Chemical Bonding

Section (A) : Introduction to Bonding, Octet rule and Ionic bond

INTRODUCTION:

It is a well known fact that none of the elements exist as independent atoms, except for noble gases, Most of the elements exist as molecules which are in a cluster. The questions that arise are. Why do atoms combine and form bonds ? How do atoms combine to form molecules? Why is a molecule more stable than the individual atom? Such doubts will be discussed in this chapter.

DEFINITION :

- (i) An attractive force that acts between two or more particles (atoms, ions or molecules) to hold them together, is known as a chemical bond.
- (ii) It is a union of two or more atoms to aquire stable inert gas configuration s^2p^6 .

To explain nature of chemical bond different theories are given. First of all KOSSEL & LEWIS proposed the theory.

Kossel & Lewis approach of chemical bonding : In early days, the ability if various elements to combine with one another was expressed in terms of their valency. The concept of valency was not based on any logical understanding. The development in the field of atomic structure provide foundations for various theories of valency. The initial contributions in this field came from W. Kossel and G. N. Lewis in 1916. They were the first to provide some logical explanation of valency which is based on the inertness of noble gases. This view, later on, came to be known as octet rule.

OCTET RULE : (Tendency to acquire noble gas configuration)

- It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.
- (ii) It means that these atoms must have a stable electronic configuration.
- (iii) These elements (noble gases) have 8 electrons (ns² np⁶) except helium which has 2 electrons (1s²) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most shell					
configuration	2s ² 2p ⁶	3s ² 3p ⁶	4s ² 4p ⁶	5s²5p ⁶	6s ² 6p ⁶

 (iv) It is therefore concluded that s²p⁶ configuration in the outer energy level constitutes a structure of maximum stability or minimum energy (v) "Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

Lewis Dot Structures :

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different.

To write the Lewis dot structure following steps are to be followed :

- (i) The total number of electrons are obtained by adding the valence electrons of combining atoms.
- (ii) For anions, we need to add one electron for each negative charge.
- (iii) For cations, we need to subtract one electron for each positive charge.
- (iv) After then the central atom is decided.
- To decide, Central atom, following steps are followed :
- (i) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF₃ and CO₃^{2–}, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- (ii) Generally the atom which is/are less in number acts as central atom.
- (iii) Generally central atom is the atom which can form maximum number of bonds(which is generally equal to the number of electrons present in the valence shell of the atom).
- (iv) Atom of highest atomic number or largest atom generally acts as central atom.

Hence fluorine and hydrogen can never act as central atoms.

After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in the following Table

M ole cule /ion	H ₂	O ₂	Ο 3	NF $_3$	C O 3 ²⁻	HNO ₃	CH₄	нсно
Lewis Representation	Н – Н	:0=0:	:0.0,0,0;	: F] - N - F]: .F]:	$\begin{bmatrix} \vdots 0 \vdots \\ \vdots 0 \vdots \\ \vdots 0 - C - 0 \vdots \end{bmatrix}^{2}$		Н-С-Н Н-С-Н Н	О Н-С-Н

Table-1

Each H-atom attains the configuration of helium (a duplet of electrons)

Limitations of the Octet Rule :

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

CHEMISTRY FOR JEE

1. The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom Is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl. BeH₂ and BCl₃.

Li. Be and B have 1,2 and 3 valence electrons only. Some other such compounds are AICl₃ and BF₃.

2. Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide. NO and nitrogen dioxide. NO₂, the octet rule is not satisfied for all the atoms

$$\dot{N} = \dot{O}$$
 $\dot{O} = \dot{N} - \dot{O}$ $\dot{C} IO_2$

3. The expanded octet/ super octet / hypervalent compound

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5 , SF_6 , $\mathsf{H}_2\mathsf{SO}_4$ and a number of coordination compounds.



10 electrons around
the P atom12 electrons around
the S atom12 electrons around
the S atom

Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.

$$|C| - S - C|$$
 Or $|C| |S| |C|$

4. Other drawbacks of the octet theory

• It is clear that octet rule is based upon the chemical Inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF₂, KrF₂, XeOF₂ etc.,

• This theory does not account for the shape of molecules.

• It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

CLASSIFICATION OF CHEMICAL BONDS :

On the basis of electronic valency theory and structure, chemical bonds can be classified as follows.



ELECTROVALENT OR IONIC BOND :

The chemical bond formed between two or more atoms as a result of complete transfer of one or more electrons from one atom to another is called ionic or electrovalent bond.

Electrovalent bond is not possible between similar atoms. This type of bonding requires two atoms of different nature. One atom should have the tendancy to loose electrons i.e. electropositive in nature and the other atom should have the tendency to accept electrons i.e. electronegative in nature.

Electropositive atom looses electrons (group IA to IIIA)

Electronegative atom gains electron (group IVA to VII A)

Example : IA and VII A group elements form strong ionic compound. Na + Cl \rightarrow Na⁺ + Cl⁻ 2, 8, 1 2, 8, 7 2, 8 2, 8, 8 (Ne configuration) (Ar configuration)

More the distance between two elements in the periodic table more will be the ionic character of the bond. Total number of electrons lost or gained is called electrovalency.

Example :

(1)

$$Mg + O \rightarrow MgO$$

$$Mg^{+2} \leftarrow Mg \qquad O \rightarrow O^{-2}$$
2, 8 2, 8, 2 2, 6 2, 8
$$2e^{-7}$$

electrovalency of Mg = 2 electrovalency of O = 2

(2) $Ca + 2CI \rightarrow CaCI_2$

$$Ca^{+2} \leftarrow Ca \qquad CI \rightarrow CI^{-}$$
2, 8, 8 2, 8, 8, 2 2, 8, 7 2, 8, 8

$$Onee^{-} CI \rightarrow CI^{-}$$

$$Onee^{-} 2, 8, 7 2, 8, 8$$

electrovalency of Ca = 2 electrovalency of Cl = 1

(3)

Ca + O −→ CaO

 $\begin{array}{ccc} Ca^{+2} \leftarrow Ca & O \rightarrow O^{-2} \\ 2, 8, 8 & 2, 8, 8, 2 & 2, 6 & 2, 8 \end{array}$

electrovalency of Ca = 2

electrovalency of O = 2

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond. Force of attraction is equal in all direction so ionic bond is non–directional.

Energy released during the formation of one mole crystal lattice is called lattice energy.

e.g. (6.023×10^{23}) Na⁺ + (6.023×10^{23}) Cl⁻ \rightarrow (6.023×10^{23}) NaCl(s) + 94.5 K.cal (Lattice energy).

lonic compounds do not have a molecular formula, they only have empirical formula.

e.g. NaCl is the empirical formula of sodium chloride.

Factors favouring formation of lonic bonds :

Formation of ionic bond depends upon three factors :

(A) Ionisation energy (IE) : Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form positve ion or cation is called ionization energy [energy is absorbed so it is an endothermic process]

$$M + I.E. \longrightarrow M_{+} + e_{-}$$

Less lonisation energy \Rightarrow Greater tendency to form cation.

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

Example :

(B) Electron affinity : Amount of energy released when an electron is added to an isotated gaseous atom to form negative ion or anion is called electron affinity [energy is released so it is an exothermic process]

$$X + e^- - \rightarrow X^- + EA$$

High electron affinity \Rightarrow Greater tendency to form anions

$$\begin{array}{c} CI^{-} > F^{-} > Br^{-} > I^{-} \\ F^{-} > O^{-2} > N^{-3} \end{array} \right\} \text{ Anion formation tendency}$$

LATTICE ENTHALPY :

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol⁻¹. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na⁺¹ (g) and one mole of Cl⁻(g) to an infinite distance.

This process involves both the attractive forces between lons of opposite charges and the repulsive forces between ions of like charge. The solid crystal being three- dimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only.

Factors associated with the crystal geometry have to be included.

 $Na^{+}(g) + CI^{-}(g) \longrightarrow NaCI(s)$ $\Delta H = \Delta H_{lattice} \Rightarrow -ve (always)$

 $Mg^{2+}(g) + 2CI^{-}(g) \longrightarrow MgCI_{2}(s)$

Factors affecting L.E.

- (i) Lattice energy (L.E.) α^{r} $r = r_{+} + r_{-}$
 - = interionic distance

(ii) L.E. α Z+, Z-

 $Z_{*} \Rightarrow$ charge on cation in terms electronic charge

- $Z_{-} \Rightarrow$ charge on anion in terms electronic charge
- (iii) Size of cation \uparrow C.N. \uparrow L.E. \uparrow
 - (a) NaCl > KCl (size)
 (b) NaCl < MgO (size, charge)
 (c) NaCl < MgCl₂ (size)

In size and charge, charge will dominate Na₂O > NaF NaCl < Na₂S

(iv) Al_2O_3 Na_2O MgO $Al_2O_3 > MgO > Na_2O$

Characteristics of ionic compounds :

(i) Physical state

(a) Electrovalent compounds are generally crystalline, hard & brittle in nature.

(b) These compounds are generally made from ions which are arranged in a regular way as a lattice structure.

(c) Thus electrovalent compounds exist as three dimensional solid aggregates.

(d) Normally each ion is surrounded by a number of oppositively charged ions and this number is called co-ordination number



{Same charged ions comes near. So they repell each other}

(ii) Boiling point and melting point :

High boiling point and melting points are due to strong electrostatic force of attraction.

(iii) Electrical conductivity :

It depends on ionic mobility. In solid state there are no free ions so they are bad conductors of electricity In fused state or aqueous solution free ions are present so they are good conductors of electricity

(Conductivity order) Solid state < Fused state < Aqueous solution

(iv) Ionic reactions :

★ Ionic compounds show ionic reactions & covalent compounds show molecular reactions.

lonic reactions are fast reactions.

Example: When NaCl is added to AgNO₃ solution, white ppt of AgCl is formed at once.

white ppt.

(v) Solubility – *lonic compounds are soluble in polar solvent like H₂O, HF etc.* To explain solubility of ionic compound consider an example of NaCl in water.



 H_2O is polar solvent it can represent as H

- The Na⁺ ions gets associated with partially negatively charged 'O' of water
- * And CI⁻ ions gets associated with partially positively charged 'H' of water.

*



Oxygen atom of H_2O gives its electron to Na

H atom of H_2O gain electron from Cl^{e}

СГ

⁺H₂O⁻

Thus charge on Na⁺ and Cl⁻ decreases and electrostatic force also decreases which leads to free ion.

-OH,

Here, attraction force between

Electrostatic force

- H_2O and Na⁺ or CI⁻ (Hydration energy) > between ions in lattice. (Lattice energy)
- * Energy released due to interaction between polar solvent molecule and ions of solute is called solvation energy. If water used as solvent it is called hydration energy.
- * Condition of the solubility of ionic compound in water is (Hydration energy > Lattice energy)

Solvation or Hydration :

Electrostatic force



Whenever any compound generally ionic or polar covalent is dissolved in an polar solvent or in water then., different ions of the compound will get separated and will get surrounded by polar solvent molecules. This process is known as solvation or hydration. Energy released in this process is known as solvation energy or hydration energy

The ionic compound will be soluble only if solvation energy (H.E.) is more than the lattice energy

Factors affecting solvtion energy or hydration energy.

S.E.
$$\alpha Z_{+} Z_{-}$$

 $\alpha \left(\frac{1}{r_{+}} + \frac{1}{r_{-}}\right)$
 $\alpha \left(1 - \frac{1}{\epsilon_{r}}\right)$ (nature of solvent) where ϵ_{r} is dielectric constant.

Greater the polarity, greater will be \in_r

 $\epsilon_r \uparrow \Rightarrow 1/\epsilon_r \downarrow$, $1-1/\epsilon_r \uparrow \Rightarrow S.E. \uparrow$

	H ₂ O	CH₃OH	C_2H_5OH	C ₆ H ₆
∈r	81	34	27	34

Applications of Hydration energy :

- (a) Size of the hydrated ions: Greater the hydration of the smaller ion, greater will be its hydrated radii Li⁺(aq) > Na⁺(aq)
- (b) Mobility of the ion: more is the hydration smaller will be the mobility of the ions Li*(aq) < Na*(aq) < K*(aq) < Rb*(aq) < Cs*(aq).</p>
- (c) Electrical conductance : is related to mobility so follows the same order

Important facts about solubility of ionic compounds in polar solvent can be predicted as

Now we have
$$\rightarrow$$
 L.E. $\alpha \frac{1}{r_+ + r_-}$ and S.E. $\alpha \left(\frac{1}{r_+ + r_-}\right)$

Section (B) : Fajan's rule

COVALENT CHARACTER IN IONIC COMPOUNDS (FAJAN'S RULE) :

When anion and cation approach each other, the valence shell of anion is pulled towards cation nucleus and thus shape of anion is deformed. This phenomenon of deformation of anion by a cation is known as polarisation and the ability of cation to polarize a near by anion is called as polarizing power of cation.



Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.

More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

(i) **Size of cation :** Smaller is the cation more is its polarizing power and thus more will be the polarisation of anion. Hence more will be covalent character in compound.

Size of cation α 1 / polarisation.						
e.g.	BeCl ₂	MgC		CaCl ₂	SrCl ₂	BaCl ₂
Size	of cation increas	ses,	Polaris	ation decreases,	Covalent of	character decreases

(ii) **Size of anion :** Larger is the anion, greater is its polarisability and, therefore, more will be the polarisation. Thus more will be covalent character in compound.

Size of anion α polarisation

- e.g., LiF LiCl LiBr Lil
 - Size of anion increases
 - Polarisation increases
 - Covalent character increases
- (iii) **Charge on cation :** Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.

Charge on cation α polarisation.

- e.g., NaCl MgCl₂ AlCl₃
 - Na⁺ Mg²⁺ Al³⁺
 - Charge of cation increases
 - Polarisation increases
 - Covalent character increases
- (iv) **Charge on anion :** Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.

Charge on anion α polarisation.

- e.g., AIF₃ Al₂O₃ AIN
 - F^- , O^{2-} , N^{3-}
 - Charge on anion increases
 - Polarisation increases
 - Covalent character increases
- (v) Pseudo inert gas configuration of cation : Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.

Application & Exceptions of Fajan's Rules :

- (i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.
- (ii) $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus charge is more. Therefore, $Fe(OH)_3$ is more covalent than $Fe(OH)_2$.
- (iii) The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example :

AgCl is white AgBr, AgI, Ag₂CO₃ are yellow. Similarly, SnCl₂ is white but SnI₂ is black. PbCl₂ is white but PbI₂ is yellow.

The bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



(iv) Variation of melting point [melting point of covalent compound < melting point of ionic compound]

 $BeCl_2$, $MgCl_2$, $CaCl_2,\,SrCl_2,\,BaCl_2$

lonic charater increases, melting point increases ; since size of cation increases & size of anions is constant.

 CaF_2 , $CaCl_2$, $CaBr_2$, CaI_2

Covalent character increase, melting point decrease ; since size of cations increase & size of anions is constant.

Solved Examples ——

- Ex-1 AgCl is colourless whereas AgI is yellow, because of :
 - (1) Ag⁺ have 18 electron shell to screen the nuclear charge.
 - (2) Ag⁺ shows pseudo inert gas configuration.
 - (3) distortion of I⁻ is more pronounced than CI⁻ ion.
 - (4) existence of d d transition.
- **Sol.** (3) the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.



Section (C) : Covalent Bond and Coordinate Bond

COVALENT BOND :

A covalent bond may be defined as the bond formed by mutual sharing of electrons between the participating atoms (which are short of electrons) of comparable electronegativity.



Covalency :

- (i) It is defined as the number of electrons contributed by an atom of the element for sharing with other atom so as to achieve noble gas configuration.
- (ii) It can also be defined as the number of covalent bonds formed by the atom of the element with other atoms.
- (iii) The usual covalency of an element except hydrogen is equal to 8 minus the number of group to which the element belongs.

Lewis structure and covalent bond :

- (i) Structures in which valency electrons are represented by dots are called Lewis structures.
- (ii) All atoms in the formulae will have eight electrons in it's valence shell. H atom is an exception for it can form large number of bonds with the atom present at the center of any crystal structure. Other atoms surround it to complete their octet.
- (iii) Lewis dot formulae shows only the number of valency electrons, the number and kinds of bonds,

but does not depict the three dimensional shapes of molecules and polyatomic ions.

 (iv) Lewis formulae are based on the fact that the representative elements achieve a noble gas configuration in most of their compounds i.e. 8 electrons in their outermost shell (except for H₂, Li⁺ and Be²⁺ ions which have only 2 electrons)

Characteristics of covalent compounds :

(i) Physical state :

- (a) Under normal temperature and pressure, they exist as gases or liquids of low boiling points.
- (b) This is due to the fact that very weak forces of attraction (Vander waal's forces) exist between
- the molecules due to which molecules are far from each other.
- (c) If their molecular masses are high they exist as soft solids ex. Sulphur, phosphorus and iodine.

(ii) Crystal structures :

Various types of structures that are present in a covalent compound are as follows.

(a) Covalent solid – In this type of structure every atom is bonded to four other atoms by single covalent bonds resulting in the formation of a giant structure e.g. SiC, AIN and diamond these crystals are very hard and possess high melting point.

Diamond is sp³ hybridized carbon atom and it forms a tetrahedral structure.

Graphite is sp² hybridized carbon atomsand it forms hexagonal layers which can slide over each other due to weak Vander waal's forces of attraction.Distance between C–C atom is 1.42 Å distance between layers is 3.6 Å. **Graphite is more stable than diamond due to high value of change in enthalpy.**

(b) Molecular solids : They are formed when one atom combines with another by a covalent bond and then the molecule combines with another similar molecule with the help of Vander waal's force of attraction or hydrogen bond

Example : CH₄(Solid), dry ice, ice

(iii) Melting and boiling points :

- (a) With the exception of a few which have giant three dimensional structures such as diamond, carborundum (SiC), Silica (SiO₂), others have relatively low melting and boiling points.
- (b) This is due to the presence of weak attractive forces between the molecules.

(iv) Electrical conductivity :

- (a) In general covalent substances are bad conductors of electricity. Since they do not contain charged particles or free electrons.
- (b) Substances which have polar character like HCl in a solution, can conduct electricity.
- (c) Graphite can conduct electricity since electrons can pass from one layer to other.
- (d) Some show conductivity due to self ionisation. example Liq NH₃

 $NH_3 + NH_3 - \rightarrow NH_4^+ + NH_2^ H_2O + H_2O - \rightarrow H_3O^+ + OH^-$

(v) Chemical reactions :

Covalent substances give molecular reactions. Reaction rate is usually low because it involves two steps (i) breaking of covalent bonds of the reactants (ii) establishing new bonds. While in ionic reactions there is only regrouping of ions.

(vi) Solubility :

- (a) Non polar compounds are soluble in non polar solvents. Non polar solvents are CCl₄, Benzene, CS₂ etc.
- (b) Polar compounds are soluble in polar solvents (i.e. ΔEN 0.9 to 1.8). Polar solvents are H₂O, CHCl₃, Alcohol etc.

(vii) Isomerism :

Covalent bonds are rigid and directional. On account of this there is a possibility of different arrangement of atoms in space. Covalent compounds can thus shows isomerism (structural and spatial)

Section (D) : Formal charge and Resonance

Formal Charge :

The formal charge of an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the lewis structure.



Let us consider the ozone molecule (O $_3$). The Lewis structure of O $_3$, may be drawn as :



The atoms have been numbered as 1. 2 and 3. The formal charge on :

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

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

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

Hence, we represent O_{3} along with the formal charges as follows :

:0.0

It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

Note : (i) The formal charge Is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

(ii) Pair of +1 and -1 formal charge on adjacent atoms is considered a coordinate bond.

:0≧0:⇒:C≦0:

(iii) Lewis dot structure with minimum formal charges is most stable.

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, O₂ molecule can be equally represented by the structures I and II shown below :



Resonance in the O3 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_2 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_2 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.





- O Stability of molecule α resonance energy.
- O More is the number of covalent bonds in molecule more will be its resonance energy.
- O Resonance energy α number of resonating structures.

Section (E) : Valence bond theory

MODERN CONCEPT OF COVALENT BOND (VBT) :

As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H₂ (435.8 kJ mol⁻, 74 pm) and F₂ (150.6 kJ mol⁻, 42 pm); although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two Important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory.

Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition. Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between :

(i) nucleus of one atom and its own electron that is $N_{\text{A}}-e_{\text{A}}$ and $N_{\text{B}}-e_{\text{B}}.$

(ii) nucleus of one atom and electron of other atom i.e., $N_{\text{A}}-e_{\text{B}}.$ $N_{\text{B}}\!-e_{\text{A}}.$

Similarly repulsive forces arise between :

(i) electrons of two atoms like $e_A - e_B$, (ii) nuclei of two atoms $N_A - N_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig.).



Attractive Forces Repulsive Forces **Fig-** Forces of attraction and repulsion during the formation of H₂ molecule.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. Conversely. 435.8 kJ of energy is required to dissociate one mole of H₂ molecule.



Fig. The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2 .

Orbital Overlap Concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present In the valence shell having opposite spins.

Main points of valence bond theory :

(i) A covalent bond is formed by partial overlapping of two atomic orbitals



(ii) More is the extent of overlapping between the two atomic orbital, stronger will be bond.



: s orbital are spherical in nature so they are least diffused hence it will provide less area for overlapping.

- (iii) Orbitals which are undergoing overlapping must be such that
 - (a) Each orbital should have one electron with opposite spin

(for formation of covalent bond)

(b) One orbital have pair of electron and the other orbital have no electron

(for formation of co-ordinate bond)

(iv) If the overlapping is along the molecular axis then bond will be sigma (σ) & in the perpendicular direction, it will be pi(π) bond.



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Examples of overlapping of pure atomic orbitals.

Types of Overlapping and Nature of Covalent Bonds :

The covalent bond may be classified into two types depending upon the type of overlapping : (i) Sigma (σ) bond, and (ii) pi (π) bond

(i) Sigma (o) bond : This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the intemuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

• s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :



• p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(ii) $pi(\pi)$ bond : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



Strength of Sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlaping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond . between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds)

Difference in σ and π bonds :

	Sigma (σ) bond	Pi (π) bond
1	It results from the end to end overlapping	It result from the sidewise (lateral)
	of two s orbitals or two p-orbitals or	overlapping of two p orbitals.
	one s and one p-orbital.	

2	Its bonded orbital consists of a single	Its bonded orbital consists of two electron
	electron cloud symmetrical about	clouds one above and the other below the plane
	internuclear axis	of symimetry
3	Strong	Weak
4	Bond energy 80 Kcals	65 Kcals
5	More stable	Less Stable
6	Less reactive	More reactive
7	Can independently exist	Always exists along with a σ bond
8	Hybridization depends upon σ bond	Hybridisation doesn't depend on $\boldsymbol{\pi}$ bond
9	The groups or atoms can undergobond	Due to resistance to rotation around the $\boldsymbol{\pi}$ bond
	rotation about single sigma (σ)bonds	the groups attached to it are not free to rotate.
10	The σ electrons are referred as localised	in π bond the electrons are held less firmly bond
		thus can be easily dissociated or
		polarised by an external charge and hence the
		$\pi \mbox{ e}^{\scriptscriptstyle -}$ are referred as mobile electrons.
11	Shape of the molecule is determined by	π bonding does not affect the shape of the
	the σ bonds present in the molecule	molecule

Section (F) : VSEPR Theory

Valence shell electron pair repulsion (VSEPR) theory :

Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957).

The main postulates of VSEPR theory are as follows :

- (i) The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded) around the central atom.
- (ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

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- (iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- (iv) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- (vi) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :

lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) - bond pair (bp)

Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

For the prediction of geometrical shapes of molecules with the help of VSEPR theory it is convenient to divide molecules into two categories as (i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom / ion has one or more lone pairs.

Shape (molecular geometry) of Some Simple Molecules / ions with central atom / ion having no Lone Pairs of Electrons (E).

Number of electron pairs	General formula type	Arrangement of electron pairs	Molecular geometry	Example
2	AB2	:	B – A – B Linear	BeCl, ,HgCl,
3	AB	Trigonal planar	B B Trigonal planar	BF_3
4	AB₄			CH_4, NH_4^-
5	AΒ _ε	120°	B 120 [°] B	PCI
6	AB ₆	Trigonal bipyramidal	Trigonal bipyramidal	SF。
7	AB,	Octahedral	Octahedral B B B B B B B B B B B B B B B B B B B	IF,

Shape (molecular geometry) of Some Simple Molecules/Ions with central atom / ions having One or More Lone Pairs of Electrons (E).

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CHEMICAL BONDING

General formula type	No.of bonding pairs	No.of Ione pairs	Arrangement of electron pairs	Shape	Examples	
AB₂E	2	1	B B B	Bent	S0₂,0₃	
AB₃E	3	1	B B B	Trigonal pyramidal	NH_{3}	H 1070 H
AB ₂ E ₂	2	2	A	Bent	H₂O	H 104.5° H
AB₄E	4	1		See saw	SF₄	F F
$AB_{3}E_{2}$	3	2	B - A	T-shape	CIF_{s}	
AB₅E	5	1		Square pyramidal	XeOF₄	F F F
A B₄E₂	4	2		S quare planar	XeF₄	F F
A B _s E ₂	5	2		Pentagonal planar	XeF₅¯	F F F

Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No.of bonding pairs	No.of lone pairs		Shape	Reason for the shape acquired
AB,E	4	1 :		Bent	It is found to be bent or v-shaped. The reason being the lone pair- bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB₄E	3	1		Trigonal pyramidal	It is found to be trigonal pyramidal due to the repulsion between lp-bp (which is more than bp–bp repulsion) the angle between bond pairs is reduced to 107° to 109.5°.
AB,E,	2	2	H 104.5 ³ H	Bent	The shape is distored tetrahedral or angular. The reason is Ip-Ip repulsion is
			H		angle is reduced to 104.5° from 109.5°.
AB₁E	4	1 (1)	F F F	See- saw s t a	in (i) the lp is present at axial position so there are three lp-bp repulsion at 90°. In (ii) the lp is an equatorial position, and there are two lp-bp repulsions. Hence, arrangement (ii) is more stable. The shape shown in (ii) is called as a distorted letrahedron, a folded square or a see-saw
		(ii		ore stable)	
AB,E2	3	2		T–shaµ	pe In (i) the lone pairs are at equatorial position (120°) so there are less lp–bp repulsions as compared to others in which the lp are at axial positions.So structure (i) is most stable. (T – shaped).
		(ii)		F	

O The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small.

Solved Examples ——

Ex-2 Use the VSEPR model to predict the geometry of the following :

(a) XeF ₂		F ₂	(b) ClO₃ [_]	
Sol.		Species	Structure	
	(a)	XeF2	⊖ ∵¦ F	lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.
	(b)	CIO₃⁻		To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Section (G) : Hybridisation and Bond angle

HYBRIDISATION:

The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. It does not give the explanation why BeCl₂ is linear, BF₃ is planar, CH₄ is tetrahedral, NH₃ is pyramidal and water is V– shaped molecule. In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and was introduced by Pauling & Slater.

According to them the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp³ hybrid orbitals.

Salient features of hybridisation : The main features of hybridisation are as under :

- **1.** The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- 2. The hybridised orbitals are always equivalent in energy and shape.
- 3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- (i) The orbitals present in the valence shell of the atom are hybridised.
- (ii) The orbitals undergoing hybridisation should have almost equal energy.
- (iii) Promotion of electron is not essential condition prior to hybridisation.
- (iv) It is the orbital that undergo hybridization and not the electrons. For example, for orbitals of nitrogen

 $(2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1)$ atom belonging to valency shell when hybridize to form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each. It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell ake part in hybridisation.

Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

Steric No. of an atom = (number of atom bonded with that atom) + (number of lone pair(s) left on that atom).

Note : This rule is not applicable to molecules/ions which have odd e^- (ClO₂, NO, NO₂), free radicals and compounds like B₂H₆ which involve 3 centre 2e⁻ bond (banana bond).

For example : O = C = O S.N O = C = O S.N

S.No. = 2 + 0 = 2 S.No. = 2 + 1 = 3 S.No. = 3 + 0 = 3

S.No. = 3 + 1 = 4

Steric number	Types of Hybridisation	Geometry	Involving orbitals
2	sp	Linear	ns, np _x /p _z /p _y
3	sp ²	Trigonal planar	ns, np_x , p_z / p_y , p_z / p_x , p_y
4	sp ³	Tetrahedral	ns, np _x , p _z , p _y
5	sp ³ d	Trigonal bipyramidal	ns, np _x , p _z , p _y d_{z^2}
6	sp ³ d ²	Octahedral	ns, np _x , p _z , p _y $d_{z^2} d_{x^2-y^2}$
7	sp ³ d ³	Pentagonal bipyramidal	ns, np _x , p _z , p _y $d_{z^2} d_{x^2-y^2} d_{xy}$

sp hybridisation :

This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation.

The two sp hybrids point in the opposite direction along the Z-axis with projecting bigger positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds.

Example of a molecule having sp hybridisation

BeCl₂ : The ground state electronic configuration of Be is 1s² 2s². In the excited state one of the 2selectrons is promoted to vacant 2p orbital to account for its divalency. One 2s and one 2p-orbitals get hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two Be-Cl sigma bonds.



Fig. (A) Formation of sp hybrids from s and p orbitals ; (B) Formation of the linear BeCl₂ molecule.

Examples of SP hybridisation.

(a)	—C≡	$H-C\equivN,$	$H-C\equivC-H$
(b)	= C =	O = C = O	$H_2C = C = CH_2$

(c) N_{3^-} (azide ion), BeF₂, HgCl₂, NO₂+ (nitronium ion), N₂O

Note : In N₃⁻ there is a total of two σ and two π bonds giving N = N = N and a bond order of two. Both N – N bonds are the same length, 1.16 Å. The hydrogen azide molecules has a bent structure and two N – N bond length are different.



sp₂ hybridisation :

In this hybridisation there is involvement of one s and two p-orbitals in order to form three equivalent sp² hybridised orbitals.

For example, in BCl₃ molecule , the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp^2 hybrid orbitals. The three hybrid orbitals so formed are oriented In trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B–Cl bonds. Therefore, in BCl₃, the geometry is trigonal planar with CIBCl bond angle of 120°.



Fig. Formation of sp^2 hybrids and the BCl₃ molecule

Steric No. = 3 Geometry = Trigonal planar Ideal bond angle = 120°

Туре	AB3	AB ₂ L
Shape	Trigonal	V-shape (bent)
Example	$C = , CH_3, CH_3$ $C_6H_6, CO_3^{2-}, HCO_3^{-}$ $H_2CO_3, \text{ graphite, BF}_3$ $B(OH)_3, SO_3, NO_3^{-}$ $C_{60} \text{ (Fullerene)}$	 -C-, SO ₂ , SnCl ₂ NOCI, O ₃ , NO ₂ NO ₂ ⁻

Example

Where A = central atom, B = side atom, L = lone pair of e⁻

sp₃ hybridisation :

This type of hybridisation can be explained by taking the example of CH_4 molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp³ hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp³ hybrid orbital. The four sp³ hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp³ hybrid orbital is 109.5° as shown in figure.



The structure of NH₃ and H₂O molecules can also be explained with the help of sp³ hybridisation. In NH₃, the valence shell (outer) electronic configuration of nitrogen in the ground state is $2s^2 2px^1 2py^1 2pz^1$ having three unpaired electrons in the sp³ hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with Is orbitals of hydrogen atoms to form three N-H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107° from 109.5°. The geometry of such a molecule will be pyramidal as shown in figure.



Ammonia NH₃

Fig. Formation of NH₃ molecule

In case of H₂O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp³ hybridisation forming four sp³ hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp³ hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° and the molecule thus acquires a V-shape or angular geometry.



Fig. Formation of H₂O molecule

Steric No. = 4

Geometry = tetrahedral

Ideal bond angle = 109° 28'

Туре	AB4	AB ₃ L	AB_2L_2	ABL_3
Shape	tetrahedral	pyramidal	V-shape or bent	Linear
Example	CH4	XeO ₃	OBr ₂	-OCI









O $NH_2 - NH_2$ or N_2H_4 (hydrazine)

Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated 95° about N – N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.



NH₂OH (hydroxylamine) sp³ lp-lp

 $\ensuremath{\mbox{lp-lp}}$ repulsion increases the N–O bond length.

O P₄ (White phosphorus)

All phosphorus atoms occupy all four vertexes of tetrahedron. There are six P–P bonds and \angle P–P–P is 60°.

Since bond angle is 60° (against normal tetrahedral bond angle, 109.5°) so, P₄ molecule is a strained molecule. So it is chemically very reactive.



0

Ρ

0



O P₄O₆

P₄O₁₀

P–O bond length shows that the bridging bonds on the edges are 1.65 Å and are normal single bonds. There is no P–P bonds.



The P–O bond lengths shows that the bridging bonds on the edges are 1.60 Å but the P = O bonds on the corners are 1.43 Å and this P=O is formed by $p\pi$ –d π back bonding. A full p-orbital on the oxygen atom overlaps sideway with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P–P bonds.

O SiO₂ is a covalent network solid like diamond



O Structures of cyclic silicates : [Si₃O₉]⁶⁻



Note : Oxygen atom bonded with two Si atoms can not have negative charge. There is no oxygen–oxygen bond. All silicates contain only Si–O bond and there is no Si – Si Bond.

O B2H6

This molecule does not have any B–B bond like C–C bond in C_2H_6 (ethane). Therefore, there is no scope of any conformations in the molecules of B_2H_6 .

Both the B atoms are in sp³ hybridization state and each boron contains two types of boron-hydrogen bond lengths.



This is an example of 3-centre 2-e⁻ bond which is also known as Banana bond.

The bridging hydrogen atom are not in the plane of the molecule, one is above the plane and the other is below the plane.



O H₂O₂

O–O bond length (148 pm) is larger than the expected due to the repulsions between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book 94°) and both the O atoms have two lone pairs each.

The H_2O_2 is the smallest molecule known to show restricted rotation, in this case about the O–O bond, and this is presumably due to repulsion between the OH groups. A similar structure is retained in the liquid and solid, but bond lengths and angles are slightly changed because of hydrogen bonding.

O **SOCI**² (Thionyl chloride)



trigonal pyramidal



O XeO₄

HYBRIDIZATION INVOLVING d-ORBITAL :

Type of 'd' orbital involved

sp ³ d	dz ²
sp ³ d ²	$dx^2 - y^2 \& dz^2$
sp ³ d ³	dxy, $dx^2 - y^2 \& dz^2$
dsp ²	$d_{x^2-y^2}$

sp₃ **d hybridiation** : Steric number = 5 Geometry = trigonal bipyramidal

Туре	AB5	AB ₄ L	$AB_{3}L_{2}$	
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	PCI_5 , PBr_5 , PF_5 etc.	SF_4 , XeO_2F_2	CIF₃, [XeF₃]⁺	XeF ₂ , I ₃ ⁻ , [ICl ₂] ⁻

Important points regarding sp³d -

(i)

According to VSEPR theory lone pair will occupy equatorial positions but not axial.



- (ii) More electronegative atoms will prefer to occupy axial positions.
- (iii) Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.

AB₅ PCI₅ (g) CI

It is covalent in the gas but in solid state exists as ionic solid consisting of $[PCI_4]^+$ (tetrahedral) and $[PCI_6]^-$ (octahedral). All P–CI bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.

Note : PF₅ (g) is trigonal bipyramidal and the electron diffraction shows that some bond angles are 90° and others are 120°, and the axial P – F bond lengths are 1.58 Å whilst the equatorial P – F lengths are 1.53 Å. But NMR studies suggest that all five atoms are equivalent because of pseudo rotation. PF₅ remains covalent and is trigonal bipyramidal in the solid state.

 $PBr_{\text{5}}(s)$ exists as $[PBr_{4}]^{+}$ Br^{-} and PI_{5} as $[PI_{4}]^{+}$ I^{-} in solution.



sp₃ d₂	hybrio	dization :
--------	--------	------------

Steric number = 6

Geometry = octahedral

Туре	AB ₆	AB ₅ L	AB_4L_2
Shape	Octahedral	Square Pyramidal	Square Planar
Example	SF ₆ , PF ₆ ⁻ , [SiF ₆] ²⁻ , [AIF ₆] ³⁻ , [XeO ₆] ⁴⁻	BrF_{5} , IF_{5} XeOF ₄	ICl₄⁻ XeF₄

Important : Since, octahedral is a symmetrical figure hence

(a) positions of a lone pair can be any where

SF6

(b) but if there are two lone pairs (max.) then these must be in the trans position.



Bond angle = 90°

 AB_6

Due to over-crowding and maximum valency of S, SF₆ is much less active (almost inert) than SF₄



 $[\overset{+8}{XeO_6}]^{4-}$ is perxenate ion & H₄XeO₆ is called perxenic acid. But H₂ $[\overset{+4}{XeO_4}]$ is called xenic acid.



 AB_4L_2

XeOF₄

XeF₄

[XeO₆]⁴⁻



Geometry = Pentagonal bi-pyramidal



0



Distorted octahedron with a nonbonding electron pair either at the center of a face or the midpoint of an edge.

O **XeF**₆ (s) is found to be ionic solid consisting of $[XeF_5]^+$ and F^- ions

It is found that F^- is forming a bridge between two XeF_{5^+} ions



Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.

O ICl₃ does not exist, but the dimer I₂Cl₆ is a bright yellow solid. Its structure is planar. The terminal I–Cl bonds are normal single bonds of length 2.38 Å and 2.39 Å. The bridgingI–Cl bonds appreciably longer (2.68 Å and 2.72 Å) suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl₂ to I.

$$\begin{array}{c|c} CI & CI & CI \\ I & I \leftarrow sp^3d^3 \\ CI & CI & CI \end{array}$$

The liquid has an appreciable electrical conductance due to self ionization. I₂Cl₆ \implies [ICl₂]⁺ (bent) + [ICl₄]⁻ (square planar)

– Solved Examples

- $\label{eq:ex-3} \quad \mbox{Which is linear PH_4^+, H_3S^+ or NO_2^+?}$
 - (1) Phosphonium ion (PH₄⁺) (2) Sulphonium (H₃S⁺)
 - (3) Nitronium ion (NO₂⁺) . (4) None of these
- **Sol.** Phosphonium ion (PH₄+) is tetrahedral, sulphonium (H₃S+) is pyramidal, but nitronium ion (NO₂+) is linear $O = \overset{\odot}{N} = O$; (sp hybridisation). **Ans. (3)**
- **Ex-4** The triodide 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.

Section (H) : Electron deficient bond and Back bonding

(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 B₂H₆, Al₂(CH₃)₆, BeH₂(s) and bridging metal carbonyls.



But Al₂Cl₆ 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 nonbonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF₃ the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.



O Decrease in B–F bond length is due to delocalised $p\pi$ – $p\pi$ 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 $p\pi$ - $p\pi$ back bonding in boron trihalide. The extent of back bonding decreases from BF₃ to BI₃ because of increasing size of p-orbitals participating in back bonding that is from 2p (in F) to 4p(in Br).

O The extent of back bonding decreases if the atom having vacant orbitals is also having some nonbonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order Si > P > S > Cl

$$P > S > C$$

O The extent of $p\pi$ - $p\pi$ overlapping

Ex-5 Silyl isocyanate (SiH₃NCO) is linear but methyl isocyanate (CH₃NCO) is bent explain !

$$\begin{array}{c} H \\ H \\ H \\ H \\ J \\ Vacant \\ d-orbitals \end{array} = C = 0 \qquad \begin{array}{c} H \\ H \\ H \\ J \\ J \\ Vacant \\ orbitals \end{array} = C = 0$$

Lone pair on nitrogen is delocalised between N and Si through $p\pi$ – $d\pi$ back bonding. So silyl isocyanate is linear.

Ex-6 Arrange in order of increasing ionic radii in water and their mobility : Be²⁺ , Mg²⁺, Ca²⁺, Sr²⁺.

Sol. (i) Size 1/degree of hydration (i.e. with increase in size, number of water molecules around central metal ions decrease). So order of increasing radii is Sr²⁺ < Ca²⁺ < Mg²⁺ < Be²⁺.

(ii) Heavily hydrated ions move slowly so the order of increasing mobility is : $Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}$.

Sol.

Section (I) : Molecular Orbital Theory (MOT)

The molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features are:

- Just as elctrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- (ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. Thus an atomic orbital is monocentric while a molecular orbital is polycentric.
- (iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- (vi) Just as the electron probability distribution around a nuclues in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by molecular orbital.
- (vii) The molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau principle obeying the Pauli Exclusion principle and the Hund's Rule of Maximum Multiplicity. But the filling order of these molecular orbitals is always experimentally decided, there is no rule like (n + l) rule in case of atomic orbitals.

Formation of Molecular Orbitals : Linear Combination of Atomic Orbitals(LCAO)

Let us begin by discussing the case of molecular hydrogen. An approximate description of the molecular orbitals in H₂ can be obtained by considering them as Linear Combinations of Atomic Orbitals (LCAOs). Let us label the nuclei A and B. The lowest energy orbital associated with each nucleus is the 1s orbital, and each of these atomic orbitals may be represented by wave function ψ_A or ψ_B . Now each molecular orbital may also be represented by a wave function which is a suitable linear combination of atomic orbitals; since A and B are identical atoms their atomic orbitals obviously contribute equally to molecular orbitals. In this case we can write down two molecular orbitals derived by combining the 1s atomic orbitals, these being represented

$$\psi_{m} = [\psi_{A} + \psi_{B}]; \psi = [\psi_{A} - \psi_{B}]$$

The molecular wave functions ψ_m and ψ_m^* are bonding and antibonding molecular orbitals; orbitals of this type, in which the line joining the two nuclei is a symmetry axis for the electron distribution, are known as σ orbitals if bonding and σ^* orbitals if antibonding, so we may alternatively denote them σ_{1s} and σ orbitals. When the two 1s wave functions are added, they reinforce one another everywhere, and especially in the region between the two nuclei; the build-up of electron density there diminishes the internuclear repulsion

and a strong bond results. When one of the two 1s wave functions is subtracted from the other, they exactly cancel in a plane midway between the nuclei, and the molecular wave function changes sign at this nodal plane. This lack of electron density raises the internuclear repulsion, the total energy becomes higher, the two nuclei are not bonded together, and the orbital is described as antibonding.

Pictorial representations of this LCAO method are given in Figs. 1, 2 and 3 In the first of these, the relative energies of 1s molecular orbitals and their constituent atomic orbitals are shown; note that the antibonding orbital is correctly shown as somewhat more destabilised relative to the atomic orbitals than the bonding orbital is stabilised (N is not strictly equal to N*, but is rather smaller, as we mentioned earlier).

In the hydrogen molecule in its ground state, both electrons occupy the σ 1s orbital ; in the hydrogen molecule ion, H⁺₂. formed by the action of an electric discharge on hydrogen at low pressures, only a single electron is in this orbital and the total bonding energy being 269 kJ mol⁻¹ compared with 458 kJ mol⁻¹ for H₂.



Figure 1. The formation of molecular orbitals for H₂.(a) ψ_A and ψ_B for individuals (b) $\psi_A + \psi_B = \psi_m$ (c) Probability function for the bonding orbital, $(\psi_m)^2$. (d) $\psi_A - \psi_B = \psi^*_m$. (e) Probability function for the antibonding orbital, $(\psi_m)^2$.



Figure 2. Another representation of the formation of molecular orbitals for H₂. The σ and σ^* orbitals

Conditions for the combination of atomic orbitals :

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied :

- 1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. It, therefore, means that only a limited number of combinations of atomic orbitals are possible.
- 2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2p_z orbital of one atom can combine with 2p_z orbital of the other atom but not with the 2p_x or 2p_y orbitals because of their different symmetries.
- **3.** The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

TYPES OF MOLECULAR ORBITALS :

Molecular orbitals of diatomic molecules are designated as $\sigma(sigma)$, $\pi(pie)$, $\delta(delta)$ etc.

In this nomenclature, the **sigma** (σ) molecular orbitals are symmetrical around the bond-axis while **pi** (π) molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ 1s and σ^*1s [Fig.(a)]. If internuclear axis is taken to be in the direction, it can be seen that a linear combination of 2p_z - orbitals of two atoms also produces two sigma molecular orbitals designated as $\sigma 2p_z$ and $\sigma^* 2p_z$. [Fig. (b)] Molecular orbitals obtained from 2p_x and 2p_y orbitals are not symmetrical around the bond axis because of the presence of positive lobes plane. Such molecular orbitals, are labelled as π and π^* [Fig. (c)]. A π bonding MO has large electron density above and below the inter nuclear axis. The π^* antibonding MO has a node between the nuclei.

 δ -type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

Difference between π molecular orbitals and the σ orbitals.

- (1) For π overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.
- (2) For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.

(3) The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the inter nuclear line a change in the sign of lobe occurs. The π bonding orbitals are therefore ungerade, where as all σ bonding MO's are gerade. Conversely the antibonding π MO's are gerade while all σ antibonding MO's are ungerade.

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

The energy levels of molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_z) < \sigma^* 2p_z.$

The increasing order of energies of various molecular orbitals for Be2, B2, C2, N2 etc., is :

 $\sigma \ 1s < \sigma^* \ 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ molecular orbital is higher

than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.





Fig. Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.

Electronic configuration and molecular behaviour :

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

- (i) The molecule is stable if N_b is greater than N_a , and
- (ii) The molecule is unstable if N_{b} is less than N_{a}

In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable. N_b is number of electrons in bonding molecular orbitals and N_a is number of electrons in antibonding molecular orbitals.

Bond order

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) = $\frac{1}{2} (N_b - N_a)$

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

Nature of the bond

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

Bond-length

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

Magnetic nature

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N₂ molecule. However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O₂ molecule.

Bonding in some Homonuclear diatomic molecules

1. Hydrogen molecule (H₂) : $H_2 : (\sigma 1s)^2$



This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol⁻¹ and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

2. Helium molecule (He₂) : He₂ : $(\sigma^* 1s)^2 (\sigma^* 1s)^2$



The molecular orbital description of He₂ predicts two electrons in a bonding orbital and two electrons in an antibonding orbital, with a bond order of zero - in other words, no bond. This is what is observed experimentally. The noble gas He has not significant tendency to form diatomic molecules and, like the other noble gases, exists in the form of free atoms. He₂ has a very low binding energy, approximately 0.01J/mol; for comparison, H₂ has a bond energy of 436 kJ/mol.

3. Lithium molecule (Li₂) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$

Its bond order, therefore, is 1/2(4-2) = 1. It means that Li₂ molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li₂, the molecules are known to exist in the vapour phase. The MO model predicts a single Li -Li bond in Li₂, in agreement with gas phase observations of the molecule.

4. Beryllium (Be₂) : $(\sigma^{1}s)^{2} (\sigma^{*}1s)^{2} (\sigma^{*}2s)^{2}$

Be₂ has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He₂, Be₂ is not a stable chemical species. 5. Boron (B₂): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1) (\sigma p_z)^0$ The bond order of B₂ is 1/2(6 - 4) = 1.

Here is an example in which the Molecular orbital model has distinct advantage over the Lewis dot picture, B₂ is found only in the gas phase; solid boron is found in several very hard forms with complex bonding, primarily involving B₁₂ icosahedra. B₂ is paramagnetic. This behaviour can be explained if its two highest energy electrons occupy separate p-orbitals. The Lewis dot model cannot account for the paramagnetic behaviour of this molecule.

 B_2 is also a good example of the energy level shift caused by the mixing of s and p orbitals.

6. Carbon molecule (C₂): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\pi 2p^2_x = \pi 2p^2_y)$ or KK $(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2$

 $(\pi 2p^{2_{x}} = \pi 2p^{2_{y}})$

The bond order of C_2 is 1/2 (8–4) = 2 and C_2 should be diamagnetic.

The simple MO picture of C₂ predicts a doubly bonded molecule with all electrons paired, but with both highest occupied molecular orbitals (HOMOs) having π symmetry.

Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond.

7. Nitrogen molecule (N₂) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$



M.O. Energy level diagram for N₂ molecule

 N_2 has a triple bond according to both the Lewis and the molecular orbital models. The bond order of N_2 is 1/2(10 - 4) = 3. It contains one sigma and two π bonds. Anionic nitrogen species (N₂⁻) : Though 15 electrons but derived from N₂, hence electronic configuration will be according to N₂ Electronic configuration : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 2s)^2 (\pi^2 2p_x^2 = \pi^2 2p_y^2) (\sigma^2 2p_z^2)^2$, $(\pi^* 2p_x)^1$ The bond order of N₂ is 1/2(10 - 5) = 2.5. It is paramagnetic species.

 N_2^+ : Bond order = 2.5, out of N_2^+ and N_2^- , N_2^- is less stable though both have equal bond order but N_2^- has greater number of antibonding electrons.

8. Oxygen molecule (O₂) : O₂ : $(\sigma^{1}s)^{2}$ $(\sigma^{*}1s)^{2}$ $(\sigma^{2}s)^{2}$ $(\sigma^{2}p_{z})^{2}$ $(\pi^{2}p_{x}^{2} = \pi^{2}p_{y}^{2})$ $(\pi^{*}2p_{x}^{1} = \pi^{*}2p_{y}^{1})$



M.O. Energy level diagram for O₂m olecule

 O_2 is paramagnetic. This property, as for B_2 , cannot be explained by the traditional Lewis dot structure , ($\dot{O} = \dot{Q}$) but is evident from the molecular orbital picture, which assigns two electrons to the degenerate π_g^* orbitals. The paramagnetism can be demonstrated by pouring liquid O_2 between the poles of a strong magnet; some of the O_2 will be held between the pole faces until it evaporates. The bond order of O_2 is

 $\frac{1}{2} \begin{bmatrix} N_b - N_a \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 10 - 6 \end{bmatrix} = 2$. So in oxygen molecule, atoms are held by a double bond. Moreover, it may be noted that it contains two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals, therefore, O_2 molecule should be paramagnetic, a prediction that corresponds to experimental observation. Several ionic forms of diatomic oxygen are known, including O_2^+ , and O_2^{2-} . The internuclear O - O distance can be conveniently correlated with the bond order predicated by the molecular orbital model, as shown in the following table.

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
$O^{+}(diaxyaanyl)$	2.5	112.3	1
O_2 (dioxygen)	2.0	120.07	2
O_2^{-} (superoxide)	1.5	128	1
O2 ²⁻ (peroxide)	1.0	149	0

Note : Oxygen-oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unsually long bond distance.

The extent of mixing is not sufficient in O_2 to push the $\sigma_g(2p)$ orbital to higher energy than the $\pi_g(2p)$ orbitals. The order of molecular orbitals shown is consistent with the photoelectron spectrum.

9. Fluorine molecule (F₂): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

The molecular orbital picture of F₂ shows a diamagnetic molecule having a single fluorine-fluorine bond, in agreement with experimental data on this very reactive molecule.

- **10.** Neon molecule (Ne₂) : $(\sigma_1 s)^2 (\sigma_1 s)^2 (\sigma_2 s)^2 (\sigma_2 s)^2 (\sigma_2 p_z)^2 (\pi_2 p_x^2 = \pi_2 p_y^2) (\pi_2 p_x^2 = \pi_2 p_y^2) (\sigma_2 p_z)^2$ All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The Ne₂ molecule is a transient species, if it exists at all.
- Note: HOMO: Highest Occupied Molecular Orbital.

LUMO : Lowest Unoccupied Molecular Orbital

Bond lengths in homonuclear diatomic molecules

Figure shows the variation of bond distance with the number of valence electrons in second-period p block homonuclear diatomic molecules. As the number of electrons increases, the number in bonding orbitals also increases, the bond strength becomes greater, and the bond length becomes shorter. This continues up to 10 valence electrons in N₂ and then the trend reverses because the additional electrons occupy antibonding orbitals. The ions N₂⁺, O₂⁺, O₂⁺, are also shown in the figure and follow a similar trend.



- **Ex-7** Though O₂ molecule is paramagnetic yet it is a colourless gas. Why ?
- Sol. It is because the energy gap between HOMO and LUMO levels in O₂ molecule is so large that radiations of visible light cannot excite a e⁻ from HOMO to LUMO. In fact O₂ gas shows absorption in UV zone. So it is colourless.
- Ex-8 Correct order of bond energy is: (1) $N_2 > N_2^+ > N_2^{--} > N_2^{2--}$ (2) $N_2^+ > N_2^{--} > N_2^{2--} > N_2$ (3) $N_2 > N_2^{--} = N_2^+ > N_2^{2--}$ (4) $N_2^- > N_2 = N_2^+ > N_2^{2--}$ Sol. (1) 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 $N_2 > N_2^+ > N_2^- > N_2^{2-}$ Which of the following species have a bond order of 3? Ex-9 (1) CO (2) CN-(3) NO+ (4) O₂+ Sol. (1,2,3) Species CO, CN⁻, NO⁺ are isoelectronic with 14 electrons to N₂ which has bond order of 3 (i.e. 10 - 43 = 3), so their bond order will be equal to three.
- **Ex-10** Which of the following are diamagnetic? (1) C_2 (2) O_2^{2-} (3) Li₂ (4) N_2^+

Sol. (1,2,3) Species C₂, O₂²⁻, Li₂ have all the electrons paired but N₂⁺ has one unpaired electron in bonding molecular orbital so it is paramagnetic.

Section (J) : Dipole Moment

POLARITY OF BONDS :

In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character.

When a covalent bond is formed between two similar atoms, for example in H₂, O₂, Cl₂, N₂ or F₂ the shared pair of electrons is equally attracted by the atoms. As a result electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond.

As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d) Dipole moment is usually expressed in Debye units (D). The conversion factors are

O 1 D = 3.33564×10^{-30} Cm, where C is coulomb and m is meter.

O 1 Debye =
$$1 \times 10^{-18}$$
 e.s.u. cm.

Further dipole moment is a vector quantity and is depicted by a small arrow with tail on the positive centre and head pointing towards the negative centre. For example the dipole moment of HF may be represented as

+ → + → + → + →

The shift in electron density is represented by crossed arrow () above the Lewis structure to indicate the direction of the shift.

In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. i.e. a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.

$$\frac{DM=P}{DM=Q} = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$$
, where R is resultant dipole moment.

For example of H₂O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5°. Net dipole moment of 6.17×10^{-30} Cm (1D = 3.33564×10^{-30} Cm) is the resultant of the dipole moments of two O—H bonds.



Net Dipole moment, $\mu = 1.85 \text{ D} = 1.85 \times 3.33564 \times 10^{-30} \text{ Cm} = 6.17 \times 10^{-30} \text{ Cm}.$

(A) Diatomic molecules :

(i) Dipole moment is a vector quantity i.e., it has magnitude as well as direction. It is often represented by an arrow with its tail at the positive centre and head pointing towards the negative end

$$(+ \rightarrow -)$$

(ii) As a polar diatomic molecule posses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond e.g. in case of HCI, the molecular dipole moment is equal to the dipole moment of H–CI bond i.e. 1.03 D. Thus.

$$H \xrightarrow{+\delta} C \stackrel{-\delta}{\longrightarrow} \mu = 1.03 D$$

(B) Polyatomic molecules :

(i) As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bonds.

(ii) For example dipole moment of H₂O is 1.84 D which is equal to the resultant dipole moment of two O– H bonds.



(iii) Think about CO_2 molecule though C=O bond is polar due to electronegativity difference but the resultant dipole moment of molecule is zero as the individual dipole moments are of equal moment and opposite sign. This shows that CO_2 is a linear molecule.

(iv) Again in case of symmetrical molecules such as BF₃, CH₄ and CCl₄ the molecular dipole moment is found to be zero. This is due to the fact that individual dipole moments cancels out on account of symmetry of the molecule.



Following compounds have zero dipole moment :
 BF₃,CO₂, SO₃, CF₄, PF₅(g), SF₆, XeF₂, CS₂, CCl₄, PCl₅(g), XeF₄

O Some important orders

HF >	HCI >	HBr >	HI
1.92 D	1.08	0.78	0.38
CH₃CI >	CH ₂ Cl ₂ >	CHCl₃ >	CCI ₄
1.86	1.6	1.0	0

O Usually for disubstituted Benzene order is o > m > p But it all depends on the substituents



Note : For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.





cis - form (low dipole moment)

trans - form (high dipole moment)

 CH_3 C = C CI

O The presence of a centre of symmetry, i, requires that the dipole moment be zero, since any charge on one side of the molecule is canceled by an equal charge on the other side of the molecule.

Thus $[CoF_6]^{3-}$, trans $-N_2F_2$ and the staggered conformer of ferrocene do not have dipole moments.



APPLICATIONS OF DIPOLE MOMENT :

(i) In determining the polarity of bonds :- As μ = q × d. obviously, greater the magnitude of dipole moment, higher will be the polarity of the bond. But in the strict sence, this concept is applicable to molecules containing only one polar bond. Further in case of non polar molecules like H₂, O₂, N₂ etc. the dipole moment is found to be zero. This is because there is no charge separation in these molecules, q = 0

(ii) In the calculation of ionic character :-

- (a) A covalent bond develops a polar character due to the difference in electronegativity of atoms forming the bond.
- (b) If the electronegativity difference between two atoms is large, the bond will be highly polar
- (c) It has been observed that when the electronegativity difference is 1.7, the bond formed between two atoms is 50% ionic and 50% covalent.
- (d) The percentage ionic character of a bond can be calculated from the ratio of the observed dipole moment to the calculated dipole moment (considering 100% ionic character)

Observed dipole moment

i.e. % ionic character = Dipole moment considering 100% ionic character $\times 100$

(iii) Shape or symmetry of molecule :-

Dipole moment is an important factor in determining the shape of molecules containing three or more atoms. For instance if any molecule possesses two or more polar bonds. It will not be symmetrical if it possesses some molecular dipole moment as in case of water ($\mu = 1.84D$) and ammonia ($\mu = 1.49$ D). But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero. This will imply that the molecule is symmetrical e.g. CH₄, CCl₄ etc.

SOME IMPORTANT POINTS ABOUT DIPOLE MOMENT :

	0	A polyatomic	molecule having	polar covalent bonds	but zero dipole moment indicates the
		symmetrical st	ructure of the mo	lecule. e.g. B - F bonds	are polar in BF ₃ but BF ₃ has $\mu = 0$ due to
		its symmetrica	l geometry.		
	0	If molecule hav	ve $\mu = 0$, then it s	hould be linear or having	g symmetrical geometry.
		e.g. linear – C	O2, CS2, BeCl2 (g); symmetrical geome	etry – BF₃, CH₄, PCl₅, SF₅, IF⁊, XeF₄.
	0	If molecule has	s $\mu \neq 0$ then it sho	ould be angular or having	g unsymmetrical geometry.
		SnCl₂	, PbCl₂ , SO₂ , an	gular molecular geomet	ry.
		NH₃, F	l₂O, NF₃, SF₄, H₂S	S, unsymmetrical molect	ular geometry.
	S	olved Ex	amples —		
Ex-11	What sl	nould be the pe	rcentage ionic ch	aracter in CsF when ele	ctronegativity difference is 3.3
	(1) 90.9	1%	(2) 0.09%	(3) 93.3%	(4) 95.7%
Ans.	(1)				
Ex-12	What is	the increasing	order of ionic cha	aracter in H2Se, H2S, H2	D
	(1) H ₂ S	e < H2S < H2O		(2) H2Se > H2S	5 > H₂O
	(3) H ₂ S	$e < H_2S > H_2O$		(4) None of the	ese
Ans.	(1)				
Ex-13	Which o	of the following	molecules should	I not have μ = 0 :	
	(1) H ₂	-	(2) CO ₂	(3) Cl ₂	(4) SO ₂
Ans.	(4)		()		.,
E 4.4	\A/b:ab	f the fellowing		le barra biaban dia da m	
EX-14		of the following	(2) L.O	(2) NU	(4) NE
Ane	(1) ПГ (2)		(∠) Π2 U	(J) INE	(4) INE3
AII5.	(∠)				

Section (K) : Hydrogen bonding

Nitrogen, oxygen and fluorine are the highly electronegative elements. When they are tied to a hydrogen atom to form covalent bond , the electrons of the covalent bond are shifted towards the more electronegative atom. This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is called as hydrogen bond and is weaker than covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as given below : $---H^{\delta_+} - F^{\delta_-} - --H^{\delta_+} - F^{\delta_-} - --H^{\delta_+} - F^{\delta_-}$ Here, hydrogen bond acts as a bridge between atoms which holds one atom by covalent bond and the

other by hydrogen bond. Hydrogen bond is represented by a dotted line (- - -) while a solid line

represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

O Hydrogen bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, N and O is held with weak electrostatic forces by the lone pair of electrons of the electronegative atom i.e. the strongly positive H and the strongly electronegative lone pairs tend to line up and hold the molecules together. Other atoms with high electronegativity, such as Cl ; can also form hydrogen bonds in strongly polar molecules such as chloroform, CHCl₃.

Conditions required for H-bond :

(i) Molecule should have more electronegative atom (F, O, N) linked to H-atom.

- (ii) Size of electronegative atom should be smaller.
- (iii) A lone pair should be present on electronegative atom.

Strength of H-bond :

The strength of H-bond is usually very low (5 - 10 kJ/mol) but in some cases this value may be as high as

50 kJ/mol. The strongest H-bonds are formed by F atoms. Deuterium is more electropositive than H, therefore it also form stronger bonds. The strength of the H-bond can be compared by the relative bond energies and the geometry of the various compounds as given below.

 $F^- + HF \longrightarrow [FHF]^-$; $\Delta H = -161 \pm 8 \text{ kJ mol}^{-1}$

 $(CH_3)_2 CO + HF \longrightarrow (CH_3)_2 CO \dots HF$; $\Delta H = -46 \text{ kJ mol}^{-1}$

 $H_2O + HOH \longrightarrow H_2O \dots HOH$ (ice) ; $\Delta H = -25 \text{ kJ mol}^{-1}$

HCN + HCN \longrightarrow HCN HCN ; $\Delta H = -12 \text{ kJ mol}^{-1}$

The magnitude of H-bonding depends on the physical state of the compounds. H-bonding is maximum in the solid state and minimum in the gaseous state. Thus hydrogen bonds have strong influence on the structure and properties of the compounds.

O Order of H-bond strength



Types of Hydrogen Bonds :

(A) Intramolecular H-Bonding :

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule i.e., it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.

(b)

(c)



(a) o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.



It has lower boiling point (i.e. more volatile) than its para-derivative (where association of molecules takes place using intermolecular H-bonding) because it exists as discrete molecules.



Nickel dimethyl glyoximate (a chelate)

Extra stability of the complex is because of intramolecular hydrogen bonding in addition to the chelating effect.



Chloral hydrate is stable only on account of intramolecular hydrogen bonding.



Persulphate ion (HSO5-)

K₁ of peroxomono sulphuric acid (i.e., caros acid) is greater than K₂. After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult.



The intramolecular hydrogen bonding attributes the stability of enolic form of aceto acetic ester.

Necessary conditions for the formation of intramolecular hydrogen-bonding :

- (a) the ring formed as a result of hydrogen bonding should be planar.
- (b) a 5- or 6- membered ring should be formed.
- (c) interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

(B) Intermolecular H-Bonding :

Exists between the negative and positive ends of different molecules of the same or different substances i.e., it is formed between two different molecules of the same or different compounds.

(a) In water molecules

Due to polar nature of H₂O there is association of water molecules giving a liquid state of abnormally high boiling point.



- O When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules. Due to this volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence, volume increases and hence density decreases. Thus, water has maximum density at 4°C.
- (b) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain (HF)ⁿ in both the solid and also in the liquid.



Some hydrogen bonding also occurs in the gas, which consists of a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$, and monomeric HF.

Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula M[HF₂]; in KHF₂, for example, an X-ray diffraction study together with a neutrons diffraction study shows that there is a liner symmetrical anion having an over all, F–H–F distance of 2.26 Å, which may be compared with the H–F bond length of 0.92Å in hydrogen fluoride monomer.

- (c) There is also similar H-bonding in alcohol (R—OH) ammonia (NH₃) and phenol (C₆H₅OH) molecules.
- (d) Carboxylic acid dimerises in gaseous state due to H-bonding



(e) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H₂O and R—OH molecules).

However isomeric ether is less soluble in water due to less polar nature of ether.



In Na⁺HCO₃⁻, the HCO₃⁻ ions are linked in to an infinite chain through intermolecular H-bonding.

Ex-15 C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.

$$CH_{3}$$

$$C = O: \dots H + \delta$$

$$CH_{3}$$

$$C = O: \dots H + \delta$$

$$C = C - H$$

$$(sp)$$

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 H₂O 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 H₂O.

Ex-16 Why SnCl₂.2H₂O readily loses one molecule of water at 80°C ?

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- **Sol.** One water molecule is coordinated to lone pair of electrons on SnCl₂ and the other is hydrogen bonded to coordinated water molecules .
- **Ex-17** Why crystalline sodium peroxide is highly hygroscopic in nature.
- **Sol.** Na₂O₂ forms stable hydrates on account of H-bonding.

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

Ex-18 Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.

Sol.

In the trimethyl compound the O–H group is hydrogen bonded to Me₃NH 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.

Section (L) : Intermolecular forces

Intermolecular forces (Van der Waal's Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

- (a) Ion-dipole attraction (b) Dipole-dipole attraction :
- (c) Ion-induced dipole attraction (d) Dipole-induced dipole attraction :
- (e) Instantaneous dipole- Instantaneous induced dipole attraction : (Dispersion force or London forces)

strength of van der Waal's forces a > b > c > d > e

(a) Ion-dipole attraction : Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion - dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as Na(OH₂)_{x⁺} and F(H₂O)_{y⁻} (for solution of NaF in H₂O) are found. Hence this force is responsible for hydration.

N a⁺ · · · · · ·
$$O^{\delta}$$
 $H^{\delta^{*}}$

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(b) **Dipole-dipole attraction :** This is electrostatic attractions between the oppositively charged ends of permanent dipoles. Exists between polar molecules and due to this force gas can be liquified.

 $H^{\delta} - CI^{\delta}$ $H^{\delta} - CI^{\delta}$

- (c) **Ion-induced dipole attraction :** Exists between ion and non-polar molecules (e.g., an atom of a noble gas such as Xenon).
- (d) Dipole-induced dipole attraction : Exists between polar and non-polar molecules.

(+

н[®] — С́Т

distribution.

Head to tail arrangement of dipoles

 $\begin{array}{c} \delta \delta \delta^{\dagger} \\ C \\ C \\ C \\ \end{array}$

Antiparallel arrangement of dipoles

(polar) (non-polar)
 (e) Instantaneous dipole- Instantaneous induced dipole attraction : Exists among the non-polar molecules like H₂, O₂, Cl₂ etc. in solid or liquid states. Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary inbalances in electron

London forces are extremely short range in action and the weakest of all attractive forces. The London forces increase rapidly with molecular weight, or more properly, with the molecular volume and the number of polarizable electrons.





- O Strength of vander waal force \propto molecular mass.
- O van der Waal's force \propto boiling point.

Solved Examples

Ex-19 Give the order of boiling point of following

Cl₂, HCl

 Sol.
 Cl₂-Cl₂
 < HCl - HCl</th>
 (boiling point)

 dispersion force
 dipole-dipole attraction

 As dipole-dipole attraction is stronger than dispersion force.

- **Ex-20** Arrange the inert gases, according to their increasing order of boiling points
- Sol.He < Ne < Ar < Kr < Xe</th>(boiling point)Because strength of van der Waal's force increases down the group with increase in molecular mass.

Section (M) : 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 (3σ s and 3σ *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.



Fig. 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 $3 \times 6.07 \times 10^{23}$ 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 $4 \times 6.02 \times 10^{23}$ orbitals. Because each orbital can hold two electrons, the resulting combination of bands is only one-eighth full.



Fig. Overlapping of a half-filled "3s" band with an empty "3p" band of NaN 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.



Fig. 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-energy 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

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

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

- 1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :
 - (a) SiSi bond in $Cl_3SiSiCl_3$ (b) SiCl bond in $Cl_3SiSiCl_3$
 - (c) CaF bond in CaF₂ (d) NH bond in NH_3
- **Sol.** (a) Covalent, due to identical electronegativity.
 - (b) Covalent, due to less electronegativity difference.
 - (c) lonic, due to more electronegativity difference.
 - (d) Covalent, due to nearly similar electronegativity.
- 2. (a) Which one has highest and lowest melting point and why?

NaCl KCl RbCl Cs

(b) Why melting points of cesium halide (CsX) decrease in the order given below ?

CsF > CsCl > CsBr > CsI.

Sol. (a) NaCl will have highest lattice energy on account of the smaller Na⁺ while CsCl has lowest lattice energy on account of the larger Cs⁺. Hence NaCl has highest melting point and CsCl has lowest melting point.

(b) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.

- **3.** Which of the compounds MgCO₃ and ZnCO₃ is thermally more stable ? Explain.
- Sol. Mg⁺² has less polarising power due to inert gas configuration while Zn⁺² has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn²⁺ with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the CO₃²⁻ ion and as such the metal carbonate (ZnCO₃) gets readily decomposed into CO₂ and the oxide of the metal, ZnO. Thus ZnCO₃ is less stable than MgCO₃.
- 4. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?
- **Sol.** It exists as HCI (bond formed by equal sharing of electrons) but in aqueous solution ionises as H⁺ (or H₃O⁺) and Cl⁻ due to polarity of HCI.

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- 5. Which type of hybridisation is found in H_3O^+ ?
- Sol. According to steric no. rule

Steric number = Number of bond pair(s) + number of lone pair(s) at central atom

$$\dot{H}$$
 So, steric number = 3 + 1 = 4.

Thus the hybridisation of oxygen in H_3O^+ is sp^3 .

6. Which of the following will be strongest Lewis base ?

(1)
$$CH_3 CN$$
 (2) $CH_3 NH_2$ (3) N_2 (4) None of these

- Sol. (2) In CH₃ NH₂, hybridisation of N is sp³ while in CH₃ CN hybridisation of N is sp. N₂ is also sp hybridised. We know that in hybridisation, as s-character increases the electronegativity of atom also increases. Due to this tendency the release of lone pair of electrons becomes some what difficult. In methyl amine the nitrogen is in sp³ hybridisation and therefore the donation of the lone pair of electron will be quite easier; so it is strongest Lewis base.
- 7. Which is **incorrect** statement ?

(1) In $CF_2 = C = CF_2$ molecule all the four fluorine atoms are not in the same plane.

(2) Ka₂ of fumaric acid is more than Ka₂ of maleic acid due to intra molecular hydrogen bonding in maleic acid.

- (3) The O O bond length in $O_2[AsF_4]$ is longer than KO_2 .
- (4) The bond angle order in halogen S halogen is $OSF_2 < OSCI_2 < OSBr_2$
- **Ans.** (3)

$$\begin{array}{c} \mathsf{F}_{\mathsf{M}} & \mathsf{C} \xrightarrow{\mathsf{p}_{z}} & \mathsf{C} \xrightarrow{\mathsf{p}_{y}} & \mathsf{C} \\ \mathsf{F}_{\mathsf{x}} & \mathsf{x} + \mathsf{p}_{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} & \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} \\ \mathsf{x} \\ \mathsf{$$

Sol.

(1)

(2)

As both carbon atoms are in different planes, all the four fluorine atoms are not in the same plane.



Due to intramolecular hydrogen bonding the maleate ion gets stabilized and thus removal of second hydrogen becomes quite difficult.

(3) $O_2[AsF_4] = O_2^+$ B.O = 2.5 KO₂ = O₂⁻ B.O = 1.5 1

Bond order \propto ; bond length so O₂⁺ has smaller bond length than O₂⁻

- (4) Greater the size of the halogen atoms greater will be the steric repulsions and thus larger will be
- the bond angles.
- 8. Why BeF₂ has zero dipole moment whereas H₂O has some dipole moment ?
- **Sol.** BeF₂ has linear molecule and H₂O has bent molecule.



- 9. Super oxides are coloured and paramagnetic why ?
- **Sol.** Super oxides contain one unpaired electron in anti bonding molecular orbital and are coloured due to transition of HOMO orbital electron within visible region.
- **10.** Of the species O_2^+, O_2^-, O_2^- and O_2^{2-} which would have the maximum bond strength ?
- **Sol.** O_{2^+} has higher bond order i.e. 2.5 than $O_2(2)$ and $O_{2^-}(1.5)$ and bond strength is directly proportional to bond order.
- **11.** A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is equal to 1.0Å then the fraction of an electronic charge on each atom is :

(1) 25% (2) 37% (3) 52% (4) 42%

- **Ans.** (1)
- **Sol.** Assuming complete charge transfer then dipole moment = $(4.8 \times 10^{-10} \text{ esu}) (10^{-8} \text{ cm}) = 4.8 \text{ D}$

so % ionic character = $\frac{1.2}{4.8} \times 100 \% = 25\%$

- **12.** The dipole moment of KCl is 3.336×10^{-29} Coulomb meter. The interionic distance in KCl is 2.6Å. Find the % ionic character in KCl.
- **Sol.** The theoretical dipole moment in KCI = $e \times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$ C meter experimental dipole moment

% ionic character = theoretical dipole moment
$$\times 100 = (3.336 \times 10^{-29}/4.1652 \times 10^{-29}) \times 100$$

13. The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67 × 10⁻⁸ cm. Calculate the percentage ionic character in KCI molecule.

CHEMISTRY FOR JEE

Sol. Dipole moment of compound would have been completely ionic

= (4.8 × 10⁻¹⁰ esu) (2.67 × 10⁻⁸ cm) = 12.8 D
% ionic character =
$$\frac{10.0}{12.8}$$
 × 100% = 78.125 % ~ 78% Ans.

- 14. CO forms weak bonds to Lewis acid such as BF₃. In contrast CO forms strong bonds to transition metals. Why explain ?
- $CO \xrightarrow{\sigma} BF_3$ Sol.

so

Transition metal $\stackrel{\pi}{\overleftarrow{\sigma}}$ CO

This is called synergic interaction and because of it the bond between CO and transition metal is stronger.

- 15. SnCl₄ has melting point - 15°C where as SnCl₂ has melting point 535°C. Why?
- Sol. According to Fajan's rule, as charge on cation increases its polarising power increases resulting in to the greater polarisation of anion. Thus covalent character increases and melting point decreases.
- 16. Inorganic benzene is more reactive than organic benzene. Why?
- Sol. Inorganic benzene (N₃B₃H₆) contains polar covalent B–N bonds while benzene (C₆H₆) contains non-polar covalent C-C bonds.
- **SbCl**₃ SbBr₃ Sbl₃ (a) (b) Pl₃ Sbl₃ Asl₃ Br CI В́г CI Sol. (a)

97.1°

Cl, the most electronegative of the halogens in this series, pulls shared electrons the most strongly away from Sb, reducing electron density near Sb. The consequence is that the lone pair exerts the strongest influence on shape in SbCl₃.

99°



Phosphorus is the most electronegative of the central atoms. Consequently, it exerts the strongest pull on shared electrons, concentrating these electrons near P and increasing bonding pair-bonding pair

17. Which compound has the smallest bond angle in each series ?

98.2°

repulsions-hence, the largest angle in PI₃. Sb, the least electronegative central atoms, has the opposite effect : Shared electrons are attracted away from Sb, reducing repulsions between the Sb–I bonds. The consequence is that the effect of the lone pair is greatest in SbI₃, which has the smallest angle. Atomic size arguments can also be used for these species. Larger outer atoms result in larger angles ; larger central atoms result in smallest angles.

- **18.** Why NO₂⁺ and I_{3}^{-} are linear species ?
- **Sol.** In NO₂⁺ the N has sp hybridisation ; so it is linear O = N = O

In I_3^- there are 5 electron pairs around central iodine atom (3 lone pairs and 2 bond pairs). The hybridisation of iodine is thus sp³d. To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.



- **19.** Draw an electron dot structure for Br₃⁻. Deduce an approximate value of the bond angle.
- **Sol.** In Br₃⁻ there are 5 electron pairs around central bromine atom (3 lone pairs and 2 bond pairs). The hybridisation of bromine is thus sp³d. To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.



- **20.** PCl₅ has the shape of a trigonal bipyramidal where as IF₅ has the shape of square pyramidal. Explain.
- **Sol.** In PCI₅ there are 5 electron pairs around central phosphorus atom and all are bond pairs. The hybridisation of phosphorus is thus sp³d. To have minimum repulsions between bp-bp it acquires trigonal bipyramidal shape as shown below.



In IF₅ there are 6 electron pairs around central iodine atom. The hybridisation of iodine is thus sp³d.



6 electron pairs contain 5 bond pairs and one lone pair so it will be square pyramidal to have minimum repulsions between lp-bp and bp-bp.

- 21. Why axial bonds of PCI₅ are longer than equatorial bonds ?
- **Sol.** This is due to greater repulsion on the axial bond pairs by the equatorial bond pairs of electrons.



- **22.** (a) NCI₅ is not possible but PCI₅ is possible. Why ?
 - (b) F_{3}^{-} does not exist but I_{3}^{-} , Br_{3}^{-} exist. Why ?
 - (c) SCI $_6$ does not exist but SF $_6$ exists. Why ?
- **Sol.** (a) This is because of the absence of d-orbitals in nitrogen for sp^3d^2 hybridisation.
 - (b) Because of the absence of d-orbitals in fluorine it can not expand its covalency.
 - (c) Bigger size of chlorine can not be accommodated around sulphur atom because of steric crowding.