Chemical Bonding

1. OCTET RULE (LEWIS-KOSSEL RULE)

Noble gases have 8 electron in their outermost shell (complete octet) and outermost configuration is ns^2p^6 . Every atom has a tendency to complete its octet by losing or gaining or by sharing electron.

1.1 Exceptions of Octet Rule

- (i) Electron-Deficient Compounds : Compounds having less than 8 electrons in the outermost shell of the central atom. e.g. BF₃, BeCl₂, AlCl₃.
- (ii) **Expansion of Octet :** The compounds having more than 8 electrons in the outermost shell of the central atom. e.g PCl₅, SF₆
- (iii) **Transition Metal lons :** Transition metal ions have 9 to 18 electrons in their outermost shell, e.g. Cr⁺³, Mn⁺², Cu⁺
- (iv) H and Li atoms attain configuration like He by gaining and losing one electron, respectively, e.g. H⁻¹, Li⁺¹.
- (v) Odd Electron Bond : Compounds having unpaired electron are also exceptions to the octet rule. The molecules having odd electrons are NO_2 , NO, CIO_2 , O_2^{-1} etc.
- **Ex.1** Octet rule is not followed in :

[1] Ti⁺³	[2] Na ⁺¹	[3] Ca⁺²	[4] K ⁺¹	Ans. [1]

- **Sol.** Ti⁺³ has 9 electron in its outermost shell.
- Ex.2 Which of the following compounds has the central atom with incomplete octet?

[1] NH₄ ⁺¹	[2] BCI	[3] CCI	[4] PCl	Ans. [2]

- **Sol.** B has 6 electron in BCl₃.
- **Ex.3** An element forms cation by losing electron. The configuration of the cation may be like that of :

[1] inert gas	[2] pseudo inert gas	[3] inert pair	[4] all above	Ans. [4]

Sol. Inert gas – 8 electron in outermost shell. Pseudo inert gas – 18 electron in outermost shell.

1.2 Inert Pair Configuration

The heavy elements of IIIA, IVA and VA groups form cations having charge equal to group number and two less than group number, e.g. Ti^{+1} , In^{+1} , Sn^{+2} , Pb^{+2} . In these elements due to more penetration power of s orbitals, the atom generally does not lose e⁻ present in ns orbital, so only np electrons are lost by the atom. This effect is called "inert pair effect".

2. IONIC BOND

- (i) Atoms get established by ion formation in formation of an ionic bond. One atom forms a cation by losing electrons and other forms anion by accepting electrons.
- (ii) The octets of the atoms are completed by transfer of electrons.
- (iii) Cations and anions are bonded by electrostatic force of attraction in ionic bond.
- (iv) Ionic bond is formed between metals (cations) and nonmetals (anions).
- (v) During the formation of an ionic bond, cation can attain one of the following configurations.

- (a) Inert Configuration : I A and II A group metals (octet configuration) Na⁺¹, Mg⁺², K⁺¹, Rb⁺¹ attain s²p⁶ inert configuration.
- (b) Pseudo Inert Configuration : Metals of I B and II B groups Cu⁺, Zn⁺², Ag⁺¹, Au⁺¹, Cd⁺², Hg⁺².
- (c) Transition metals, e.g. Ti^{+3} (9), Ti^{+2} (10).

(vi) Energies involved in ionic bond formation :

(a) Sublimation Energy – The energy required to convert solid metal to gaseous state.

 $Na(s) \xrightarrow{+S.E.} Na(g)$

- (b) Ionisation Energy The energy required to remove an electron from the outermost shell of metal in gaseous state.
- (c) Dissociation Energy The energy required to convert the nonmetal molecule to atoms.

 $CI - CI + Dissociation Energy \longrightarrow 2CI$

- (d) Electron Affinity The energy required during formation of an anion by addition of an electron to a nonmetal in gaseous state.
- (e) Lattice Energy -
 - (i) The energy released during the formation of ionic bond.
 - (ii) Cations and anions form crystal lattice of ionic crystal in space by electrostatic force of attraction.

(iii) Lattice Energy $\propto \frac{1}{r^+ + r^-}$

(f) lonic compound is formed when the energy required (Sublimation energy + lonisation energy +

Dissociation energy) is less than energy released (Electron affinity + Lattice energy) So total energy change

$$-\Delta H = S + I + \frac{D}{2} - E - U$$

(Borne-Haber Equation)

2.1 Factors Affecting Formation of Ionic Bond

- (a) The sublimation energy and ionisation potential of a metal should be minium so that it may easily form a cation.
- (b) The dissociation energy and electron affinity of a nonmetal should be high so that if may easily form an anion.
- (c) There should be a strong electrostatic force of attraction between cation and anion.
- (d) Metals have low ionisation potential and nonmetals have high electron affinity, so ionic bond is formed between metals and nonmetals.

2.2 Characteristic of Ionic Compounds

(i) Solid and Crystalline Structure :

lonic compounds do not show molecular structure.

lonic compounds have definite crystal structures.

CsCl has body centered cubic (BCC) structure.

(ii) Melting and Boiling Point :

lonic compounds have high melting and boiling points.

(iii) Hardness :

lonic compounds are solid with brittle nature.

(iv) Conductivity:

lons are not free in solid state so ionic compounds are bad conductor of electric current in solid state but in solution and fused state electric current passes through and the ionic compound becomes good conductor of electricity

(v) Solubility of Ionic Compounds :

lonic compounds are soluble in solvents which have high dielectric constant like water.

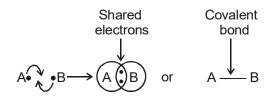
(vi) Solvation of Hydration Energy :

The energy released by the attraction of ions and solvent molecules is called solvation energy and when solvent is water this is called hydration energy.

Solubility in water = Lattice energy < Hydration energy

3. COVALENT BOND

A covalent bond is formed between two nonmetal atoms. e.g. in H–H, O=O and N=N.



Formation of a covalnet bond

(a) Nonpolar Covalent Bonds :

Covalent bond between two identical atoms (e.g. H–H, O=O) electronegativity of both atom is same.

(b) Polar Covalent Bond :

When covalent bond is formed between two different atoms. e.g. HCI, HF

3.1 Characteristics of Covalent Compounds

1. Physical State :

Covalent compounds generally occur in gaseous and liquid states, but sometimes in solid state also.

(a) Diamond :

- (i) In the structure of diamond, every carbon atom is attached to four other carbon atoms, tetrahedrally.
- (ii) Density of diamond is high.
- (iii) Every carbon atom is sp³ hybridised and forms four C–C σ bond by sp³–sp³ overlapping
- (iv) Electrons are not free, so diamond is bad conductor of electricity.
- (v) Oxidation number of C in diamond is zero

(b) Graphite :

- (i) In the structure of graphite, every carbon atom is attached to three other carbon atoms forming hexagonal layers.
- (ii) Every carbon atom is sp² hybridised and forms three σ bonds by sp²-sp² overlapping.
- (iii) Every carbon atom has one free electron. So graphite is a good conductor of electricity
- (iv) C–C bond length is 1.42 Å in plane.
- 2. Boiling and Melting Points :

Melting and boiling points of covalent compounds are generally low due to weak van der Waals forces between molecules.

3. Conductivity:

Covalent compounds are bad conductors of electricity.

- **Ex.4** F₂ and Cl₂ are gases, Br₂ is liquid and l₂ is solid why?
- Sol. Intermolecular distance is high in gaseous state, low in solid state and intermediate in liquid state. When

molecular weight increases, van der Waals forces also increase. So F_2 and Cl_2 are gases due to weak van der Waals forces and I_2 is solid.

- **Ex.5** CHCl₃ is liquid but CHl₃ is solid. Why?
- **Sol.** Due to increase in molecular weight, intermolecular force in CHI₃ is greater than in CHCI₃.
- **Ex.6** CO₂ is gas but SiO₂ is solid. Why ?
- **Sol.** CO₂ has only weak van der Walls forces, but in SiO₂, one silicon atom is surrounded by four oxygen atoms tetrahedrally forming macromolecular structure. So SiO₂ is sold.
- **Ex.7** H₂O is liquid but H₂S is a gas. Why?
- Sol. H₂O is liquid due to strong H-bonding.
- **Ex.8** NH₃ can be liquefied easily but PH₃ is not. Why?
- **Sol.** H-bonding present in NH₃, while PH₃ is nonpolar due to same value of electronegativity of P and H.

4. **DIPOLE MOMENT**

Polarity of bond is measured by dipole moment. The product of charge (e) and internuclear distance (d) between two poles of polar molecule is called dipole moment (μ). The unit of dipole moment is Debye (D). μ = e.d.

Percentage of ionic character = $\frac{\mu(obs.)}{\mu(cal.)}$ × 100 [1D = 10⁻¹⁸ e.s.u cm]

- (i) Dipole moment of nonpolar compounds is zero.
- (ii) When the electronegativity difference of atoms in compounds increases dipole moment also increases.
- (iii) If the structure of a compounds is symmetric like linear, trigonal planer & Tetrahedral the dipole moment will be zero. e.g. BF_3 , BCI_3 , CF_4 , CCI_4 , CH_4 etc.
- (iv) Structure of CHCl₃, CH₂Cl₂, CHCl₃, CH₃F is tetrahedral, but due to different bonds, dipole moment will not be zero.
- **Ex.9** What will be the dipole moment of HCl if d = 1.34 Å and charge = 4.8×10^{-10} esu ? Calculate ionic character of the bond when observed value of μ is 1.08D.

Sol. $\mu_{(cal.)}$

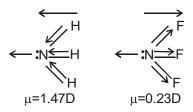
 $= 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$ $= 6.4 \times 10^{-18} \text{ esu cm}$

Percentage of ionic character = $\frac{1.08 \times 10^{-18}}{6.40 \times 10^{-18}} \times 100 = 16.88\%$

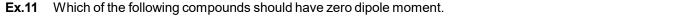
Ex.10 Dipole moment of NH₃ is greater than that of NF₃.

= e.d.

Sol. N–H bond moment and lone pair moment in NH₃ add up because they are in NF₃ ionisation lone pair moment and N–F bond moment are in opposite direction. So dipole moment will decrease.



Dipole Moments of some Compounds



[1] CO [2]
$$CCI_4$$
 [3] NH_3 [4] CH_3CI Ans. [2]

Sol. Tetrahedral geometry of CCl_4 in which four C–Cl bond moments balance each other.

Ex.12 Which of the following compounds should have higher dipole moment than the remaining three?

[1] HF [2] H_2O [3] NH_3 [4] NF_3 Ans. [2]

Sol. Higher dipole moment of H_2O is due to H-bonding.

5. BOND PAIR AND LONE PAIR

(i) In covalent compounds, the number of bond pairs is equal to the number of shared pairs of electron.

Number of bond pairs = Number of bonds

- (ii) The electron pair, which does not participate in bond formation, is called lone pair.
- (iii) $N \equiv N$ (N₂) 2 lone pairs and 3 bond pairs.
- (iv) $:CI CI: (CI_2)$ 6 lone pairs and 1 bond pairs.
- **Ex.13** What are the numbers of lone pairs and bond pairs in H_2O_2 molecule?

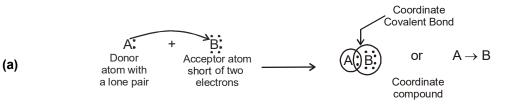
Ex.14 What are the numbers of lone pairs and bond pairs on B in BF₃?

Sol.

6.

COORDINATE BOND OR DATIVE BOND OR COORDINATE COVALENT BOND

- (i) Coordinate bond is formed by unequal sharing of electron pair between two atoms, one of which, called the donor atom, provides the electron pair and the other atom, called the acceptor atom, receives that electron pair.
- (ii) The donor should have complete octet with a lone pair of electrons and acceptor atom should have incomplete octet and a vacant orbital to accept the electron pair.



It is also known as Dative Bond, according to Scientist, Menzie.

- (iii) Formation of covalent bond is essential before formation of coordinate bond.
- (iv) This bond is different from a covalent bond, in the latter one electron provided by each of the bonding atoms.
- (v) Coordinate bond is also different from ionic bond because electrons are not completely transferred.
- (vi) In this bond, electrons are donated only in the form of pairs.
- (vii) Electron pair is provided by only one atom and shared equally by both the atoms. So according to Sugden it is a polar bond.

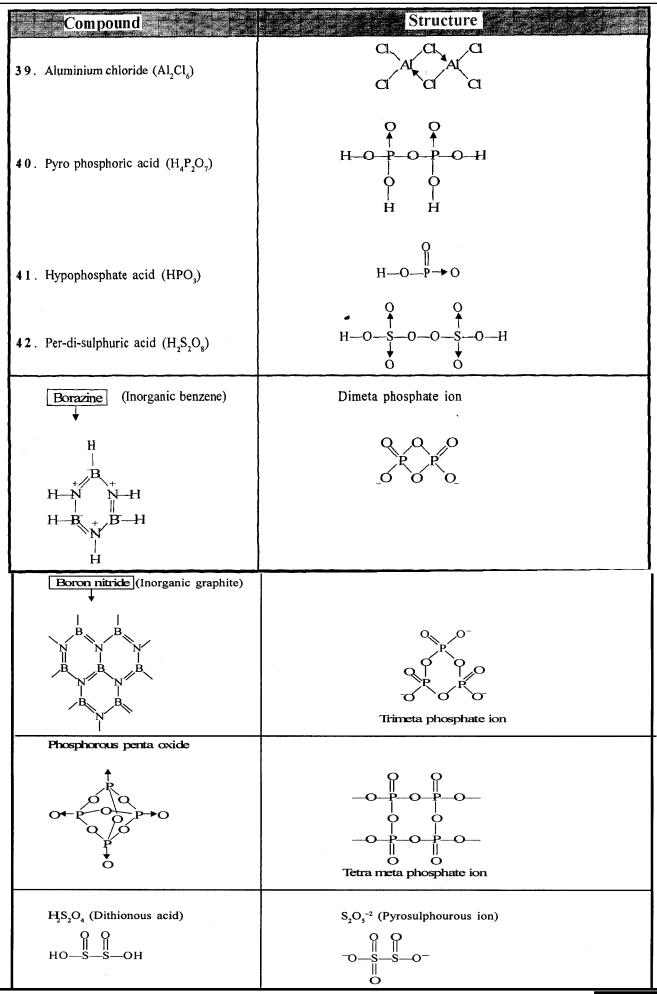
- (viii) Once a coordinate bond is formed, there remains no difference between the coordinate and covalent bonds. So the property of coordinate compounds are similar to those of covalent compounds.
- Ex.15 Which of the following compounds has coordinate bond?
 - [1] Methyl cyanide [2] Methyl isocyanate [3] Methyl cyanate [4] None of these Ans. [3]
- $\textbf{Sol.} \qquad CH_{_3}C{\equiv}N{\rightarrow}O$

STRUCTURES \ FORMULAE OF IMPORTANT COMPOUNDS

Compound	Structure	Electron dot / Cross Formula
1. Sodium Sulphide (Na ₂ S)	$(Na^{+})_{2}S^{-}$	Na ⁺ : Š. Na ⁺
2. Calcium Hydride (CaH ₂)	Ca ⁺⁺ (H ⁻) ₂	$H\overline{i}$ Ca^{++} $H\overline{i}$
3. Hydrogen Peroxide (H_2O_2)	H – O – O – H	н: ё:ё :н
4. Phosphene (PH ₃)	H HPH	
5. Carbon mone-oxide (CO)	C ≡ 0	:c : :: o :
6. Carbon di-oxide (CO ₂)	$\mathbf{O} = \mathbf{C} = \mathbf{O}$	ö ∷C ∷ ö
7. Hydrogen Cyanide (HCN)	HC≡N	Н ; С 🕌 🔥
8. Potassium Isocyanide (KNC)	$K^+ \cap N \cong C$	ĸ['näc]
9. Sodium Hydroxide (NaOH)	Na ⁺ ⁻ O—H	Na [†] .O.* H
10. Nitrous oxide (N_2O)	N≡N →O	≈n≞n÷ Ö:
11. Nitric oxide (NO or N_2O_2)	O=N-N=O	ġ : : Ň : Ň :: ġ
12. Dinitrogen tri oxide (N_2O_3)	o=n−n=o	;ö: ö:::Ň::Ň::ö
13. Dinitrogen tetraoxide (N_2O_4)	$ \begin{array}{c} 0 & 0 \\ \uparrow & \uparrow \\ 0 = N - N = 0 \end{array} $:ö: :ö: ö: :: Ň : Ň:: ö
14. Nitrogen Penta oxide (N ₂ O ₅)	$ \begin{array}{c} 0 & 0 \\ \uparrow & \uparrow \\ 0 = N - 0 - N = 0 \end{array} $:ö: :ö: ö::Ň:ö:Ň::ö
15. Nitrous acid (HNO ₂)	H-O-N=0	H:Ö:N::Ö
16. Nitric acid (HNO_3)	0 ↓ H−O−N=0	;ö: H:Ö: N::Ö
17. Nitrate Ion (NO ₃ ⁻)	0 ∥ 0 ← N—0 ⁻	[;ö: ;ö: N: ö:]

Compound	Structure	Electron dot / Cross Formula
18. Ammonium Chloride (NH_4CI)	$\begin{bmatrix} H \\ I \\ H - N \rightarrow H \\ I \\ H \end{bmatrix} C \Gamma$	$\begin{bmatrix} H \\ \vdots \\ H^* \cdot N^* \cdot H \\ \vdots \\ H \end{bmatrix}^+ \overset{\circ}{\underset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\overset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\overset{\circ}{\otimes}} \overset{\circ}{\underset{\circ}{\circ}} \overset{\circ}{\underset{\circ}{\mathrel}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\underset{\circ}{\sim}} \overset{\circ}{\overset{\circ}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}{\overset}$
19 . Carbonate Ion (CO_3^{-})	o " -o-c-o-	
20 . Sulphur di-oxide (SO_2)	0 ← s=0	: ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ;
21 . Sulphur Tri-oxide (SO_3)	O → S=O	:ö: :ö :š: ö
22 . Sulphite Ion (SO_3^{-})	o to-s-o	:ö: :ö: š: ö:
23 . Sulphate Ion (SO_4^{-})	-0 <u>s</u> -0- •	:ö: :ö: : : :ö: :o:
24 . Thio-sulphate Ion $(S_2O_3^{-})$::::::::::::::::::::::::::::::::::::::
25 . Phosphoric Acid (H_3PO_4)	H O H—O—P—O—H ↓ O	H ∷Ω: H∷Ö: P: Ö: ∷H :α
26 . Phosphorous acid (H ₃ PO ₃)	H HOPOH ↓ O	ਸ਼ ਸ਼:: ਹੁੱ: P: ਹੁੰ :: ਸ :ਹੁ:
27 . Phosphate Ion (PO $_4^{}$)		
28. Potassium Permagnate (KMnO₄)	$\mathbf{K}^{+}\begin{bmatrix}\mathbf{O}\\\mathbf{A}\\\mathbf{A}\\\mathbf{A}\\\mathbf{A}\\\mathbf{A}\\\mathbf{A}\\\mathbf{A}\\A$: : : : : : : : : : : :

Compound Compound	server and a Structure
29 . Carbon di-sulphide (CS_2)	S=C=S
30 . Nitronium Ion (NO_2^*)	$o = \overset{+}{N} = o$
31. Nitrite Ion (NO_2)	$O = N - O^{-}$
32 . Hydronium Ion (H_3O^+)	H-O-H ↓ H
33 . Sulphuryl chloride (SO_2Cl_2)	C1 $C1$ $C1$
34. Potassium chlorate (KClO ₃)	K ⁺ [0 ← CI−0]
35. Potassium per-chlorate (KClO ₄)	
36. Potassium dichronmate $(K_2 Cr_2 O_7)$	$(\mathbf{K}')_{2} \begin{bmatrix} \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} \end{bmatrix}^{-2}$
37 . Ferry - cyanide Ion [Fe(CN) ₆] ⁻³	$\begin{bmatrix} N \equiv C & C \equiv N \\ N \equiv C & C \equiv N \\ N \equiv C & C \equiv N \end{bmatrix}^{-3}$
38 . Fero cyanide Ion $[Fe(CN)_6]^{-4}$	$\begin{bmatrix} N \equiv C & C \equiv N \\ N \equiv C & Fe^+ & C \equiv N \\ N \equiv C & C \equiv N \end{bmatrix}^{-4}$



Compound's Name	Formula	Structure
Sulphurous acid	H ₂ SO ₃	0 ↑ H-O-S-O-H
Persulphuric acid Peroxo monosulphuric acid (caro's acid)	H ₂ SO ₅	HOSOOH
Thiosulphuric acid	H ₂ S ₂ O ₃	H-O-S-O-H
Chlorous acid	HClO2	H -Ö -Ö
Chloric acid	нсю,	H-O-CCO
Perchloric acid	HClO₄	
Perchloric anhydride	Cl ₂ O ₇	
Hypophosphorous acid	H ₃ PO ₂	H H−O−P→O H
Perchromate	QQ,	
Chromyl Chloride	CrO ₂ Cl ₂	$ \begin{array}{c} \mathbf{O} \\ \parallel \\ \mathbf{CI} - \mathbf{Cr} - \mathbf{CI} \\ \parallel \\ \mathbf{O} \end{array} $
Carbon suboxide	$C_{3}O_{2}$	0=C=C=0
Bleaching Powder	CaOCl ₂	

Compound's Name	Formula	Structure
Calcium carbide	CaC ₂	$\mathbf{Ca} \begin{pmatrix} \mathbf{C} \\ \mathbf{M} \\ \mathbf{C} \end{pmatrix} \mathbf{Ca}^{+2} \begin{bmatrix} \mathbf{C} \\ \mathbf{M} \\ \mathbf{C} \end{bmatrix}^{-2}$
Ozone	Ο,	
Ground state of phosphorous	P 4	P: P: P: P: P:
Ground state of sulphur	S ₈	
Nitrosyl choride (Tilden reagent)	NOCI	Cl—N== O
Sodium thiosulphate	Na ₂ S ₂ O ₃	$2Na^{+}\begin{bmatrix}S\\ \uparrow\\ O\\ -S\\ \downarrow\\ O\end{bmatrix}$

6.1 Characteristics of Coordinate Compounds

- (i) These compounds show partial ionic character due to polar nature.
- (ii) Melting and boiling points of these compounds are less than those of ionic compounds are less then those of ionic compounds and more than those of covalent compounds.
- (iii) Solubility : These are partially soluble in water (polar solvent) and soluble in nonpolar solvents.
- (iv) **Conductivity :** Coordinate compounds are bad conductor of electricity due to absence of ions.
- (v) Stability : These are stable due to polar nature. When bonding molecules are independently stable, the coordinate bond is less stable, e.g. in $H_3N \rightarrow BF_3$ molecule, the coordinate bond is less stable because NH_3 and BF_3 are themselves stable.

6.2 Compounds Having Ionic, Covalent and Coordinate Bonds

Some compounds have all the three types of bonds, i.e. ionic, covalent and coordinate bond, e.g.

(i) NH_4CI – Ionic bond between NH_4^+ and CI^- and covalent bonds and a coordinate bond are present in NH_4^+ .

7. IONIC CHARACTER IN COVALENT COMPOUNDS

- (i) When electronegativity difference of two atoms is less than 0.8, the covalent bond is nonpolar, e.g. PH₃.
- (ii) When electronegativity difference of atoms is 0.1 to 0.8, the bond between them is nonpolar covalent bond. When electronegativity difference of atoms is 0.8 to 1.6, the bond between them is polar covalent bond. Then electronegativity difference is 1.7 to 3.2, the bond is ionic.

lonic character \propto Electronegativity difference of bonded atoms

- (iii) Pauling used dipole moment for depicting percentage of polarity and ionic character of the bond. According to Pauling, a bond can never be 100% ionic.
- (iv) When electronegativity difference between two atoms is 2.1, there is 50% ionic character in the bond.
- (v) When electronegativity difference is zero (identical atoms), the bond will be 100% covalent.
 According to Haney and Smith, the percentage of ionic character of a polar covalent bond can be calculated with help of the following expression.

% lonic character = $(0.16\Delta + 0.035\Delta^2) \times 100$

Where Δ = Electronegativity difference between bonded atoms.

Ex.16 Atomic number of A, B and C are Z, Z + 1 and Z + 2, respectively, and C is an alkali metal. What should be the nature of bond between A and C?

	[1] Ionic	[2] Coordinate	[3] Covalent	[4] Hydrogen bond	Ans. [1]
Sol.	(Z + 2) stands for alkali the nature of bond will b	· · · ·	s and Z for halogen. Sinc	e A is halogen and C is alk	ali metal,
Ex.17	Three electrons are pres will be formed by A and		of an element A and six el	ectrons in that of B. What co	ompound
	$[1] A_2 B_3$	[2] AB ₂	[3] A ₆ B ₆	[4] All of the above	Ans. [1]
Sol.	A has 3 electrons in out AI_2O_3 , i.e. A_2B_3 .	ermost shell, like Al. B has	s 6 electrons in outermost	t shell, like O, their compou	nd will be
Ex.18	Compound having dativ	e and covalent bond, is :			
	[1] SO ₂	[2] NH ₄ Cl	[3] CuSO ₄ , 5H ₂ O	[4] AgCl	Ans. [1]
Sol.	All the three types of bobonds in SO_2 .	nds are present in NH_4CI	and $CuSO_4$, ionic bond in	n AgCl and both dative and	covalent
Ex.19	Compound formed by the	ne elements having atom	ic number 6 and 16, will b	e:	
	[1] Ionic	[2] Covalent	[3] Coordinate	[4] Hydrogen bonded	Ans.[2]
Sol.	Atomic number 6 = Carl	oon ; Atomic	number 16 = Sulphur		
	The compound will be C	S ₂ (covalent)			
Ex.20	Diamond and graphite a	ire :			
	[1] isotone	[2] isomers	[3] isotope	[4] allotropes	Ans.[4]

Sol. Diamond and graphite are allotropic forms of carbon.

 Ex.21
 Which of the following compounds has ionic and covalent bonds ?

 [1] NaCN
 [2] CO2
 [3] NaCI

	\oplus	Θ
Sol.	Na	C≡N

[4] N₂

	IIOAL DONDING				ULL # 5]
Ex.22	Inorganic graphite is :				
	[1] boron nitrate	[2] boron nitride (BN)	[3] boron carbonate	[4] None of the above	Ans. [2]
Ex.23	In disulphuric acid (H ₂	S_2O_7), the number of cova	lent bonds and coordinat	te bonds, respectively, are	
	[1] 6 and 4	[2] 6 and 6	[3] 4 and 4	[4] 4 and 6	Ans. [1]
Sol.	Structure of $H_2S_2O_7$ is				
		0	0		
			1		
		H–S–C	р_о_ş_о_н У		
		0	0		
Ex.24	When electronegativi	ty difference of B and Cl is	s 1.0, the % ionic charact	ter in the bond will be :	
	[1] 10%	[2] 19.5%	[3] 30%	[4] 45.5%	Ans. [2]
Sol.	Δ = 1.0				
	% ionic character	= (0.16 × 1 + 0.035 × 1	1²) × 100		
		= 0.195 × 100 = 19.5%	0		
Ex.25	What should be the p	ercentage ionic character	in CsF when electronega	ativity difference is 3.3 ?	
	[1] 90.9%	[2] 0.09%	[3] 93.3%	[4] 95.7%	Ans. [1]
Sol.	% ionic character				
	= (0.16 × 3.3 + 0.035	× 3.3 ²) × 100			
	= 90.9%				
Ex.26	What is the increasing	g order of ionic character i	n H_2O , H_2S and H_2Se ?		
Sol.	Electronegativity diffe	erence is maximum in H ar	nd O. So H_2 Se < H_2 S < H	0 ₂ 0	
Ex.27	What is the increasing	g order of ionic character i	n OF ₂ and Cl ₂ O ?		
Sol.	Electronegativity diffe	erence in F–O is greater the	en in O–CI. \therefore Cl ₂ O < OF	2	
8.	COVALENT CHAR	RACTER IN IONIC CO	OMPOUNDS (FAJAN	N'S RULE)	
	Some ionic compoun	d show that covalent chara	acter by polarization of ar	nion	
(i)	Size of Cation : Size	e of cation must be small			
			1		
		Covalent chara	$rac{1}{rcter} \propto \frac{1}{Size of cation}$		
		ionic charac	ter ∞ Size of cation		

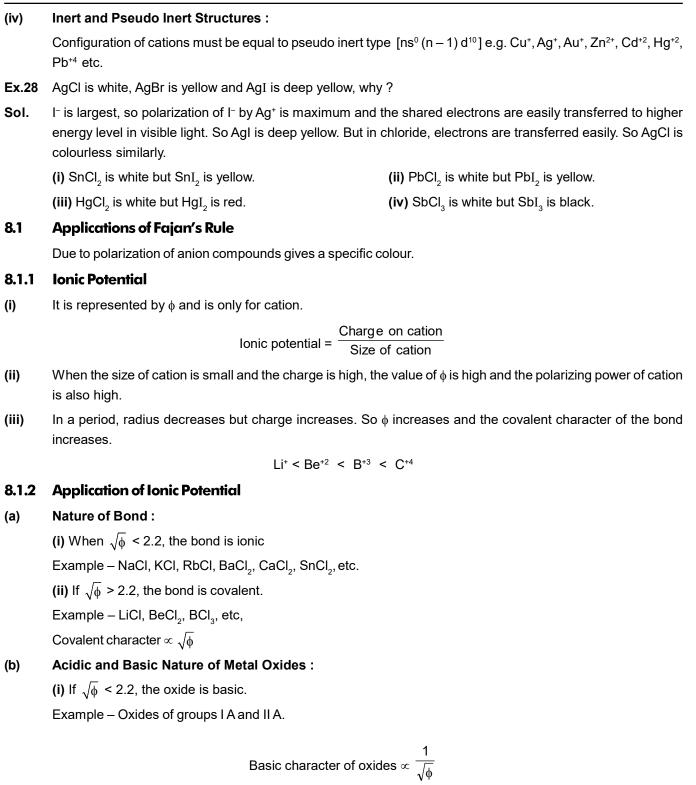
(ii) Size of Anion : Size of anion must be large

Covalent character ∞ Size of anion

lonic character $\infty \frac{1}{\text{Size of anion}}$

(iii) Charge on Cation and Anion :

Covalent character \propto Charge on cation and anion



(ii) If $\sqrt{\phi}$ = 2.2 to 3.2, the oxide is amphoteric.

Example – Oxides of groups III A and IV A

(iii) If $\sqrt{\phi} > 3.2$ then oxide will be acidic

Example - Oxides of VA, VIA and VIIA

(c) Boiling and Melting Points of Compounds :

In a group, $\sqrt{\phi}$ decreases and the ionic character also increases. Therefore, melting points and boiling points increase.

CHEN	IICAL BONDI	NG				[MODULE # 5]
(d)	Nature of Met	al Halides :				
	When $\sqrt{\phi}$ of r	metal < 2.2, the ionic	characte	r and conduct	vity increase and when $$	$\sqrt{\phi}$ > 2.2, the covalen
	character incre	eases and conductivity	/ decreas	es.		
		F	ormation	of complex ion	$\propto \sqrt{\phi}$	
Ex.29	Which of the fo	ollowing compounds h	as minim	um melting poir	nt?	
	[1] PbCl ₂	[2] SnCl ₂		[3] NaCl	[4] SnF ₄	Ans. [4
Sol.	Covalent chara	acter ∞ Charge on cati	on			
Ex.30	Which of the fo	ollowing compounds h	as maxim	ium melting poi	nt?	
	[1] CaF ₂	[2] CaCl ₂		[3] CaBr ₂	[4] Cal ₂	Ans. [1
Sol.	F⁻ is smallest,	so CaF ₂ is most ionic	. Thus, m	elting point and	l boiling point are maximu	n.
		lo	nic chara	$cter \propto \frac{1}{Size of}$		
Ex.31			and $S^{-2} > 0$		ese compounds is least sol	
	[1] MgS	[2] Na ₂ S			[4] MgCl ₂	Ans. [1]
Sol.			-	-	ovalent, so least soluble in	polar solvents.
Ex.32		f SnCl ₂ is 606° while r		oint of SnCl ₄ is 7	114ºC. Why ?	
Sol.	-	ent due to small size o				
Ex.33	Which of the fo	blowing compounds h	as least i	onic character '	?	
	[1] NaCl	[2] BaCl ₂	[3] ł		[4] HgCl ₂	Ans. [4
Sol.	Hg⁺² is pseudo	inert ion, but others a	are inert io	ons.		
9.	BOND LENGTH					
	The distance b	etween nuclei of two	conded at	oms is called b	ond length.	
	Factors effecting	ng Bond Length				
1.	Radius of Bor	nded Atoms :				
	Bond length in	creases with increase	in radii o	the bonded at	oms.	
			H-0-H <	H–S–H < H–S	e-H	
2.	Difference Between Electronegativity of Two Bonded Atoms :					
	Bond length can be determined by the relation given by Shoemaker and Stevension.					
		$d_{A-B} = r_A + r_B$	_в – 0.09 (Δ)		
		d _{A-B} = Bond	l length	r _A = Radius	s of A	
				r _B = Radius	s of B	
		Δ = Differen	nce in eleo	ctronegativity o	f A and B.	
3.	Bond Order :					
	Bond length of that of triple bo		than that o	of the double bo	nd and bond length of dout	ble bond is greater that
		C -	-C >	C = C >	$C \equiv C$	
		4 6	1 8	4.04 Å	1.20Å	

C – C	>	C = C >	$C \equiv C$
1.54 Å		1.34 Å	1.20Å
$\boldsymbol{C}\equiv\boldsymbol{C}$	>	$C \equiv N$ >	$N \equiv N$

Ans. [4]

4. Hybridization :

When s character in hybrid orbitals increases, bond length decreases, because s orbital as attracted by the nucleus with greater force.

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

or bond length ∞ p character in hybrid orbital

Ex.34 Which of the following statements is not true ?

[1] N–N bond length in N_2 is less than in NH_2 – NH_2

[2] O–O bond length in O_3 is less than in H_2O_2

[3] Bond length in H–CI is greater than in H–F

[4] Bond length in H₂S is greater than in H₂Se

- **Sol.** Electronegativity of S is greater than that of Se. So bond length in H_2S is less than bond length in H_2Se .
- **Ex.35** Correct order of bond length of N-H in NH_3 , and bond length of N-F in NF_3 is :

[1] N - H = N - F [2] N - F < N - H [3] N - F > N - H [4] None of these Ans. [3]

Sol. The electronegativity difference of N–F is less than that in N–H. So N–H bond is more polar.

10. BOND ANGLE

Bond angle between two adjacent bonds in a molecule is called bond angle.

Factors effecting Bond Angle

1. Type of Hybridization :

Bond angle depends on hybridization of an atom. Increasing order of bond angle is as follows :

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

Hybridization	sp ³	sp²	sp
Bond angle	109°28'	120°	180°

Bond angle \propto s – character in hybrid orbitals

Bond angle ∝	1
	p-character in hybrid orbitals

2. Lone Pair of Electrons :

Bond angle decreases with increase in the number of lone pairs on the central atom.

Bond angle $\propto \frac{1}{\text{Number of lone pairs}}$

3. Electronegativity of Central Atom :

Bond angle will be high if the electronegativity value of the central atom is high.

Bond angle \propto Electronegativity of central atom

Molecule	H ₂ O	H ₂ S	H ₂ Se
Bond angle	105°	92°	37.5°

11. BOND ENERGY

The energy released during formation of one mole gaseous substance from two neutral gaseous species is called bond energy of the bond formed.

(a) Dissociation Energy :

The energy required to dissociate the bond into two neutral atoms is called dissociation energy.

(b) Bond Energy :

More than one bond is present in a polyatomic molecule. So, the average of bond dissociation energies of different bonds is called bond energy.

11.1 Factors Affeting Bond Energy

(1) Atomic Radius :

Bond energy decreases with increase in atomic size because overlapping decreases.

C-H < N-H < O-H < F-H Bond energy $\propto \frac{1}{1}$

atomic radius
$$\alpha$$

(2) Bond length :

Bond energy increase with decrease in bond length because of more effective orbital overlap.

CI-CI > F-F > Br-Br > I-I
Bond energy
$$\propto \frac{1}{\text{Bond length}}$$

(3) Polarity of the Bond :

Bond energy increases with polarity of bond and polarity depends on difference in electronegativity.

HF > HCl > HBr > HI

(4) Hybridization :

Bond energy increases with increase in s-character or decrease in p-character in hybrid orbital.

C–C	<	C=C	<	C=C
sp³		sp ²		sp

Bond energy \propto s – character in hybrid orbital

Bond energy $\propto \frac{1}{p - character in hybrid orbital}$

(5) Bond Order :

Bond energy increases with bond order.

 $N \equiv N > O = O > H - H$ $C \equiv C > C = C > C - C$

Ex.36 Highest bond energy will be.

- [1] F F [2] Cl Cl [3] I F [4] Br Br **Ans. [2**]
- **Sol.** Due to small size of F atoms, electron-electron (I.p.) repulsion will be effective, so bond energy of F₂ will be less than Cl₂.
- **Ex.37** NF₃ is more stable than NCl₃. Why ?
- **Sol.** NF₃ is more polar than NCl₃. So bond energy of will be higher.
- **Ex.38** The bond energy of I₂ and Cl₂ is 150.6 and 247.8 kJ./mole. Calculate the bond energy of ICl bond.

Sol. I₂ = 150.6 Cl₂ = 247.8

I = 75.3 Cl = 123.9

ICl = 75.3 + 123.9 = 199.2 KJ/mole.

12. VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- This theory was put forward by Sidgwick and Powell in 1940 and was further improved by Nyholm and
 Gillespie in 1957
- The electron pairs surrounding the central atom repel one another and move so far apart from one another that there are no further repulsions between them. As a result, the molecule has minimum energy and maximum stability.
- The basic assumptions of the VSEPR theory

(1) The shape of a molecule containing only two atoms is always linear.

(2) For molecules containing 3 or more atoms, one of the atoms is called the central atom to which other atoms are linked.

(3) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons only, the repulsions between them are similar. As a result, the shape of the molecule is *symmetrical* and the molecule is said to have a *regular geometry*.

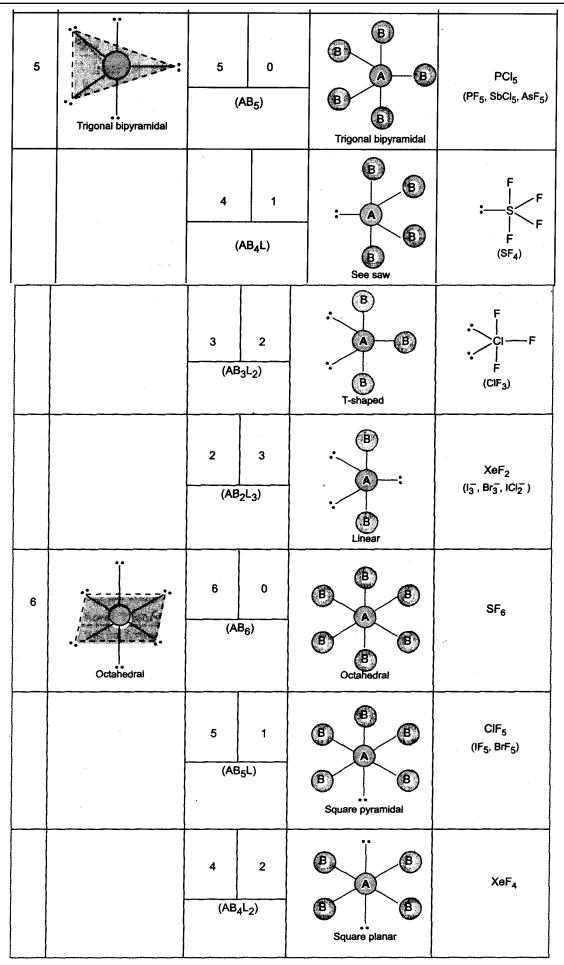
(4) If the central atom is linked to different atoms or is surrounded by bond pairs as well as lone pairs of electrons, the repulsions between them are different. As a result, the molecule has an *irregular* or *distorted geometry*. The order of repulsions between electron pairs is as follows :

Lone pair—Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

(5) The exact shape of the molecule depends upon the total number of electron pairs present around the central atom.

Table : Shapes (Geometry) fo molecules containing bond pairs only or bond pairs and lone pairs

Total No. of Geometry of the		Bond pairs	Lone pairs	Geometry (Shape) of the	illustrative Example
electron pairs			ar Formula)	molecule	(Other Examples)
2	:0:	2	0	B — A — B	0 = C = 0
	Linear	(A	мВ ₂)	Linear	(BeF ₂ , BeCl ₂ , HgCl ₂)
3	Triangular planar	3 (A	0 B ₃)	BBB	
			· · · · · · · · · · · · · · · · · · ·	Triangular planar	(AICl ₃ , SO ₃)
		2	1 	ÿ	Ň
			5 <u>2</u> ⊏)	B Bent (V-shape)	:O: :O: (SO ₂ , O ₃ , SnCl ₂)
4	, ,	4	0	B	H
	 Tetrahedral	(A	AB ₄)	Tetrahedral	H / H H (SiF ₄ , NH ₄ *)
		3	1	ï	_N_
		(Al	B ₃ L)	E Trigonal pyramidal	H H (PCl ₃ , NCl ₃ ,NF ₃ , PH ₃ , H ₃ O ⁺)
		2	2	Ä	ŗ
		(AB	₂ L ₂)	B B Bent	$H H H (H_2S, NH_2^-)$



☆ Calculation of total number of electron pairs, bond pairs and lone pairs and predicting the shapes of the molecules and ions.

(i) Total no. of electron pairs around the central atom

= $\frac{1}{2}$ (No. of valence electrons of central atom + No. of atoms linked to central atom by single bonds)

For negative ions, add number of electrons equal to the units of negative charge on the ion to the valence electrons of the central atom.

For positive ions, subtract number of electrons equal to the units of positive charge on the ion from the valence electrons of the central atom.

(ii) No. of bond pairs (shared pairs) = No. of atoms linked to central atom by single bonds.

(iii) No. of lone pairs = Total no. of electron pairs - No. of shared pairs.

13. VALENCE BOND THEORY

This theory was first put forward by Heitler and London in 1927.

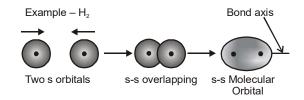
(A) Covalent bond is formed between atoms by sharing of unpaired electrons of the outermost shell in order to attain greater stability.

(B) **Overlapping**

- (i) Overlapping does not take place in ionic bond, only takes plac valent bond.
- (ii) The orbitals of unpaired electrons overlap in the formation of covalent bond.
- (iii) When overlapping is coaxial, a σ bond is formed and when overlapping is collateral, a π bond is formed.
- (iv) A σ bond is stronger than a π bond.
- (v) A π bond is never formed along as it is very weak. It is formed after a σ bond is formed.
- (vi) s-Orbital always forms σ bond.

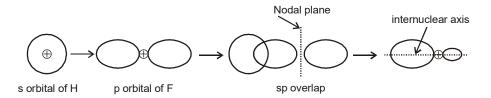
13.1 Types of Overlapping

(i) s-s Overlapping – When two s orbitals of two atoms each having an unpaired electron, participate in overlapping, it is called s-s overlapping.



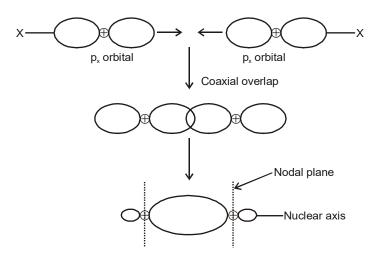
Formation of H₂ by s-s overlapping

(ii) **s-p Overlapping –** When s orbital of an atom and p orbital of the other atom, each having one unpaired electron, participate in overlapping, a sausage-shaped σ molecular orbital is formed.



(iii) **p-p Overlapping –** Two p orbitals can form either a σ bond or a π bond by different type of overlapping. When overlapping of p orbital is coaxial, a σ bond is formed and when it is collateral, a π bond is formed.

F = 1s², 2s², 2p⁵



The order of bond strength is as follows

1. p–p (coaxial) > s–p > s–s

2. p-p (coaxial) > p-p- (collacteral)

- **Ex.39** Four bonds are never formed between two atoms. Why?
- **Sol.** There are three axes (x, y and z) perpendicular to each other. A maximum of two π bonds can be formed by collateral overlapping and one σ bond is formed by coaxial overlapping. Thus, highest bond order between two atoms can be three and never four.
- **Ex.40** p-p Overlapping is not possible in :

[1] Cl_2 [2] O_2 [3] N_2 [4] H_2 Ans. [4]

Sol. p-Orbital is not present in H atom.

Ex.41 A σ bond is formed in O₂ by overlapping of :

[1] $2p_y - 2p_z$ [2] $2p_y - 2s$ [3] $2p_z - 2s$ [4] $2p_z - 2p_z$ **Ans. [4]**

- **Sol.** Extent of $p_v p_z$ and $p_v s$ overlapping is zero.
- Ex.42Which of the following orbitals will form a weak bond by the overlapping ? $[1] sp^2 sp^2$ $[2] sp^2 s$ [3] s s[4] p p (coaxial)Ans. [3]
- **Sol.** Due to non directional character of s orbital, bond formed by s-s orbitals will be weak.
- **Ex.43** Which of the following overlapping will form a π bond ?
 - [1] sp-p [2] sp²-s [3] sp³-sp³ [4] None of these **Ans. [4**]
- **Sol.** Hybrid orbitals always form a σ bond.

14. HYBRIDIZATION

- (1) Hybridization occurs in the central atom of a compound, e.g. in CH_4 , H_2O .
- (2) Generally, the orbitals of the outermost shell of the central atom participate in hybridization.
- (3) In hybridization, all types of orbitals (empty and half-filled and fully-filled) can participate.
- (4) If the orbitals participating in hybridization have paired electrons, the new orbitals formed will also have paired electrons.
- (5) The σ bonds formed by hybrid orbitals are strong and their orientation is different in space.
- (6) All hybrid orbitals are generally identical having one larger lobe and one smaller lobe.

Total no. of hybrid orbitals = No. of σ bonds + No. of lone pairs

- (7) In hybridization, the orbitals of the outermost shell of central atom having almost equal energy, combine and form new hybrid orbitals of identical energy.
- (8) The number of hybrid orbitals formed will be equal to the number of orbitals participating in hybridization e.g. 2,
 3 and 4 hybrid orbitals are formed in sp, sp² and sp³ hybridization, respectively.
- (9) Orbitals having unpaired electrons overlap for pairing and overlapping occurs in the orbitals having paired electrons.
- (10) Bond pair is formed by overlapping of hybrid orbitals. So lone pair or bond pair is present in a hybrid orbital.
- (11) The hybridization of central atom of a molecule can be determined by the following formula.

Total no. of hybrid orbitals = No. of σ bonds + No. of lone pairs

(12) Hybrid orbitals have directional property, so more the directional property of hybrid orbital, stronger will be the bond formed : $sp < sp^2 < sp^3 < sp^3d < sp^3d^2 < sp^3d^3$

14.1 Types of Hybridisation

sp³ Hybridisation :

- (i) In this hybridisation, one s orbital and three p orbitals join up and form four sp³ hybrid orbitals of same energy.
- (ii) The geometry of the compound will be tetrahedral and bond angle will be about 109° 28'.e.g. CH₄,CCl₄ & Diamond

sp² Hybridisation :

- (i) One s and two p orbitals join up and form three new sp^2 hybrid orbitals.
- (ii) The geometry of the molecule will be trigonal and bond angle will be 120°.

Examples – BF₃, BCl₃, BH₃, C₂H₄ and graphite.

sp Hybridisation :

- (i) In sp hyrbridisation, one s orbital and one p orbital join up and form two sp hybrid orbitals of equal energy.
- (ii) Geometry of along sp hybrid orbital will be linear and bond angle will be 180°.
- (iii) Two σ bonds will be formed by sp hybridised atom.
- (iv) The dipole moment will be zero.

Examples – BeF_2 , $BeCI_2$, C_2H_2 , CO_2 etc.

sp³ d Hybridisation :

One s, three p and one d orbitals join up and form five sp³d hybrid orbitals of same energy.

Example – PCI_5 , CIF_3 , SF_4 , XeF_2 , $TeCI_4$, ICI_2 etc.

sp³d² Hybridisation :

One s, three p and two d orbitals combine and form six sp³ d² hybrid orbitals of same energy.

 $\mathsf{Example} - \mathsf{SF}_6, \mathsf{CIF}_5, \mathsf{XeF}_4, \mathsf{IF}_4, \mathsf{SiF}_6^{-2}, \mathsf{ICI}_4^{-}.$

sp³d³ Hybridisation :

One s, three p and three d orbitals join up and form seven new sp³ d³ hybrid orbitals of same energy. Example – IF_{τ} , SeF₆, etc.

Ex.44 Which of the following molecules is bent?

[1] CO_2 [2] O_3 [3] N_2O [4] None of these Ans. [2]

Sol.

Ex.45 What is the type of hybridisation in H_3O^+ ?

Sol. O atom is sp³ hybridised and has one lone pair. Its geometry is pyramidal.

	Ground state $O^8 = 1s^2$,	2s²2p⁴			
	Hybrised state	ℓ .p. Geometr	sp ³ sp ³ sp ³ sp ³ ↓ I I H ⁺ H H angle – 107°		
Ex.46	Which of the following s	species is planar ?			
	[1] [⊕] _{NH4}		[3] XeF ₄	[4] SiCl ₄	Ans. [3]
Sol.	Types of hybridisation a	are sp ³ in $\overset{\oplus}{N}H_4^+, \overset{\Theta}{B}F_4^-$ and	$I SiCl_4$ and sp^3d^2 in XeF_4 .		
Ex.47	Which of the following i	ons has tetrahedral geon	netry ?		
	[1] Na⁺	[2] NH ₄ ⁺	[3] Mg ⁺²	[4] CO ₃ ⁻²	Ans. [2]
Sol.	NH ₄ ⁺ is sp ³ hybridisatio	n so structure will be tetra	ahedral.		
Ex.48	What should be the geo atom ?	ometry of the molecule wh	hen there are three bond p	pairs and one lone pair on	the central
	[1] Tetrahedral	[2] Pyramidal	[3] Trigonal	[4] Octahedral	Ans. [2]
Sol.	For example, $\mathrm{NH}_{_3}$ has t	hree N–H bond pair and	one lone pair. Its geometr	y is trigonal pyramidal.	
Ex.49	Which of the following r	molecules has sp² hybrid	isation on N atom ?		
	[1] NH ₃	[2] NOCI	[3] N ₂ H ₄	[4] All of the above	Ans. [2]
Sol.	Nitrogen atom in Cl–Ň sp² hybridisation.	= O has one lone pair, tw	No σ bond pairs and one π	bond pair. So, N atom is i	n a state of
Ex.50	If hybridisation on Co a	tom is sp³d², the geomet	ry of [Co(NH₃)₀]⁺³ will be s	imilar to that of :	
	[1] SiF ₆ ⁻²	[2] SF ₆	[3] both 1 and 2 [4] Nor	ne of these	Ans. [3]
Sol.	S is in a state of sp ³ d ² h	nybridisation in SiF ₆ ⁻² and	I SF $_6$ and the geometry of	^s sp ³ d ² and d ² sp ³ will be or	ctahedral.
14.2	Hybridisation in Tra	nsition Metal Ions			

14.2 Hybridisation in Transition Metal Ions

In sp³d hybridisation, d orbital of the outermost orbit participates. But in dsp³ hybridisation, the d orbital of inner orbit (n - 1), which is vacant in transition elements, participates.

14.3 Examples on sp hybridisation

Example	σ bond	l.p.e.	Hybridisation	Bond angle	Shape
BeH,	2	-	sp	180°	Linear
BeF ₂	2	-	sp	180°	Linear
BeCl,	2	-	sp	180°	Linear
BeBr,	2	-	sp	180°	Linear
Bel ₂	2	- /	sp	1 80 °	Linear
CO ₂	2	-	sp	180°	Linear
Ω Î	1	1	sp	1 80°	Linear
NO_2^+	2	-	sp	1 80 °	Linear
C ₂ H ₂	2	-	sp	1 80°	Linear
HCN	2	-	sp	1 80°	Linear
ZnCl ₂	2	-	sp	1 80°	Linear
HgCl ₂	2	-	sp	1 80°	Linear
CdCl ₂	2	-	sp	180°	Linear
R-Mg-X	2	-	sp	1 80°	Linear
[Ag(CN) ₂] [−]	2	-	sp	1 80°	Linear
[Cu(CN) ₂] ⁻	2	-	sp	1 80°	Linear
N ₂ O	2	-	sp	1 80°	Linear
N ₃ -	2	-	sp	1 80°	Linear

Examples on sp² hybridisation

Example of bon	d	l.p.e.	Hybridisation	Bond angle	Shape
BH,	3	-	sp²	120°	Trigonal planar
BF ₃	3	-	sp²	120°	Trigonal planar
BCl,	3	-	sp²	120°	Trigonal planar
CH ₃ (radical)	3	-	sp²	120°	Trigonal planar
CH ₂ =CH ₂	3,3	-	sp²	120°	Trigonal planar
Graphite 3		-	sp ²	120°	Trigonal planar
HNO,	3	-	sp²	120°	Trigonal planar
NO ₃ -	3	-	sp²	120°	Trigonal planar
HNO ₂	2	1	sp²	<120°	Angular (V)
SO ₂	2	1	sp²	<120°	Angular (V)
SO ₃	3	- 1	sp²	120°	Trigonal planar
HCO,-	3	-	sp²	120°	Trigonal planar
CO_3^{-2}	3	-	sp²	120°	Trigonal planar
SnCl ₂	2	1	sp²	<120°	Angular (V)
SnBr ₂	2	1	sp²	<120°	Angular (V)
SnI ₂	2	1	sp ²	<120°	Angular (V)
AlCl ₃	3	-	sp ²	120°	Trigonal planar
GaCl ₃	3	-	sp ²	120°	Trigonal planar
PbCl ₂	2	1	sp²	<120°	Angular (V)

Example	σbond	l.p.e.	Hybridisation	Shape
CH ₄	4	-	sp ³	Tetrahedron
CCl ₄	4	-	sp ³	Tetrahedron
CBr ₄	4	-	sp ³	Tetrahedron
PCl ₄ ⁺	4	-	sp ³	Tetrahedron
$\mathrm{NH_4^+}$	4	-	sp ³	Tetrahedron
BF ₄	4	-	sp ³	Tetrahedron
AlF ₄ -	4	-	sp ³	Tetrahedron
GaF₄ [−]	4	-	sp ³	Tetrahedron
BeF ₄ ⁻²	4	-	sp ³	Tetrahedron
MgF ₄ ⁻²	4	-	sp ³	Tetrahedron
Ni(CO) ₄	4	-	sp ³	Tetrahedron
$Zn(CN)_4^{-2}$	4	-	sp ³	Tetrahedron
$Cd(CN)_4^{-2}$	4	-	sp ³	Tetrahedron
Hg(CN) ₄ ⁻²	4	-	sp ³	Tetrahedron
NF ₃	3	1	sp ³	Pyramidal
NCl ₃	3	1	sp ³	Pyramidal
N(CH ₃) ₃	3	1	sp ³	Pyramidal
PF ₃	3	1	sp ³	Pyramidal
PCl ₃	3	1	sp ³	Pyramidal
AsCl ₃	3	1	sp ³	Pyramidal
SbCl ₃	3	1	sp ³	Pyramidal
BiCl ₃	3	1	sp ³	Pyramidal
NH ₃	3	1	sp ³	Pyramidal
∶⁻СӉ	3	1	sp ³	Pyramidal
H₃O⁺	3	1	sp ³	Pyramidal
SO ₃ ²⁻	3	1	sp³	Pyramidal
ClO ₃	3	1	sp ³	Pyramidal
XeO ₃	3	1	sp³	Pyramidal
H ₂ O	2	2	sp ³	Angular (V)
H ₂ S	2	2	sp³	Angular (V)
NH ₂ -	2	2	sp ³	Angular (V)
OF ₂	2	2	sp ³	Angular (V)
Cl ₂ O	2	2	sp ³	Angular (V)
SCl ₂	2	2	sp ³	Angular (V)
Diamond	4	-	sp ³	Tetrahedron
SiO2	4	-	sp ³	Tetrahedron
SiC	4	-	sp³	Tetrahedron

Examples on sp³ Hybridisation

Example	σbond	l.p.e.	Hybridisation	Bond angle	Shape
PF,	5	-	sp³d	120° & 90°	Trigonal bipyramidal
PCI,	5	-	sp ³ d	120°&90°	Trigonal bipyramidal
AsF,	5	-	sp ³ d	120°&90°	Trigonal bipyramidal
AsCl,	5	_	sp ³ d	120°&90°	Trigonal bipyramidal
SbCl,	5	-	sp ³ d	120°&90°	Trigonal bipyramidal
BiCl	5		sp ³ d	120°&90°	Trigonal bipyramidal
SbF	5	-	sp ³ d	120°&90°	Trigonal bipyramidal
SF4	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
SeF	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
TeF	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
PoF	4	1	sp ³ d	<1 80°, <90°,<120°	Irregular tetrahedron
PF ₄	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
AsF ₄	. 4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
SbF ₄ ⁻	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
SCl ₄	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
SeCl₄	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
TeCl	4	1	sp ³ d	<180°,<90°,<120°	Irregular tetrahedron
ClF,	3	2	sp ³ d	87.6°	T-shape
BrF,	3	2	sp³d	87.6°	T-shape
IF,	3	2	sp ³ d	87.6 °	T-shape
ICl ₃	3	2	sp³d	87.6°	T-shape
I_3^-	2	3	sp³d	180°	Linear
Br ₃ -	2	3	sp ³ d	180°	Linear
ICl ₂ -	2	3	sp ³ d	1 80 °	Linear
IBr ₂ -	2	3	sp ³ d	180°	Linear
ClF ₂ ⁻	2	3	sp³d	1 80°	Linear
XeF ₂	2	3	sp³d	180°	Linear

EXAMPLES ON sp³d HYBRIDISATION

15. MOLECULAR ORBITAL THEORY

- (a) There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Muliken (1932) and Hund. Which explains the bonding characteristics in a better way.
- (b) The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecular.
- (c) This approach recognizes that each electron belongs to the molecule as a whole and may move within the entire molecule.

15.1 Important Features of M.O.T.

- (i) Like an A.O. (atomic orbital) which is around the nucleus of an atom there are M.O. (Molecular orbital) which are around the nuclei of a molecule.
- (ii) The molecular orbitals are entirely different from the atomic orbitals from which they are formed.
- (iii) The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.
- (iv) The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.
- (v) Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.

- (vi) The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.
- (vii) Like atomic orbitals, the filling of electron in molecular orbitals is governed by the three principles such as Aufbau principle, Hund's rule and Pauli's exclusion principle.

15.2 Conditions for atomic orbitals to form M.O.

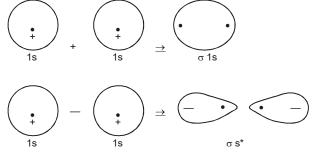
- (i) The combining A.O. should be a comparable energy
- (ii) The combining atomic orbitals must overlap to a large extent greater the overlap, stable is the molecule formed.

15.3 Different between A.O. and M.O.

A.O. (Atomic orbital)	M.O. (Molecular Orbital)
1. An e ⁻ in an A.O. is under the influence	An e- in a M.O. is under the influence
of only one nucleus.	of nuclei of two or more atoms of a molecule.
2. Their existence is because of inherent	These are formed by the combination of atomic
property of the atoms	orbitals of comparable energies
3. They are less stable than bonding M.O.	They are less or more stable than A.O.
Which are more stable than antibonding M.O.	
4. They have simple shapes	They have complex shapes
5. They are represented by s, p, d, f	They are represented by σ , σ^* , π , π^* etc.

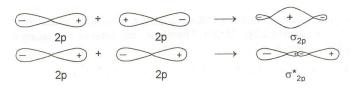
15.4 Formation of Bonding and Antibonding Molecular orbitals (LCAO method)

- (i) An electron in an atom is described by a wave function, ψ called an atomic orbitals. Similarly, the behavior of an electron in a molecule is described by a molecular wave function called molecular orbitals.
- (ii) Quantum mechanics shows that linear combination of two functions gives, not one but two combination and hence two molecule orbitals; a bonding orbital and an antibonding orbital.
- (iii) Such an orbital. Obviously cannot lead to the formation of a chemical bond and is therefore, termed as an antibonding M.O. combination of atomic orbitals-sigma (σ) and Pi (π) molecular orbitals.
- (iv) In the M.O. theory, orbitals are identified as σ or π depending upon the type of the symmetry of the molecular orbital.
- (v) A sigma (σ) M.O. is one that has cylindrical symmetry around the internuclear axis, i.e. it does not show any change of sigma on rotation through 180° about the axis.
- (vi) It can be said that a sigma M.O. has no nodal plane (in which the electron density is zero) along the inter nuclear axis.

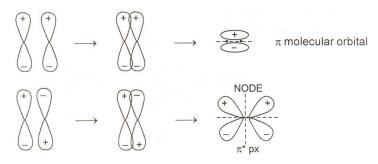


Formation of σ 1s and σ^* is bonding anti bonding M.O.

- (vii) The bonding orbital is designated simply as σ orbital and antibonding as σ^* .
- (viii) Such a sigma (σ) orbital is also formed when any two p-atomic orbitals overlap in end -on (along their axes) position.



(ix) Since the energy of a molecular orbital is directly related to the number of nodal planes, the π -orbital is more energetic then the σ -orbital. The explains why a π -bond is weaker bond then a σ -bond.



15.5 Relative energies of M.O. and filling of e-

(i) Two general criteria, which determine the energy of the molecular orbitals are

(i) Initial energy of the atomic orbitals

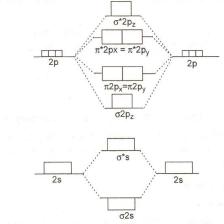
(ii) The extent of the overlap of the atomic orbitals

- (ii) It is obvious that molecular orbitals formed from lower energy atomic orbitals have lower energy than the molecular orbitals formed from higher energy atomic orbitals.
- (iii) As the σ overlap is much more effective than π -overlap, σ p-molecular orbital is of lowest energy, even through originally all the three π -orbitals are of equal energy.
- (iv) The relative energies of the M.O. are obtained experimentally from spectroscopic data.
- (v) The sequence in the order of increasing energy is given below i.e., for less than N_2 .

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

(vi) The sequence in the order of increasing energy is given below i.e., for more than N_2 .

 $^{1s} < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_z = \pi 2p_z < \pi^* 2pz = \pi^* 2p_z < \sigma^* 2\pi_z$



M.O. Energy level diagram for O₂, F₂ and Ne.

- (vi) Using preceding figures for respective molecules as a guide, we can build up the electronic structure of simple diatomic molecules.
- (vii) The filling of electrons in various M.O. follows similar rules to those for filling A.O. similar M.O. belongs to entire molecule, the total number of electrons are taken into consideration and accommodated in molecular orbitals according to the following rules.

(i) Aufbau principle : The M.O. of lower energy is filled up first.

(ii) Pauli exclusion principles. Each M.O. can accommodate a maximum of two electrons having opposite spins.

(iii) Hund's rule. Whenever two equal energy M.O. are available electrons prefer to remain unpaired. This is particularly significant for π -orbitals because π -bonding and π -antiboding M.O. have equal energies.

15.6 Stability of Molecules

(A) Stability of molecules in terms of bonding and antibonding electrons :

(i) If $N_{b} > N_{a}$, the molecule is stable.

(ii) If $N_{h} < N_{a}$, the molecule is unstable.

(iii) Even if $N_{b} = N_{a}$, the molecule is unstable. This is due to the fact that antibonding effect is some what stronger than the bonding effect.

(B) Stability of molecules in terms of bond order :

- (a) The relative stability of a molecule is further evaluated by a parameter known as bond order.
- (b) It can be defined as number of covalent bonds formed in molecule.
- (c) It is given by one half of the difference between the number of electrons in bonding orbitals and those in antibonding orbitals.

(d) Bond order = $\frac{1}{2}$ [No. of electrons in bonding orbitals – No. of electrons in antibonding orbitals]

$$= \frac{1}{2}[N_b - N_a]$$

(e) The bond order of 1, 2 and 3 corresponds to single, double and triple bonds respectively. It may be mentioned that according to MO theory, even a frictional bond order is possible.

(f) Stability of molecule ∞ bond order

(g) Dissociation energy ∞ bond order

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

(i) If all the electrons in a molecule are paired the substance is diamagnetic on the other hand it there are unpaired electron in the molecules, the substance is paramagnetic. More the number of unpaired electron in the molecule greater is the paramagnetism of the substance.

15.7 M.O. Configuration

(h)

(A) Homonuclear diatomic species : These types of ions have two identical atoms linked together of A₂ type.
 N₂: (a) The electron configuration of N is 1s², 2s², 2p³. In N₂ molecule, there are 14 electrons of which 4 are in K shell and are nonbonding. Each atom contributes four atomic orbitals and thus, the molecule consists of 8 M.O. Then ten electron are allotted to M.O. as follows

 $[\mathsf{KK}\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_x)^2\,(\pi_y 2p_y)^2\,(\pi_z 2p_z^{-2})]$

where KK denotes the closed K shell structure $(\sigma 1s)^2\,(\sigma^* 1s)^2$

(b) Bond order $\rightarrow 1/2 (8-2) = 3$

(c) Thus N₂ molecule has three bonds, one sigma and two pi.

(B) Heteronuclear diatomic molecules

(a) **CO**: (a) We know that total number of valence electrons = 8 + 6 = 14The distribution of electrons in various molecular orbitals of CO molecule is done in the following manner $KK(\sigma^2s)^2(\sigma^2s)^2(\pi^2p_y)^2(\pi^2p_z)^2(\sigma^2p_x)^2$

(b) Bond order =
$$\frac{1}{2}$$
 (8–2) = 3

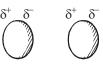
(c) It represents one sigma bond and two π -bonds (d) The molecule is stable and diamagnetic in nature.

16. SECONDARY FORCES :

16.1 Vander waal's forces

- (I) These are weak; non directional, non valence force of attraction among neutral species.
- (II) These are electrical in nature, due to induced polarity caused by temporary displacement of electrons towards one end of the inert atoms, becoming a temporary dipole.
- (III) This temporary dipole in one molecule can induce opposite dipoles in

surrounding molecule.due to diplacement of electrons, one end becomes -ve and other +ve. These partially charged ends, induce surrounding molecules accordingly.



- (IV) Strength of vander waal force depends on ease of distortion of electron cloud. Vander waal force ∞ size of atom or molecule ∞ atomic wt. or molecular weight.
- (V) Therefore m.p. and b.p. of noble gas elements (inert gas atom) and halogens increases down the group.
- (VI) These force originate from three different causes -
- (a) Keesom force or dipole dipole force one dipole molecule orient the other dipole molecule, to bring opposite ends close to each other for attraction. This is called orientation effect. Example HCl, H₂O, NH₃ etc.
- (b) Debye force or dipole induce dipole force :- Forces which results from the interaction of a permanent dipole and induced dipole are called Debye force.
 eg. When non-polar substance like benzene come in contact with polar molecules like NH₃, induced dipole moment in benzene appears (Induction effect).
- (c) London force or Instantaneous dipole instantaneous induce dipole attraction :-Due to vibration or moment of atom electron cloud and nuclei shifts temporarily towards opposite ends, leads to attraction between them, eg. In atoms of noble gases.

16.2 Hydrogen Bond

- (1) Hydrogen bond is formed in covalent compounds and not in ionic compounds.
- (2) H-bond is not formed in nonpolar covalent compounds.
- (3) H-bond is the attraction between H atom and strongly electronegative atom.

16.2.1 Intermolecular Hydrogen Bond : Bond between two nearest molecules.

(a) Homointermolecular H-Bond : This type of H-bond is formed between same molecules. For example, H₂O, HF, NH₃, ROH, CH₃COOH, etc.

(b) Heterointermolecular H-Bond : The type of H-bond is formed between molecules of different compounds.

16.2..2 Intramolecular Hydrogen Bond : Bond in a single molecule e.g. Nitrophenol

- (i) Due to higher electronegative in nature of O, electron density transfers from electron-rich $O^{\delta-}$ to electron deficient $H^{\delta+}$ bonded to the electronegative atom of the other molecule.
- (ii) H-bond is formed between two molecules, so this is called intermolecular H-bond.
- (iii) One H₂O molecule can form a maximum of four H-bonds.

17. RESONANCE

- (a) The concept of resonance was introduced by Heisen berg (1920), and later developed by pauling and ingold, to explain the properties of certain molecules.
- (b) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure. The molecule is then supposed to have many structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules. The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.
- (c) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O-O = 1.48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.

$$\mathcal{O}_{\mathcal{O}} \longleftrightarrow \mathcal{O}_{\mathcal{O}} \equiv \mathcal{O}_{\mathcal{O}}$$

Resonance hybrid

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

-0

P - O

Bond order =
$$\frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$

e.g.

O

Bond order =
$$\frac{4}{3}$$
 = 1.33

4

Bond order =
$$\frac{5}{4}$$
 = 1.25

$$O = CI - O$$

Bond order = $\frac{7}{4}$ = 1.75

18. METALLIC BOND

- (a) The constituent particles of metallic solids are metal atoms which are held together by metallic bond.
- (b) In order to explain the nature of metallic bond Lorentz proposed a simple theory known as electron gas model or electron sea model.
- (c) A metal atom is supposed to consist of two parts, valence electrons and the remaining part (the nucleus and the inner shells) called kernel.
- (d) The kernels of metal atoms occupy the lattice sites while the space between the kernel is occupied by valence electrons.
- (e) Due to small ionisation energy the valence electrons or metal atoms are not held by the nucleus firmly. Therefore, the electrons leave the field of influence of one kernel and come under the influence of another kernel. Thus the electrons are not localised but are mobile.
- (f) The simultaneous attraction between the kernels and the mobile electrons which hold the kernel together is known as metallic bond.

19. SOME USEFUL FORMULAE

Ionic character :

