramagnetic
NO^-	16	Same as in O_2	2	Paramagnetic
CN	13	Same as in NO^{2+}	2.5	Paramagnetic
CN^-	14	Same as in N_2	3	Diamagnetic

Ex. Though O_2 molecule is paramagnetic yet it is a colourless gas. Why ?

Sol. It is because the energy gap between HOMO and LUMO levels in O_2 molecule is so large that radiations of visible light cannot excite a e^- from HOMO to LUMO. In fact O_2 gas shows absorption in UV zone. So it is colourless.

Ex. Correct order of bond energy is:

(A) $N_2 > N_2^+ > N_2^- > N_2^{2-}$ **(B)** $N_2^+ > N_2^- > N_2^{2-} > N_2$ **(C)** $N_2 > N_2^- = N_2^+ > N_2^{2-}$ **(D)** $N_2^- > N_2 = N_2^+ > N_2^{2-}$

Sol. **(A)** Bond order is directly proportional to the bond energy.

Bond order of $N_2 = 3$, N_2^+ , $N_2^- = 2.5$ $N_2^{2-} = 2$

But N_2^- has more electrons in antibonding MO's and thus N_2^+ is more stable than N_2^-. So correct order of bond energy will be $N_2 > N_2^+ > N_2^- > N_2^{2-}$

Ex. Which of the following species have a bond order of 3 ?

(A) CO **(B)** CN^- **(C)** NO^+ **(D)** O_2^+

Sol. **(A,B,C)** Species CO, CN^-, NO^+ are isoelectronic with 14 electrons to N_2 which has bond order of 3 (i.e. $\frac{10-4}{3} = 3$), so their bond order will be equal to three.

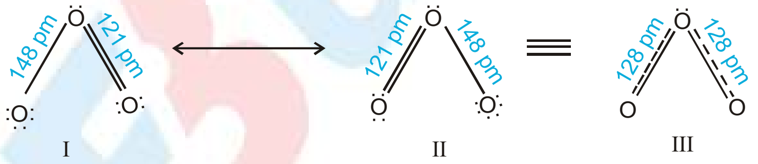
Ex. Which of the following are diamagnetic ?

(A) C_2 **(B)** O_2^{2-} **(C)** Li_2 **(D)** N_2^+

Sol. **(A,B,C)** Species C_2, O_2^{2-}, Li_2 have all the electrons paired but N_2^+ has one unpaired electron in bonding molecular orbital so it is paramagnetic.

RESONANCE

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O_3 molecule can be equally represented by the structures I and II shown below :



Resonance in The O_3 Molecule

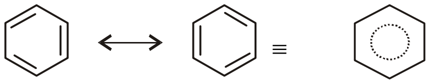
(structures I and II represent the two canonical forms while the structure III is the resonance hybrid)

In both structures we have a O – O single bond and a O = O double bond. The normal O – O and O = O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above.

The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like O_3. According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3, more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

Definition : Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound

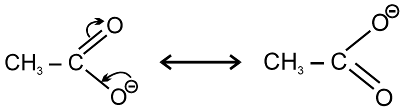
Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



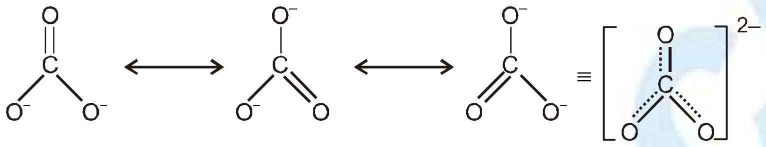
Resonance hybrid

Ex.

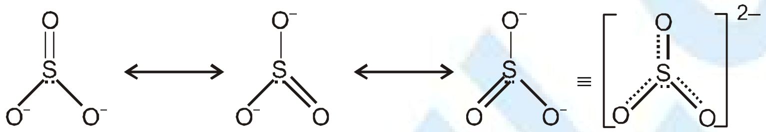
(i)



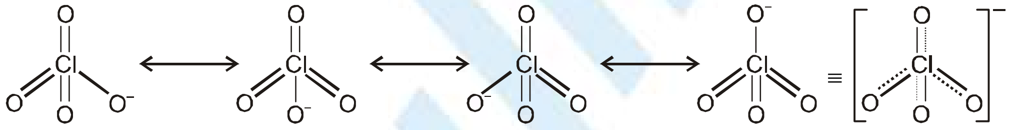
(ii)



(iii)

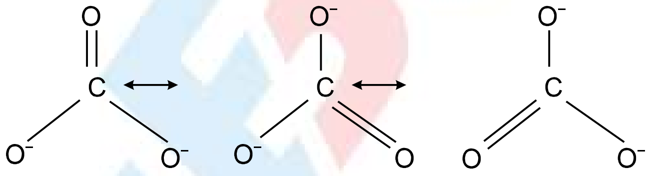


(iv)



- $$\text{Bond order} = \frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}}$$

Ex.



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

- Resonance energy = Actual bond energy – Energy of most stable resonating structure.
- Stability of molecule α resonance energy.
- More is the number of covalent bonds in molecule more will be its resonance energy.
- Resonance energy α number of resonating structures.

HYDROGEN BOND

(a) An atom of hydrogen linked covalently to a strongly electronegative atom can establish an extra weak attachment to another electronegative atom in the same or different molecules. This attachment is called a hydrogen bond.

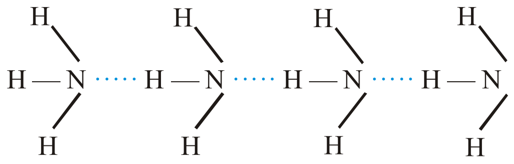
(b) To distinguish from a normal covalent bond, a hydrogen bond is represented by a broken line,
Ex. X – H ... Y where X and Y are two electronegative atoms. The strength of hydrogen bond is quite low about 2-10 kcalmol^{-1} or 8.4-42 kJmol^{-1}.

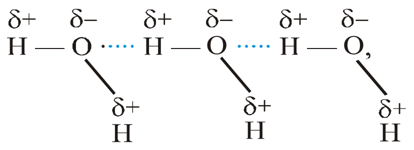
(c) Conditions of hydrogen bonding:

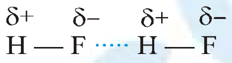
(i) The molecule must contain a highly electronegative atom linked to H-atom. (If E.N. ↑ polarity of bond ↑)

(ii) The size of the electronegative atom should be small.(size ↓ electrostatic attraction ↑)

Ex.







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

(d) Strength of H-bond :

H .... F bond dissociation energy = 41.8 kJ mol^{-1}

H .... O bond dissociation energy = 29.3 kJ mol^{-1}

H .... N bond dissociation energy = 12.6 kJ mol^{-1}

(e) Effect of H-bond

- (i) It causes the association of many molecules.
- (ii) Due to hydrogen bond molecules are associated and show high molecular weight.
- (iii) M.P. & B.P. of the molecules increases
- (iv) Viscosity & surface tension of the molecules increases.
- (v) The compounds which can form H-bond with the covalent molecules are soluble in such solvents.

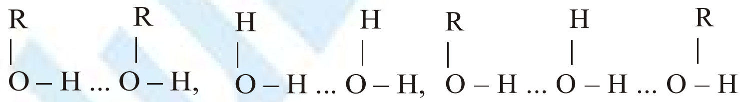
Ex. : Alcohol & Ammonia are water soluble.

TYPE OF H-BONDING

(a) Intermolecular (b) Intramolecular

(a) Intermolecular H-bond

(i) This type of H-bonding takes place between two molecules. **Ex.** ROH, H_2O, R - OH & H_2O



$$\overset{R}{\overset{|}{O}}-H\ldots\overset{R}{\overset{|}{O}}-H,\quad \overset{H}{\overset{|}{O}}-H\ldots\overset{H}{\overset{|}{O}}-H,\quad \overset{R}{\overset{|}{O}}-H\ldots\overset{H}{\overset{|}{O}}-H\ldots\overset{R}{\overset{|}{O}}-H$$

(ii) In such compounds molecular wt., M.P, & B.P. are high.

(iii) Extent of H-bonding ↑ viscosity & density ↑.

(b) Intramolecular Bond

(i) It is the H-bonding in the same molecule of a compound. The bonding also known as chelation.

(ii) Solubility in water, M.P. & B.P. of these compounds decreases.

(iii) The value of acid strength of acid depends on the relative stability of the acid and its conjugated base if the intramolecular H-bonding stablises the conjugate base then, the acid strength increase and if the conjugate acid is stabilised in this way then the acid strength decreased.

H-bond has serious consequences on the physical properties. These are –

(i) H_2O is liquid at room temperature whereas H_2S is gas at room temperature although H_2S has greater molecular weight.

(ii) Ice is lighter than water, although it solid because in ice H_2O molecules are extending their H-bonds to full length and six water molecules produce a cage like structure which is porous in nature leading to smaller mass and larger volume, thus lowering the density.

(iii) Alcohols have higher boiling points than corresponding alkanes and there of the same molecular mass. This can be explained by the intermolecular H-bonds existing among the R-OH molecules whereas ethers and hydrocarbon are not capable to have such strong intermolecular forces. thus they have lower boling points.

$H_2O > \text{R-OH} > \text{R-OH} \rightarrow$ Exceptional

$H_2S < \text{R-SH} < \text{R-S-R} \rightarrow$ Normal

$$\xleftarrow{\text{H-bond increases}}$$

$$H_2O > \text{R-OH} > \text{R-O-R}$$

$$\xleftarrow[\text{B.P. increases}]{}$$

R-O-R → no H-bond

$H_2O \rightarrow$ H-bonds

R-OH → H-bond.

(iv) Alcohol and water are miscible in any proportion due to formation of H-bonds.

(v) Ammonia is excessively soluble in water whereas other gases are partially soluble. This is due to the tremendous capacity of NH_3 molecule to generate 4-H-bonds.

$NH_3 > RNH_2 > R_2NH$

(vi) Solubility order of different amines and ammonia in water follows the order $NH_3 > RNH_2 > R_2NH$. This can be explained by the capacity of these elements to form H-bonds.

(vii) KHF_2 exists whereas $KHCl_2$, $KHBr_2$, KHI_2 do not because KHF_2 is constituted by 2 ions

i.e. K^+ & HF_2^-

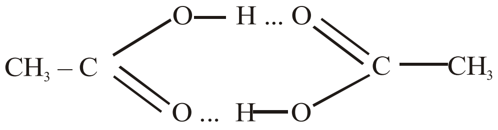
$[\overset{-}{F} \ldots \overset{\delta+}{H} - \overset{\delta-}{F}\ ]$ $\qquad$ $[Cl^- \ldots H-Cl]$

exist $\qquad$ does not exist

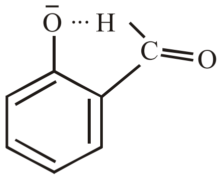
KHF_2 is a red orange coloured solid.

(viii) o-nitro phenol is steam volatile and less H_2O soluble than its coresponding para isomer because in o-nitro phenol, intra molecular H-bond exists which reduces the capacity of the molecule to produce intermolecular H-bonds with other molecules like water. This brings interamolecular forces among the o-nitrophenol molecules resulting into high volatility.

(ix) Acetic acid has a molecular weight of 60 in benzene and it shows a very high boiling points. This is due to dimerization of molecule.

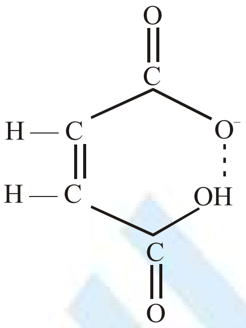


(x) Salicylic acid has very high acidity due to chelation of salicylate ion through the H-bond

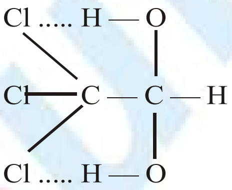


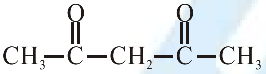
(xi) Chelation means to grab atoms in vicinity as much as possible.

(xii) Maleic acid has greater acidity than furmaric acid. This can also be explained by chelation of monomaleate anion which has a H-bond between carboxylate anion adn the unionized carboxylic acid.



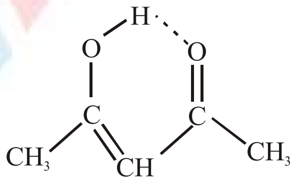
(xiii) Normally when 2 hydroxyl groups are present on the same carbon atom i.e. gem diols are unstable, but "chloralhydrate" is a stable molecule due to formation of H-bond.



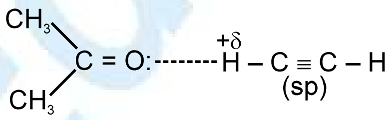
(xiv) 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

In the above compound, (acetyl acetone) enol form is stable because of the intramolecular H-bond.



Ex. C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.

Sol. 

In hybridisation as %S character increase, electronegativity increase hence C_2H_2 forms H–bonds with O–atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O.

Ex. Why $SnCl_2.2H_2O$ readily loses one molecule of water at 80ºC ?

Sol. One water molecule is coordinated to lone pair of electrons on $SnCl_2$ and the other is hydrogen bonded to coordinated water molecules .

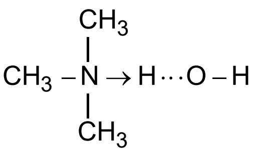
Ex. Why crystalline sodium peroxide is highly hygroscopic in nature.

Sol. Na_2O_2 forms stable hydrates on account of H-bonding.

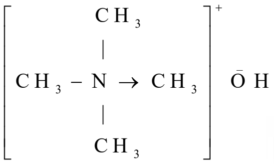
$$---O_2^{2-}---(H_2O)_8---O_2^{2-}---(H_2O)_8---$$

Ex. Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.

Sol.



$$\begin{array}{c} \quad CH_3 \\ \quad | \\ CH_3-N\rightarrow H\cdots O-H \\ \quad | \\ \quad CH_3 \end{array}$$



$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3-N\rightarrow CH_3 \\ | \\ CH_3 \end{array}\right]^+ \bar{O}H$$

In the trimethyl compound the O–H group is hydrogen bonded to Me_3NH group and this makes it more difficult for the OH group to ionize and hence it is a weak base.

In the tetramethyl compound, hydrogen bonding can not occur, so the OH^- group ionizes easily and thus it is a much stronger base.

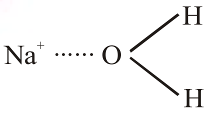
VANDERWAAL'S FORCES

(a) These are the weakest type of inter molecular forces that exist among the molecules which being significant change in physical properties.

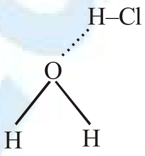
(b) These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.

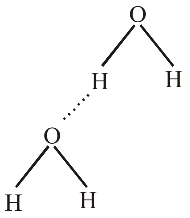
(c) Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Walls forces and may be of the following types:

(d) **Ion-Dipole Attraction :** Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride ($Na^+ Cl^-$) is dissolved in water because negative poles of water aggregate around Na^+ ions and positive poles around Cl^- ions.



(e) **Dipole-Dipole Attraction :** The force of attraction between the oppositely charged poles of two polar molecules (for example : H_2O, H–F, NH_3 etc.) is called dipole-dipole attraction. This type of attraction is weaker than the ion-dipole attraction.

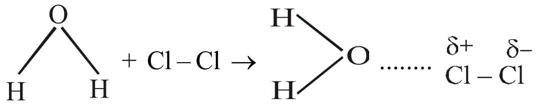




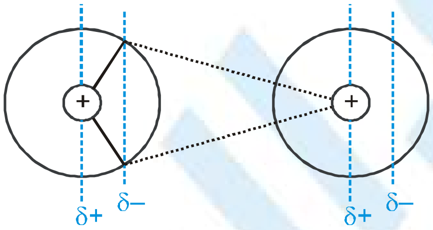
(f) **Ion-Induced Dipole Attraction :** When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between Na^+ and Cl_2 molecule.

$$Na^+ + Cl-Cl \rightarrow Na^+ \ldots\ldots \overset{\delta-}{Cl} - \overset{\delta+}{Cl}$$

(g) **Dipole-Induced Dipole Attraction :** This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between Cl_2 and H_2O.



(h) **Induced-Induced Dipole :** The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in F_2, Cl_2, N_2, molecules and in noble gasses.



Ex. Give the order of boiling point of following

Cl_2, HCl

Sol. Cl_2-Cl_2 $<$ HCl – HCl (boiling point)

dispersion force dipole-dipole attraction

As dipole-dipole attraction is stronger than dispersion force.

Ex. Arrange the inert gases, according to their increasing order of boiling points

Sol. $He < Ne < Ar < Kr < Xe$ (boiling point)

Because strength of van der Waal's force increases down the group with increase in molecular mass.

METALLIC BOND

Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electrons interactions among 8 to 12 nearest neighbours (which is also called coordination number). Bonding in metals is called metallic bonding. It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.

Two models are considered to explain metallic bonding:

(A) Band model (B) Electron-sea model

(A) Band Model

The interaction of two atomic orbitals, say the 3s-orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital. If N atomic orbitals interact, N molecular orbitals are formed. Atoms interact more strongly with nearby atoms than with those farther away . The energy that separates bonding and antibonding molecular orbitals decreases as the interaction (overlap) between the atomic orbitals decreases. When we consider all the possible interactions among one mole of Na atoms, there is formation of series of very closely spaced molecular orbitals ($3\sigma s$ and $3\sigma^*s$). This consists of a nearly continuous band of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole (6.02×10^{23}) of valence electrons thus, 6.02×10^{23} orbitals in the band are half-filled.

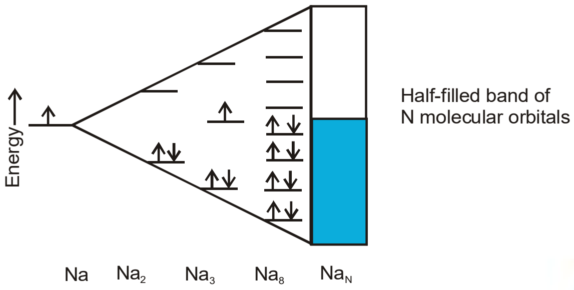


Figure. The band of orbitals resulting from interaction of the 3s - orbitals in a crystal of sodium

The empty 3 p atomic orbitals of Na atoms also interact to form a wide band of 3 × 6.07 × 10^{23} orbitals. The 3s and 3p atomic orbitals are quite close in energy , so that these bands of molecular orbitals overlap. The two overlapping bands contain 4 × 6.02 ×10^{23} orbitals. Because each orbital can hold two electrons, the resulting combination of bands is only one-eighth full.

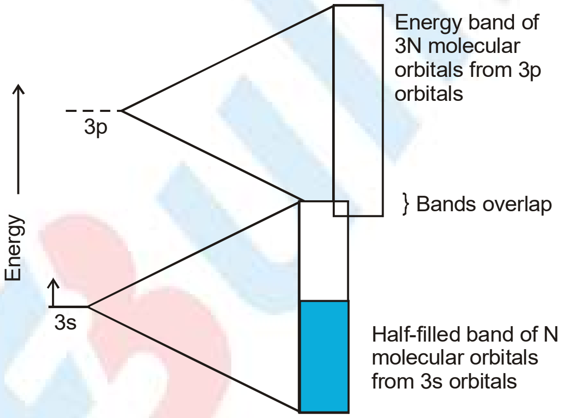


Figure. Overlapping of a half–filled “3s” band with an empty “3p” band of Na_N crystal

According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band within which (or into which) electrons must move to allow electrical conduction is called a conduction band. The electrical conductivity of a metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

Crystalline non-metals, such as diamond and phosphorus, are insulators, they do not conduct electricity. It is due to the fact that their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty bond (conduction band) by an energy difference called the band gap. In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band.

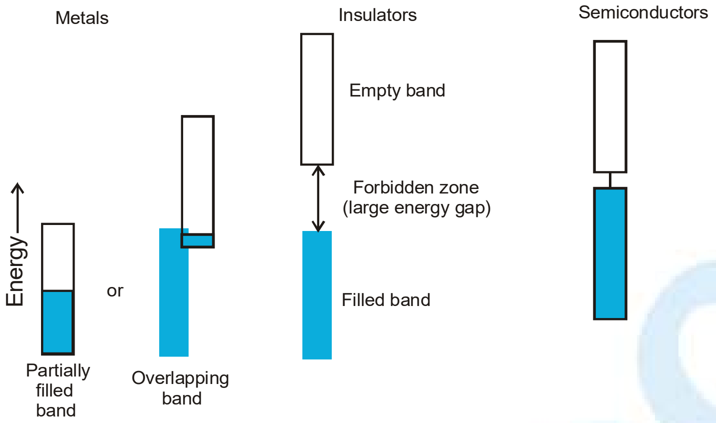


Figure. Distinction among metals, insulators and semiconductors. In each case an unshaded area represents a conduction band.

Elements that are semiconductors have filled bands that are only slightly below, but do not overlap with empty bands. They do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest-ene rgy electrons into the empty conduction band.

(B) Electron-Sea Model

Metals have ability to conduct electricity, ability to conduct heat, ease of deformation [that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility)] and lustrous appearance.

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a “sea of electrons” . In lithium the ions would be Li^+ and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

In thermal conductivity no electrons leave or enter the metal but those in the region being heated gain kinetic energy and transfer this to other electrons.

According to the electron-sea model, the case of deformation of metals can be thought of in this way : If one layer of metal ions is forced across another, perhaps by hammering, the internal structure remains unchanged as the sea of electrons rapidly adjusts to the new situation.

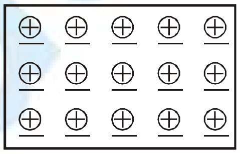


Fig. Metallic Bonding in Electron-Sea Model

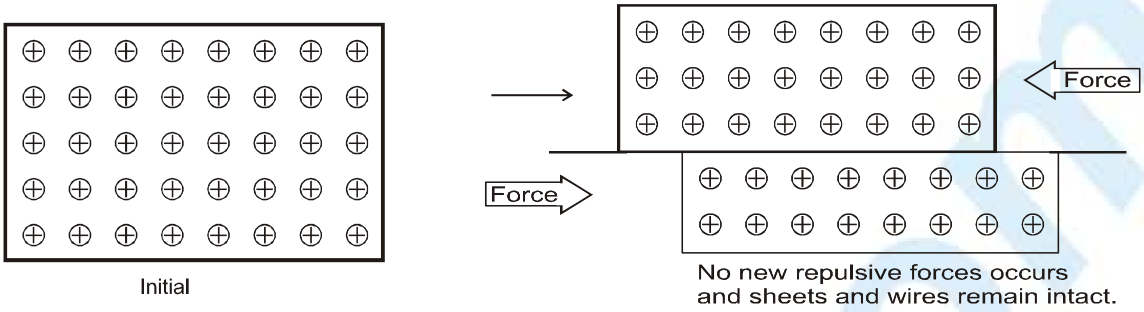


Figure. Effect of Distortion (by hammering) on Metal Sheet (assuming Electron Sea Model)

Ex. Why transition element have high heat of atomization.

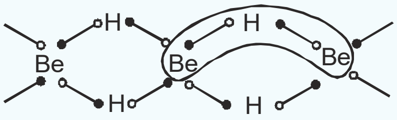
Sol. Transition metals may use inner -d-electrons along with the outer s-electrons for bonding as (n–1) d and ns have nearly same energy. So in them number of metallic bonds per atoms is quite large (more than two always). Hence element have high heat of atomization.

EDUBULL KEY POINTS

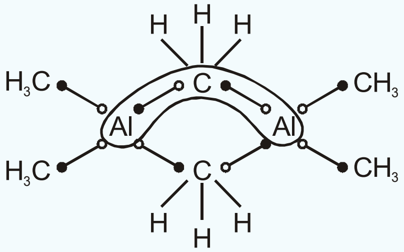
Some Special Bonding Situations

(a) Electron Deficient Bonding

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bonds(two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6, $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

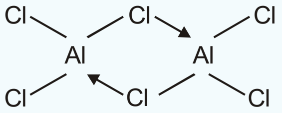


$BeH_2(s)$



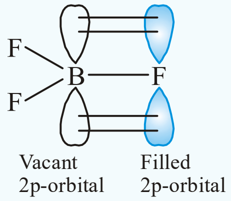
$Al_2(CH_3)_6$

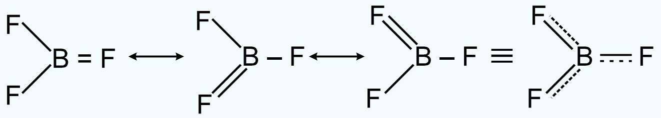
But Al_2Cl_6 have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



(b) Back Bonding

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3 the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.





(i) Decrease in B–F bond length is due to delocalised pπ–pπ bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :

$$BF_3 > BCl_3 > BBr_3$$

There is pπ-pπ back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

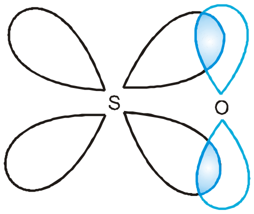
(ii) The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order

$$Si > P > S > Cl$$

(iii) The extent of pπ-pπ overlapping $\propto \dfrac{1}{\text{Lewis acid character}}$

(c) BOND LENGTHS AND pπ – dπ BONDING

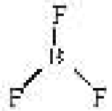
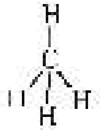
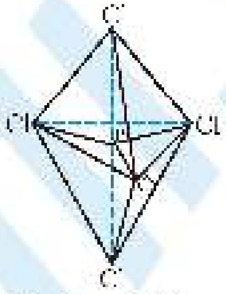
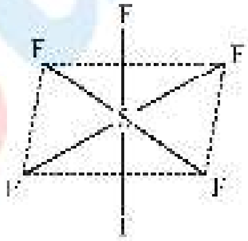
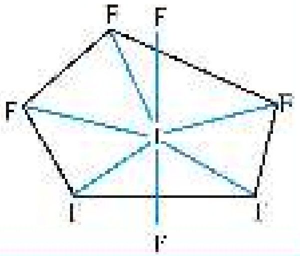
The bonds between S and O, Se and O, are much shorter than might be expected for a single bond. In some cases, they may be formulated as localized double bonds. A σ bond is formed in the usual way, In addition a π bond is formed by the sideways overlap of a p orbital on the oxygen with a d orbital on the sulphur giving a pπ – dπ interaction. This pπ – dπ bonding is similar to that found in the oxides and oxo-acids of phosphorus, and is in contrast to the more common pπ – pπ type of double bond found in ethene.



pπ – dπ overlap

To obtain effective pπ – dπ overlap the size of the d orbital must be similar to size of the p orbital. Thus sulphur forms stronger π bonds than the larger elements in the group. On crossing a period in the periodic table, the nuclear charge is increased and more s and p electrons are added. Since these s and p electrons shield the nuclear charge incompletely, the size of the atom and the size of the 3d orbitals in this series of elements leads to progressively stronger pπ – dπ bonds. Thus in the silicates there is hardly any pπ–dπ bonding. Thus SiO_4^{4-} units polymerize into an enormous variety of structures linked by Si—O—Si σ bonds. In the phosphates, π bonding is stronger, but a large number of polymeric phosphates exist. In the oxo-acids of sulphur, π bonding is even stronger and has become a dominant factor. Thus only a small amount of polymerization occurs, and only a few polymeric compounds are known with S—O—S linkages. For chlorine, pπ – dπ bonding is so strong that no polymerization of oxo-anions occurs.

EDUBULL TIPS & FORMULAS

Sr. No.	Hybridisation	Structure		Bond Angle	Examples
1.	sp	Linear	F — Be — F	180°	BeF_2
2.	sp^2	Trigonal planar		120°	BF_3
3.	sp^3	Tetrahedral		109°28'	CH_4
4.	sp^3d	Trigonal bipyramidal	 Structure of PCl_5	3 orbitals-120° 2 perpendicular orbitals	PCl_5
5.	sp^3d^2	Octahedral		90° between all hybrid orbitals	SF_6
6.	sp^3d^3	pentagonalbipiramidal		5 bond angle 72° and [illegible] angle 90°	IF_7