# **Chemical Bonding**

## Chemical Bond :

The attractive force which holds various constituents such as atoms, ions etc., together in different chemical species is called a chemical bond.

A chemical species i.e. molecule will only be formed if it is more stable and has a lower energy than the individual atoms.

In the formation of a chemical bond, only the electrons of the outermost shell of an atom are involved. In the process each atom attains a stable outer electronic configuration of inert gases.

**KOSSEL-LEWIS APPROACH**: Lewis postulated that atoms achieve the stable octet (i.e. 8 electrons in their outer most shells), when they are linked by chemical bonds. This can happen (i) by the transfer of electron(s) from one atom to another and (ii) by the sharing of a pair of electrons between the atoms.

**Lewis symbols** : In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols. For example, the Lewis symbols for the elements of second period are as follow :



SIGNIFICATION OF LEWIS SYMBOLS : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons help to calculate the common or group valence of the elements.

The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.

## Kossel put forward the following facts with respect to chemical bonding.

- (i) In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.
- (ii) The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.
- (iii) The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium) have a particularly stable outer shell configuration of eight (octet) electrons, ns<sup>2</sup> np<sup>6</sup>.

(iv) The negative and positive ions are stabilized by electrostatic attraction.

The bond formed, as a result of the electrostatic attraction between the positive and negative ions is termed as the ionic bond or the electrovalent bond. The electrovalence is thus equal to the number of unit charge (s) on the ion. Kossel's postulations provide the basis for the concepts regarding ion - formation by electron transfer and the formation of ionic crystalline compounds.

#### Ionic or Electrovalent Bond :

It is cleared from the Kossel and Lewis approach that the formation of an ionic compound would primarily depends upon :

\* The ease of formation of the positive and negative ions from the respective neutral atoms.

\* The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

## Conditions for the formation of ionic compounds :

- (i) Electronegativity difference between two combining elements must be larger.
- (ii) Ionization enthalpy  $(M(g) \rightarrow M^{+}(g) + e^{-})$  of electropositive element must be low.
- (iii) Negative value of electron gain enthalpy (X (g) +  $e^- \rightarrow X^-(g)$ ) of electronegative element should be high.
- (iv) Lattice enthalpy  $(M^+(g) + X^-(g) \rightarrow MX(s))$  of an ionic solid must be high.

## 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.



## General properties of ionic compounds :

- (a) **Physical state :** At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.
- (b) **Isomorphism :** Simple ionic compounds do not show isomerism but isomorphism is their important characteristic. Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.

e.g. , FeSO₄ .7H₂O | MgSO₄ . 7H₂O

## Conditions for isomorphism

(i) The two compounds must have the same formula type e.g.,  $MgSO_4 \& ZnSO_4$ ;  $BaSO_4 \& KMnO_4$  are isomorphous because they have same formula type. All alums are isomorphous because they have same general formula :

 $M_2SO_4 \cdot M_2' (SO_4)_3 \cdot 24H_2O$ M = monovalent ; M' = trivalent

- (ii) The respective structural units, atoms or ions need not necessarily be of same size in the two compounds but their relative size should be little different.
- (iii) The cations of both compound should be of similar shape or structure (isostructural). Similarly anions of both compounds should be isostructural.
  - (a)  $SO_4^{2-}$  and  $MnO_4^{-}$  have same shape i.e. tetrahedral, so isomorphous.



(b) NaNO<sub>3</sub> & NaClO<sub>3</sub> they have same formula type yet they are not isomorphous because NO<sub>3</sub><sup>-</sup> is trigonal planar but ClO<sub>3</sub><sup>-</sup> pyramidal.

$$-0$$
  $NO_{3}^{-}$  (sp<sup>2</sup>)  $O_{0}^{-}$   $O_$ 

(iv) The respective structural units should have same polarisation property.

#### (c) Electrical conductivity :

lonic solids are almost non-conductors. However they conduct a very little amount of current due to crystal defects. All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

## (d) Solubility of ionic compounds :

Soluble in polar solvents like water which have high dielectric constant

## 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:

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.

e.g.	BeCl <sub>2</sub>		n. CaCl <sub>2</sub>	SrCl <sub>2</sub>	BaCl <sub>2</sub>	
Size	Size of cation increases		arisation decreases	Covalent	character decreases	



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

Resonance

# Solved Examples Example-1. AgCl is colourless whereas AgI is yellow, because of : (A) Ag<sup>+</sup> have 18 electron shell to screen the nuclear charge. (B) Ag<sup>+</sup> shows pseudo inert gas configuration. (C) distortion of l<sup>-</sup> is more pronounced than Cl<sup>-</sup> ion. (D) existence of d – d transition. Solution. (C), the bigger anions are more polarised and hence their electrons get excited by partial absorption of visible light.

## **Covalent Bond :**

(i)

The **Lewis-Langmuir theory** can be understood by considering the formation of the chlorine molecule,  $Cl_2$ . The Cl atom with electronic configuration,  $[Ne]^{10} 3s^2 3p^5$ , is one electron short of the argon configuration. The formation of the  $Cl_2$  molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both

$$: \ddot{\mathbb{C}}^{I} + : \ddot{\mathbb{C}}^{I} \longrightarrow : \ddot{\mathbb{C}}^{I} : \ddot{} : \ddot{\mathbb{C}}^{I} : \ddot{} : \ddot{$$

Figure-2

chlorine atoms attain the outer shell octet of the nearest nobe gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.

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

- Each bond Is formed as a result of sharing of an electron pair between the atoms.
- (ii) Each combining atom contributes at least one electron to the shared pair.
- (iii) The combining atoms attain the outer- shell noble gas configurations as a result of the sharing of electrons. Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:



## Figure-3

Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds between atoms. The formation of multiple bonds involves the sharing of more than one electron pair between two atoms. If two atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.



Double bonds in CO<sub>2</sub> molecule

**Kesonance** 



#### Figure-4

When combining atoms share three electron pairs as in the case of two nitrogen atoms in the  $N_2$  molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



#### Figure-5

#### Lewis Representation of Simple Molecules (the Lewis Structures)

The Lewis dot structures can be written by adopting the following steps : The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the  $CH_4$  molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms).

For anions, each negative charge would result in to addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the  $CO_3^{2-}$  ion, the two negative charges Indicate that there are two additional electrons than those provided by the neutral atoms. For NH<sub>4</sub><sup>+</sup> ion, one positive charge indicates the loss of one electron from the group of neutral atoms. Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound, it is easy to distribute the total number of electrons as bonding shared pairs between the atoms In proportion to the total bonds.

### TO DECIDE THE CENTRAL ATOM

- (1) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF<sub>3</sub> and CO<sub>3</sub><sup>2-</sup>, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- (2) Generally the atom which is/are less in number acts as central atom.
- (3) 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).
- (4) 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 Table-1

Molecule / Ion	Le	wis Representation
H <sub>2</sub>	H : H*	H – H
O <sub>2</sub>	:Ö::Ö:	:Ö=Ö:
O <sub>3</sub>	0. 0. O.	:0 <u>0:   </u>
$NF_3$	:F:N:F: :F:	:FNF.: .F.:
CO <sub>3</sub> <sup>2-</sup>	::::::::::::::::::::::::::::::::::::::	$\begin{bmatrix} :O:\\ :O:\\ :O-C-O:\\ \end{bmatrix}^{2-}$
HNO3	Ö::N:Ö:H : <u>Ö:</u>	Ö = Ň – Ö –H I : <u>O:</u>

## Solved Examples

Example-2. Solution. Write the Lewis structure of the nitrite ion,  $NO_2^{-}$ .

**Step 1.** Count the total number of valence electrons of the nitrogen atom , the oxygen atoms and the additional one negative charge (equal to one electron).

$$5 + (2 \times 6) + 1 = 18$$
 electrons

**Step 2.** The skeletal structure of  $NO_2^-$  is written as : O N O

**Step 3.** Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This , however , does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.

## **Coordinate Bond (Dative Bond):**

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.



## Formal Charge :

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be 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. It is expressed as :





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:

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

## 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.

## 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, BeH<sub>2</sub> and BCl<sub>3</sub>.

CI Li CI H:Be:H CI:B:CI Some other such compounds are AICI, and BF,.

## 2. Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide. NO<sub>2</sub>, the octet rule is not satisfied for all the atoms

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

## 3. The expanded octet

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.



Resonance

Some of the examples of such compounds are:  $PF_5 SF_6$ ,  $H_2 SO_4$  and a number of coordination compounds.



10 electrons around the P atom 12 electrons around the S atom 12 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.

#### 4. Other drawbacks of the octet theory

- (i) 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  $XeF_2$ ,  $KrF_2$ ,  $XeOF_2$  etc.,
- (ii) This theory does not account for the shape of molecules.
- (iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

#### 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  $H_2$  (435.8 kJ mol<sup>-</sup>, 74 pm) and  $F_2$  (150.6 kJ mol<sup>-</sup>, 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  $N_A - e_A$  and  $N_B - e_B$ .

(ii) nucleus of one atom and electron of other atom i.e.,  $N_A - e_B N_B - e_A$ .

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.).



Figure-6- Forces of attraction and repulsion during the formation of H, 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 H<sub>2</sub> molecule.



**Figure-7.** 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.

#### **Directional Properties of Bonds**

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like  $CH_4$ ,  $NH_3$  and  $H_2O$ , etc. in terms of overlap and hybridisation of atomic orbitals.

#### Overlapping of Atomic Orbitals

When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/ heteronuclear diatomic molecules and polyatomic molecules. In the case of polyatomic molecules like  $CH_4$ ,  $NH_3$  and  $H_2O$ , the VB theory has to account for their characteristic shapes as well. We know that the shapes of  $CH_4$ ,  $NH_3$ , and  $H_2O$  molecules are tetrahedral, pyramidal and bent respectively.



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Figure-8. Positive , negative and zero overlaps of s and p atomic orbitals

## Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping : (i) sigma( $\sigma$ ) bond, and (ii) pi ( $\pi$ ) bond

(i) Sigma (σ) bond : This type of covalent bond is formed by the end to end (hand-on) overlap of bonding orbitals along the internuclear 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 :



(ii)  $pi(\pi)$  bond : In the formation of  $\pi$  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 overlapping 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)

Solved Examples -

III

N

Example-3.

What are the total number of  $\sigma \& \pi$  bonds in tetracyanomethane.

Solution

 $N \equiv C - \dot{C} - C \equiv N \qquad (in triple bond = \frac{\pi}{\sigma})$ 

From the structure it is clear that it has 8  $\sigma$  and 8  $\pi$  bonds.

## 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.
- (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.
- (v) 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  $(\ell p)$  - lone pair  $(\ell p)$  > lone pair  $(\ell p)$  - 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 - 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).

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

Molecule type       No.of pairs       No.of lone pairs       Arrangement of electron pairs       Shape       Examples         AB,E       2       1       Image: Book of the second se
AB,E21 $\overrightarrow{B}$ BentSO, 0,AB,E31 $\overrightarrow{B}$ $\overrightarrow{B}$ $\overrightarrow{Trigonal}$ NH;AB,E22 $\overrightarrow{B}$ BentH <sub>2</sub> OAB,E41 $\overrightarrow{B}$ See sawSF <sub>4</sub> AB,E32 $\overrightarrow{B}$ T-shapeCIF <sub>3</sub> AB,E51 $\overrightarrow{B}$ $\overrightarrow{B}$ SquareAB,E42 $\overrightarrow{B}$ $\overrightarrow{B}$ SquareAB,E,42 $\overrightarrow{B}$ $\overrightarrow{B}$ $\overrightarrow{B}$ AB,E,42 $\overrightarrow{B}$ $\overrightarrow{B}$ $\overrightarrow{B}$ AB,E,4333 $\overrightarrow{A}$ AB,E,4333AB,E,E,43
AB,E31Image: Big
$AB_2E_2$ 22 $B_B$ Bent $H_2O$ $AB_4E$ 41 $B_B$ $B_B$ $Beet$ saw $SF_4$ $AB_4E_2$ 32 $B_B$ $T$ -shape $CIF_3$ $AB_4E_2$ 51 $B_A$ $B_B$ $Square$ pyramidal $BrF_5$ $AB_4E_2$ 42 $B_A$ $B_B$ $Square$ planar $XeF_4$
$AB_{4}E$ 41 $\vdots$ $B_{B}$ See saw $SF_{4}$ $AB_{3}E_{2}$ 32 $B_{-A}$ $T_{-shape}$ $CIF_{3}$ $AB_{5}E$ 51 $B_{A}$ $B_{B}$ $Square$ pyramidal $BrF_{5}$ $AB_{4}E_{2}$ 42 $B_{-A}$ $B_{-A}$ $Square$ planar $XeF_{4}$
$AB_3E_2$ 32 $B - A$ T-shape $CIF_3$ $AB_5E$ 51 $B - A$ $AB_5E$ 51 $B - A$ $AB_4E_2$ 42 $B - A$ $AB_4E_2$ 42 $B - A$ $AB_4E_2$ 42 $B - A$ $AB_4E_2$ 42 $B - A$ $A - A$
AB <sub>3</sub> E     5     1     B     AB     Square pyramidal     BrF <sub>5</sub> AB <sub>4</sub> E <sub>2</sub> 4     2     B     B     B     Square planar     XeF <sub>4</sub>
AB <sub>4</sub> E <sub>2</sub> 4 2 B A B B A B B A B B A B B A B B A B B A B B A B B B A B B

Shapes of Molecules containing Bond Pair and Lone Pair
Table-4

Molecule type	No.of bonding pairs	No.of lone pairs		Shape	Reason for the shape acquired
AB <sub>2</sub> 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°.
AB₃E	3	1	H 107° H	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 $107^{\circ}$ to $109.5^{\circ}$ .
					,005
	2	2	Н 104.5° Н	Bent	The shape is distored tetrahedral or angular. The reason is Ip-Ip repulsion is more than Ip-bp repulsion. Thus , the angle is reduced to 104.5° from 109.5°.
				~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	
AB₄E	4	1 (i		See- Ir saw so Ir th a si	n (i) the lp is present at axial position o there are three lp-bp repulsion at 90°. n (ii) the lp is an equatorial position, and here are two lp-bp repulsions. Hence , rrangement (ii) is more stable. The shape hown in (ii) is called as a distorted etrahedron, a folded square or a see-saw.
		(i		More stable)	
AB <sub>3</sub> E <sub>2</sub>	3	2		T–shap	e 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).
	ò	(ii) F			

• The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of pblock 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 2	Examples						_
Example-4.	Use the VS (a) XeF <sub>2</sub>	EPR model to pr (b) C	edict the g CIO <sub>3</sub> <sup>-</sup>	geometry of t	he following	<b>]</b> :	2	
Solution	Species	Structure						
(a)	XeF <sub>2</sub>		minim	lone pairs o num repulsior	occupy the e n. Thus it is I	equatorial pos inear.	itions to have	
(b)	CIO3-			To minimiz bond, spec	e the repuls ies acquires	ion between lo s trigonal pyra	one pair and doubl midal.	е
Example-5.	Discuss the	bond angle in ca	bonyl hali	des $COF_2$ , C	$OCl_2$ , $COBr_2$	2, COI2		
Solution	F Bond angle	$\begin{array}{c} O \\ O $	Q CI CI CI₂ < CO	$ \begin{array}{c}                                     $		S		
	Double bond bond angle of because of h decreases re	ls require more ro lecrease maximu igh electronegativ epulsion between	om than si m in COF <sub>2</sub> ity of fluori bond pairs	ingle bonds. H as bond pairs ne. As size of I s increases ar	lence C = O g of electrons halogen atom nd therefore (	group compres are more close is increase and θ increase.	ses the molecule a r to the fluorine ator their electronegativ	nd ns ity
Example-6.	Compare bo	ond angle of $OF_2$	, $Cl_2O$ and	Br <sub>2</sub> O.				
Solution	OF <sub>2</sub>	F F	Cl <sub>2</sub> O	CI CI	Br <sub>2</sub> O	Br Br		
	Bond pairs of fluorine). So from 109.5 <sup>0</sup> electronega CI—O—Cl in	of electrons are r the $\ell p - \ell p$ repulsi 0. In Cl <sub>2</sub> O, the b tivity of oxygen. Increases to $\approx 1116$	nore close on is more ond pair a So the bp due to bp	er to the fluori than bp - bp. are more clo o - bp repulsi - bp repulsior	ne atoms (b Thus the F— ser to the c on is more to and repulsion	ecause of hig O—F bond an oxygen atom I than ℓp - ℓp. on between lai	h electronegativity gle decreases to 10 because of the hi Thus the bond ang ger Cl atoms.	of )2º gh gle

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

## 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  $BeCl_2$  is linear,  $BF_3$  is planar,  $CH_4$  is tetrahedral,  $NH_3$  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 sp<sup>3</sup> 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.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
   These hybrid orbitals are directed in space in some preferred direction to have minimum
  - 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 atom

 $(2s^2 2p_x^1 2p_y^1 2p_z^1)$  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 take 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  $e^-$  (ClO<sub>2</sub>, NO, NO<sub>2</sub>), free radicals and compounds like B<sub>2</sub>H<sub>6</sub> which involve 3 centre 2e<sup>-</sup> bond (banana bond).



**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 central 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

**BeCl<sub>2</sub>**: The ground state electronic configuration of Be is 1s<sup>2</sup> 2s<sup>2</sup>. In the excited state one of the 2s-electrons 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.



Figure-11 (A) Formation of sp hybrids from s and p orbitals; (B) Formation of the linear  $BeCl_2$  molecule.

### Examples of SP hybridisation.

- (a)  $-C \equiv H C \equiv N$ ,  $H C \equiv C H$
- (b) = C = O = C = O  $H_2C = C = CH_2$
- (c)  $N_3^-$  (azide ion), BeF<sub>2</sub>, HgCl<sub>2</sub>, NO<sub>2</sub><sup>+</sup> (nitronium ion), N<sub>2</sub>O

**Note :**  $\ln N_3^-$  there is a total of two  $\sigma$  and two  $\pi$  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.



**sp<sup>2</sup> hybridisation :** In this hybridisation there is involvement of one s and two p-orbitals in order to form three equivalent sp<sup>2</sup> hybridised orbitals.

For example, in  $BCl_3$  molecule, the ground state electronic configuration of central boron atom is  $1s^22s^22p^1$ . 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 a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B–Cl bonds. Therefore, in BCl<sub>3</sub>, the geometry is trigonal planar with CIBCl bond angle of 120°.





Where A = central atom, B = side atom, L = lone pair of  $e^{-1}$ 

**sp**<sup>3</sup> **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 sp<sup>3</sup> hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp<sup>3</sup> hybrid orbital. The four sp<sup>3</sup> hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp<sup>3</sup> hybrid orbital is 109.5° as shown in figure.



The structure of NH<sub>3</sub> and H<sub>2</sub>O molecules can also be explained with the help of sp<sup>3</sup> hybridisation. In NH<sub>3</sub>, the valence shell (outer) electronic configuration of nitrogen in the ground state is  $2s^2 2p_x^{-1} 2p_y^{-1} 2p_z^{-1}$  having three unpaired electrons in the sp<sup>3</sup> 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.

Example

Figure-14. Formation of NH, molecule Н н In case of H<sub>2</sub>O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp<sup>3</sup> hybridisation forming four sp<sup>3</sup> hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp<sup>3</sup> 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. Figure-15. Formation of H<sub>2</sub>O molecule  $H_2O$ Steric No. = 4 Geometry = tetrahedral Ideal bond angle = 109° 28' Table-5 Type AB, AB, L AB, L ABL, tetrahedral V-shape or bent Shape pyramidal Linear -OCI Example CH₄ XeO<sub>2</sub> OBr, Some other Examples of sp<sup>3</sup> hybridisation (a) Be Ο Re steric number = 4 (i.e.  $sp^3$ ) BeCl<sub>2</sub> (s) 11 0 |1↓ В BF,⁻ **B** = (b) SD<sup>°</sup>hvbridisatior , diamond,  $CCI_4$ ,  $:CH_3^{\Theta}$ ; (C) С Ο  $\mathbf{S}iCl_{4}$ ,  $SiO_{2}$ , Silicates etc. (d) S (e) NH<sub>2</sub><sup>-</sup> (amide ion) V-shape sp³ sp³ H N→N√  $NH_2 - NH_2$  or  $N_2H_4$  (hydrazine) Ο 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.

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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  $p\pi - d\pi$  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 SiO, is a covalent network solid like diamond

Ο

 $P_4O_6$ 



O Structures of cyclic silicates : [Si<sub>3</sub>O<sub>0</sub>]<sup>6-</sup>



**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 B<sub>2</sub>H<sub>6</sub>

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 sp<sup>3</sup> 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.

0

H<sub>2</sub>O<sub>2</sub>



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  $\approx 94^{\circ}$ ) 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.



## Hybridization Involving d-orbital :

Type of 'd' or	bital involved
sp³d	d <sub>z2</sub>
sp <sup>3</sup> d <sup>2</sup>	$d_{x^2-y^2} \& d_{z^2}$
2 -12	
spaas	$a_{x^2 - y^2}, a_{z^2} \& a_{xy}$
dsp <sup>2</sup>	$d_{x^2-v^2}$

sp<sup>3</sup> d hybridisation : Steric number = 5

Geometry = trigonal bipyramidal

×.C

## Table-6

Туре	AB5	AB₄L	$AB_{3}L_{2}$	AB <sub>2</sub> L <sub>3</sub>
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	$PCI_{5}$ , $PBr_{5}$ , $PF_{5}$ etc.	$SF_4$ , $XeO_2F_2$	CIF₃, [XeF₃]⁺	¥ XeF₂ , I₃⁻ , [ICI₂]⁻

## Important points regarding sp<sup>3</sup>d -

(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.



It is covalent in the gas but in solid state exists as ionic solid consisting of [PCl<sub>4</sub>]<sup>+</sup> (tetrahedral) and [PCl<sub>4</sub>]<sup>-</sup> (octahedral). All P-CI bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.

Note: PF<sub>5</sub> (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 while 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.

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





Important : Since, octahedral is a symmetrical figure hence

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

 $SF_6$ 

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

AB<sub>6</sub>

Due to over-crowding and maximum valency of S,  $SF_6$  is much less active (almost inert) than  $SF_4$ 

Bond angle = 90°





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

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Ο  $ICl_3$  does not exist, but the dimer  $I_2Cl_6$  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 bridging I – Cl bonds appreciably longer (2.68 Å and 2.72 Å) suggesting delocalized bonding rather than simple halogen bridges formed by coordinate bonds from Cl<sub>2</sub> to I.



The liquid has an appreciable electrical conductance due to self ionization.  $I_2Cl_6 \Longrightarrow [ICl_2]^+$  (bent) +  $[ICl_4]^-$  (square planar)

## Solved Examples

The triodide ion  $(I_3^-)$  in which the I atoms are arranged in a straight line is stable, but the Example-9.

corresponding  $F_3^-$  ion does not exist.  $F_3^-$  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. Solution.

## 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 electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in (i) various molecular orbitals.
- Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry. (ii)
- (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.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic (iv) orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular** orbital are formed.
- The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding (v) molecular orbital.
- (vi) Just as the electron probability distribution around a nucleus 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 H<sub>2</sub> 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  $\psi_{A}$  or  $\psi_{B}$ . 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 by :

$$\Psi_{\rm m} = \left[\Psi_{\rm A} + \Psi_{\rm B}\right]; \Psi_{\rm m}^* = \left[\Psi_{\rm A} - \Psi_{\rm B}\right]$$

The molecular wave functions  $\psi_m$  and  $\psi^*_m$  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  $\sigma$  orbitals

if bonding and  $\sigma^*$  orbitals if antibonding, so we may alternatively denote them  $\sigma_{1s}$  and  $\sigma_{1s}^*$  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  $\sigma$ 1s orbital; in the hydrogen molecule ion, H<sup>+</sup><sub>2</sub>, 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<sup>-1</sup> compared with 458 kJ mol<sup>-1</sup> for H<sub>2</sub>.



Figure-16 The relative energy levels of molecular orbitals and their constituent atomic orbitals for H<sub>2</sub>.



**Figure-17**. The formation of molecular orbitals for H<sub>2</sub>. (a)  $\psi_A$  and  $\psi_B$  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-18.** Another representation of the formation of molecular orbitals for  $H_2$ . Since the  $\sigma$  and  $\sigma^*$  orbitals are respectively centrosymmetric and non-centrosymmetric these orbitals may also be denoted by the symbols  $\sigma_g$  and  $\sigma^*_u$ .

Molecular orbital wave functions are designated as  $\psi_q$  and  $\psi_u$ . g and u refer to the symmetry of the orbital about its centre. If the wave function is centrosymmetric, i.e. has the same sign at the same distance in opposite directions from the centre of symmetry. The orbital is said to gerade (German, even); if it changes sign on inversion about the centre it is said to ungerade (German, uneven).

Alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remain the same, the orbital is gerade, and if the sign changes, the orbital is ungerade.

Thus  $\sigma$  and  $\pi^*$  molecular orbitals are gerade and  $\sigma^*$  and  $\pi$  molecular orbitals are ungerade.

## 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** ( $\sigma$ ) **molecular orbitals are symmetrical around the bond-axis while pi** ( $\pi$ ) **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 orbital's are of the  $\sigma$  type and are designated as  $\sigma$  1s and  $\sigma^*$ 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  $\pi$  and  $\pi^*$  [Fig. (c)]. A  $\pi$  bonding MO has large electron density above and below the inter nuclear axis. The  $\pi^*$  antibonding MO has a node between the nuclei.

 $\delta$ -type of molecular orbitals are obtained by involvement of d-orbitals into bonding.

## Difference between $\pi$ molecular orbitals and the $\sigma$ orbitals.

- (1) For  $\pi$  overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, while for  $\sigma$  overlap the lobes point along the line joining the two nuclei.
- (2) For  $\pi$  molecular orbitals,  $\psi$  is zero along the internuclear line and consequently the electron density  $\psi^2$  is also zero. This is in contrast to  $\sigma$  orbitals.
- (3) The symmetry of  $\pi$  molecular orbitals is different from that shown by  $\sigma$  orbitals. If the bonding  $\pi$  MO is rotated about the inter nuclear line a change in the sign of lobe occurs. The  $\pi$  bonding orbitals are therefore ungerade, where as all  $\sigma$  bonding MO's are gerade. Conversely the antibonding  $\pi$  MO's are gerade while all  $\sigma$  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<sub>z</sub> < ( $\pi$ 2p<sub>x</sub> =  $\pi$ 2p<sub>y</sub>) < ( $\pi$ \*2p<sub>x</sub> =  $\pi$ \*2p<sub>z</sub>) <  $\sigma$ \*2p<sub>z</sub>.

The increasing order of energies of various molecular orbitals for Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub> etc., is :  $\sigma$  1s <  $\sigma$ <sup>\*</sup> 1s <  $\sigma$ 2s <  $\sigma$ <sup>\*</sup>2s < ( $\pi$ 2p<sub>x</sub> =  $\pi$ 2p<sub>y</sub>) <  $\sigma$ 2p<sub>z</sub> < ( $\pi$ <sup>\*</sup>2p<sub>x</sub> =  $\pi$ <sup>\*</sup>2p<sub>y</sub>) <  $\sigma$ <sup>\*</sup>2p<sub>z</sub>

The important characteristic feature of this order is that the energy of  $\sigma 2p_z$  molecular orbital is higher than that of  $\pi 2p_z$  and  $\pi 2p_z$  molecular orbitals.



**Figure-19.** Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) 2p, atomic orbitals and (c) 2p, 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.

- The molecule is stable if  $N_{h}$  is greater than  $N_{a}$ , and (i) (ii)
  - The molecule is unstable if N<sub>b</sub> is less than N<sub>a</sub>

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<sub>b</sub> is number of electrons in bonding molecular orbitals and N<sub>a</sub> 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.,  $N_{h} = N_{a}$ ) 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**

1.

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., N, molecule. However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O<sub>2</sub> molecule.

## BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

Hydrogen molecule (H<sub>2</sub>) :  $H_2$  :  $(\sigma 1s)^2$ 

Bond order = 
$$\frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 2$$

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<sup>-1</sup> and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

#### 2. Helium molecule (He<sub>3</sub>) : He<sub>3</sub> : $(\sigma^{1}s)^{2}$

Bond order of He<sub>2</sub> is  $\frac{1}{2}(2-2) = 0$ 

The molecular orbital description of He, 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. He, has a very low binding energy, approximately 0.01J/mol; for comparison, H, has a bond energy of 436 kJ/mol.

#### 3. Lithium molecule (Li,): $(\sigma^{+}1s)^{2}$ $(\sigma^{+}1s)^{2}$ $(\sigma^{2}s)^{2}$

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

## **Beryllium (Be**): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\sigma^* 2s)^2$

Be, has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He<sub>2</sub>, Be<sub>2</sub> is not a stable chemical species.

## **Boron** (**B**<sub>2</sub>): $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_1^1 = \pi 2p_1^1) (\sigma p_2^1)^0$

Here is an example in which the Molecular orbital model has distinct advantage over the Lewis dot picture, B, is found only in the gas phase; solid boron is found in several very hard forms with complex bonding, primarily involving B<sub>12</sub> icosahedra. B<sub>2</sub> 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. In the absence of mixing, the  $\sigma_g$  (2p) orbital is expected to be lower in energy than the  $\pi_u$ (2p) orbitals and the resulting molecule would be diamagnetic. However, mixing of the  $\sigma_g$ (2s) orbital with the  $\sigma_g$ (2p) orbital lowers the energy of the  $\sigma_g$ (2s) orbital and increases the energy of the  $\sigma_g$ (2p) orbital to a higher level than the  $\pi$  orbitals, giving the order of energies shown above. As a result, the last two electrons are unpaired in the degenerate (having the same energy)  $\pi$  orbitals, and the molecule is paramagnetic. Overall, the bond order is 1, even though the two p electrons are in different orbitals. The bond order of  $B_2$  is 1/2(6-4) = 1.

4. **Carbon molecule (C**<sub>2</sub>) :  $(\sigma 1s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$  or KK  $(\sigma 2s)^2 (\sigma 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ The simple MO picture of C<sub>2</sub> predicts a doubly bonded molecule with all electrons paired, but with both highest occupied molecular orbitals (HOMOs) having  $\pi$  symmetry. It is unusual because it has two  $\pi$  bonds and no  $\sigma$  bond. The bond dissociation energies of B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub> increase steadily, indicating single, double, and triple bonds with increasing atomic number. Although C<sub>2</sub> is not a commonly encountered chemical species (carbon is more stable as diamond, graphite, and the fullerenes), the acetylide ion, C<sub>2</sub><sup>2-</sup>, is well known, particularly in compounds with alkali metals, alkaline earths, and lanthanides. According to the molecular orbital model, C<sub>2</sub><sup>2-</sup> should have a bond order of 3 (configuration  $\pi_u^2 \pi_u^2 \sigma_g^2$ ). This is supported by the similar C – C distances in acetylene and calcium carbide (acetylide) :

Table-9		
C – C Distance	(pm)	
$C = C (gas phase)$ $H - C \equiv C - H$ $CaC_2$	132 120,5 119,1	, V

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

5. Nitrogen molecule  $(N_2)$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$ 

 $N_2$  has a triple bond according to both the Lewis and the molecular orbital models. This is in agreement with its very short N–N distance (109.8 pm) and extremely high bond dissociation energy (942kJ/mol.). Atomic orbitals decrease in energy with increasing nuclear charge Z; as the effective nuclear charge increases, all orbitals are pulled to lower energies. The shielding effect and electron-electron interactions cause an increase in the difference between the 2s and 2p orbital energies as Z increases, from 5.7 eV for boron to 8.8 eV for carbon and 12.4 eV for nitrogen. As a result, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  levels of  $N_2$  interact (mix) less than the  $B_2$  and  $C_2$  levels, and the  $\sigma_g(2p)$  are very close in energy.

The bond order of N<sub>2</sub> is 1/2(10 - 4) = 3. It contains one sigma and two  $\pi$  bonds.

- 6. Anionic nitrogen species (N<sub>2</sub>): Though 15 electrons but derived from N<sub>2</sub>, hence electronic configuration will be according to N<sub>2</sub> Electronic configuration :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\pi^2 2s)^2 (\pi^2 2p_x^2 = \pi^2 2p_y^2) (\sigma^2 2p_z^2)^2$ ,  $(\pi^* 2px)^1$ The bond order of N<sub>2</sub> is 1/2(10-5) = 2.5. It is paramagnetic species.
- 7.  $N_2^+$ : 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  $(O_2): O_2: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_z^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$

 $O_2$  is paramagnetic. This property, as for  $B_2$ , cannot be explained by the traditional Lewis dot structure (O = O), but is evident from the molecular orbital picture, which assigns two electrons to the degenerate  $\pi_g^*$  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  $\frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$ . 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.



Table-10

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
	25	112 3	1
$O_2$ (dioxygen)	2.0	120.07	2
$O_2^{-}$ (superoxide)	1.5	128	1
$O_2^{2-}$ (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<sub>2</sub> 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.

Fluorine molecule (F<sub>2</sub>):  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^2 2s)^2 (\sigma^2 2p_z)^2 (\pi^2 2p_z^2 = \pi^2 2p_y^2) (\pi^* 2p_z^2 = \pi^* 2p_y^2)$ 

The molecular orbital picture of  $F_2$  shows a diamagnetic molecule having a single fluorine-fluorine bond, in agreement with experimental data on this very reactive molecule.

The net bond order in N<sub>2</sub>, O<sub>2</sub>, and F<sub>2</sub> is the same whether or not mixing is taken into account, but the order of the filled orbitals is different. The switching of the order of the  $\sigma_{q}(2p)$  and  $\pi_{u}(2p)$  orbitals can occur because these orbitals are so close in energy; minor changes in either orbital can switch their order. The energy difference between the 2s and 2p orbitals of the atoms increases with increasing nuclear charge, from 5.7 eV in boron to 27.7 eV in fluorine. Because the difference becomes greater, the s-p interaction decreases and the "normal" order of molecular returns in O<sub>2</sub> and F<sub>2</sub>. The higher  $\sigma_{q}$  orbital is seen again in CO.

**Neon molecule (Ne<sub>2</sub>) :**  $(\sigma 1s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\sigma 2s)^2 (\sigma 2p_z)^2 (\pi 2p_z^2 = \pi 2p_z^2) (\pi 2p_z^2 = \pi 2p_z^2) (\sigma 2p_z^2)^2$ All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The Ne<sub>2</sub> 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  $N_2$  and then the trend reverses because the additional electrons occupy antibonding orbitals. The ions  $N_2^+$ ,  $O_2^{-2+}$  are also shown in the figure and follow a similar trend.



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# Solved Examples

Example-10. Solution.	Though $O_2$ molecule is paramagnetic yet it is a colourless gas. Why? It is because the energy gap between HOMO and LUMO levels in $O_2$ molecule is so large that radiations of visible light cannot excite a e <sup>-</sup> from HOMO to LUMO. In fact $O_2$ gas shows absorption in UV zone. So it is colourless.
Example-11.	Correct order of bond energy is: (A) $N_2 > N_2^+ > N_2^{} > N_2^{2} > N_2^{} > N_2^{} > N_2^{} = N_2^+ > N_2^{2} (D) N_2^- > N_2^{} = N_2^+ > N_2^{2} (D) N_2^{} > N_2^{} > N_2^{} > N_2^{} > N_2^{} > N_2^{} = N_2^+ > N_2^- = N_2^+ > N_2^{} = N_2^+ > N_2^- = N_2^+ = N_2^+ > N_2^- = N_2^+ = N_2^+ > N_2^- = N_2^+ = N_$
Solution.	(A) Bond order is directly proportional to the bond energy. Bond order of $N_2 = 3$ , $N_2^+$ , $N_2^- = 2.5$ $N_2^{2-} = 2$ But $N_2^-$ has more electrons in antibonding MO's and thus $N_2^+$ is more stable than $N_2^-$ . So correct order of bond energy will be $N_2 > N_2^+ > N_2^{-2} > N_2^{2-}$
Example-12.	Which of the following species have a bond order of 3? (A) CO (B) $CN^-$ (C) $NO^+$ (D) $O_2^+$
Solution.	(A,B,C) Species CO, CN <sup>-</sup> , NO <sup>+</sup> are isoelectronic with 14 electrons to N <sub>2</sub> which has bond order of 3 (i.e. $\frac{10-4}{3} = 3$ ), so their bond order will be equal to three.
Example-13.	Which of the following are diamagnetic? (A) C (D) N +
Solution.	(A) $O_2$ (B) $O_2^{-1}$ (C) $II_2$ (D) $N_2^{-1}$ (A,B,C) Species $C_2$ , $O_2^{-2-}$ , $II_2$ have all the electrons paired but $N_2^{+1}$ has one unpaired electron in bonding molecular orbital so it is paramagnetic.

## 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  $H_2$ ,  $O_2$ ,  $CI_2$ ,  $N_2$  or  $F_2$  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 ( $\delta^+$  or  $\delta^-$ ) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment ( $\mu$ ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (D). The conversion factors are

• 1 D =  $3.33564 \times 10^{-30}$  Cm, where C is coulomb and m is meter.

• 1 Debye =  $4.80 \times 10^{-18}$  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.

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

For example of H<sub>2</sub>O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5°. Net dipole moment of  $6.17 \times 10^{-30}$  Cm (1D =  $3.33564 \times 10^{-30}$  Cm) is the resultant of the dipole moments of two O—H bonds.

DM=



Net Dipole moment,  $\mu = 1.85 \text{ D} = 1.85 \times 3.33564 \times 10^{-30} \text{ Cm} = 6.17 \times 10^{-30} \text{ Cm}.$ 0 Following compounds have zero dipole moment :  $\mathsf{BF}_3, \mathsf{CO}_2, \mathsf{SO}_3, \mathsf{CF}_4, \mathsf{PF}_5(\mathsf{g}), \mathsf{SF}_6, \mathsf{XeF}_2, \mathsf{CS}_2, \mathsf{CCI}_4, \mathsf{PCI}_5(\mathsf{g}), \mathsf{XeF}_4$ Ο Some important orders HF HCI HBr ΗI 0.78 CHCl<sub>3</sub> > 1.0 1.92 D 1.08 0.38 CH<sub>2</sub>Cl<sub>2</sub> > 1.6 CH<sub>3</sub>Cl > CCI, 1.86 Ο Usually for disubstituted Benzene order is o > m > pBut it all depends on the substituents O ] D.M ≠ 0 D.M = 0 Note : For geometrical isomers usually the dipole moment of cis is more than trans but again there can be exceptions.  $CH_3$  C = C H $\square^3 C = C$ For example : cis - form (low dipole moment) trans - form (high dipole moment)

• 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.



## Some important points about dipole moment :

- A polyatomic molecule having polar covalent bonds but zero dipole moment indicates the symmetrical structure of the molecule. e.g. B F bonds are polar in  $BF_3$  but  $BF_3$  has  $\mu = 0$  due to its symmetrical geometry.
- O If molecule have  $\mu = 0$ , then it should be linear or having symmetrical geometry. e.g. linear  $-CO_2$ ,  $CS_2$ ,  $BeCI_2(g)$ ; symmetrical geometry  $-BF_3$ ,  $CH_4$ ,  $PCI_5$ ,  $SF_6$ ,  $IF_7$ ,  $XeF_4$ .
  - If molecule has  $\mu \neq 0$  then it should be angular or having unsymmetrical geometry.
    - $\int$  SnCl<sub>2</sub>, PbCl<sub>2</sub>, SO<sub>2</sub>, angular molecular geometry.

 $\rm NH_{_3},\, \rm H_2O,\, \rm NF_{_3},\, \rm SF_{_4},\, \rm H_2S,$  unsymmetrical molecular geometry.

% Ionic character =  $\frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100 = \frac{\mu_{(\text{Observed})}}{\mu_{(100\% \text{ lonic compound})}} \times 100$ 

 $\cap$ 

# Solved Examples





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

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

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

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

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



## Hydrogen Bond :

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 :  $---\mathsf{H}^{\delta +}-\mathsf{F}^{\delta -}---\mathsf{H}^{\delta +}-\mathsf{F}^{\delta -}---\mathsf{H}^{\delta +}-\mathsf{F}^{\delta -}$ 

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.

Ο 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, CHCl<sub>3</sub>.

## **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.

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

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

 $H_{2}O + HOH \longrightarrow H_{2}O \dots HOH$  (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.

#### Ο Order of H-bond strength



## **TYPES OF H-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.



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.


(b)

o-nitro phenol

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.



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



Chloral hydrate

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



K, of peroxomono sulphuric acid (i.e., caros acid) is greater than K<sub>2</sub>. 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.



 – OEt Aceto acetic ester (enolic form) 

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 H<sub>2</sub>O there is association of water molecules giving a liquid state of abnormally high boiling point.



- 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), 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)<sub>6</sub> polymers, dimeric (HF)<sub>2</sub>, and monomeric HF.

Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula  $M[HF_2]$ ; in  $KHF_2$ , 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 ( $NH_3$ ) and phenol ( $C_6H_5OH$ ) 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  $H_2O$  and R—OH molecules).



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

$$CH_3 - CH_2 - \underbrace{\overset{\delta-}{\overset{\delta+}{\overset{0}{\phantom{0}}}}_{\text{polar}}H^+$$
  $CH_3 - \underbrace{\overset{\delta-}{\overset{\delta+}{\overset{0}{\phantom{0}}}}_{\text{less polar}}CH_3$ 

f)  $HCO_3^-$  ions exist as dimer in KHCO\_3^-

In Na<sup>+</sup>HCO<sub>3</sub><sup>-</sup>, the HCO<sub>3</sub><sup>-</sup> ions are linked in to an infinite chain through intermolecular H-bonding.

	Solved Examples ———
Example-18.	$C_2H_2$ is not soluble in $H_2O$ but it is highly soluble in acetone.
Solution.	$CH_{3}$ $C = 0: \dots H + \delta$ $CH_{3}$ $C = 0: \dots H + \delta$ $C = C - H$ $CH_{3}$
	In hybridisation as %S character increase, electronegativity increase hence $C_2H_2$ forms H–bonds with O–atom of acetone and get dissolved. But $H_2O$ molecules are so much associated that it is not possible for $C_2H_2$ molecules to break that association, hence $C_2H_2$ is not soluble in $H_2O$ .
Example-19. Solution.	Why $SnCl_2.2H_2O$ readily loses one molecule of water at 80°C? One water molecule is coordinated to lone pair of electrons on $SnCl_2$ and the other is hydrogen bonded to coordinated water molecules.
Example-20. Solution.	Why crystalline sodium peroxide is highly hygroscopic in nature. Na <sub>2</sub> O <sub>2</sub> forms stable hydrates on account of H-bonding. $O_2^{2^-} (H_2O)_8 O_2^{2^-} (H_2O)_8$
Example-21.	Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.
	CH <sub>2</sub> [ CH <sub>2</sub> ] <sup>+</sup>

Solution.

$$\begin{bmatrix} \mathsf{CH}_{3} \\ \mathsf{H}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \end{bmatrix}^{+} \overline{\mathsf{OH}}$$

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

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

### 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 (ii) 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  $Na(OH_2)_x^+$  and  $F(H_2O)_y^-$  (for solution of NaF in  $H_2O$ ) are found. Hence this force is responsible for hydration.

Na⁺-----ð

#### (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 liquefied.

 $H^{\delta^{+}}$   $Cl^{\delta^{-}}$   $Cl^{-}$ 

#### (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.



Head to tail arrangement of dipoles



Figure-22

#### (e) Instantaneous dipole-Instantaneous induced dipole attraction;

Exists among the non-polar molecules like  $H_2$ ,  $O_2$ ,  $CI_2$  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 unbalances in electron distribution.

Antiparallel arrangement of dipoles

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.



Strength of vander waal force  $\infty$  molecular mass.

van der Waal's force  $\infty$  boiling point.

Ο

Solved Examples

Example-22.	Give the order of $Cl_2$ , HCl	boilin	g point of following		
Solution.	Cl <sub>2</sub> -Cl <sub>2</sub> dispersion force As dipole-dipole	< attrac	HCl – HCl dipole-dipole attraction tion is stronger than dispe	(boiling point) rsion force.	col.
Example-23.	Arrange the inert gases, according to their increasing order of boiling points				
Solution.	He < Ne < Ar < h Because strength	Kr < X n of va	e an der Waal's force increas	(boiling point) es down the group with incr	ease in molecular mass.

#### Metallic bond :

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

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

#### (A) Band Model

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



Half-filled band of N molecular orbitals

**Figure-24.** 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.



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

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



Figure-26. 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<sup>+</sup> 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.



## Solved Examples

Example-24. Solution

Why transition element have high heat of atomization.

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

## Some special bonding situations:

## (a) Electron deficient bonding:

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bonds( two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane  $B_2H_6$ ,  $AI_2(CH_3)_6$ ,  $BeH_2(s)$  and bridging metal carbonyls.



But Al<sub>2</sub>Cl<sub>6</sub> have covalent bond only and there is no electron deficient bonding as depicted in the given structure.



### (b) Back Bonding :

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



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 :

 $BF_3 > BCI_3 > BBr_3$ 

There is  $p\pi$ - $p\pi$  back bonding in boron trihalide. The extent of back bonding decreases from BF<sub>3</sub> to BI<sub>3</sub> because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 4p(in Br).

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

The extent of  $p\pi$ -p $\pi$  overlapping  $\propto \frac{1}{\text{Lewis acid character}}$ 

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#### (c) BOND LENGTHS AND $p\pi - d\pi$ BONDING :

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



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

Solved Examples —

Gaseous silyl isocyanate (SiH, NCO) is linear but gaseous methyl isocyanate (CH, NCO) is bent Example-25. explain!

Solution	$H = Si = N = C = O \qquad H = C = O \qquad H = C = O$	
	vačant No vacant	
	orbitals orbitals	
	Lone pair on nitrogen is delocalised between N and Si through $p\pi$ -d $\pi$ back bonding. So silvl isocyanate is linear.	е
Example-26.	Arrange in order of increasing ionic radii in water and their mobility : Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> .	
Solution	(i) Size $\infty$ 1/degree of hydration (i.e. with increase in size, number of water molecules around centra	al
	metal ions decrease). So order of increasing radii is $Sr^{2+} < Ca^{2+} < Mg^{2+} < Be^{2+}$ .	
	(ii) Heavily hydrated ions move slowly so the order of increasing mobility is	
	$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}$ .	

## MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Example-1	Classify the following bonds as ionic, polar covalent or covalent and give your reasons : (a) SiSi bond in Cl <sub>3</sub> SiSiCl <sub>3</sub> (b) SiCl bond in Cl <sub>3</sub> SiSiCl <sub>3</sub> (c) CaF bond in CaF <sub>2</sub> (d) NH bond in NH <sub>3</sub>
Solution	<ul> <li>(a) Covalent, due to identical electronegativity.</li> <li>(b) Covalent, due to less electronegativity difference.</li> <li>(c) Ionic, due to more electronegativity difference.</li> <li>(d) Covalent, due to nearly similar electronegativity.</li> </ul>
Example-2	<ul> <li>(a) Which one has highest and lowest melting point and why?</li> <li>NaCl KCl RbCl CsCl</li> <li>(b) Why melting points of cesium halide (CsX) decrease in the order given below?</li> <li>CsF &gt; CsCl &gt; CsBr &gt; CsI.</li> </ul>
Solution	<ul> <li>(a) NaCl will have highest lattice energy on account of the smaller Na<sup>+</sup> while CsCl has lowest lattice energy on account of the larger Cs<sup>+</sup>. Hence NaCl has highest melting point and CsCl has lowest melting point .</li> <li>(b) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.</li> </ul>
Example-3 Solution	Which of the compounds MgCO <sub>3</sub> and ZnCO <sub>3</sub> is thermally more stable ? Explain. Mg <sup>+2</sup> has less polarising power due to inert gas configuration while Zn <sup>+2</sup> has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn <sup>2+</sup> with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the CO <sub>3</sub> <sup>2-</sup> ion and as such the metal carbonate (ZnCO <sub>3</sub> ) gets readily decomposed into CO <sub>2</sub> and the oxide of the metal, ZnO. Thus ZnCO <sub>3</sub> is less stable than MgCO <sub>3</sub> .
Example-4 Solution	Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution? It exists as HCl (bond formed by equal sharing of electrons) but in aqueous solution ionises as $H^+$ (or $H_3O^+$ ) and $Cl^-$ due to polarity of HCl.
Example-5 Solution	Which type of hybridisation is found in $H_3O^+$ ? According to steric no. rule Steric number = Number of bond pair(s) + number of lone pair(s) at central atom
	$H \rightarrow H^+$ So, steric number = 3 + 1 = 4.
	Thus the hybridisation of oxygen in $H_3O^+$ is sp <sup>3</sup> .
Example-6	Which of the following will be strongest Lewis base ?
Solution	(B) In CH <sub>3</sub> NH <sub>2</sub> , hybridisation of N is sp <sup>3</sup> while in CH <sub>3</sub> CN hybridisation of N is sp. N <sub>2</sub> 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 sp <sup>3</sup> hybridisation and therefore the donation of the lone pair of electron will be quite easier; so it is strongest Lewis base.
Example-7	<ul> <li>Which is <u>incorrect</u> statement ?</li> <li>(A) In CF<sub>2</sub>=C=CF<sub>2</sub> molecule all the four fluorine atoms are not in the same plane.</li> <li>(B) Ka<sub>2</sub> of fumaric acid is more than Ka<sub>2</sub> of maleic acid due to intra molecular hydrogen bonding in maleic acid.</li> <li>(C) The O-O bond length in O<sub>2</sub>[AsF<sub>4</sub>] is longer than KO<sub>2</sub>.</li> <li>(D) The bond angle order in halogen - S - halogen is OSE &lt; OSEI &lt; OSBr</li> </ul>
Ans.	(C)
Solution	(A) $ \int \frac{F}{r_{z}} c = c = c = c = c = c = c = c = c = c$
	$F^{(s+p_{x}+p_{y})} (s+p_{x}) (s+p_{x}+p_{z}) F$
	As both carbon atoms are in different planes, all the four fluorine atoms are not in the same plane.
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(B) maleic acid fumaric acid Due to intramolecular hydrogen bonding the maleate ion gets stabilized and thus removal of second hydrogen becomes quite difficult.  $O_2[AsF_4] = O_2^+$  $KO_2 = O_2^-$ (C) B.O = 2.5B.O = 1.5 Bond order  $\propto \frac{1}{\text{bond length}}$ ; so  $O_2^+$  has smaller bond length than  $O_2^-$ 

(D) Greater the size of the halogen atoms greater will be the steric repulsions and thus larger will be the bond angles.

Example-8 Why BeF, has zero dipole moment whereas H,O has some dipole moment? Solution BeF<sub>2</sub> has linear molecule and H<sub>2</sub>O has bent molecule.



Example-9 Why crystals of hydrated calcium sulphate are soft and easily cleaved where as anhydrous calcium sulphate are very hard and very difficult to cleave? With in the Ca<sup>2+</sup> / SO<sub>4</sub><sup>2-</sup> layer the ions are held together by strong electrovalent bonds but these Solution

separated Ca<sup>2+</sup> / SO<sub>4</sub><sup>2-</sup> layers are linked by relative weak H–bond. The weak H-bonds link SO<sub>4</sub><sup>2-</sup> ion in the intermediate region.

- Example-10 Super oxides are coloured and paramagnetic why? Solution Super oxides contain one unpaired electron in anti bonding molecular orbital and are coloured due to transition of HOMO orbital electron within visible region.
- Of the species  $O_2^+, O_2^-, O_2^-$  and  $O_2^{2-}$  which would have the maximum bond strength ? Example-11
- $O_2^+$  has higher bond order i.e. 2.5 than  $O_2(2)$  and  $O_2^-(1.5)$  and bond strength is directly proportional to Solution bond order.

Example-12 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 : (C) 52% (D) 42% (A) 25% (B) 37%

(A) Solution Assuming complete charge transfer then dipole moment =  $(4.8 \times 10^{-10} \text{ esu}) (10^{-8} \text{ cm}) = 4.8 \text{ D}$ 

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

The dipole moment of KCl is 3.336 × 10<sup>-29</sup> Coulomb meter. The interionic distance in KCl is 2.6Å. Find Example-13 the % ionic character in KCI. The theoretical dipole moment in KCl =  $e \times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$  C meter

Solution

Ans.

experimental dipole moment % ionic character =  $\frac{0.29 \text{ cm} \text$ 

Resonance

SO

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**CHEMICAL BONDING - I** 

# **Exercise #1**

## **PART - I : SUBJECTIVE QUESTIONS**

## Section (A): Types of chemical bond and octet rule

- A-1. Identify the following compounds as Ionic, Metallic, Network solid and Molecular solids-(a) CsCl (b) Nal (c) Diamond (d) Iodine (s) (e) Cu (f) quartz
- A-2. Indicate what is wrong with each of the following Lewis structures ? Replace each with a more acceptable structure.

(a)  $[:S - C = N;]^{-}$  (b)  $[:CI]^{+}[:O;]^{2-}[CI:]^{+}$  (c) :O = N = O:

- **A-3.** Why is  $CCl_4$  insoluble in water while NaCl is soluble ?
- A-4. Solid sodium conducts electricity but solid NaCl does not. Explain.
- Section (B) : Limitations of octet rule, formal charge, lewis dot structures, resonance
- **B-1.** Why  $CIF_3$  exists but  $FCI_3$  does not?
- **B-2.** Draw the Lewis structures of the following molecules and ions  $PH_3$ ,  $H_2S$ ,  $BeF_2$ ,  $SiCl_4$ , HCOOH,  $H_2SO_4$ ,  $O_2^{2-}$ ,  $F_2O_1O_4^{-4}$
- B-3. In how many of the following species, the central atoms have two lone pairs of electrons?

XeF <sub>4</sub>	XeF <sub>5</sub> <sup>-</sup>	F <sub>2</sub> SeO <sub>2</sub>
XeF <sub>3</sub> +	XeOF <sub>4</sub>	CIOF <sub>3</sub>
	SCI <sub>2</sub>	$OSF_4$

- **B-4.** With the help of Lewis dot structure find the number of total covalent bonds formed in the following species. (i)  $CO_3^{2-}$ , (ii)  $CCI_4$ , (iii)  $NF_3$ , (iv)  $HNO_3$ .
- **B-5.** Draw Lewis structure of (i)  $S_3^{2-}$  (ii) NOCI (iii) SOBr<sub>2</sub> (iv)  $SO_2CI_2$
- **B-6.** Assign formal charges to the following species. If there are no formal charges present for certain of these species, so indicate.



## Section (C) : Bond order in oxoanions and corresponding acids

**C-1.** Compare bond length of S–O bond in  $SO_3^{2-}$  and  $HSO_3^{-}$ .

## Section (D): VBT, Overlapping of orbitals

- **D-1.** Find number of sigma bonds and pi bonds in  $CH_2 = C = C = CH_2$ .
- **D-2.** Draw the orbital overlapping diagram for  $O_2$  molecule.

## Section (E) : Hybridisation

E-1. Explain hybridisation of central atom in :

(1)	XeF	(2)	XeF₄	(3)	PCl <sub>3</sub>	(4)	PCI
(5)	SF	(6)	IF	(7)	١F	(8)	IF,
(9)	CH	(10)	CČl₄	(11)	SiCl	(12)	SiH
(13)	H,Õ	(14)	NH	(15)	PO, <sup>3</sup> -	(16)	BrF
(17)	NÔ,⁻	(18)	CO <sup>2-</sup>	(19)	NH ً⁺	(20)	CIO

- E-2. Draw the shape of sp<sup>3</sup> hybridised orbital. Locate the nodal surface if any.
- **E-3.** The order of size of the hybrid orbitals is as follows  $sp < sp^2 < sp^3$ . Explain.

## Section (F): VSEPR theory

- **F-1.** Why  $NO_2^+$  and  $I_3^-$  are linear species ?
- F-2. PCl<sub>5</sub> has the shape of a trigonal bipyramidal where as IF<sub>5</sub> has the shape of square pyramidal. Explain.
- **F-3.** Write the geometry of XeF<sub>4</sub> and OSF<sub>4</sub> using VSEPR theory and clearly indicate the position of lone pair of electrons.
- **F-4.** Explain the structure of CIF<sub>3</sub> on the basis of VSEPR theory.

## Section (G) : Bond angle, bond length comparison

- **G-1.** Draw an electron dot structure for  $Br_3^-$ . Deduce an approximate value of the bond angle.
- G-2. Which compound has the smallest bond angle in each series ?

(a)	SbCl <sub>3</sub>	SbBr <sub>3</sub>	Sbl
(b)	Pl,	Asl	Sbl

**G-3.** Why  $[SiCl_6]^{2-}$  does not exist?

G-4. (a) NCl<sub>5</sub> is not possible but PCl<sub>5</sub> is possible. Why ?
(b) F<sub>3</sub><sup>-</sup> does not exist but l<sub>3</sub><sup>-</sup>, Br<sub>3</sub><sup>-</sup> exist. Why ?
(c) SCl<sub>6</sub> does not exist but SF<sub>6</sub> exists. Why ?

**G-5.** Compare the C–H bond strength in  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$ .

## **PART - II : OBJECTIVE QUESTIONS**

#### \* Marked Questions may have more than one correct option.

## Section (A) : Types of chemical bond and octet rule

- A-1. Which of the following compound has electrovalent linkage ? (A) CH<sub>3</sub>Cl (B) NaCl (C) CH<sub>3</sub>OH
- **A-2.** An ionic bond  $A^+ B^-$  is most likely to be formed when :
  - (A) the ionization energy of A is high and the electron affinity of B is low
  - (B) the ionization energy of A is low and the electron affinity of B is high
  - (C) the ionization energy of A and the electron affinity of B is high
  - (D) the ionization energy of A and the electron affinity of B is low
- A-3. An element has electronegativity 1. The bonds formed between atoms of this elements are (A) covalent (B) metallic (C) ionic (D) hydrogen bond
- A-4. Electrovalent compound's (A) Melting points are low (C) Conduct current in fused s
  - (C) Conduct current in fused state (D) Insoluble in polar solvent
- A-5. Among the following which property is commonly exhibited by a covalent compound
  - (A) High solubility in water
    - (C) Low boiling point
- (B) High electrical conductance(D) High melting point

(B) Boiling points are low

(D) CH<sub>2</sub>COOH





D-4.	$C_3^{4-}$ has (A) two $\sigma$ and two $\pi$ bond (C) two $\sigma$ and one $\pi$ bond	d d	(B) three $\sigma$ and one $\pi$ bo (D) two $\sigma$ and three $\pi$ bo	and		
D-5.	How many bonds are the	nere in O ?				
	(A) 13	(B) 23	(C) 20	(D) 26		
D-6.	What is covalency of I in (A) 5	n IF <sub>7</sub> ? (B) 3	(C) 7	(D) 1		
D-7.	The covalency of nitroge	en in HNO <sub>3</sub> is	$(\mathbf{O})$			
	(A) 0	(D) 3	(C) 4	(D) 5		
Section F-1	on (E) : Hybridisatic	<b>on</b> has been arranged in incr	easing order of size of th	e hybrid orbitals ?		
<b>-</b>	(A) $sp < sp^2 < sp^3$	(B) $sp^3 < sp^2 < sp$	(C) $sp^2 < sp^3 < sp$	(D) $sp^2 < sp < sp^3$		
		( ) -F · -F · -F				
E-2.	The hybridization of car	bon atoms in $C_2 - C_3$ sing	gle bond of $H\vec{C} = \vec{C} - \vec{C}H$	CH <sub>2</sub> is:		
	(A) $sp^3 - sp^3$	(B) sp <sup>2</sup> – sp	(C) sp $-$ sp <sup>2</sup>	(D) sp <sup>3</sup> - sp		
E-3.	Specify the hybridisation (A) sp , sp <sup>2</sup> , sp	ns of central atom in the fo (B) sp , sp , sp³	ollowing species respecti (C) sp² , sp , sp	vely {N <sub>3</sub> <sup>-</sup> , NOCI, N <sub>2</sub> O} (D) sp <sup>2</sup> , sp <sup>2</sup> , sp.		
E-4.	In pent-3-en-1-yne the te (A) sp & sp <sup>2</sup>	erminal carbon-atoms hav (B) sp <sup>2</sup> & sp <sup>3</sup>	e following hybridisation (C) sp <sup>2</sup> & sp	(D) sp & sp <sup>3</sup>		
E-5.	In which of the following (A) $(CH_3)_3N$	N is in the sp <sup>2</sup> hybridisat (B) $CH_3CONH_2$	ion state (C) CH <sub>3</sub> CN	(D) NO <sub>2</sub> <sup>+</sup>		
E-6.	In $H_2SO_4$ molecule (A) S-atom is $sp^3d^2$ hybridised and there are 4 lone pair electrons on 'O' atoms. (B) S-atom is $sp^3$ hybridised and there are no lone pair of electrons in the molecule. (C) S-atom is $sp^3$ hybridised and there are 8 lone pair of electrons on the 'O' atoms. (D) S-atom is $sp^2$ hybridised and these are 8 lone pair of electrons 'O' atoms.					
E-7.	$S_1$ : [XeF <sub>7</sub> ] <sup>+</sup> has sp <sup>3</sup> d <sup>3</sup> hy S <sub>2</sub> : [SF <sub>6</sub> ] has sp <sup>3</sup> d <sup>2</sup> hyb	ybridisation pridisation	; S <sub>2</sub> : [PCl <sub>4</sub> ] <sup>+</sup> has ; S <sub>4</sub> : [PF <sub>4</sub> ] <sup>+</sup> has	sp <sup>3</sup> d <sup>2</sup> hybridisation sp <sup>3</sup> hybridisation		
	(A) TFFT	(B)TTET	(C)TFTT	(D) FFFT		
E-8.	In which of the following (A) $CIF_3$ , $CIF_3O$	pairs hybridisation of the (B) $CIF_3O$ , $CIF_3O_2$	central atoms are differe (C) $[CIF_2O]^+$ , $[CIF_4O]^-$	ent ? (D) [CIF <sub>4</sub> O] <sup>–</sup> , [XeOF <sub>4</sub> ]		
E-9.	$BF_3 + F^- \rightarrow BF_4^-$ What is the hybridiation (A) $sp^2$ , $sp^3$	state of B in BF <sub>3</sub> and BF (B) sp <sup>3</sup> , sp <sup>3</sup>	' - : (C) sp², sp²	(D) sp³, sp³d		
Sectio	on (F): VSEPR the	ory				
F-1.	Which is the right struct	ure of XeF <sub>4</sub> ?				
2	(A) F F F F	F (B)	(C) F (I	D) F F		
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F-2.	Identify the correct match	า.						
	(i) XeF <sub>2</sub>	(a	a) Central atom	has sp	<sup>3</sup> hybridis	sation an	d bent geometry.	
	$(II) N_3^{-}$	(t	b) Central atom	has sp <sup>.</sup>	<sup>o</sup> d <sup>2</sup> hybrid bybridio	disation a	and octahedral.	
	(iii) $PCI_6$ ( $PCI_5$ (s) anion) (iv) $ICI + (I CI (\ell) cation)$	(0	) Central atom	nas sp has sp	<sup>3</sup> d hybrid	isation a	nd linear geometry	
	(A) $(i - a)$ , $(ii - b)$ , $(iii - c)$	. (iv – d)		(B) (i –	d). (ii – t	b). (iii – d	). (iv $-c$ )	•
	(C) $(i - b)$ , $(ii - c)$ , $(iii - a)$	, (iv – d)		(D) (i –	d), (ii – d	c), (iii – b	), (iv – a)	
F-3.	Which of the following sta (A) The electrons are loca	atement is ated at the	true for $IO_2F_2$ corners of a tri	-? gonal bi	pyramida	al but one	e of the equatorial pairs is unshar	ed.
	<ul> <li>(B) It has sp<sup>3</sup>d hybridisati</li> <li>(C) Its structure is analog</li> <li>(D) (A) and (C) both</li> </ul>	ion and is gous to SF	T–shaped. ₄.					
F-4.	Which reaction involves a	a change i	n the electron-	-pair geo	ometry fo	or the unc	der lined element ?	
	$(A) \underline{B}F_{3} + F^{-} \longrightarrow \underline{B}F_{4}^{-}$	-		(B) <u>N</u> H	₃ + H⁺ —	—→ <u>N</u> H	4	
	$(C) 2 \underline{SO}_2 + O_2 \longrightarrow 2$	<u>S</u> O <sub>3</sub>		(D) H <sub>2</sub>	<u>)</u> + H⁺ —	$\longrightarrow H_{3}$	<u>2</u> +	
F-5.	In which of the following r (A) $H_2O$	molecules (B) I <sub>3</sub> <sup>-</sup>	number of lon	e paris a (C) O <sub>2</sub> F	and bonc	l pairs on	central atom are not equal ? (D) SCl <sub>2</sub>	
E 6	The structure of E SoO is	o opologoj	in to t			<b>N</b>	•	
Γ-0.	(A) $SO_3$	(B) $CIO_{3}^{-}$	1510.	(C) XeC	) <sub>3</sub>		(D) (B) and (C) both	
F-7.	Which of the following sp	ecies give	n below have s	shape si	milar to 🕽	(eOF <sub>4</sub> ?		
	(A) XeO <sub>3</sub>	(B) IOF <sub>4</sub> <sup>+</sup>		(C) PC	5		(D) $XeF_5^{\oplus}$	
				C				
Sectio	on (G) : Bond angle,	bond le	ength com	oariso	n			
G-1.	The ONO angle is maxim	num in :			_			
	(A) $HNO_3$	(B) $NO_{2}^{+}$		(C) HN	$D_2$		(D) $NO_2$	
G-2.	Which statement is corre	ect for N <sub>a</sub> −i	ion 🖌					
	(A) It is bent molecule	3	<u> </u>	(B) Bor	nd angle	is < 120°		
	(C) Central atom is sp <sup>2</sup> hy	ybridized	× U	(D) Nor	ne of the	se		
G-3.	Consider the following mo	olecules ;	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te		
	Arrange these molecules	s in increas	sing order of bo	nd and	es.	1 V		
	(A) I < II < III < IV	(B) IV < II	I <ii<i< th=""><th>(C) I &lt;</th><th>II &lt; IV &lt; I</th><th>Π</th><th>(D) II &lt; IV &lt; III &lt; I</th><th></th></ii<i<>	(C) I <	II < IV < I	Π	(D) II < IV < III < I	
G-4.	In which of the following b	oond angle	is maximum					
	(A) NH <sub>3</sub>	(B) NH <sub>4</sub> +		(C) PC	3		(D) SCl <sub>2</sub>	
G-5.	Consider the following sta	atement a	nd arrange in t	he orde	of true /	false.		
	$S_1$ : In SnCl <sub>2</sub> the bonding	takes pla	ce in ground s	tate and	the bond	d angle C	CI-Sn-CI is slightly less than 12	0º.
	$S_2$ : The molecular geome	etry of XeF	$-7^+$ is pentagon	al bipyra	amidal ha	aving two	o different Xe-F bond lengths.	o of
	$3_3 \cdot 113F_4$ , the bolid angle	es, instead			ale 09		respectively due to the presence	eoi
	(A)TTT	(B) F T T		(C) T T	F		(D) T F T	
G-6.	In which of the following o	central ato	m is unhvbridi	sed?				
••••	(A) $S(CH_3)_2$	(B) $SO_2$		(C) SiH	4		(D) PCl <sub>3</sub>	
G-7.	Consider the following sta	atements						
	1. Steric number '7'	' gives 'sp	<sup>3</sup> d <sup>3</sup> hybridisatic	0n.				
	3 Lone pair does n	of cause a	any distortion i	n the bo	nd angle	•		
	The above statements 1,	, 2, 3 respe	ectively are (T	= True,	F = False	∋)		
	(Ă) T F F	(B) T T F	- 、	(C) F T	F		(D) T T T	
_	•							
							CHEMICAL BONDING-1 - 1	24

G-8.	All the following specie (A) $AsF_3$	s have all their bon (B) AsF <sub>4</sub> <sup>-</sup>	nd lengths identical except (C) $AsF_4^+$	: (D) AsF <sub>6</sub> <sup>-</sup>	
G-9.	Which of the following $(A) C_2 H_2$	nas maximum (C–C (B) C <sub>2</sub> H <sub>4</sub>	C) bond length (C) C <sub>2</sub> H <sub>6</sub>	(D) $C_2 H_2 Br_2$	
G-10.	Which one has highest (A) NH <sub>3</sub>	bond angle. (B) PH <sub>3</sub>	(C) H <sub>2</sub> O	(D) CH <sub>4</sub>	0
	Р	ART - III : A	SSERTION / REAS	SONING	
	Each question has 5 ( (A) STATEMENT-1 is tr (B) STATEMENT-1 is tru (C) STATEMENT-1 is tr (D) STATEMENT-1 is fa (E) Both STATEMENTS	choices (A), (B), (C) ue, STATEMENT-2 ie, STATEMENT-2 is, STATEMENT-2 alse, STATEMENT- S are false	<b>C), (D) and (E) out of whic</b> is true and STATEMENT-2 s true and STATEMENT-2 is is false 2 is true	ch ONLY ONE is correct. It is correct explanation for not correct explanation for	STATEMENT-1 STATEMENT-1
1.	<b>Statement-1</b> : In CH <sub>3</sub> N <b>Statement-2</b> : N–atom does not have lone pair	ICO , the bond ang has a lone pair of e of electrons.	V = V - V - C and $V - C - Celectrons which is involved$	O are not identical. In $p\pi$ -d $\pi$ delocalisation w	here as C–atom
2.	Statement-1 : $[SiC\ell_6]$ Statement-2 : Interactions can not be accommons	<sup>2-</sup> does not exist. tion between lone p modated around S	pairs of chloride ions and S i⁴+ due to limitation of its si	it is not very strong and s ze.	six large chloride
3.	Statement-1 : Molecu Statement-2 : Compo	lar species like SF ounds with an expa	$I_6^{-}$ , $PF_5^{-}$ , $\mathrm{I}_3^{-}$ and $XeF_2^{-}$ violate nded octet are called hyper	e the octet rule. rvalent compounds.	
4.	<b>Statement-1 :</b> In tetrahedral hybridisation i.e., in sp <sup>3</sup> hybridisation all p–orbitals of valence shell are involved and no p–orbital is left for forming $\pi$ –bonds. <b>Statement-2 :</b> Central atom can not form double bonds in the molecules or species having sp <sup>3</sup> hybridisation.				
5.	Statement-1 : All F-S- Statement-2 : The bon	F angles in SF <sub>4</sub> are d pair-bond pair rej	e greater than 90° but less t pulsion is weaker than lone	than 180º. Pair-bond pair repulsion.	
6.	Statement-1: The bond angles of BrNO, CINO and FNO are approximately 114.5°, 113.3° and 110.1° respectively.				
7.	Statement-2 : The hyb	F F F F F	Bond angle R is a normal t	ounds is sp². riangular angle 120º.	
	Statement-2 : ∠P ≠ 1	80♥; ∠Q ≠ 90° and	thus $\angle R \neq 120^{\circ}$ but less th	en 120° due to the presen	ice of a lone pair.
8.	Statement-1 : In IOF	a single lone pai	r is present on iodine atom	n trans to oxygen atom to	have minimum

repulsion between the I = O and the lone pair of electrons. **Statement-2**: The VSEPR model considers double and triple bonds to have slightly greater repulsive effect than single bonds because of the repulsive effect of  $\pi$  electrons.

Statement-1: Molecules having different hybridisation can have same shape.
 Statement-2: The shape of a molecule does not depend on the hybridisation but it depends on the energy factor.

**10. Statement-1** :  $SO_2$ ,  $NO_3^-$  and  $CO_3^{2-}$  are isoelectronic as well as isostructural species. **Statement-2** : The d and f-orbitals do not shield the nuclear charge very effectively. Therefore, there is significant reduction in the size of the ions, just after d or f orbitals have been completely filled.

- Statement-1: NO<sub>3</sub><sup>-</sup> and PO<sub>3</sub><sup>-</sup> have similar formula type but differ structurally i.e. they have different type of hybridisation.
   Statement-2: NO<sub>3</sub><sup>-</sup> ion exists as free ion. On the other hand PO<sub>3</sub><sup>-</sup> exists as cyclic or linear polymeric structure.
- **12. Statement-1**: Carbon has unique ability to form  $p\pi$ – $p\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity. **Statement-2**: Heavier elements of group 14<sup>th</sup> do not form  $p\pi$ – $p\pi$  bonds because their atomic orbitals are too large and diffuse to have effective side ways overlapping.
- Statement-1 : The hybridisation of N atom in acetamide is sp<sup>3</sup>.
   Statement-2 : There occurs delocalisation of lone pair of electrons present on N atom.

$$CH_{3} - C - \dot{N}H_{2} \longleftrightarrow CH_{3} - C = NH_{2}$$

**14.** Statement-1 : CI P F, bond angle P is equal to the bond angle Q but not precisely equal to 90°.

Statement-2 : The molecule is T - Shaped and there is repulsion between lone pairs of electrons

**15.** Statement-1 : The electronic structure of azide ion  $(N_3^-)$  is N = N:

Statement-2:  $\begin{bmatrix} \dot{N} \\ \dot{N} \\ \vdots \\ N = N \end{bmatrix}^{-}$  is not a resonating structure of azide ion, because the position of atoms cannot be

changed.

- **16. Statement-1** : Elemental nitrogen exists as a diatomic molecule and phosphorous as tetratomic molecule. **Statement-2** : Nitrogen does not have vacant d-orbital whereas phosphorus have vacant d-orbital.
- Statement-1 : Single N–N bond is weaker than the single P–P bond.
   Statement-2 : In N–N bond there is high interelectronic repulsion of the non–bonding electrons, owing to the weker bond.

# **Exercise #2**

## **PART - I : SUBJECTIVE QUESTIONS**

- 1. NaCl<sub>a</sub>, gives a white precipitate with AgNO<sub>3</sub> solution but  $CCl_4$  or  $CHCl_3$  does not. Explain.
- 2. Draw the Lewis structures of the following species :

$$NO_2^-$$
,  $NH_4^+$ ,  $O_3^-$ ,  $CO$ ,  $HNO_3^-$ ,  $NO_2^-$ ,  $COF_2^-$ ,  $XeOF_4^-$ ,  $TeO_3^{2-}$ ,  $XeF_5^{--}$ 

3. Write down the resonance structure(s) for : (i)  $CH_2COQ^-$  (ii)  $HCO_3^-$ 

(iii) O<sub>3</sub> (vii) H<sub>2</sub>PO<sub>2</sub>-

(iv) NO<sub>3</sub><sup>-</sup> (viii) SO<sub>4</sub><sup>2-</sup>

(ix)  $PO_4^{3}$  (x)  $HPO_3^{2-}$ Also calculate average bond order of M–O bond in

(vi) HN

(i), (ii), (iii), (iv), (vii), (viii), (ix), (x), where M is central atom (And M–O bonds considered are the one which involve delocalization)

4. How many types of N–O bondlengths are present in (a)  $HNO_3$  (b)  $NO_3^-$ ?

(v) CO<sub>2</sub>

5. Draw the type of overlaps between (b) s and  $d_{x^2-y^2}$  (c) s and  $d_{yz}$ (a) s and  $d_{-2}$ (d)  $p_z$  and  $d_{2}$ (e)  $p_{_{T}}$  and  $d_{_{M}}$ (f) p, and d, (g)  $p_x$  and  $d_{2}$ (h)  $p_x$  and  $d_{x^2-y^2}$ (i)  $d_{x^2-y^2}^{}$  and  $d_{x^2-v^2}^{}$  (j)  $d_{xy}^{}$  and  $d_{xy}^{}$  $(k) d_{xy}$  and  $d_{yz}$ if internuclear axis is z-axis. Identify them as  $\sigma,\pi,\delta$  bond wherever bond is formed In which of the following species all bond lengths are not identical? 6. (b) CHCl<sub>3</sub> (c) NH<sub>3</sub> (f) PCI (a) CH<sub>4</sub> (d) CIF<sub>3</sub> (e) SF (g) XeO (h) SF<sub>6</sub> (i) CO<sub>2</sub>  $(j) H_2 CO_2$ (k) PCl<sub>2</sub> (I) SO 7. Draw the structure of the following compound and identify the hybridisation of the central atom, also count the Sigma and  $\pi$ -bond. (iii) NH<sub>2</sub>OH (iv) Anion of PCI<sub>c</sub>(s) (i) XeO<sub>2</sub>F<sub>2</sub> (ii) PF<sub>3</sub>Cl<sub>2</sub> Prove that 8. (i): N<sub>2</sub>H<sub>4</sub> is pyramidal about each N atom (ii): NH<sub>2</sub>OH is pyramidal about the N atom and bent about the O atom (iii): CH,COCI is trigonal about the carbon atom (attached to O and CI) 9. Why is oxygen atom in XeOF, in equatorial plane? 10. The POCI, molecule has the shape of an irregular tetrahedron with the P atom located centrally. The CI-P-CI angle is found to be 103.5°. Give a qualitative explanation for the deviation of this structure from a regular tetrahedron. Which one has highest and least bond angle in the following? 11. PH, AsH H<sub>0</sub> SbH<sub>2</sub> (2) H<sub>2</sub>S H,Te (1) CH<sup>1</sup> CO CĪ<sub>2</sub>O (3)PH HO (4) CĪO, BF<sub>3</sub> (5) PF. PH. (6) NF, PF<sub>3</sub> NF, (7)NH (8) PCL Explain why the experimentally determined N  $\leftarrow$  F bond length in NF<sub>3</sub> is greater than the sum of single bond 12. covalent radii of N and F. 13. Arrange the following in the increasing order of bond angles : (i) NO<sub>2</sub><sup>+</sup>, BF<sub>4</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> (ii)  $SO_2CI_2$ ,  $SO_3$ ,  $SF_6$ (iii) OCl<sub>2</sub>, OF<sub>2</sub>, OBr<sub>2</sub> (iv) Equitorial bond angle in PCl<sub>5</sub>, XeO<sub>2</sub>F<sub>2</sub>, PBr<sub>5</sub> 14. Explain why PCl<sub>5</sub> is formed but PH<sub>5</sub> is not known. PART - II : OBJECTIVE QUESTIONS Single choice type Which of the following contains both electrovalent and covalent bonds? 1 (A) CH<sub>4</sub> (B) H<sub>2</sub>O<sub>2</sub> (C) NH<sub>4</sub>Cl (D) none In the following which substance will have highest boiling point 2. (A) He 🕨 (B) CsF (C) NH<sub>2</sub> (D) CHCl<sub>2</sub> Arrange the following in order of decreasing N – O bond length :  $NO_2^+$ ,  $NO_2^-$ ,  $NO_3^-$ 3. (A)  $NO_3^- > NO_2^+ > NO_2^-$ (B)  $NO_3^- > NO_2^- > NO_2^+$ (D)  $NO_2^- > NO_3^- > NO_2^+$ (C)  $NO_2^+ > NO_3^- > NO_2^-$ In the thiocyanate ion, SCN<sup>-</sup> three resonating structure are possible with the electron-dot method as shown in 4. figure:  $S \equiv C - N$  $\dot{S} - C \equiv N$ S = C = N: (x) (Z) The decreasing order of % contribution in resonance hybrid is : (B) y > z > x(D) cannot predicted. (A) y > x > z(C) z > x > yCHEMICAL BONDING-1 - 127 |Kesonance|

5.	The correct order of C– P : $CH_3CN$ (A) P > Q > R	N bond length in the giver Q : HNCO (B) P = Q = R	n compounds is : R : CH <sub>3</sub> CONH <sub>2</sub> (C) R > Q > P	(D) R > P > Q
6.	Which of the following s (A) Free rotation of ator (B) Sigma -bond deterr regard (C) Sigma-bond is stron (D) Bond energies of sig	statements is not correct f ms about a sigma - bond mines the direction betwe nger than a pi-bond gma- and pi-bonds are of	for sigma and pi bond forr is allowed but not in case een carbon atoms but a p the order of 264 kJ/mol a	med between two carbon atoms? of a pi-bond bi-bond has no primary effect in this nd 347 kJ/mol. <b>res</b> pectively.
7.	Number and type of bor (A) one sigma ( $\sigma$ ) and o (C) one $\sigma$ and one and a	nds between two carbon a ne pi ( $\pi$ ) bond a half $\pi$ bond	atoms in CaC <sub>2</sub> are : (B) one $\sigma$ and two $\pi$ bon (D) one $\sigma$ bond	nds
8.	The number of $\sigma$ and $\pi$ (A) $2\sigma$ + $3\pi$	t bonds in dicyanogen (C (B) $3\sigma$ + $2\pi$	CN) <sub>2</sub> are : (C) 3σ + 4π	(D) $4\sigma + 3\pi$
9.	Indicate the incorrect st (A) An 'sp' hybrid orbita (B) $2p_x$ and $2p_y$ - orbital (C) Effective hybridisati (D) The concept of hybri theory.	atement : I is not lower in energy th s of carbon can be hybric on is not possible with orb idisation has a greater sig	an both s- and p-orbitals dized to yield two new mo bitals of widely different er gnificance in the VB theor	re stable orbitals hergies y of localised orbitals than in the MO
10.	The correct order of ind (assume all hybrid orbit $CO_3^{2-}$ I (A) II < III < IV < I < V (C) W. W. L. V(-V)	creasing s character (in p als are exactly equivalen XeF <sub>4</sub> $I_3^-$ I II	ercentage) in the hybrid t) : IV (B) II < IV < III < V < I	orbitals in below molecules / ions is BeCl <sub>2</sub> (g) V
	(C) III < II < I < V < IV		(D) II < IV < III < I < V	
11.	(A) I in IC $\ell_4^-$	(B) S in SO <sub>3</sub> (PO <sub>4</sub> <sup>3-</sup> ) (B) S in SO <sub>3</sub> (B) S in SO <sub>3</sub> (B) $(B_{1})$	s the same as : (C) N in $NO_3^-$	(D) S in SO $_3^{2-}$
12.	Choose the molecules (a) $BCI_3$ The correct answer is : (A) a b d	in which hybridisation oct (b) NH <sub>3</sub> (B) a b c	curs in the ground state ? (c) PCl <sub>3</sub>	(d) BeF <sub>2</sub>
40	(A) a, b, u			(D) C, C
13.	ions. The hybrid state c (A) sp <sup>3</sup> d, sp <sup>3</sup> d <sup>2</sup>	onde in gaseous phase e f P-atom in PCI <sub>5</sub> is sp <sup>3</sup> d. (B) sp <sup>3</sup> ,sp <sup>3</sup> d <sup>2</sup>	The hybrid states of P–at (C) sp <sup>3</sup> d <sup>2</sup> , sp <sup>3</sup> d	toms in $PCI_4^+$ and $PCI_6^-$ will be : (D) sp <sup>3</sup> , sp <sup>3</sup> d
14.	In which of the following	g cyclic compound the nit	rogen atom is sp <sup>3</sup> hybridis	sed
	(A) 1 & III	(B) I, II, III	(C) 111 & IV	(D) I, III & IV
15.	The bent or V–shape of (A) sp <sup>3</sup>	the molecule can be resu (B) sp <sup>2</sup>	Ited from which of the fol (C) Both (A) and (B)	lowing hybridization. (D) None of these
16.	A σ bonded molecule N (A) 0	IX₃ is T-shaped. The num (B) 2	ber of non-bonding pairs ( (C) 1	of electrons can be (D) none of these
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17.	Which of the following p (A) $BaSO_4$ , $KMnO_4$ (C) $FeSO_4$ .7 $H_2O$ , $MgSO_4$	pairs does not contain iso 0 <sub>4</sub> .7H <sub>2</sub> O	morphous species : (B) KClO <sub>4</sub> , KBF <sub>4</sub> (D) NaClO <sub>3</sub> , NaNO <sub>3</sub>	
18.	sp <sup>3</sup> d hybridization is cor (A) $p^3$ + sd	nsidered to be a combina (B) sp² + pd	tion of two hybridization. (C) spd + p <sup>2</sup>	They are (D) none of these
19.	Which of the following s (A) $[CIOF_2]^+$	hould have pyramidal sha (B) ICl <sub>3</sub>	ape : (C) [BrICl]⁻	(D) All of these
20.	Which of the following s (A) $N_2O$	pecies have a non linear (B) I <sub>3</sub> +	shape? (C)SCN⁻	(D) NO <sub>2</sub> <sup>+</sup>
21.	The correct order of inc	reasing $X - O - X$ bond a	angle is $(X = H, F \text{ or } CI)$ :	
	(A) $H_2O > CI_2O > F_2O$		(B) $CI_2O > H_2O > F_2O$	
	(C) $F_2O > CI_2O > H_2O$		(D) $F_2O > H_2O > Cl_2O$	Nº I
22.	When NH <sub>3</sub> is treated wit (A) Increases	th HCl, in the product spec (B) Decreases	cies H—N—H bond angl (C) Remains same	e (in comparison to ammonia) (D) Depends upon temperature
23.	The correct order of bor (A) $H_2S < NH_3 < BF_3 <$ (C) $H_2S < NH_3 < CH_4 <$	nd angle is : CH <sub>4</sub> : BF <sub>3</sub>	(B) NH <sub>3</sub> < H <sub>2</sub> S < CH <sub>4</sub> < (D) H <sub>2</sub> S < CH <sub>4</sub> < NH <sub>3</sub> <	BF <sub>3</sub> BF <sub>3</sub>
24.	Arrange the following in (A) $P_4 < PH_3 < H_2O$	n the increasing order of (B) $PH_3 < H_2O < P_4$	deviation from normal te (C) $P_4 < H_2 O < PH_3$	etrahedral angle : (D) H <sub>2</sub> O < PH <sub>3</sub> < P <sub>4</sub>
25.	In XeF <sub>2</sub> molecule the an orbital is $\beta$ and the angl (A) $\alpha = \beta = \gamma$	gle between two lone pair e between bond pair orbit (B) $\alpha > \beta > \gamma$	orbitals is $\alpha$ , the angle betals is $\gamma$ : (C) $\gamma > \beta > \alpha$	tween lone pair orbital and bond pair (D) $\gamma > \alpha > \beta$
26.	In which of the following (A) $NF_3$	molecules are all the bor (B) $CIF_3$	nds not equal? (C) BF <sub>3</sub>	(D) AIF <sub>3</sub>
27.	Which of the following is (A) $BF_4^- < BF_3$	s correct order of bond ler (B) $NO_2^+ < NO_2^-$	gth ? (C) CCl <sub>4</sub> < CF <sub>4</sub>	(D) $^{+}CH_{_{3}} > CH_{_{4}}$
28.	In which of the following (A) C– H bond in cyclop (C) N–N bond in $N_2O_4$	g cases the stated bond is ropane and propane and and $N_2H_4$	Bonger in first species th (B) Equatorial P –Cl bo (D) C – C bond in benze	an in second species? nd in PCI <sub>5</sub> and P–CI bond in PCI <sub>6</sub> <sup>-</sup> ne and $C_2H_6$
29.	Identify the correct sta (A) single N–N bond is (B) single N–N bond is (C) N $\equiv$ N is weaker the (D) None of these	tement : s stronger than single P - s weaker than single P – an P≡ P	– P bond P bond	
30.	In $O_2F_2$ , which of the fo (A) O–F bond length in (B) The O.N. of oxygen (C) The O–O bond leng (D) None of these	Nowing statement is incor $O_2F_2$ is longer than O–Fbo in $O_2F_2$ is +1. th in $O_2F_2$ is shorter than 0	rect. and length in $OF_2$ . D–O bond length in $H_2O_2$ .	
More	than one choice ty	ре		
31.	All bond : (A) dissociations are ex	othermic	(B) dissociations are end	dothermic
32.	Which of the following c	compounds contain(s) bot	יט) enmaiples are negati h ionic and covalent bond	
			(C) CUSO <sub>4</sub> ·5H <sub>2</sub> O	(D) NAUH
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**33.** Which of the following Lewis diagram is/are incorrect ?



46. Identify the correct option(s) (A)  $NH_4^+ > NH_3 > NH_2^-$  order of bond angle (B)  $(CH_3)_3$  B is a trigonal planar molecule (not considering the H-atoms on 'C') (C) In NH<sub>4</sub>Cl 'N' atom is in sp<sup>3</sup>d hybridisation (D) In S<sub>8</sub> molecule a total of 16 electrons are left on all the 'S' atoms after bonding . 47. Which of the following molecule (s) has/have bond angle close to 90°? (D) ICl<sub>3</sub> (A) NH<sub>2</sub> (B) H<sub>2</sub>S (C) PH PART - III: MATCH THE COLUMN 1. Column – I Column – II sp<sup>3</sup> and bent (A) SF (p) (B) KrF (q) two lone pairs (C) NOĊI bond angle < 109°28' (r) (D) NF<sub>3</sub> (s) sp<sup>2</sup> and bent sp<sup>3</sup>d<sup>2</sup> and square planar (t) 2. Match the compounds listed in column-I with characteristic(s) listed in column-II Column – I Column-II (A)  $CIF_{2}^{-}, CIF_{2}^{+}$ (B)  $IO_{2}F_{2}^{-}, F_{2}SeO$ (C)  $IOF_{4}^{-}, XeOF_{2}$ Square pyramidal. (p) See - saw and pyramidal shaped respectively. (q) (r) Linear and bent shaped respectively. (D)  $BrF_5$ , XeOF\_4 (s) Square pyramidal and T-shaped respectively. Both sp<sup>3</sup>d<sup>2</sup> (t) 3. Match the species given in column-I with the type of hybridisation given in column-II. Column-I Column-II sp<sup>3</sup>d (A)  $IO_{2}F_{2}^{-}$ (p) (B) F<sub>2</sub>SeO sp<sup>3</sup> (q) sp<sup>2</sup>

## **PART - IV : COMPREHENSION**

sp<sup>3</sup>d<sup>2</sup>

Read the following comprehension carefully and answer the questions.

(r)

(s)

### **Comprehension : 1**

(C) CIOF<sub>3</sub>

(D) XeF5+

## VSEPR THEORY

The trigonal bipyramid is not a regular shape since the bond angles are not all the same. It therefore follows that the corners are not equivalent in CIF<sub>3</sub> molecule. Lone pairs occupy two of the corners, and F atoms occupy the other three corners. These different arrangements are theoretically possible, as shown in figure.

(i) The most stable structure will be the one of lowest energy, that is the one with the minimum repulsion between the five orbitals. The greatest repulsion occurs between two lone pairs. Lone pair bond pair repulsions are next strongest, and bond pair-bond pair repulsions the weakest.



E - Equatorial position a - Axial position

Resonance

(1)

A rule of thumb can be theorised, that the position having maximum repulsion amongst them are occupied at equatorial points. Therefore (3) structure is right.

(ii) Since double bond occupies more space compared to single bond therefore it will prefer equatorial position. (iii) More electronegative element will occupy axial position in case of trigonal bipyramidal geometry (iv) In case of  $sp^3d^2$  hybridisation lone pairs should be placed opposite to each other because all the corners are identical.

- 1. Geometry (i.e. arrangement of electron pairs around central atom) of  $ClOF_3$  is similar to the : (A)  $XeF_4$  (B)  $SOCl_2$  (C)  $I_3$  (D)  $ClO_4$
- **2.** The shape of  $SF_5^-$  can be :



- 3. Actual shape of the molecule  $BrF_5$  is similar to the molecule : (A)  $PCI_5$  (B)  $XeF_4$  (C)  $PCI_4^+$ 
  - (A)  $PCI_5$  (B)  $XeF_4$  (C)  $PCI_4^+$ Which of the following statements is/are correct for  $CIO_4^-$  oxoanion?
  - (A) It does not have any tendency of polymerisation.
  - (B) It has strong  $p\pi$ - $p\pi$  bonding between chlorine and oxygen.
    - (C) All Cl–O bonds are identical and chlorine atom is sp<sup>3</sup> hybridised.
    - (D) The chemical bonding takes place in ground state and charge dispersion is more than  $CIO_3^-$  oxo anion.

(C) SI

(D) None of these

(D) HCIO<sub>3</sub>

5. Which of the following do not exist ? (A)  $SH_6$  (B)  $HFO_4$ 

4.

# **Exercise #3**

## PART - I : IIT-JEE PROBLEMS (LAST 10 YEARS)

#### \* Marked Questions may have more than one correct options. 1. The hybridization of atomic orbitals of nitrogen in $NO_2^+$ , $NO_3^-$ and $NH_4^+$ are : [JEE-2000, 1/35] (A) sp, sp<sup>3</sup> and sp<sup>2</sup> respectively (B) sp, sp<sup>2</sup> and sp<sup>3</sup> respectively (C) sp<sup>2</sup>, sp and sp<sup>3</sup> respectively (D) sp<sup>2</sup>, sp<sup>3</sup> and sp respectively 2. Molecular shapes of $SF_{a}$ , $CF_{a}$ and $XeF_{a}$ are respectively : [JEE-2000, 1/35] (A) the same with 2,0 and 1 lone pair of electrons respectively. (B) the same with 1,1 and 1 lone pair of electrons respectively. (C) different with 0,1 and 2 lone pair of electrons respectively. (D) different with 1, 0 and 2 lone pair of electrons respectively. Draw the molecular structures of XeF<sub>2</sub>, XeF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>, indicating the location of lone pair of electrons. 3. [JEE-2000, 3/100] The correct order of hybridisation of the central atom in the following species; NH<sub>3</sub>, PCI<sub>5</sub> and BCI<sub>3</sub> is : 4. [Atomic number Pt = 78] [JEE-2001, 1/35] (C) dsp<sup>2</sup>, sp<sup>3</sup>, dsp<sup>3</sup> (D) dsp<sup>2</sup>, sp<sup>2</sup>, dsp<sup>3</sup> (A) $dsp^2$ , $sp^2$ , $sp^3$ (B) sp<sup>3</sup>, dsp<sup>3</sup>, sp<sup>2</sup> Which of the following are isoelectronic and isostructural ? 5. NO<sub>3</sub><sup>-</sup> , CO<sub>3</sub><sup>2-</sup> , CIO<sub>3</sub><sup>-</sup> , SO<sub>3</sub> . (A) NO<sub>3</sub><sup>-</sup> , CO<sub>3</sub><sup>2-</sup> (B) SO<sub>3</sub> , NO<sub>3</sub><sup>-</sup> [JEE-2003, 3/84] (C) CIO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> (D) $CO_{3}^{2-}$ , $SO_{3}$ . CHEMICAL BONDING-1 - 132 Kesonance

6.	Which of the following r (A) $H_2C = CH - C \equiv N$	hich of the following represent the given mode of hybridisation $sp^2 - sp^2 - sp - sp$ $H_2C = CH - C \equiv N$ (B) $HC \equiv C - C \equiv CH$							
	(C) $H_2C = C = C = CH_2$		(D) CH <sub>2</sub>						
7.	Using VSEPR theory, d	Jsing VSEPR theory, draw the shape of PCI <sub>5</sub> and $BrF_5$ .							
8.	The number of lone pair (A) 3	(s) of electrons in XeOF <sub>4</sub> (B) 2	is : (C) 1	(D) 4	[JEE-2004, 3/84]				
9.	Use VSEPR model to d specify their geometry.	Use VSEPR model to draw the structures of $OSF_4$ and $XeF_4$ (indicate the lone p specify their geometry.							
10.	In which of the following	n which of the following the maximum number of lone pairs is present on the cent							
	(A) [CIO <sub>3</sub> ] <sup>-</sup>	(B) XeF <sub>4</sub>	(C) SF <sub>4</sub>	(D) I <sub>3</sub>					
11.	Based on VSEPR theor	Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF <sub>5</sub> is [JEE–2010, 3/163]							
12.	The shape of $XeO_2F_2$ mo (A) trigonal bipyramidal (C) tetrahedral	olecule is :	<ul><li>(B) square plannar</li><li>(D) see-saw</li></ul>	0	[JEE–2012, 3/136]				
13.*	The correct statement(s (A) O-O bond lengths ar (C) $O_3$ is diamagnetic in	s) about O <sub>3</sub> is (are) re equal. nature.	(B) Thermal decomposit (D) O <sub>3</sub> has a bent structu	[JEE(Ad ion of O <sub>3</sub> ure.	dvanced) 2013, 3/120] is endothermic.				
	PART - II : AIEEE PROBLEMS (LAST 10 YEARS)								
1.	The number of lone pair (A) 3, 2, 1	s on Xe in Xe $F_2$ , Xe $F_4$ and (B) 2, 4, 6	XeF <sub>6</sub> respectively are : (C) 1, 2, 3	(D) 6, 4	[ <b>AIEEE-2002</b> ]				
2.	The hybridisation of the underline atom changes in : (A) AlH <sub>3</sub> changes to $AlH_4^-$ (B) $H_2O$ changes to $H_3O^+$ (C) $NH_3$ changes to $NH_4^+$ (D) in all cases				[AIEEE-2002]				
3.	Bond angle of $109^{\circ} 28' i$ (A) NH <sub>3</sub>	s found in : (B) H <sub>2</sub> O	(C) CH <sub>3</sub> <sup>+</sup>	(D) NH <sub>4</sub>	[AIEEE-2002]				
4.	In the anion HCOO <sup>-</sup> the (A) Electronic orbits of a (B) The C = O bond is w (C) The anion HCOO <sup>-</sup> h (D) The anion is obtained	two C – O bonds are four carbon atom are hybridise veaker than the C – O bor as two resonating structur d by removal of a proton f	nd to be of equal length. d. nd. res. from the acid molecule.	What is t	he reason for it ? <b>[AIEEE-2003]</b>				
5.	Which of the following $c$ (A) SO <sub>2</sub>	compounds has the small $(B) H_2O$	est bond angle in its mole (C) H <sub>2</sub> S	cule? (D) NH <sub>3</sub>	[AIEEE-2003]				
6.	The pair of species have $(A) CF_4$ , $SF_4$	ing identical shapes for m (B) $XeF_2$ , $CO_2$	olecules of both species $(C) BF_3, PCI_3$	is : (D) PF <sub>5</sub> ,	[AIEEE-2003] IF <sub>5</sub> .				
7.	The maximum number of	of 90º angles between bor	nd pair-bond pair of electi	rons is ob	served in :				
	(A) dsp <sup>3</sup>	(B) sp <sup>3</sup> d	(C) dsp <sup>2</sup>	(D) sp³d	[AILL-2004]				
8.	The correct order of bor (A) $H_2 S < SiH_4 < NH_3 <$ (C) $H_2 S < NH_3 < SiH_4 <$	nd angles (smallest first) i $BF_3^{}$ BF $_3^{}$	n $H_2S$ , $NH_3$ , $BF_3$ and $SiH_4$ (B) $NH_3 < H_2S < SiH_4 <$ (D) $H_2S < NH_3 < BF_3 < SiH_3 < Si$	is∶ BF₃ SiH₄	[AIEEE-2004]				
9.	Which one of the followi (A) $XeF_4$ (Atomic number : B = 5	ing has the regular tetrahe (B) SF <sub>4</sub> , S = 16, Ni = 28, Xe = 54	edral structure ? (C) BF <sub>4</sub> <sup>-</sup> !)	(D) [Ni(C	[AIEEE-2004] CN) <sub>4</sub> ] <sup>2-</sup>				

10.	Which one of the followi (A) Acetone	ng does not have sp² hyb (B) Acetic acid	ridized carbon? (C) Acetonitrile	(D) Acetamide	[AIEEE-2004]
11.	The molecular shapes c (A) the same with 2, 0 a (B) the same with 1, 1 a (C) different with 0, 1 an (D) different with 1, 0 an	of $SF_4$ , $CF_4$ and $XeF_4$ are : nd 1 lone pairs of electron nd 1 lone pair of electron id 2 lone pairs of electrons id 2 lone pairs of electrons	ns on the central atom, re s on the central atom, res s on the central atom, res s on the central atom, res	espectively. pectively. pectively. pectively.	[AIEEE-2005]
12.	The number and type of (A) one sigma, one pi (C) two sigma, one pi	bonds between two carb	on atoms in calcium carb (B) one sigma, two pi (D) two sigma, two pi	ide are : [AIEEE	E-20 <b>05, 2</b> 011, 4/120]
13.	The hybridisation of orb (A) sp, sp <sup>2</sup> , sp <sup>3</sup>	itals of N atom in NO <sub>3</sub> <sup>-</sup> , N (B) sp <sup>2</sup> , sp, sp <sup>3</sup>	$IO_2^+$ and $NH_4^+$ are respective (C) sp, sp <sup>3</sup> , sp <sup>2</sup>	ctively : <b>[AIEEE</b> (D) sp <sup>2</sup> , sp <sup>3</sup> , sp	- <b>2011, 4/120]</b>
14.	The structure of IF <sub>7</sub> is : (A) square pyramid (C) octahedral		(B) trigonal bipyramid (D) pentagonal bipyrami	d [AIEEE	E -2011, 4/120]
15.	Which of the following h (A) $XeF_4$	as maximum number of I (B) XeF <sub>6</sub>	one pairs associated with (C) $XeF_2$	Xe ? [AIEEE (D) XeO <sub>3</sub>	E -2011, 4/120]
16.	The molecule having sn (A) $\mathrm{NCl}_3$	nallest bond angle is : (B) AsCl <sub>3</sub>	(C) SbCl <sub>3</sub>	(D) PCl <sub>3</sub>	E -2012, 4/120]
17.	In which of the following (A) $CO_3^{2-}$ and $NO_3^{-}$	pairs the two species are (B) $PCl_4^+$ and $SiCl_4$	e not isostructural ? (C) PF <sub>5</sub> and BrF <sub>5</sub>	[AIEEB (D) $AIF_6^{3-}$ and S	E - <b>2012, 4/120]</b> SF <sub>6</sub>
18.	Which of the following e (A) lodine	exists as covalent crystal (B) Silicon	s in the solid state ? (C) Sulphur	[AIEEE (D) Phosphorus	E <b>-2013, 4/120]</b> S

Resonance

# Answers

## **EXERCISE - 1**

## **PART-I**

- A-1. Ionic : CsCl, Nal, metallic -Cu Network solid -diamond, guartz Molecular solid -iodine,ice
- A-2.
- (a)  $[::: C \equiv N]^{-}$  (b) Covalent compound :: Ci: :Ci: :Ci:

(c) (c)

- A-3. In CCl<sub>4</sub>, covalent bond is present and also it is non polar in nature, whereas in NaCl ionic bond is present.
- Solid sodium has the loosely bound electron, where as solid NaCl does not have any free electron. A-4.
- B-1. (i) Chlorine has vacant d-orbital and thus it can expand its covalence (ii) The contraction of d-orbital of chlorine by the inductive effect of the fluorine atoms permits the sp<sup>3</sup>d hybridisation of chlorine to have trigonal bipyramidal arrangement of five electron pairs. Fluoride does not have empty d-orbital like chlorine and thus cannot expands its covalence.



(a) All have zero except single bonded oxygen have -1 charge. **B-6**.

(b) All zero.

- (c) All 'F' have zero but 'B' have -1 charge.
- (d) Central atom has +1 charge and others have -1 charge.
- (e) Central atom has +1 and one have -2 and other have zero
- (f) Oxygen has zero and nitrogen has +1 charge

**C-1.** 
$$\rightarrow$$
 average B.O.=  $1\frac{1}{3}$ ;  $H \rightarrow average B.O.= 1\frac{1}{2}$   
Hence one bond in HSO<sub>3</sub><sup>-</sup> is longer than S–O bond in SO<sub>3</sub><sup>2-</sup>. But other two S–O bond in HSO<sub>3</sub><sup>-</sup> are shorted

er bonds.

Number of sigma bonds is 7 & number of pi bonds is 3. D-1.

人 **Resonance** 





In  $IF_5$  there are 6 electron pairs around central iodine atom. The hybridisation of iodine is thus sp<sup>3</sup>d. 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.



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**G-1.** In Br<sub>3</sub><sup>-</sup> there are 5 electron pairs around central bromine atom (3 lone pairs and 2 bond pairs). The hybridisation of bromine is thus sp<sup>3</sup>d. To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.



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 SbCl<sub>2</sub>.



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 repulsions–hence, the largest angle in Pl<sub>3</sub>. 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 Sbl<sub>3</sub>, 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.

- **G-3.** (i) Interaction between lone pair of electrons of chloride ion and Si<sup>4+</sup> is not very strong and (ii) Six large chloride ions can not be accommodated around Si<sup>4+</sup> due to limitation of its size.
- G-4. (a) This is because of the absence of d-orbitals in nitrogen for sp<sup>3</sup>d 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.
- **G-5.** Order of C–H bond strength is  $C_2H_2 > C_2H_4 > C_2H_6$  as % s character decreases in the same order.

A-1.	(B)	A-2.	(B)	A-3.	(B)	A-4.	(C)	A	-5.	(C)
A-6.	(B)	A-7.	(B)	B-1.	(D)	B-2.	(D)	В	-3.	(B)
B-4.	(D)	B-5.	(D)	B-6.	(C)	B-7.	(D)	В	-8.	(C)
C-1.	(D)	C-2.	(D)	D-1.	(C)	D-2.	(C)	D	-3.	(B)
D-4.	(A)	D-5.	(B)	D-6.	(C)	D-7.	(C)	E	·1.	(A)
E-2. E-7.	(B) (C)	E-3. E-8.	(A) (C)	E-4. E-9.	(D) (A)	E-5. F-1.	(B) (C)	E: F:	·6. ·2.	(C) (D)
F-3.	(D)	F-4.	(A)	F-5.	(B)	F-6.	(D)	F	7.	(D)
G-1.	(B)	G-2.	(D)	G-3.	(B)	G-4.	(B)	G	-5.	(A)
G-6.	(A)	G-7.	(A)	G-8.	(B)	G-9.	(C)	G	-10.	(D)

## PART-II

Resonance







- **13.** (i)  $NO_2^+ > CO_3^{2-} > BF_4^-$  (ii)  $SO_3 > SO_2CI_2 > SF_6$  (iii)  $OBr_2 > OCI_2 > OF_2$  (iv)  $PCI_5 = PBr_5 > XeO_2F_2$
- 14. If central P atom is bonded to highly electronegative elements such as F, O, or Cl then electronegative element attracts more than its share of bonding electrons and the F or Cl atom attains δ<sup>-</sup> charge. This leaves δ<sup>+</sup> charge on P, which makes the orbital contact. Since the 3d orbital contracts in size very much more than 3s and 3p orbitals, the energies of 3s, 3p and 3d orbitals may become close enoguh to allow sp<sup>3</sup>d hybridization in PCl<sub>5</sub>. Hydrogen cannot cause this large contraction so PH<sub>3</sub> does not exist.



- **4.** (B) **5.** (A) **6.** (A)
- 7. There are 5 electron pairs and all are bonds pairs in  $PCI_5$ . So to have the minimum repulsions between bond pairs it acquires trigonal bipyramidal shape. In  $BrF_5$ , there are 6 electrons pairs out of which one lone pair and rest all are bond pairs. So to have the minimum repulsions between bond pairs and lone pairs it acquires square pyramidal shape.



8. 9. (C)

According to VSEPR theory two lone pairs out of six electron pairs are trans to each other to have minimum repulsion. The shape of  $XeF_4$  is square planar and geometry is octahedral with  $sp^3d^2$  hybridisation. The molecule looks like :

F Ve

In OSF<sub>4</sub>, there are five electron pairs and all are bond pairs. So geometry is trigonal bipyramidal. As double bond creates more repulsion than singles bond, the double bond acquires one of equatorial position of trigonal bipyramidal to have minimum repulsions. The structure looks like:



## **Advanced Level Problems**

## **PART - I : OBJECTIVE QUESTIONS**




11.	The correct order or molecules / ions is (assi	f increasing s ume all hybrid or	charact bitals are	ter (in exactly	percentage) in equivalent):	n the hybrid c	orbitals in below
	SnCl <sub>2</sub>	XeF <sub>4</sub>	I 3			HgCl <sub>2</sub> (g)	$\mathbf{\wedge}$
	ı (A) II < III < IV < I < V	II	111	(B) II < I	1v V < 111 < V < 1	V	
	(C) III < II < I < V < IV			(D) II < I	V < III < I < V		
12.	The hybrid state of posit	ively charged ca	arbon in vi	invl catio	on (CH <sub>2</sub> = $\stackrel{\oplus}{C}$ H) is	5:	
	(A) Unpredicatable	(B) sp <sup>2</sup>		(C) sp	( <u>2</u> - )	(D) sp <sup>3</sup>	<b>U</b>
13.	If the equatorial plane is	s x– v plane in sp	<sup>3</sup> d hybridi	sation th	nen the orbital us	sed in pd hybridis	ation are -
	(A) $p_z$ and $d_{z^2}$	(B) $p_x$ and $d_{xy}$	,	(C) p <sub>y</sub> ar	nd d <sub>yz</sub>	(D) none of thes	e
14.	In the cation [H–C–N–X	e–F]⁺ which is lin	hear, the h	ybridisa	tions of C, N & X	e atoms respect	ively are -
	(A) sp, sp, sp	(B) sp , sp <sup>2</sup> , sp <sup>2</sup>	<sup>3</sup> d	(C) sp, :	sp, sp³d	(D) sp <sup>2</sup> , sp, sp <sup>3</sup>	'nd
15.	The structure of $IO_2F_2^{-1}$	s analogous to :				5	
	(A) SF <sub>4</sub>	(B) $XeO_2F_2$		(C) $F_2Se$	$\Theta_2$	(D) (A) and (B) I	ooth
16.	Which of the following a (A) Equitorial FSF bond (B) Hybridisation states (C) The bond angle FCC (D) The axial FSF bond	bout SF <sub>4</sub> , SOF <sub>4</sub> angle in SOF <sub>4</sub> w of sulphur in SF <sub>2</sub> will be < 120° ir angle in SF <sub>4</sub> is e	and OCF <sub>2</sub> vill be great and SOF molecule exactly 18	$_{2}$ moleculater than $F_{4}$ moleculater than e OCF <sub>2</sub> 0°	les is correct. in SF $_4$ molecule ules will be diffe	rent.	
17.	Which of the following n (A) $SF_2$	nolecules has tw (B) KrF <sub>4</sub>	o lone pai	irs and b (C) ICl <sub>4</sub> -	ond angle (need	I not be all bond a (D) All of these	angles) < 109.5°?
18.	Incorrect order about b (A) $H_2O > H_2S > H_2Se >$ (C) $SF_6 < NH_3 < H_2O <$	ond angle is : • H <sub>2</sub> Te OF <sub>2</sub>		(B) C <sub>2</sub> H (D) ClO	$_{2} > C_{2}H_{4} > CH_{4} > 2$ $_{2} > H_{2}O > H_{2}S > 2$	> NH <sub>3</sub> • SF <sub>6</sub>	
19.	In the structure of $H_2CS$ given : Axial FSF angle (idealise Equatorial FSF angle (idealise Equatorial FSF angle (idealise After deciding the plane (A) two C – H bonds are (B) two C – H bonds are (C) total five atoms are id (D) equatorial S – F bon	$F_4$ , to decide the ed = 180°) dealised = 120°) of double bond, in the same pla in the same plan ds are perpendic	which of t ne of axia ne of equa	which C which C the follow al S – F I atorial S ane of $\pi$ -	C = S is present t 170° 97° wing statement is bonds F – F bonds bond	he following bon s/are correct ?	d angle values are
20.	The bond length in LiF v (A) less than that of Naf (C) more than that of KF	vill be		(B) equa	al to that of KF al to that of NaF		
21.	$S_1$ : Oxidation number $S_2$ : The anhydride of H $S_3$ : As the electroneg terminal atoms increas $S_4$ : For heteronucles electronegativity value (A) T T T F	of N in $N_2O_5$ is solve the set of N in N_2O_5 is solve the set of the set	5 cid is Cl <sub>2</sub> C al atom ir increase: ecies A ·	) n a mole s. – B, the (C) F F	ecule having sa e bond length T F	me hybridisatio decreases as (D) T T F T	n state and same
More	than one choice ty	pe		(-)			
22*.	Most ionic compounds h (A) high melting points a (B) high melting points a (C) high solubilities in po (D) three-dimensional c	nave : and low boiling po and non-direction plar solvents and rystal structures.	oints Ial bonds I low solub , and are g	bilities in good coi	nonpolar solven nductors of elect	its ricity in the molte	en state.

Resonance

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### **PART - II : SUBJECTIVE QUESTIONS**

- What type of bonding is expected between.
   (a) a metal and a non-metal
   (b) two non-metal
- **2.** Write down the resonating structures for  $SO_4^{2-}$  and  $NO_3^{-}$ .
- 3. Identify the type of overlapping in N–H bond in  $N_2H_4$  molecule?
- 4. One of the first drugs to be prepared for use in treatment of acquired immuno deficiency syndrome (AIDS) was azidothymidine (AZT).

- (a) How many carbon atoms have sp<sup>3</sup> hybridisation?
- (b) How many carbon atoms have sp<sup>2</sup> hybridisation ?
- (c) How many nitrogen atoms (central atom not terminal) have sp hybridisation ?

I

- (d) How many  $\pi$  bonds are in the molecule ?
- 5. Compare the bond angle in  $O_3$  and  $SO_2$ .
- Draw the structure of the following compounds. Clearly indicate the number of bond pairs and lone pairs involved on central atom. Write (i) number of bond pairs and lone pairs on the central atom (ii) the shape of the molecules (iii) hybridization of the central atom.
   (a) SF<sub>4</sub>
   (b) XeOF<sub>4</sub>
- 7. Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron. Calculate the distance between the terminal carbon atoms in propane. Given, C—C single bond length is 1.54 Å.
- 8. There will be three different flourine-flourine distances in molecule  $F_2C=C=C=CF_2$ . Assuming ideal bond angles for a particular hybridisation (assume no distortion due to double bonds), find out the two smaller flourine-flourine distances (in pm).

(Given that C–F bond length = 134 pm, C = C bond length = 134 pm,  $\sqrt{3}$  = 1.7)

- 9. The cynate ion (OCN)<sup>-</sup> form stable series of salts, but many fulminates (CNO)<sup>-</sup> are explosive. Explain.
- 10. Why electrovalent compounds do not show stereoisomerism?
- **11.**  $SF_4$  and  $SF_6$  are known but  $OF_4$  and  $OF_6$  are not. Explain only in one or two lines.
- 12. Draw orbital overlap diagram for the cases given below. consider internuclear axis as y-axis. Also classify them as  $\sigma,\pi,\delta$  if bond is formed by their overlap
  - (a) s and  $p_y$ (b)  $d_{xy}$  and  $p_y$ (c) s and  $p_z$ (d)  $p_x$  and  $p_x$ (e)  $p_z$  and  $p_z$ (f)  $d_{xz}$  and  $d_{xz}$ (d)  $p_x$  and  $p_y$

Resonance



### **CHEMICAL BONDING - II**

# **Exercise #1**

### **PART - I : SUBJECTIVE QUESTIONS**

#### Section (A) : Lewis acids, coordinate bond, electrondeficient bond A-1. Explain why (i) NH<sub>3</sub> is better e<sup>-</sup> pair donor than PH<sub>3</sub>. (ii) Why NH<sub>3</sub> is a better base than CH<sub>3</sub>CN? A-2. Why BCl<sub>3</sub> and SiF<sub>4</sub> act as Lewis acids ? Explain. A-3. BF<sub>3</sub> exists but BH<sub>3</sub> does not. Why explain? Section (B) : Back bonding The B–F bond length in Me<sub>3</sub>N.BF<sub>3</sub> is 1.35 Å, much longer than 1.30 Å in BF<sub>3</sub>. Explain. B-1. B-2. Explain why SiH<sub>3</sub>NCO is linear (expect H atoms) but CH<sub>3</sub>NCO is non linear. B-3. Draw the structure : Identify the type ( $p\pi - p\pi$ , $p\pi - d\pi$ ) of bonds and number of these bonds in the following molecule : (ii) H<sub>2</sub>PO<sub>4</sub> (iv) HClO (i) SO<sub>3</sub> (iii) N Why (CH<sub>3</sub>)<sub>3</sub>COH is less acidic than (CH<sub>3</sub>)<sub>3</sub>SiOH ? B-4. BCl<sub>3</sub> is more acidic than BF<sub>3</sub>. Why? B-5. Section (C) : MOT C-1. Find out the bond order of :

- (a)  $H_2$  (b)  $H_2^+$  (c)  $H_2^-$  (d)  $Li_2$  (e)  $Be_2$  (f)  $B_2$
- **C-2.** Identify the molecules or atoms or ions from the following molecular orbital energy level formulations. The species should be selected from  $(B_2, C_2, O_2^{2+}, O_2, F_2, N_2)$ 
  - (a) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \pi (2p_x)^1 \pi (2p_y)^1$
  - (b) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \pi (2p_x)^2 \pi (2p_y)^2$
  - (c) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \sigma (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2$
  - (d) KK  $\sigma (2s)^2 \sigma^* (2s) \sigma (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2 \pi (2p_x)^1 \pi^* (2p_y)^1$
  - (e) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \sigma (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2 \pi (2p_y)^2 \pi^* (2p_y)^2$
  - (f) KK  $\sigma$  (2s)<sup>2</sup>  $\sigma$  (2s)<sup>2</sup>  $\pi$ (2p<sub>y</sub>)<sup>2</sup> $\pi$ (2p<sub>x</sub>)<sup>2</sup> $\sigma$ (2p<sub>z</sub>)<sup>2</sup>

### Section (D) : Applilcation of MOT

- **D-1.** How would you explain that  $B_2$  molecule is not diamagnetic?
- D-2. Explain why NO<sup>+</sup> is more stable towards dissociation into its atoms than NO?
- **D-3.** Which of the following are gerade molecular orbitals? (i)  $\sigma^*2s$  (ii)  $\sigma^2p_z$  (iii)  $\pi^2p_y$  (iv)  $\pi^*2p_x$

### Section (E) : Multicentered species

- E-1. Explain the structure, hybridisation and oxidation state of S in sulphuric acid, Marshall's acid, Caro's acid and oleum.
- **E-2.** Find number of  $p\pi$ -d $\pi$  bonds in (a) Disulphate (d) trimer of SO<sub>2</sub>

(b) triphosphate (e)  $P_4O_{10}$  (c) trimetaphosphate (f)  $P_4O_6$ 

**E-3.** In which of the following compounds, the  $p\pi$ -d $\pi$  back bonding take place ? (a)  $P_4O_{10}$  (b)  $HNO_3$  (c)  $N_2O_5$  (d)  $HCIO_4$ 

**E-4.** Give the number of characteristic bond(s) found in the various oxy-acids of phosphorus as given below. (P) Number of P-O-P bond(s) in cyclotrimetaphosphoric acid.

- (Q) Number of P-P bond(s) in hypophosphoric acid.
- (R) Number of P-H bond(s) in hypophosphorus acid.
- (S) Number of P-OH bond(s) in pyrophosphoric acid.

Р	0	R	S

**E-5.** Draw the structure of cyclic metaphosphoric acid,  $(HPO_3)_3$  and give how many P—O—P bonds are there in the structure ?

# **PART - II : OBJECTIVE QUESTIONS**

#### \* Marked Questions may have more than one correct option.

#### Section (A) : Lewis acids, coordinate bond, electrondeficient bond

A-1. Which of the following contains a coordinate covalent bond (A)HNO (B) BaCl (C) HCI  $(D) H_0 O$ A-2. Bonds present in  $CuSO_4$ .  $5H_2O(s)$  is (B) Electrovalent and coordinate (A) Electrovalent and covalent (C) Electrovalent, covalent and coordinate (D) Covalent and coordinate A-3. Which combination is best explained by the co-ordinate covalent bond (C) Mg +  $\frac{1}{2}O_2$  (D) H<sub>2</sub> + I<sub>2</sub> (A) H<sup>+</sup> + H<sub>2</sub>O (B) Cl + Cl A-4. For B<sub>2</sub>H<sub>6</sub> **S<sub>1</sub>**: Each boron is sp<sup>3</sup> hybridised  $S_2$ : from terminal 'H' & two 'B' atom are in same plane but two bridge hydrogen in different plane.  $S_3$ : It has 4  $\sigma$  bond & 2 bridge bond  $\mathbf{S}_{\mathbf{A}}$ : 8  $\sigma$  bonds are present in it (A) TTFF (B) TTTF (C) F F T F (D) FTFT Identify the species containing Banana bonds A-5.  $(A) (BeH_2)_n$ (B) BF<sub>2</sub>  $(C) (AICI_3)_2$  $(D) (BeCl_2)_n$ Which of the following compounds has coordinate (dative) bond A-6. (A) CH<sub>3</sub>NC (B) CH<sub>3</sub>OH  $(C) CH_3CI$  $(D) NH_3$ Which is not true about  $B_2H_6$ A-7. (A) Both 'B' atoms are sp<sup>3</sup> hybridised (B) Boron atom is in ground state (C) Two hydrogens occupy special positions (D) There are two, three centre two electron bonds

#### Section (B) : Back bonding

- For BF<sub>3</sub> molecule which of the following is true? B-1.
  - (A) B-atom is sp<sup>2</sup> hybridised.
  - (B) There is a  $P\pi P\pi$  back bonding in this molecule.
  - (C) Observed B–F bond length is found to be less than the expected bond length.
  - (D) All of these
- B-2. Which of the following statements regarding the structure of SOCI, is not correct?
  - (A) The sulphur is sp<sup>3</sup> hybridised and it has a tetrahedral shape.
  - (B) The sulphur is sp<sup>3</sup> hybridised and it has a trigonal pyramid shape.
  - (C) The oxygen -sulphur bond is  $p\pi d\pi$  bond.
  - (D) It contain one lone pair of electrons in the sp<sup>3</sup> hybrid orbital of sulphur.
- B-3. Respective order of strength of back-bonding and Lewis acidic strength in boron trihalides is : (A) BF<sub>3</sub> < BCl<sub>3</sub> < BBr<sub>3</sub> and BF<sub>3</sub> < BCl<sub>3</sub> < BBr<sub>3</sub> (B) BF<sub>3</sub> > BCl<sub>3</sub> > BBr<sub>3</sub> and BF<sub>4</sub> > BCl<sub>3</sub> > BBr<sub>3</sub> (C)  $BF_3 > BCI_3 > BBr_3$  and  $BF_3 < BCI_3 < BBr_3$ (D) BF<sub>3</sub> < BCl<sub>3</sub> < BBr<sub>3</sub> and BF<sub>3</sub> > BCl<sub>3</sub> > BBr<sub>3</sub>
- For BF, molecule which of the following will not be true **B-4**.
  - (A) It has less bond length than  $BF_{4}^{-}$
  - (B) It has less bond length than the compound  $[NH_3 \rightarrow BF_3]$
  - (C) It's bond strength is increased because of  $p\pi$ -d $\pi$  back bonding
  - (D) It forms  $BF_4^{-}$  when hydrolysed in water.

#### Section (C) : MOT

- C-1. During the formation of a molecular orbital from atomic orbitals of the same atom, probability of electron density is :
  - (A) none zero in the nodal plane
  - (C) zero in the nodal plane

- (B) maximum in the nodal plane
- (D) zero on the surface of the lobe
- C-2. If Z-axis is the molecular axis, then  $\pi$ -molecular orbitals are formed by the overlap of (A) s + p  $(C) p_{7} + p_{7}$ (B) p, + p, (D) p + p

C-3. Bond order is a concept in the molecular orbital theory. It depends on the number of electrons in the bonding and antibonding orbitals. Which of the following statements is true about it? The bond order (A) Can have a negative quantity (B) Has always an integral value

- (C) Can assume any positive or integral or fractional value including zero
- (D) Is a non zero quantity
- C-4. Which of the following pairs have identical values of bond order? (A)  $N_2^+$  and  $O_2^+$ (B) F, and Ne<sub>2</sub>  $(C) O_2$  and  $B_2$ (D)  $C_2$  and  $N_2$
- Which of the following molecules /ions exhibit sp mixing? C-5.  $(A) B_{2}$ (B) C<sub>2</sub><sup>2</sup>  $(C) O_{2}^{+}$ (D) Both (A) and (B)
- The common features of the species  $N_2^{2-}$ ,  $O_2$  and  $NO^{-}$  are : C-6. (A) bond order three and isoelectronic. (B) bond order two and isoelectronic. (C) bond order three but not isoelectronic. (D) bond order two but not isoelectronic.
- Which of the following molecular orbitals has two nodal planes C-7.

(B) π2p<sub>v</sub> (C)  $\pi^{*} 2p_{v}$ (A) σ2s  $(D) \sigma^{*} 2p_{x}$ 

#### Section (D) : Applilcation of MOT

- Among the following species, which has the minimum bond length? D-1.  $(A) B_2$  $(B) C_2$  $(C) F_{2}$  $(D) O_{2}^{-}$ Which of the following species is paramagnetic? D-2.
- $(B) O_2^{2-}$ (C) CN-(A) NO-(D) CO

D-3.	The following molecules correct order. (I) $O_2$ ; (II) $O_2^-$ ; (III) $O_2^-$ ; (A) I I I < I I < I V	s / species have been arra $_{2}^{2-}$ ; (IV) O <sub>2</sub> <sup>+</sup> (B) IV < I I I < I I < I	anged in the order of their (C)III <ii<iv<i< th=""><th>increasing bond orders, Identify the (D) II &lt; III &lt; IV</th></ii<iv<i<>	increasing bond orders, Identify the (D) II < III < IV
D-4.	Which of the following s (A) Among $O_2^+$ , $O_2^-$ and (B) He <sub>2</sub> molecule does n (C) $C_2^-$ , $O_2^{2-}$ and Li <sub>2</sub> are c	statements is incorrect? $O_2^{-}$ the stability decrease not exist as the effect of b liamagnetic	is as $O_2^+ > O_2^- > O_2^-$ onding and anti-bonding	orbitals cancel each other.
	(D) In $F_2$ molecule, the	energy of $\sigma_{2p_z}$ is more the	nan $\pi_{2p_x}$ and $\pi_{2p_y}$	×.
D-5.	Which one is paramagn (A) $O_2^-$	etic from the following (B) NO	(C) Both (A) and (B)	(D) CN-
D-6.	Which of the following of (A) $N_2^+ > N_2^-$	orders is correct in respec (B) $O_2^+ > O_3^-$	t of bond dissociation en∉ (C) NO⁺ > NO	ergy? (D) All of those
D-7.	Which of the following s (A) During $N_2^+$ formation (B) During $O_2^+$ formation (C) During $O_2^-$ formation (D) During CN <sup>-</sup> formation	statement is incorrect ? n, one electron is removed n, one electron is removed n, one electron is added to on, one electron is added t	from the bonding molect from the antibonding mo the bonding molecular o o the bonding molecular	ular orbital of $N_2$ . Diecular orbital of $O_2$ . Orbital of $O_2$ . Orbital of CN.
D-8.	S <sub>1</sub> : The HOMO in $F_2^{-1}$ is S <sub>2</sub> : Bond order of $O_2^{-1}$ is S <sub>3</sub> : NO <sup>+</sup> is more stable S <sub>4</sub> : C <sub>2</sub> is more stable the State, in order, whether	s $\pi^* 2p_x = \pi^* 2p_y$ molecula s more then $O_2^+$ . e than $N_2^+$ han $C_2^+$ $S_1, S_2, S_3, S_4$ are true or	false	
D-9.	Which the following mo (I) $O_{a^+}$ ; (II) NO; (III) N	lecules / species have ide	ntical bond order and sar	me magnetic properties ?
	(A) (I), (II) only	(B) (I) and I I I only	(C) (I) ,(I I) and (I I I)	(D) (I I) and (I I I) only
Section	on (E) : Multicente	red species		
E-1.	Which of the following s $(A) N_2O_3$	species does not contain $(B) N_2 O_2^{2-}$	$N - N \text{ covalent bond } ?$ $(C) N_2O_5 \qquad (D) N_2C$	) <sub>4</sub>
E-2.	The no. of S-O-S bonds (A) 1	s in the trimer of SO $_3$ is (B) 2	(C) 3	(D) None
E-3.	Which of the following s (A) $H_2S_2O_5$	species do not contain S– (B) H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	S linkage? (C) $H_2S_2O_3$	(D) $H_2S_4O_6$
E-4.	Number of sigma bond (A) 6	ls in P₄O₁₀ is : (B) 7	(C) 17	(D) 16
E-5.	Which statement is <b>inc</b> (A) sp <sup>3</sup> hybridisation (C) there are eight Si–C	<b>orrect</b> about pyrosilicate D bond	ion. (B) One oxygen atom is (D) There is one Si-Si bo	shared between two tetrahydron ond
E-6.	The specie which does (A) NO	not contain an odd numbe (B) NO <sub>2</sub>	er of valence electrons an (C) CIO <sub>2</sub>	nd is diamagnetic: (D) $N_2O_4$
E-7.	Which is correct about (A) The value of n is 12 (B) each Si atom is bon (C) each oxygen atom i (D) all the above are cor	the cyclic silicate [Si <sub>6</sub> O <sub>18</sub> ] ded with three oxygen ato s bonded with two Si ator rect.	n- : oms ns	

# PART - III : ASSERTION / REASONING

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct. (A) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is correct explanation for STATEMENT-1 (B) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is not correct explanation for STATEMENT-1 (C) STATEMENT-1 is true, STATEMENT-2 is false (D) STATEMENT-1 is false, STATEMENT-2 is true (E) Both STATEMENTS are false

- Statement-1 : Amongst the oxo acids of halogens, HOCI, HOBr and HOI, the HOI is the most acidic acid.
   Statement-2 : The conjugate base stability is CIO<sup>-</sup> > BrO<sup>-</sup> > IO<sup>-</sup>
- **2.** Statement-1 : Si F, Si C $\ell$  and Si O bonds are stronger than the corresponding bonds with C.



Si

 $p\pi - d\pi$  overlapping

- 3. Statement-1 : Aluminium chloride in acidified aqueous solution forms octahedral  $[Al(H_2O)_6]^{3+}$  ion. Statement-2 : In  $[Al(H_2O)_6]^{3+}$  complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp<sup>3</sup>d<sup>2</sup>.
- 4. Statement-1 : In graphite, on increasing the temperature the conductivity decreases along the layers of carbon atoms.

**Statement-2**: Graphite cleaves easily, because the force of attraction between the layers is weak van der Waal's force.

- Statement-1 : A molecule of buckminister fullerene exhibits aromatic character.
   Statement-2 : All the carbon atoms undergo sp<sup>2</sup> hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals.
- 6. Statement-1 :  $PF_5$  keeps trigonal bipyramidal structure in gas as well as in solid state. Statement-2 :  $PC\ell_5$  in gas and liquid state is covalent but in solid state it is ionic and exist as  $[PC\ell_4]^+$  and  $[PC\ell_5]^-$
- 7. Statement-1: Atomic orbitals are monocentric while molecular orbitals are polycentric. Statement-2: In an atomic orbital the movement of an electron is influenced by only one positive nucleus, while that of an electron in a molecular orbital is influenced by two or more nuclei depending on the number of atoms contained in the molecule.
- 8. Statement-1 : The double bond in  $C_2$  molecule consists of both  $\pi$ -bonds. Statement-2 : Four electrons are present in two  $\pi$ -bonding molecular orbitals in  $C_3$ .
- 9. Statement-1 : Anhydrous A( $C\ell_3$  is more soluble in diethyl ether than hydrous A $\ell C\ell_3$ . Statement-2 : Anhydrous A $\ell C\ell_3$  is electron deficient. The oxygen atom of ether donates a pair of electrons to vacant p-orbital on the A $\ell$  atom forming a co-ordinate bond.
- Statement-1 : To obtain effective pπ-dπ overlap, the size of the d-orbital must be similar to the size of the p-orbital. So for chlorine pπ-dπ bonding is strongest in their oxoanions.
   Statement-2 : On moving a period from left to right in the periodic table, the nuclear charge is increased and more s and p-electrons are added. Since these s- and p-electrons shield the nuclear charge incompletely, the size of the atom and that of the d-orbitals decreases. This leads to progressively stronger pπ-dπ bonding.
- 11. Statement-1 : Dimethyl ether and disilyl ether both readily form complexes with trimethyl borane



Resonance

# **Exercise #2**

# **PART - I : SUBJECTIVE QUESTIONS**

- 1. Which orbitals are involved in banana bonding in  $Al_2(CH_3)_6$ .
- 2. BF<sub>3</sub>(g) dissolves in diethyl ether forming a viscous liquid. Explain ?
- 3. The correct order of extent of polymerisation is  $SiO_4^{4-} > PO_4^{3-} > SO_4^{2-} > CIO_4^{-}$ . Why, explain briefly?
- 4. Give your answers in not more then 4 lines.
  - What is wrong about the following statement and give the correct statement:
     "In CH<sub>4</sub>(methane), sp<sup>3</sup> hybridisation involves mixing of p-orbitals of Carbon atom and s-orbitals of Hydrogen atom."
  - (b) Formation of molecular orbitals and hybridised orbitals involve mixing of pure atomic orbitals. Is there any difference between these mixings (combinations)?
- 5. At high temperatures sulphur vapour is predominantly in the form of S<sub>2</sub>(gas) molecules. Assuming that the molecular orbitals for third row diatomic molecules (homonuclear) are analogous to those for second-row molecules. Answer the following questions by putting correct number in the boxes provided at the bottom.
  - P: The number of unpaired electrons in  $S_{a}$ .
  - Q: The bond order of  $S_2$ .
  - R: The number of  $\pi$  bond(s) in S<sub>2</sub>.
  - S: The bond order of  $S_2^{2-}$ , disulphide ion formed by the gain of two electrons.



- 6. What is the bond order of underlined species in NO [BF<sub>4</sub>]?
- 7. Draw the bonding and antibonding molecular orbital diagram  $3p_x$  and  $3d_{xy}$  orbital with z-axis inter nuclear axis. Also locate nodal planes in it.
- **8.** Explain the hybridisation in solid form of  $POI_{s}$ ,  $N_2O_5$  and  $XeF_6$ .
- 9. Interpret the general formula of

   (a) single chain silicate
   (b) double chain silicate
   (c) trisilicate
   (c) trisilicate
- **10.** Draw the structure and identify the bond orders of all bonds in (a) trisulphate (b) dithionate (c) tetrametaphosphate (d)  $Cl_2O_7$ (e)  $MnO_4^{-}$  (f)  $MnO_4^{2-}$  (g)  $Mn_2O_7$
- 11. Arrange the following boron trihalides in the increasing order of their ease of hydrolysis. Also give the reason for the same. BF<sub>3</sub>, BCl<sub>3</sub>, BBr<sub>5</sub>
- **12.** Phosphorus acid, dimeta phosphoric acid and Pyro phosphoric acid have basicity respectively as x, y and z. Then fill your answer as x, y, z in the bubbles.
  - **13.** Draw structure of (a) dimeta borate (b) cyclic trimetaborate. Write their formula.
  - **14.** Arrange following compounds in the order of increasing order of O–O bond length.

(ii)  $O_2[BF_4]$  (iii)  $KO_2$ 



 $(i) O_2$ 

	F	PART - II : OBJE	CTIVE QUESTIO	NS
Single	e choice type			
1.	Which of the following (A) [(CH <sub>3</sub> ) <sub>3</sub> N $\rightarrow$ BF <sub>3</sub> ] (C) [(CH <sub>3</sub> ) <sub>3</sub> N $\rightarrow$ B(CH <sub>3</sub> ) <sub>2</sub> F	has the minimum heat of -]	dissociation of N $\rightarrow$ B bo (B) [(CH <sub>3</sub> ) <sub>3</sub> N $\rightarrow$ B(CH <sub>3</sub> )F <sub>2</sub> (D) [(CH <sub>3</sub> ) <sub>3</sub> N $\rightarrow$ B(CH <sub>3</sub> ) <sub>3</sub> ]	nd ? 2 <sup>]</sup>
2.	In which of the following (a) Tetrahedral hybridisat (b) Hybridisation can be (c) All bond lengths are (A) $B_2H_6$	molecules/species all fol- tion considered to have taken identical i.e. all $A - B$ bor (B) $Al_2Cl_6$	lowing characteristics are n place with the help of er nd lengths are identical. (C) $BeCl_2$	e found ? npty orbital(s). (D) BF <sub>4</sub>
3.	In which of the following	g compounds B – F bond	length is shortest ?	
	(A) BF <sub>4</sub>	(B) $BF_3 \rightarrow NH_3$	(C) BF <sub>3</sub>	$(D) BF_{3} \leftarrow N(CH_{3})_{3}$
4.	Which of the following s (A) Three sp <sup>2</sup> orbitals are (B) The lone pair of elect p-orbitals on each of the (C) The N-Si bond leng (D) It is a weaker Lewis	tatement is false for trisily e used for $\sigma$ bonding, givin trons occupy a p-orbital at e three silicon atoms resu th is shorter than the expension base than trimethyl amin	ylamine ? ng a plane triangular struct right angles to the plane to ulting in π bonding. ected N–Si bond length. e.	cture. triangle and this overlaps with empty
5.	Gaseous SO <sub>3</sub> molecule (A) is planar triangular in overlap and two $p\pi - d\pi d$ (B) is a pyramidal molec (C) planar triangular in (D) is planar triangular in overlap and one $p\pi - d\pi$	shape with three $\sigma$ -bonds overlap. cule with one double bond shape with two double bo shape with three $\sigma$ bonds overlap.	s from sp <sup>2</sup> – p overlap and d and two single bonds onds between S and O and s from sp <sup>2</sup> – p overlap and	three $\pi$ -bonds formed by one $p\pi - p\pi$ d one single bond three $\pi$ -bonds formed by two $p\pi - p\pi$
6.	Number of antibonding (A) 4	electrons in $N_2$ is : (B) 10	(C) 12	(D) 14
7.	Consider the following s $S_1$ : Fluorine does not for $S_2$ : In CIF <sub>3</sub> , the three lo $S_3$ : In B <sub>2</sub> and N <sub>2</sub> molecu Of these statements : (A) S <sub>1</sub> , S <sub>2</sub> and S <sub>3</sub> are co	tatements. frm any polyhalide because one pairs of electrons occ ules mixing of s- and p- at prrect	se it does not have d-orbin upy the equatorial positio tomic orbitals takes place (B) $S_1$ and $S_2$ are correc	tals in valence shell. on. e.
_	(C) $S_1$ and $S_3$ are correc		(D) $S_2$ and $S_3$ are correc	t
8.	According to Molecular (A) LUMO level for $C_2$ m (C) In $C_2^{2-}$ ion there is c	orbital theory which of the tolecule is $\sigma_{2p_x}$ orbital one $\sigma$ and two $\pi$ bonds	e following is correct ? (B) In C <sub>2</sub> molecules both (D) All the above are cor	n the bonds are $\pi$ bonds rect
9.	Which species can exis (A) B <sub>2</sub>	t among the following : (B) Be <sub>2</sub>	(C) Ne <sub>2</sub>	(D) He <sub>2</sub>
10.	Among the following wh $(A) \text{ KO}_2$	ich one will have the larg (B) $O_2$	est O – O bond length ? (C) $O_2^+[AsF_6]^-$	(D) K <sub>2</sub> O <sub>2</sub>
11.	The correct order in whi (A) $H_2O_2 < O_2 < O_3$	ch the O - O bond length (B) $O_2 < H_2O_2 < O_3$	increases in the following (C) $O_2 < O_3 < H_2O_2$	g is : (D) $O_3 < H_2O_2 < O_2$
12.	Which of the following is (A) $O_2^{2-} > O_2 > O_2^+$ [Para (C) $H_2 > H_2^+ > He_2^+$ [bon	s a <u>wrong</u> order with resp amagnetic moment] d energy]	Dect to the property menti (B) $(NO)^{-} > (NO) > (NO)$ (D) $NO_{2}^{+} > NO_{2} > NO_{2}^{-}$	oned against each ? )* [bond length] [bond angle]

13.	Which of the following of (A) NO < $C_2 < O_2^- <$ He (C) He <sub>2</sub> <sup>+</sup> < $O_2^- <$ NO < C	pption with respect to increase $\frac{2}{2}$	easing bond dissociation (B) $C_2 < NO < He_2^+ < O_2^-$ (D) $He_2^+ < O_2^- < C_2^- < NC_2^-$	energies is correct ?
14.	Two types of carbon-car (A) diamond	bon covalent bond length (B) graphite	s are present in (C) C <sub>60</sub>	(D) benzene
15.	In which of the following (A) $[B_4O_5(OH)_4]^{2-}$	g species peroxide group i (B) [S <sub>2</sub> O <sub>8</sub> ] <sup>2-</sup>	is not present : (C) CrO <sub>5</sub>	(D) HNO <sub>4</sub>
16.	Which of the following s (A) (BN) <sub>x</sub>	solids is a good conductor (B) SiO <sub>2</sub>	of electricity (C) SiC	(D) none of these
17.	Consider the following s (I) The hybridisation fou (II) In $AB_2L_2$ type the BA (III) In $CIO_3^-$ , $NH_3$ and X (IV) In $P_4$ molecule, the of these statements : (A) I, II and III are correct (C) III and IV are correct	statements ; and in cation of solid PCl <sub>5</sub> B bond angle is always gr $eO_3$ , the hybridisation and re are six P – P bonds and ct only	is sp <sup>3</sup> . reater than the normal tet I the number of lone pairs I four lone pairs of electro (B) I, III and IV are corre (D) All are correct	rahedral bond angle. s on the central atoms are same. ons.
18.	Which of the following i (A) $S_3O_9$ – contains no $S_3O_9$ – contains $S_3O_9$ – contains $S_3O_9$ – contains $S_3O_9$	s correct ? S–S linkage. P – P linkage	(B) $S_2O_6^{2-}$ – contains – C (D) $S_2O_8^{2-}$ contains S–S	O−O− linkage. S linkage
19.	The percentage of s–ch (A) 25	naracter in the orbital form (B) 33	hing P – S bonds in $P_4S_3$ i (C) 75	s : (D) 50
More 20.	than one choice ty Which of the following is (A) NaBH <sub>4</sub>	<b>pe</b> s/are electron deficient co (B) $B_2H_6$	mpounds ? (C) AICI <sub>3</sub>	(D) LiAlH₄
21.	Which of the following r (A) $(CH_3)_2O + BF_3 \rightarrow$	eactions is/are likely to be (B) (SiH <sub>3</sub> ) <sub>2</sub> O + BF <sub>3</sub>	impossible. (C) (SiH <sub>3</sub> ) <sub>3</sub> N + BF <sub>3</sub> $\rightarrow$	(D) All the above
22.	Which of the following h (A) $O_2^{2+}$	ave bond order three ? (B) NO <sup>+</sup>	(C) CN⁻	(D) CN+
23.	Which of the following s (A) Out of trimethylamin (B) Out of $(SiH_3)_2O$ and (C) C – C bond length (i (D) N(SiMe <sub>3</sub> ) <sub>3</sub> and BF <sub>3</sub> n	statements is/are correct $f$ the and trimethylphosphine (CH <sub>3</sub> ) <sub>2</sub> O, (SiH <sub>3</sub> ) <sub>2</sub> O is more n pm) in C <sub>2</sub> molecule is gr nolecules are isostructura	? e, trimethylamine has high e basic. reater than O – O bond le II.	her dipole moment. Ength in $O_2$ molecule.
24.	The species which are p (A) NO	paramagnetic is/are : (B) NO <sub>2</sub>	(C) CIO <sub>2</sub>	(D) N <sub>2</sub> O <sub>4</sub>
25.	Which of the statement (A) There is a single bo (B) The F and O are fur (C) There is a double bo (D) It would take more e	(s) are correct ? nd in FO⁺ ther apart in FO⁻ than in F ond in FO⁻. energy to break F – O bor	<sup>:</sup> O⁺. nd in FO⁺ than in FO⁻.	
26.	Which of the following s (A) Each 'P' atom can b (B) There are six POP b (C) There are two types (D) POP angle is 180°.	statements is incorrect ab be considered to be sp <sup>3</sup> hy bonds in the molecule of P— O bond lengths	out P <sub>4</sub> O <sub>10</sub> molecule ? /bridised	

Resonance

- 27. Which of the following statements is /are true about the structure of fullerene (Buckminister fullerene) ?

  (A) All the carbon atoms undergo sp<sup>2</sup> hybridisation.
  (B) Remaining fourth electron at each carbon is delocalised in molecular orbitals which in turn gives aromatic character to molecule.
  (C) It has a shape like rugby ball.
  (D) It contains both single and double bonds and has two C–C distances of 143.5 pm and 138.3 pm respectively.
- 28. Identify the correct statement (A)  $H_2S_2O_7$  has peroxy linkage (C)  $H_2S_2O_8$  has peroxy linkage
- (B)  $H_2S_2O_6$  has S–S linkage (D)  $H_2SO_3$ (Sulphurous acid) has S in +4 oxidation state
- **29.** Which of the following statements is /are true for  $P_4S_3$  molecule ?
  - (A) It contains six P-S bonds and three P-P bonds.
  - (B) It contains six P–S bonds and ten lone pairs.
  - (C) It has all atoms sp<sup>3</sup> hybridised.
  - (D) It contains six  $\ensuremath{\mathsf{P}}\xspace -\ensuremath{\mathsf{P}}\xspace$  bonds and ten lone pairs.
- **30.** Identify the correct statement (s)
  - (A) in H-atom bond is formed by non direction orbital
  - (B) graphite behaves as conductor as well as semi conductor.
  - (C) in  $SiO_2$  molecule Si-atom is sp<sup>3</sup> hybridised
  - (D)  $CIF_3$  is hyper valent molecule.

# PART - III : MATCH THE COLUMN

- 1. Column I
  - (A) BF<sub>3</sub>
  - (B)  $(SiH_3)_3 N$ (C)  $B_2H_6$ (D)  $SiO_2$
- 2. Column I (A)  $O_2$  and  $NO^-$ (B)  $O_2^+$  and NO(C) CO and  $CN^-$ (D)  $C_2$  and  $CN^+$

#### 3. Column (I)

- (A) P<sub>4</sub> (B) SO<sub>4</sub><sup>2-</sup> (C) C<sub>2</sub>H<sub>6</sub> (D) P<sub>4</sub>O<sub>10</sub>
- 4. Column-I (A)  $H_3P_3O_9$ 
  - (B)  $H_2S_2O_7$ (C)  $H_2S_4O_6$ (D)  $H_4P_2O_5$
- 5. Match the following : Column-I

(A)  $N_2^+$  is stable than  $N_2^-$ 

- (B) NO can easily lose its electron than  $N_2$  (C) NO have large bond length than NO<sup>+</sup>
- (D)  $He_2^+$  exists, but is less stable than  $H_2^+$

# Column - II

- (p) sp<sup>3</sup> hybridization
- (q)  $p\pi p\pi$  back bond
- (r)  $p\pi d\pi$  back bond
- (s) 3c 2e bond

#### Column – II

- (p) Same magnetic property and bond order as that in  $N_2^+$
- (q) Same bond order but not same magnetic property as that in  $O_2$
- (r) Same magnetic property and bond order as that  $N_2^{2-}$
- (s) Same magnetic property and bond order as that in NO+

#### Column (II)

- (p) 7 σ bond
- (q) central atom is in sp<sup>3</sup> hybridisation
- (r) No, 'P-P' bond
- (s) No, 'O-O' bond

#### Column-II

- (p) S–O–S bond is present
- (q) Di-basic acid
- (r) P–O–P bond is present
- (s) Central atom (S or P) in maximum oxidation state.

#### Column-II

(p) due to one have greater number of electrons in antibonding molecular orbitals than other(q) one has B.O. 3 and other has 2.5

- (r) both are paramagnetic with same bond order
- (s) one is paramagnetic and other diamagnetic

## **PART - IV : COMPREHENSION**

#### **COMPREHENSIONS:**

#### Read the following passage carefully and answer the questions.

#### **COMPREHENSION #1**

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule which provides us the following very important informations about the molecule .

(A) Stability of molecule : The molecule is stable if number of bonding molecular orbital electrons  $(N_{\rm e})$  is greater than the number of antibonding molecular orbital electrons (N) and vice-versa. (B) Bond order :

Bond order = 
$$\frac{1}{2}(N_{b} - N_{a})$$

A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule. (C) Nature of the bond :

Bond order 1, 2, or 3 corresponds to single, double or triple bonds respectively.

(D) Bond length :

Bond length decreases as bond order increases.

(E) Magnetic nature :

Molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic and if one or more molecular orbitals are singly occupied, it is paramagnetic.

1. Which of the following statements is incorrect?

(A) Among  $O_2^+$ ,  $O_2$  and  $O_2^-$  the stability decreases as  $O_2^+ > O_2^- > O_2^-$ (B) He<sub>2</sub> molecule does not exit as the effect of bonding and anti-bonding molecular orbitals cancel each other (C)  $C_2, O_2^2$  and  $Li_2$  are diamagnetic

(D) In  $F_2$  molecule, the energy of  $\sigma 2 P_z$  is more than  $\pi_{2px}$  and  $\pi_{2py}$ 

2. The bromine (Br<sub>2</sub>) is coloured because:

(A) the difference in energy ( $\Delta E$ ) between HOMQ and LUMO is large and the electronic excitation take place by absorption of light which falls in ultra violet region.

(B) the difference in energy ( $\Delta E$ ) between HOMO and LUMO is small and the electronic excitation take place by absorption of light which falls in infrared region.

(C) the bromine molecule is paramagnetic and the difference in energy ( $\Delta E$ ) is such that the electronic excitation take place in visible light.

(D) the difference in energy ( $\Delta E$ ) between HOMO and LUMO is such that the electronic excitation take place by absorption of light which falls in visible region and bromine molecule is diamagnetic.

- N<sub>2</sub> has greater bond dissociation energy than N<sub>2</sub><sup>+</sup>, where as O<sub>2</sub> has a lower bond dissociation energy than O<sub>2</sub><sup>+</sup> 3. because:
  - (A) Bond order is reduced when  $O_2$  is ionized to  $O_2^+$  and bond order is increased when  $N_2$  is ionized to  $N_2^+$
  - (B) Bond order is increased when  $O_2$  is ionized to  $O_2^+$  and bond order is decreased when  $N_2$  is ionized to  $N_2^+$
  - (C) Bond order is decreased when  $O_2$  is ionized to  $O_2^+$  and bond order is decreased when  $N_2^-$  is ionized to  $N_2^+$
  - (D) None of these.

Jun?

		Exer	<b>cise # 3</b>		
	PART	- I : IIT-JEE PR	OBLEMS (LAST	10 YEARS)	
* Mark	ed Questions may ha	ave more than one co	prrect option.		<u> </u>
1.	The number of P—O— (A) zero	-P bonds in tricyclic met (B) two	taphosphoric acid is : (C) three	(D) four	[JEE-2000, 1/35]
2.	Write the Molecular or	bital electron distributior	n of $O_2$ . Specify its bond or	der and magnetic	property. [JEE–2000, 3/100]
3.	The number of S–S bo (A) three	nds, in sulphur trioxide t (B) two	trimer (S <sub>3</sub> O <sub>9</sub> ) is : (C) one	(D) Zero	[JEE-2001, 1/35]
4.	The common feature c (A) bond order three ar (C) bond order two and	of the species CN $$ , CO, nd isoelectronic. I $\pi$ acceptor.	NO <sup>+</sup> are : (B) bond order three a (D) isoelectronic and	nd weak field ligan weak field ligands.	<b>[JEE–2001, 1/35]</b> d.
5.	Specify the coordinatio	n geometry around and	hybridisation of N and Ba	atoms in a 1 : 1 com	plex of BCl <sub>3</sub> & NH <sub>3</sub> .
	<ul><li>(A) N : tetrahedral sp<sup>3</sup>,</li><li>(C) N : pyramidal sp<sup>3</sup>,</li></ul>	B : tetrahedral sp <sup>3</sup> B : planar sp <sup>2</sup>	(B) N : pyramidal sp³, (D) N : pyramidal sp³,	B : pyarmidal sp <sup>3</sup> B : tetrahedral sp <sup>3</sup>	[, 0,00]
6.	Which of the following (A) $N_2$	molecular species has u (B) F <sub>2</sub>	Inpaired electron(s) ? (C) $O_2^-$	(D) O <sub>2</sub> <sup>2-</sup>	[JEE-2002, 3/90]
7.	Which one is more sol	uble in diethyl ether anh	ydrous AICl <sub>3</sub> or hydrous A	ICl <sub>3</sub> ? Explain in te	rms of bonding. [JEE–2003, 2/60]
8.	Amongst the following (A) $H_2S_2O_3$	the acid having $-O-O-$ (B) $H_2S_2O_5$	bond is : (C) H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	(D) H <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	[JEE-2004, 3/84]
9.	According to molecular correct ? (A) It is paramagnetic a (B) It is paramagnetic a (C) It is diamagnetic ar (D) It is diamagnetic ar	r orbital theory, which on and has less bond order and more bond order tha nd has less bond order th nd has more bond order	e of the following stateme than $O_2$ an $O_2$ han $O_2$ than $O_2$	ents about the mole	ecular species O <sub>2</sub> *is [JEE–2004, 3/84]
10.	Arrange the following	three compounds in terr	ns of increasing O — O b	ond length :	
	Justify your answer ba compounds.	sed on the ground state	electronic configuration	of the dioxygen spe	ecies in these three [JEE–2004, 2/60]
11.	$AIF_3$ is insoluble in and of $BF_3$ , $AIF_3$ is precipita	ydrous HF but when little ated. Write the balanced	e KF is added to the comp I chemical equations.	bound it becomes s	oluble. On addition [JEE-2004, 2/60]
12.	Which of the following (A) Sheet silicate (C) Three dimensional	silicate is formed when silicate	three oxygen atoms of [Si (B) Pyrosilicate (D) Linear chain silica	iO₄]⁴- tetrahedral u te	nits are shared ? [JEE–2005, 3/84]
13.	Predict whether the fol (i) NMe <sub>3</sub> (ii) N(S	lowing molecules are iso SiMe <sub>3</sub> ) <sub>3</sub>	o-structural or not. Justify	your answer.	[JEE–2005, 2/60]
14.	Write the structure of F	P <sub>4</sub> O <sub>10</sub> .			[JEE-2005, 1/60]
15.	The species having bo (A) NO <sup>−</sup>	nd order different from tł (B) NO⁺	nat in CO is : (C) CN⁻	(D) N <sub>2</sub>	[JEE-2007, 3/162]
	-				

16.	Among (A) Na <sub>2</sub>	the following, th $O_2$	e paramagnetic (B) O <sub>3</sub>	compour	nd is : (C) N <sub>2</sub> O	(D) KO	2	[JEE-2007, 3/162]
17.	The per (A) 25	rcentage of p-ch	naracter in the orb (B) 33	oitals forr	ning P – P bonds in $P_4$ is (C) 50	: (D) 75		[JEE-2007, 3/162]
18.	Match e	each of the diato <b>Column I</b>	omic molecules in	n <b>Colum</b> i	n I with its property/prop Column II	erties in	Column	II. [JEE-2009, 8/160]
	(A)	B <sub>2</sub>		(p)	Paramagnetic			
	(B)	N <sub>2</sub>		(q)	Undergoes oxidation			
	(C)	O_2 <sup>-</sup>		(r)	Undergoes reduction			
	(D)	O <sub>2</sub>		(s)	Bond order $\geq$ 2		$\mathbf{\hat{n}}$	
				(t)	Mixing of 's' and 'p' orbi	tals	X	
19.	The nitr (A) N <sub>2</sub> O	rogen oxide(s) th )	nat contain(s) N— (B) N <sub>2</sub> O <sub>3</sub>	-N bond(	s) is(are) : (C) N <sub>2</sub> O <sub>4</sub>	(D) N <sub>2</sub> C	) <sub>5</sub>	[JEE-2009, 4/160]
20.	Assumi (A) 1 ar (C) 1 ar	ing that Hund's r nd diamagnetic nd paramagnetic	ule is violated, th	ne bond o	rder and magnetic natur (B) 0 and diamagnetic (D) 0 and paramagnetic	e of the o	diatomic	molecule B <sub>2</sub> is : [ <b>JEE-2010, 5/163]</b>
		PART -	II : AIEEE	PROE	BLEMS (LAST 1	0 YEA	RS)	
1.	Increas (A) $O_2^+$ (C) $O_2^-$	sing order of bon $< O_2 < O_2^- < O_2^-$ $< O_2^{2^-} < O_2^+ < O_2^+$	d strength of $O_2$ , $O_2$	O <sub>2</sub> <sup></sup> , O <sub>2</sub> <sup>-2-</sup>	and $O_2^+$ is : (B) $O_2^- < O_2^+ < O_2^- < O_2^-$ (D) $O_2^{-2^-} < O_2^- < O_2^- < O_2^- < O_2^-$	2- + 2		[AIEEE-2002]
2.	The bo species (A) Bor (C) Bor	nd order in NO 6? nd length in NO <sup>+</sup> nd length in NO <sup>+</sup>	is 2.5 while that is greater than ir is equal to that in	in NO⁺ is n NO n NO	s 3. Which of the follow (B) Bond length in NO i (D) Bond length is unpre-	ing state s greater edictable	ments is r than in l	true for these two [AIEEE-2004] NO <sup>+</sup>
3.	The stru (A) four (C) two	ucture of diborar 2c–2e bonds ar 2c–2e bonds an	ne (B <sub>2</sub> H <sub>6</sub> ) contains nd four 3c–2e bor nd four 3c–2e bor	s: nds nds	(B) two 2c–2e bonds ar (D) four 2c–2e bonds a	nd two 3c nd two 3c	:–3e bon :–2e bon	<b>[AIEEE-2005]</b> ds ds
4.	Which $(A) He_2^2$	one of the follow	ing species is dia (B) H <sub>2</sub>	amagneti	c in nature ? (C) H <sub>2</sub> +	(D) H <sub>2</sub> -		[AIEEE-2005]
5.	Which $(A) O_2^2$	of the following r	molecules/ions de (B) B <sub>2</sub>	oes not c	ontain unpaired electron: $(C) N_2^+$	s? (D) O <sub>2</sub>		[AIEEE-2006]
6.	Which $_{2}^{0}$ (A) $O_{2}^{2-}$	of the following s	species exhibits the (B) $O_2^+$	he diama	gnetic behaviour? (C) $O_2$	(D) NO	[AIEEE	-2007, 3/120]
7.	In whicl change	h of the following d ?	g ionization proc	esses, th	e bond order has increas	sed and t	he magn [AIEEE	etic behaviour has - <b>2007, 3/120]</b>
	(A) O <sub>2</sub>	$\longrightarrow O_2^+$			(B) $N_2 \longrightarrow N_2^+$			
	(C) C <sub>2</sub> -	$\longrightarrow C_2^+$			(D) NO $\longrightarrow$ NO <sup>+</sup>			
8.	Which (A) CN-	one of the follow and CN⁺	ring pairs of spec (B) O₂⁻ and CN	ies has th -	ne same bond order? (C) NO⁺ and CN⁺	(D) CN	[AIEEE <sup>-</sup> and NC	:- <b>2008, 3/105]</b> )⁺
							Снеміса	al Bonding-2 - 159

9. The bond dissociation energy of B – F in BF<sub>3</sub> is 646 kJ mol<sup>-1</sup> whereas that of C – F in CF<sub>4</sub> is 515 kJ mol<sup>-1</sup>. The correct reason for higher B - F bond dissociation energy as compared to that of C - F is : [AIEEE-2009, 4/144] (A) stronger  $\sigma$  bond between B and F in BF<sub>3</sub> as compared to that between C and F in CF<sub>4</sub>. (B) significant  $p\pi - p\pi$  interaction between B and F in BF<sub>3</sub> whereas there is no possibility of such interaction between C and F in  $CF_4$ . (C) lower degree of  $p\pi - p\pi$  interaction between B and F in BF<sub>3</sub> than that between C and F in CF<sub>4</sub> (D) smaller size of B - atom as compared to that of C - atom. 10. Using MO theory predict which of the following species has the shortest bond length ? [AIEEE-2009, 4/144] (D) O<sub>2</sub><sup>2+</sup>  $(A) O_{2}^{+}$  $(C) O_{2}^{2-}$  $(B) O_{2}^{-}$ 11. Which one of the following molecules is expected to exhibit diamagnetic behaviour? [JEE-Mains 2013 4/120] (D) S<sub>2</sub>  $(B) N_2$  $(C) O_{2}$  $(A) C_{2}$ 12. In which of the following pairs of molecules/ions, both the species are not likely to exist? [JEE-Mains 2013, 4/120] (B) H<sub>2</sub><sup>-</sup>, He<sub>2</sub><sup>2-</sup> (D) H<sub>2</sub><sup>-</sup>, He<sub>2</sub><sup>2+</sup> (A) H<sub>2</sub><sup>+</sup>, He<sub>2</sub><sup>2-</sup> (C) H<sub>2</sub><sup>2+</sup>, He<sub>2</sub> Stability of the species  $Li_2$ ,  $Li_2^-$  and  $Li_2^+$  increases in the order of : 13. [JEE-Mains 2013, 4/120] (A)  $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (B)  $Li_2^- < Li_2^+ < Li_2$ (C)  $Li_2 < Li_2^- < Li_2^+$ (D)  $\text{Li}_{2}^{-} < \text{Li}_{2} < \text{Li}_{2}^{+}$ 

# **Answers**

### **EXERCISE - 1**

#### PART-I

- A-1. (i) In NH<sub>3</sub> molecule N atom has lone pair in sp<sup>3</sup> hybrid orbital while in PH<sub>3</sub> as suggested by its bond angle ( $\approx$  92°) the lone pair must be present in 'S' orbital which is much more contracted than sp<sup>3</sup>. Hence PH<sub>3</sub> becomes a poor donor than NH<sub>3</sub>.
- A-2. In BCl<sub>3</sub>, octet of Boron is incomplete. In SiF<sub>4</sub>, silicon has vacant d-orbitals, by which it can accept electron pair.
- A-3. BF<sub>3</sub> molecule being electron deficient gets stabilised through  $P\pi P\pi$  back bonding. where as BH<sub>3</sub> removes its electron deficiency through dimerisation and thus exists as B<sub>2</sub>H<sub>6</sub>.
- **B-1.** In Me<sub>3</sub> N  $\longrightarrow \stackrel{\mathsf{F}}{\underset{\mathsf{F}}{\overset{\mathsf{B}}{\longrightarrow}}}$ , the electron deficiency of boron is compensated by the lone pair of electron donated by

nitrogen atom. Where as in  $BF_3$  it is compensated by back bonding with F atom; back bonding is delocalised thus B - F bond has partial double bond character.



- **B-4.** After removal of H<sup>+</sup>, (CH<sub>3</sub>)<sub>3</sub>SiO gets stabilised by  $p\pi$ -d $\pi$  back bonding due to the presence of empty d-orbital in silicon. In (CH<sub>3</sub>)<sub>3</sub>CO, there is no such  $p\pi$ -d $\pi$  delocalisation of electrons as there is no empty d-orbital in carbon.
- **B-5.** In BF<sub>3</sub> vacant p-orbital of boron undergoes  $2p\pi$ - $2p\pi$  back bonding with fluorine atom, which is stronger than  $2p\pi$ - $3p\pi$  back bonding in BCl<sub>3</sub>. So BCl<sub>3</sub> is more electron deficient than BF<sub>3</sub>. Thus BCl<sub>3</sub> is more acidic than BF<sub>3</sub>.
- **C-1.** (a) 1 (b) 1/2 (c) 0 (d) 1 (e) 0 (f) 1
- **C-2.** (a)  $B_2(b) C_2(c) O_2^{2+}(d) O_2$ , (e)  $F_2(f) N_2$
- **D-1.** Boron (B<sub>2</sub>) : B<sub>2</sub> is a good example of the energy level shift caused by the mixing of s and p orbitals. In the absence of mixing, the  $\sigma_g$  (2p) orbital is expected to be lower in energy than the  $\pi_u$ (2p) orbitals and the resulting molecule would be diamagnetic. However, mixing of the  $\sigma_g$ (2s) orbital with the  $\sigma_g$ (2p) orbital lowers the energy of the  $\sigma_g$ (2s) orbital and increases the energy of the  $\sigma_g$ (2p) orbital to a higher level than the  $\pi$  orbitals, giving the order of energies shown below. As a result, the last two electrons are unpaired in the degenerate (having the same energy)  $\pi$  orbitals, and the molecule is paramagnetic. ( $\sigma$ 1s)<sup>2</sup> ( $\sigma$ \*1s)<sup>2</sup> ( $\sigma$ 2s)<sup>2</sup> ( $\sigma$ \*2s)<sup>2</sup> ( $\pi$ 2p<sup>1</sup><sub>x</sub> =  $\pi$ 2p<sup>1</sup><sub>y</sub>) ( $\sigma$ p<sub>2</sub>)<sup>0</sup>.

**D-2.** NO<sup>+</sup> and NO are derivative of N<sub>2</sub>; so NO<sup>+</sup> bond order = 3 and NO bond order = 2.5; B.O.  $\infty$  bond strength.

- D-3. (ii) & (iv)
- Sulphuric acid  $(H_2SO_4)$ E-1.

ric acid (H<sub>2</sub>SO<sub>3</sub>)  
H-O-
$$\stackrel{0}{=}$$
-O-H S.No. = 4, Hybridisation = sp<sup>3</sup>, Oxidation state of Sulphur = + 6  
II's acid (H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)  
H-O- $\stackrel{0}{=}$ -O-O- $\stackrel{0}{=}$ -O-H  
Sp<sup>3</sup> Oxidation state of both sulphur atoms = + 6  
acid (H<sub>2</sub>SO<sub>5</sub>)  
H-O-O- $\stackrel{0}{=}$ -O-H Oxidation state of sulphur = +6

Marshall's acid (H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>)

Caro's acid (H<sub>2</sub>SO<sub>5</sub>)



Oleum (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>)



(b) 3 (c) 3 (d) 6 (e) 4 (f) 0 E-2. (a) 4

**E-3.** (a) 
$$P_4O_{10}$$
,  $O = P$   $O = O$   
 $O =$ 

(b) and (c) nitrogen does not have empty d-orbital.

ρπ-dπ (d) HCIO<sub>4</sub> 4 2 E-4. R S

人 **Resonance** 



According to the structure of cyclic metaphosphoric acid,  $(HPO_3)_3$ , there are three P – O – P bonds

				PA	RT-II				
A-1.	(A)	A-2.	(C)	A-3.	(A)	A-4.	(B)	A-5.	(A)
A-6.	(A)	A-7.	(B)	B-1.	(D)	B-2.	(A)	B-3.	(C)
B-4.	(C)	C-1.	(C)	C-2.	(D)	C-3.	(C)	C-4.	(A)
C-5.	(D)	C-6.	(B)	C-7.	(C)	D-1.	(B)	D-2.	(A)
D-3.	(A)	D-4.	(D)	D-5.	(C)	D-6.	(D)	D-7.	(C)
D-8.	(D)	D-9.	(C)	E-1.	(C)	E-2.	(C)	E-3.	(B)
E-4.	(D)	E-5.	(D)	E-6.	(D)	E-7.	(A)		
				PA	RT-III	7			
1.	(D)	2.	(A)	3.	(A)	4.	(B)	5.	(A)
6.	(B)	7.	(A)	8.	(A)	9.	(A)	10.	(A)
11.	(D)								

**EXERCISE - 2** 

#### PART-I

- 1. sp<sup>3</sup> hybridised orbital of both aluminium and sp<sup>3</sup> hybridised orbital of carbon.
- 2. In diethyl ether oxygen atom has two lone pairs of electrons and BF<sub>3</sub>(g) has vacant 2p-orbital in valence shell. BF<sub>3</sub> being electron deficient compensates its deficiency by accepting a lone pair of electrons from diethyl ether forming a complex as given below.



- 3. As the difference in the size of p and d orbitals decreases the extent of  $p\pi d\pi$  overlapping increases and thus tendency of polymerisation decreases.
- 4. (a) The given statement is wrong. Infact pure atomic orbitals of carbon atom only (s, p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>) participate in mixing.
  - (b) Molecular orbitals : mixing of pure orbitals of two or more different atoms (may be same type or different type); Hybridisation : Mixing of pure atomic orbitals of the same atom only.





node

8. Solid PCl<sub>5</sub> exists as  $[PCl_4]^+$  (sp<sup>3</sup>) and  $[PCl_6]^-$  (sp<sup>3</sup>d<sup>2</sup>); N<sub>2</sub>O<sub>5</sub> as NO<sub>2</sub><sup>+</sup> (sp) and NO<sub>3</sub><sup>-</sup> (sp<sup>2</sup>); XeF<sub>6</sub> as XeF<sub>5</sub><sup>+</sup> (sp<sup>3</sup>d<sup>2</sup>) and F<sup>-</sup> (as bridging ion).



- **11.**  $BF_3 < BCI_3 < BBr_3$ Electron acceptor strength of boron halides on the basis of back bonding is  $BBr_3 > BCI_3 > BF_3$  Hydrolysis takes place through coordinate bond formation, easier the coordinate bond formation greater is the extent of hydrolysis.
- **12.** 224

7.

**13.**  $\overline{O} - B \longrightarrow B + \overline{O}$  dimetaborate  $(B_2O_4)^{2^-}$   $O = B \longrightarrow O$  trimetaborate  $(BO_2)_3^{3^-}$ **15.** O-O bond length order is ii < i < iii

×.CC

**PART-II** 



Similarly electronic configuration of  $O_2^-$  (in KO<sub>2</sub>) will be  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^1$ 

Bond order =  $\frac{10-7}{2} = \frac{3}{2} = 1.5$ 

In O<sub>2</sub> [AsF<sub>4</sub>]<sup>-</sup>, O<sub>2</sub> is O<sub>2</sub><sup>+</sup>. The electronic configuration of O<sub>2</sub><sup>+</sup> will be  $\sigma$ 1s<sup>2</sup>  $\sigma$ <sup>\*</sup>1s<sup>2</sup>  $\sigma$ 2s<sup>2</sup>  $\sigma$ <sup>\*</sup>2s<sup>2</sup>  $\sigma$ 2p<sup>2</sup><sub>z</sub>  $\pi$ <sup>2</sup>p<sup>2</sup><sub>x</sub>, =  $\pi$ 2p<sup>2</sup><sub>y</sub>  $\pi$ <sup>\*</sup>2p<sup>1</sup><sub>x</sub>

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

Hence bond length order will be  $O_{2}^{+} < O_{2} < O_{2}^{-}$  because Bond order  $\propto \frac{1}{Bond length}$ 

11. There is inter molecular hydrogen bonding in HF and because of this it is weakly dissociated. So AlF<sub>3</sub> is not soluble in anhydrous HF. On the other hand KF is ionic compound and thus it is highly dissociated giving a high concentration of F<sup>-</sup> ion which leads to the formation of a colourless soluble complex,

$$AIF_3 + KF \longrightarrow K_3[AIF_6].$$

BF<sub>3</sub> is more acidic than AIF<sub>3</sub> because of the small size of B than that of AI. Thus BF<sub>3</sub> pulls out F<sup>-</sup> from  $[AIF_6]^{3-}$  forming  $[BF_4]^-$  and AIF<sub>3</sub>. Hence AIF<sub>3</sub> is precipitated on adding BF<sub>3</sub> to  $[AIF_6]^{3-}$ .

$$K_3[AIF_6] + 3BF_3 \longrightarrow 3K[BF_4] + AIF_3 \downarrow$$

- **12.** (A)
- **13.** (i)  $N(SiMe_3)_3$  is trigonal planar because in it silicon uses its vacant d-orbital for  $p\pi$ -d $\pi$  back bonding with lone pair of electrons of central N-atom and the  $p\pi$ -d $\pi$  bonding is delocalised as given in the structure. So,  $N(SiMe_3)_3$  with steric number three is trigonal planar.

(ii) In N(Me<sub>3</sub>), there is no such  $p\pi$ -d $\pi$  delocalisation of lone pair of electrons on N atom as carbon does not have vacant d-orbital. So N(Me)<sub>3</sub> with steric number four is trigonal pyramidal with a lone pair at the apex.



# **Advanced Level Problems**

# **PART - I : OBJECTIVE QUESTIONS**

# Single choice type

1.	In the coordinate valen (A) Electrons are equa (C) Hydrogen bond is fo	cy Illy shared by the atoms ormed	(B) Electrons of one ato (D) None of the above	om are shared with two atoms
2.	What is the nature of t	he bond between B and O	in (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> OBH <sub>2</sub>	
	(A) Covalent (B) Co	o-ordinate covalent	(C) Ionic bond	(D) Banana shaped bond
3.	Which of the following (A) $N_2F_3^+$ is planar at ea (C) The shape of N(SiN	statements is correct ? ach nitrogen atom. $Me_3)_3$ , is trigonal planar.	(B) In $N_3H$ , the H – N – I (D) (A) and (C) both.	N bond angle is exactly of 120°.
4.	Which of the following (A) The B - F bond leng (B) The N is pyramidal (C) The coordination g (D) (A) and (C) both.	statement is correct for the gth in the complex is longed with sp <sup>3</sup> hybridisation and eometry of N and B both a	e 1 : 1 complex of trimeth er than that of in BF <sub>3</sub> . I B is planar with sp <sup>2</sup> hybri re tetrahedral with sp <sup>3</sup> hyb	yl amine and boron tri fluoride ? idisation. pridisation each.
5.	The molecular orbital c	configuration of a diatomic	molecule is	
	σ 1s <sup>2</sup> $σ$ <sup>*</sup> 1s <sup>2</sup> $σ$ 2s <sup>2</sup> $σ$ <sup>*</sup> 2	$2s^2 \sigma 2p_x^2 \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$		
	Its bond order is	C		
	(A) 3	(B) 2.5	(C) 2	(D) 1
6.	The bond order of $He_2^+$	molecule ion is :		
	(A) 1	(B) 2	(C) $\frac{1}{2}$	(D) $\frac{1}{4}$
7.	Pick out the incorrect s	statement.	(P) O has lower discos	intion one ray than 0 t
	(C) Bond length in $N_2^+$	is less than $N_2$	(D) Bond length in NO <sup>+</sup>	is less than in NO.
8.	The species which are	diamagnetic :		
	(A) $O_2^{-}$	(B) NO <sub>2</sub>	(C) $CIO_2$	(D) $N_2O_4$
9.	When $N_2$ goes to $N_2^+$ , (A) Decrease, Increase (C) Increases, Increase	the N– N bond distance es es	and when $O_2$ goes to $O_2$ (B) Increases ,Decrease (D) None of these	+, the O – O bond distance e
10.	Which of the following (A) The O – O bond ler (B) The O – O bond ler (C) $O_2^-$ and $O_2^+$ species (D) None	is incorrect ? ngth in $H_2O_2$ is larger than ngth in $H_2O_2$ is very slightly s are paramagnetic and ha	that in $O_2F_2$ . y smaller than in $O_2^{2-}$ ion. we same number of unpa	ired electrons.
11.	A simplified application	n of MO theory to the hypo	thetical 'molecule' OF wo	ould give its bond order as :
	(A) 2	(B) 1.5	(C) 1.0	(D) 0.5
八尺				CHEMICAL BONDING-2 - 167



Resonance

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## **PART - II : SUBJECTIVE QUESTIONS**

- **1.**  $BF_3$  and graphite both are coplanar having sp<sup>2</sup> hybridisition yet graphite is a conductor. Explain.
- 2. Discuss the bond order and magnetic nature of following species. NO, NO<sup>+</sup> NO<sup>2+</sup>, NO<sup>-</sup>
- **3.** (a) Number of shared 'O' atoms in  $[Si_{6}O_{18}]^{12-}$  cyclic silicate.
  - (b) Number of S S bond present in  $H_2S_4O_6$  (tetrathionic acid).
  - (c) Number of P P bonds in  $P_4S_3$  molecule.
  - (d) Maximum number of equilvalent N O bonds in  $N_2O_5$  (g).
  - (e) Number of S O S bonds in cyclic trimer of  $SO_3^{-}$ .
- **4.** Draw structures for the polymeric  $(BeH_2)_n$  and  $(BeCl_2)_n$ . Explain in brief why the hydride bridge in  $(BeH_2)_n$  is considered to be electron deficient but not the halide bridge in  $(BeCl_2)_n$ ?
- 5. Find number of bonds in : (a)  $P_3 O_{10}^{5-}$  with bond order =  $\frac{4}{3}$  (b)  $S_2 O_7^{2-}$  with bond order =
- 6. The number of P–S bonds and P– P bonds in  $P_4S_3$  are x and y respectively. The number of  $\pi$ -bonds in  $P_4O_{10}$  is z. Fill answer in bubbles as xyz.
- 7. Find number of 3c-2e bond in  $(BeH_2)_n$
- 8. In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine N(SiH<sub>3</sub>)<sub>3</sub> it has a planar geometry. Explain? Out of trimethylamine and trisilyamine which one is more basic and why?
- **9.**  $O_2$ ,  $N_2$  are colourless gases but  $Cl_2$ ,  $Br_2$ ,  $l_2$  are coloured gases. Explain on the basis of M.O. theory.
- **10.** Draw the molecular orbital (both bonding and antibonding) and identify the number of nodal planes in the following combination of atomic orbitals with z as internuclear axis:  $d_{yz}$  and  $d_{yz}$
- 11. Draw structure of boron nitride and express the hybridisation of B and N. Will it conduct electricity like graphite?
- 12. Answer the following questions with respect to the compound <u>NO[BF<sub>4</sub>]</u>.
  - (P) Bond order of the part underlined.
    - (Q) Total number of  $\sigma$  bonds in the compound.
    - (R) Total number of  $\pi$  bonds in the compound.
    - (S) Number of hybrid orbitals involved in the hybridisation of boron.

Ρ	Q	R	S

- **13.** (a) Number of unpaired electrons in  $O_2[AsF_6]$ .
  - (b) Bond order of O O bond in  $Na_2O_2$ 
    - (c) Number of polar bonds in  $H_2O_2$
    - (d) Number of  $\pi$  bonds in carbon suboxide molecule.
    - (e) Number of non bonded electron pairs is present in  $N(SiMe_3)_3$ .
  - Fill your answer in the box provides :

- 14. Answer the following questions about the structure of the dimer of phosphorus pentaoxide.
  - (i) The number of P O linkages which have bond length equal to 1.43Å.
  - (ii) The number of covalent bonds which have bond length equal to 1.60Å.
  - (iii) The number of P O P linkages.
  - (iv) The number of lone pair(s) of electrons on each phosphorus atom.



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					Ar	16'	Wi	ers					
			<b>^</b>	(D)	2	F/-						-	
۱. د	(D) (C)	-	Z. 7	(D)	ు	•	(D)		4.	(D)		Э. 10	(A) (D)
0.	(C) (D)		/. 40	(C)	0		(D)		9.	(D)		10.	(D)
11.	(D)		12.	(C) (D)	1	ა. ი	(A) (D)		14.			15.	
10. 21			17. วว		1	0.	(D)		19.	(A,D,C		20.	(B,C,D)
21.	(B,C,D)		۲۲.	(A,D,C)		PA	RT-I				Q.		
1	In BF	R is electi	ron deffi	icient wher	eas in c	nranhi <sup>.</sup>	te 'C'	has one t	free eler	ctron wh	ich can c	onduct	electricity
י. כ	, in Di <sub>3,</sub> i											onddot	cicothony.
Ζ.	Species	M.O.Con	figuration	Bond	Magr	netic Pro	perties	-		$\mathbf{O}$			
	NO	$\sigma 1 s \sigma 1 1 \sigma c 1 s \sigma $	$s_{\sigma} \sigma^{2} s_{\sigma} \sigma^{2} s_{\sigma$	$\left[ \frac{1}{2} [10-5]=2 \right]$	.5 Pa	aramagne	etic		X				
	NO <sup>+</sup>	$\sigma 1s' \sigma^* 1s' \sigma^* 1s' \sigma^2 p_x^2 \begin{bmatrix} \pi 2p_y^2 \\ \pi 2p_z^2 \end{bmatrix}$	$ \frac{\sigma 2 s \sigma^* 2 s}{\left[ \frac{\pi^* 2 p_y^0}{\pi^* 2 p_z^0} \right] } $	1 <u>2</u> [10-4]=3	Di	amagnel	tic	C	?				
	NO <sup>2+</sup>	$ \begin{array}{c} \sigma 1 s' \sigma^* 1 \\ \sigma 2 p_x^{-2} \left[ \begin{array}{c} \pi 2 p_y^{-2} \\ \pi 2 p_z^{-1} \end{array} \right] $	$ \begin{array}{c} s^{3}\sigma 2s^{3}\sigma^{*}2s^{2} \\ \pi^{*}2p_{y}^{0} \\ \pi^{*}2p_{z}^{0} \end{array} $	$\frac{1}{2}[9-4]=2.5$	Pa	ramagne	tic						
	NO <sup>-</sup>	$\sigma 1s^{i}\sigma 1t^{j}\sigma 1t^{j}\sigma 2t^{j}\sigma 2t$	$s \sigma 2 s \sigma^{*} 2 s \pi^{*} 2 s \pi^{*} 2 \pi^{*} 2 p_{z}^{1} \pi^{*} 2 p_{z}^{1}$	1 <u>2</u> [10-6]=2	Pa	ramagne	;tic						
3.	a b 6 3	c d e 3 4 3			X	0.	/						
4.		Be	H H H	H H H									
	(BeH <sub>2</sub> ) <sub>n</sub>	contains	2e – 3c	bonds whe	reas								
		Be		Be	>Be<	~							
	(BeCl <sub>2</sub> )	contain	the usua	al 2e – 2c b	onds.								
5.	(a) 6	?	(b) 6		6	) <b>_</b>	634			7.	2n		
8.	The lon electror donation	e pair of is not ea n as carbo	electror asily ava on does	ns on N ato nilable for th not have d-	m in tri ne dona orbital t	silyl a ition. C for pπ-	mine ι On the ·dπ del	undergoe other ha ocalisatio	es pπ-dπ nd, in tri on.	delocalis methyl ar	ation. Th nine it is	us this easily a	lone pair of available for

In O<sub>2</sub> and N<sub>2</sub> energy gap between HOMO and LUMO is large so electronic excitation is not possible with visible light. But for halogens, the electronic excitation can be done with visible light because energy difference between HOMO and LUMO is small.

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# **CHEMICAL BONDING - III**

# **Exercise #1**

### **PART - I : SUBJECTIVE QUESTIONS**

#### Section (A) : Fajan's Rule and its applications

- A-1. Arrange the following in the increasing order of their covalent character. (a) NaF, Na<sub>3</sub>N and Na<sub>2</sub>O (b) NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>, SiCl<sub>4</sub> and PCl<sub>5</sub>
- A-2. SnCl<sub>4</sub> has melting point  $15^{\circ}$ C where as SnCl<sub>2</sub> has melting point 535°C. Why?
- A-3. Arrange the following cations in the order of increasing polarising power. (i) V<sup>3+</sup>, Sc<sup>3+</sup>, Ti<sup>3+</sup>, Cr<sup>3+</sup> (ii) Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> (iii) Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Au<sup>3+</sup>
- A-4. SnCl<sub>2</sub> is white but  $Snl_2$  is red. Why?
- A-5. Why lithium salts are most hydrated amongst alkali metals salts?

#### Section (B) : Metallic bonding

- B-1. Zinc has lowest melting point in 3d-series elements. Why?
- B-2. Among Be and Li, which should have higher melting point and why?

# PART - II : OBJECTIVE QUESTIONS

\* Marked Questions may have more than one correct option.

#### Section (A) : Fajan's Rule and its applications

- A-1. Which of the following is in order of increasing covalent character?
  - (A)  $CCl_4 < BeCl_2 < BCl_3 < LiCl$  (B)  $LiCl < CCl_4 < BeCl_2 < BCl_3$
  - (C)  $\text{LiCl} < \text{BeCl}_2 < \text{BCl}_3 < \text{CCl}_4$  (D)  $\text{LiCl} < \text{BeCl}_2 < \text{CCl}_4 < \text{BCl}_3$
- A-2.Which of the following combination of ion will have highest polarisation ?(A)  $Fe^{2+}$ ,  $Br^-$ (B)  $Ni^{4+}$ ,  $Br^-$ (C)  $Ni^{2+}$ ,  $Br^-$ (D) Fe,  $Br^-$
- A-3. The correct order of decreasing polarizability of ion is :

(A)  $CL^{-}, Br^{-}, I^{-}, F^{-}$ (B)  $F^{-}, I^{-}, Br^{-}, Cl^{-}$ (C)  $L^{-}, Br^{-}, Cl^{-}, F^{-}$ (D)  $F^{-}, Cl^{-}, Br^{-}, I^{-}$ 

- A-4. SnCl<sub>4</sub> is a covalent liquid because :
  - (A) electron clouds of the Cl<sup>-</sup> ions are weakly polarized to envelop the cation.
  - (B) electron clouds of the Cl<sup>-</sup> ions are strongly polarized to envelop the cation.
  - (C) its molecules are attracted to one another by strong van der Waals forces.
  - (D) Sn shows inert pair effect.
- A-5. Which of the following has highest melting point according to Fajan's rule :

	-
(A) NaCl	
(C) AICl <sub>2</sub>	

(B) MgCl<sub>2</sub> (D) LiCl

#### Section (B) : Metallic bonding

- B-1. Iron is harder than sodium because :
  - (A) iron atoms are smaller.

- (B) iron atoms are more closely packed.
- (C) metallic bonds are stronger in sodium.
- (D) metallic bonds are stronger in iron.
- B-2. The enhanced force of cohesion in metals is due to
  - (A) The covalent linkages between atoms
  - (B) The electrovalent linkages between atoms
  - (C) The lack of exchange of valency electrons
  - (D) The delocalization of valence electron between metallic kernels.
- B-3. In the following metals which one has lowest probable interatomic forces (B) Silver
  - (A) Copper
  - (C) Zinc

# PART - III: ASSERTION / REASONING

#### Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

(A) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is correct explanation for STATEMENT-1

(D) Mercury

- (B) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is not correct explanation for STATEMENT-1.
- (C) STATEMENT-1 is true, STATEMENT-2 is false
- (D) STATEMENT-1 is false, STATEMENT-2 is true
- (E)Both STATEMENTS are false
- 1. Statement-1 : Solubility of Lil is more than that of LiBr. Statement-1 : LiI has more lattice energy and more hydration energy in comparison to LiBr.
- 2. **Statement-1**: Al<sup>3+</sup> form more ionic compound in comparison to Ga<sup>3+</sup>, with identical anion. Statement-2 :  $r_{AI3+} \approx r_{Ga3+}$  and  $Z_{eff}$  of  $Ga^{3+}$  is more than that of  $AI^{3+}$ .

#### **Exercise #2 PART - I : SUBJECTIVE QUESTIONS** More is the polarising power of cation, lesser is the basic strength of anion. Using this, arrange the following oxides and hydroxides in increasing order of basic character. (ii) $NH_4OH$ and $[N(CH_3)_4]OH$ (iii) NaOH Mg(OH), AI(OH) (i) LiOH, NaOH, HOH (vi) MgO, FeO, ZnO, NiO (iv) TiO, Ti<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (v) MnO, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>7</sub> Arrange the following in increasing order of thermal stability. (ii) LiO<sub>2</sub>, NaO<sub>2</sub>, KO<sub>2</sub>, RbO<sub>2</sub>, CsO<sub>2</sub> (i) Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Cs<sub>2</sub>O (iii) LiOH, NaOH, KOH, RbOH, CsOH Arrange the following in the increasing order of their solubility in water. (b) BeF<sub>2</sub>, BeCl<sub>2</sub>, BeBr<sub>2</sub>, Bel<sub>2</sub> (a) AgCl, AgBr, AgI, AgF (c) PbF<sub>2</sub>, PbCl<sub>2</sub>, PbBr<sub>2</sub>, Pbl<sub>2</sub> (d) $Na_2SO_4$ , $MgSO_4$ , $Al_2(SO_4)_3$ (e) LiCl, BeCl<sub>2</sub>, BCl<sub>3</sub>

4. Why d-block elements (except group 12) usually have higher melting points as compared to metals of s and p block ?

# **PART - II : OBJECTIVE QUESTIONS**

#### Single choice type

1.

2.

3.

1.	The correct order	The correct order of the increasing ionic character is :							
	(A) BeCl <sub>2</sub> < MgCl	$_2$ < CaCl $_2$ < BaCl $_2$	(B) BeCl <sub>2</sub> < MgC	(B) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$					
	(C) $BeCl_2 < BaCl_2$	$_2 < MgCl_2 < CaCl_2$	(D) $BaCl_2 < MgC$	(D) $BaCl_2 < MgCl_2 < CaCl_2 < BeCl_2$					
2.	Which of the follo	owing compounds of eleme	ents in group IV is expe	cted to be most ionic?					
	(A) PbCl <sub>2</sub>	(B) PbCl <sub>4</sub>	(C) CCl <sub>4</sub>	(D) SiCl <sub>4</sub>					
3.	3. Least melting point is shown by the compound :								
	(A) PbCl <sub>2</sub>	(B) SnCl <sub>4</sub>	(C) NaCl	(D) AICI <sub>3</sub>					
4.	Which of the following cannot be explained on the basis of Fajan's Rules?								
	(A) Ag <sub>2</sub> S is much	less soluble than Ag <sub>2</sub> O	(B) Fe(OH) <sub>3</sub> is m	(B) $Fe(OH)_3$ is much less soluble than $Fe(OH)_2$					
(C) BaCO <sub>3</sub> is much less soluble than $MgCO_3$ (D) Melting point of AlCl <sub>3</sub> is much					at of NaCl				
5. $S_1$ : AgI is less soluble in water than AgF due to more polarisation of I in comparison to F <sup>-</sup> ion.									
$S_2$ : Melting point of BaCl <sub>2</sub> is higher than the melting point of BeCl <sub>2</sub> due to greater ionic nature of BaCl <sub>2</sub> .									
S₃ : Order of hydrated radii is : Al³+ (aq) > Mg²+ (aq) > Na⁺ (aq)									
	(A) T T T	(B) T T F	(C)TFT	(D) F T T					

- 6. Which of the following is observed in metallic bonds?
  - (A) Mobile valence electrons
  - (C) Highly directed bond

- (B) Localised electrons
- (D) None of these

#### More than one choice type

- 7. Which of the following factors do not favour electrovalency?
  - (A) Low charge on ions
  - (C) Large cation and small anion
- (B) High charge on ions(D) Small cation and large anion

x.or

- 8. Which statement(s) is/are correct?
  - (A) Polarising power refers to cation.
  - (B) Polarisability refers to anion.
  - (C) Small cation is more efficient to polarise anion.
  - (D) Molecules in which cation having pseudo inert gas configuration are more covalent.
- **9.** Which of the following is/are correct statement(s).
  - (A) Increasing covalent character : NaCl < MgCl<sub>2</sub> < AlCl<sub>3</sub>
  - (B) Increasing covalent character : LiF < LiCl < LiBr < LiI.
  - (C) Increasing polarizability :  $F^- < CI^- < Br^- < I^-$
  - (D) Decreasing ionic nature : MCl<sub>3</sub> > MCl<sub>2</sub> > MCl
- 10. Which of the following statements is / are true for the metallic bond?
  - (A) It is an electrical attraction between delocalised electrons and the positive part of the atom.
  - (B) Transition metals may use inner d- electrons along with the outer s-electrons for metallic bonding.
  - (C) Strength of metallic bond does not depend on the type of hybrid orbitals participating in metallic bonding.
  - (D) Strength of metallic bond is inversely proportional to the radius of metallic atom.

### PART - III : COMPREHENSION

#### **COMPREHENSIONS :**

Read the following passage carefully and answer the questions.

#### Comprehension: 1

A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge, is called a polar covalent bond. Bond polarity is described in terms of ionic character. Similarly in ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. The magnitude of covalent character in the ionic bond depends upon the extent of polarization caused by cations.

In general :

(i) Smaller the size of cation, larger is its polarizing power.

(ii) Larger the anion, more will be its polarisability.

(iii) Among two cations of similar size, the polarizing power of cations with pseudo - inert gas configuration  $(ns^2np^6nd^{10})$  is larger than cation with noble gas configuration  $(ns^2np^6)$  e.g. polarizing power of Ag<sup>+</sup> is more than K<sup>+</sup>.

1. Which of the following will be most covalent ?								
(A)	NaCl	(B) $Na_2S$	(C) MgCl <sub>2</sub>	(D) MgS				
<b>2.</b> Wł	nich of the following is	least ionic?						
(A)	Bel <sub>2</sub>	(B) BeCl <sub>2</sub>	(C) BeBr <sub>2</sub>	(D) BeF <sub>2</sub>				
				CHEMICAL BONDING-3 - 175				

Arrange the following compounds in increasing order of their ionic character : 3.

SnCl<sub>2</sub>, SnCl<sub>4</sub>, SiCl<sub>4</sub>, SnF<sub>4</sub>, SnF<sub>2</sub>

(A)  $SnF_2 < SnCl_2 < SnF_4 < SnCl_4 < SiCl_4$  (B)  $SnF_2 < SnCl_2 < SnF_4 < SiCl_4 < SnCl_4$ (C) SiCl<sub>4</sub> < SnCl<sub>4</sub> < SnF<sub>4</sub> < SnCl<sub>2</sub> < SnF<sub>2</sub>

- 4. Which is the correct order of covalent character (A)  $BeF_2 < BeCl_2 < BeBr_2 < Bel_2$ (C)  $Bel_2 < BeBr_2 < BeCl_2 < BeF_2$
- 5. Which of the following combination of cation and anion has maximum covalent character. (A) K<sup>+</sup>, Cl<sup>-</sup> (B) Na+, CI-(C) Cs<sup>+</sup>, Cl<sup>-</sup> (D) Mg<sup>+2</sup>, Cl

# **Exercise** # 3

(D)  $SnCl_4 < SnF_4 < SnCl_2 < SnF_2 < SiCl_4$ 

(B)  $\operatorname{BeCl}_2 < \operatorname{BeF}_2 < \operatorname{Bel}_2 < \operatorname{BeBr}_2$ 

(D)  $Bel_2 < BeCl_2 < BeBr_2 < BeF_2$ 

# PART - I : IIT-JEE PROBLEMS (LAST 10 YEARS)

#### \* Marked Questions are having one or more than one correct option.

- 1. Statement-1 : Band gap in germanium is small, because Statement-2 : The energy spread of each germanium atomic energy level is infinitesimally small. [JEE-2007, 3/162]
  - (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
  - (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
  - (C) Statement-1 is True, Statement-2 is False
  - (D) Statement-1 is False, Statement-2 is True
- 2. Statement-1 : Boron always forms covalent bond, because

Statement-2: The small size of B<sup>3+</sup> favours formation of covalent bond. [JEE-2007, 3/162]

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.

# PART - II : AIEEE PROBLEMS (LAST 10 YEARS)

- 1. A metal, M forms chlorides in + 2 and + 4 oxidation states. Which of the following statements about these chlorides is correct? [AIEEE-2006] (A) MCl<sub>2</sub> is more volatile than MCl<sub>4</sub>

  - (C)  $MCl_2$  is more ionic than  $MCl_4$
- (B) MCl<sub>2</sub> is more soluble in anhydrous ethanol than MCl<sub>4</sub>
- (D) MCl<sub>2</sub> is more easily hydrolysed than MCl<sub>4</sub>
- 2. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of these cationic species, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Be<sup>2+</sup>? (A)  $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

(C) Mg<sup>2+</sup> < Be<sup>2+</sup> < K<sup>+</sup> < Ca<sup>2+</sup>

- (B)  $Ca^2 < Mg^{2+} < Be^{2+} < K^+$ [AIEEE-2007, 3/120] (D)  $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
- 3. Among the following the maximum covalent character is shown by the compound : [AIEEE -2011, 4/120] (A) FeCl<sub>2</sub> (B) SnCl<sub>2</sub>  $(C) AICI_3$ (D) MgCl<sub>2</sub>

# Answers EXERCISE - 1



- A-1. (a) NaF < Na<sub>2</sub>O < Na<sub>3</sub>N (b) NaCl < MgCl<sub>2</sub> < AlCl<sub>3</sub> < SiCl<sub>4</sub> < PCl<sub>5</sub> A-2. 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. (i) Sc<sup>2+</sup> < Ti<sup>3+</sup> < V<sup>3+</sup> < Cr<sup>3+</sup> (ii)  $Cd^{2+} < Zn^{2+} < Hg^{2+}$ (iii)  $Ag^+ < Cu^+ < Au^+ < Au^{3+}$ A-3. A-4. Bigger anion has higher polarisability; more polarisation greater is the intensity of colour (valence shell electrons are loosely bound with the nucleus). It has highest polarising power due to smallest ionic radius amongst alkali metal, therefore, greater degree of A-5. hydration is observed in Li<sup>+</sup> salts. Weakest metallic bonding amongst the 3d – series elements  $\rightarrow$  no unpaired electrons available for B-1.
- metallic bonding in case of zinc.
- **B-2.** Be should have higher melting point as it contain 2 electrons for metallic bonding where as Li contain only one. Further more, size of Be is smaller than that of Li.



PART-II

1.	(A)	2.	(A)	3.	(B)	4.	(C)	5.	(A)		
6.	(A)	7.	(B,D)	8.	(A,B,C,D)	9.	(A,B,C)	10.	(A,B,D)		
	PART-III										
1.	(D)	2.	(A)	3.	(C)	4.	(A)	5.	(D)		
			E	EXER	CISE - 3						
				PA	RT-I						
1.	(C)	2.	(A)				S				
				PA	RT-II						
1.	(C)	2.	(A)	3.	(C)						
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# **Advanced Level Problems**

# **PART - I : OBJECTIVE QUESTIONS**

#### Single choice type

- Cul₂ is unstable even at ordinary temperature because :

   (A) the Cu<sup>2+</sup> ion with a comparatively small radius has a strong polarising power.
   (B) the Cu<sup>2+</sup> ion with a 17 electron outer shell has weak polarising power.
   (C) the I<sup>-</sup> ion with a larger radius has a high polarisability.
   (D) both (A) and (C)
- 2. Which of the following statements is incorrect ?
  - (A)  $N_2$  and  $C_2$  molecules contain both  $\sigma$  and  $\pi$  bonds.
    - (B)  $Cu^{2+}$  is more stable than  $Cu^{+}$  in aqueous medium.
  - (C) The electrical conductivity of metals can not be explained by electron sea model.
  - (D) (A) and (C) both
- 3. Which anion has the highest polarisability?

(A) I<sup>\_</sup> (B) CI<sup>\_</sup>

(C) F⁻

(B) Higher ionization energy

(D) Both (A) and (B)

(D) Br-

- Boron forms covalent compound due to
   (A) Small size
  - (C) Lower ionization energy

#### More than one choice type

- 5. Which of the following statements are correct?
  - (A) Pbl<sub>2</sub> is yellow due to high polarization of Pb<sup>2</sup>
  - (B) Beryllium chloride exists in a polymeric chain like structure in solid state.
  - (C) The thermal stability of alkalline earth metal carbonates follow the order :  $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
  - (D) CuI has higher covalent character than NaI.

# **PART - II : SUBJECTIVE QUESTIONS**

- 1. Arrange the following compounds in the order of increasing ionic character : KI,  $A\ell P$ , CaS, MgO.
- **2.** The M.P. of NaCl is higher than that of  $AlCl_3$ . Explain.
- 3. Alkali metals impart colour to the flame. Explain.
- Radii of the following cations are nearly same. Arrange them in the increasing order of polarising power :
   (i) Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>
   (ii) Ga<sup>3+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>
- Arrange the following in increasing order of melting points.
   (i) XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub> (ii) TiCl<sub>2</sub>, TiCl<sub>3</sub>, TiCl<sub>4</sub> (iii) NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>

6. Out of the given species, which one has highest polarising power and why.

Na+, Ca2+, Mg2+, Al3+

				Ans	<b>SWEI</b>	rs		
				F	PART-I			
1.	(D)	2.	(D)	3.	(A)	4.	(D)	<b>5.</b> (B,C,D)
				F	ART-II			X·
1.	AℓP, CaS, K	I, MgO						
2.	AICI <sub>3</sub> shows predominan	significaı tly ionic.	nt covalent o Hence NaC	character du I has higher	e to high pol M.P. and B.I	arising powe P. against Al	er of Al <sup>3+</sup> . ( Cl <sub>3</sub> .	Fajan's rule) while NaCl is
3.	Alkali metals electron imp	s have on arts colou	e loosly bou Ir to the flam	nd electron v e.	which can ea	asily be excit	ed by heat	. During de- excitation the
4.	(i) Mg <sup>2+</sup> < Fe <sup>2</sup>	<sup>2+</sup> < Ni <sup>2+</sup> <	Zn <sup>2+</sup> (i	i) Al <sup>3+</sup> < Fe <sup>3</sup>	⁺ < Ga³+			
5.	(i) XeF <sub>2</sub> > Xe (ii) TiCl <sub>2</sub> > Ti (iii) NaCl> M	F <sub>4</sub> > XeF <sub>6</sub> Cl <sub>3</sub> > TiCl <sub>4</sub> gCl <sub>2</sub> >AIC	<sub>3</sub>			S.		
	and and	0						


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- **B-2.** In SF<sub>6</sub>, PCl<sub>5</sub> and IF<sub>7</sub> the valence shell has 12, 10 and 14 electrons. As all contain more than 8 electrons in their valence shell they are example of super octet molecules.
- **B-4.**  $N_3^-$ , (CNO)<sup>-</sup> and (NCN)<sup>2-</sup> all have same number of electrons i.e., 22; so all are isoelectronic with CO<sub>2</sub> which also has 22 electrons.

J.CC Bond length  $\propto \frac{1}{\text{Bond order}}$ B-5. Bond order of CO = 3 (as isoelectronic with  $N_2$ ) No. of bonds in all possible sides Bond order = No. of resonating structures Bond order of  $CO_2 = \frac{4}{2} = 2$ Bond order of  $CO_3^{2-} = \frac{4}{3} = 1.33$ So, order of bond length of C – O is CO <  $CO_2 < CO_3^{2-}$ B-6.  $\therefore$  Bond order = 1.5. B-8. (D) Position of atoms are different. (E) Has unpaired electrons and this is not possible since the molecule is diamagnetic. C-1.  $\therefore x > y = z$ D-1. (A) (B) Ζ (C) > Z (D) Zero overlap Ζ D-3. (A)  $\sigma$  bond is formed by axial over lapping. (B) p-orbital have both axial and side ways over lapping







orbital is left for side wise overlapping.

**Statement-2**: XeO<sub>3</sub> is sp<sup>3</sup> hybridised and Xe form three double bonds through  $p\pi$ -d $\pi$  overlapping.



- Statement-1 : To have minimum repulsion between the I = O and the lone pair of electrons (has greater repulsive effect), the lone pair is opposite to the I = O bond.
   Statement-2 : correct statement.
- 9. Statement-1 and Statement-2 both are correct statement and Statement-2 is the correct statement of Statement-1, e.g.,  $NO_2^+$  and  $I_3^-$  have different hybridisation but on account of stability they have linear shape as given below.



**10.**  $S_1$ : SO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> have same number of electrons (i.e. 32) but have different molecular geometry.



 $S_2$ : The d and f-orbitals do not shield the nuclear charge very effectively. Therefore, there is significant reduction in the size of the ions, just after d or f orbitals have been completely filled. This is called lanthanide contraction.

**12.** Both Statement-1 and Statement-2 are true but Statement-2 is not true explanation (directly not but indirectly true) of Statement-1.

Atomic size of carbon is smaller and thus it has effective overlapping with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are C = C, C = C, C = O, C = S and C = N. Heavier elements do not form  $p\pi$ - $p\pi$  bonds because their atomic orbital are too large and diffuse to have effective overlapping.



**16.** Elemental nitrogen exists as a diatomic molecule because nitrogen can form  $p\pi$ – $p\pi$  multiple bonds which is not possible in case of phosphorus due to repulsion between non–bonded electrons of the inner core. There is no such repulsion in case of smaller nitrogen atoms as they have only 1s<sup>2</sup> electrons in their inner core.

## EXERCISE # 2

## PART - I

Solutions of problems have already been given in Answer Key of Chemical Bonding Sheet.



(b) Electronic configuration of nitrogen in ground state is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>.



(c) Electronic configuration of phosphorus in ground state is 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>3</sup>.



(d) Electronic configuration of boron in ground state is  $1s^22s^2$ .





**17.** The hybridization & shape of  $CIO_3^{\Theta}$  is sp<sup>3</sup> & pyramidal but hybridization & shape of NO<sub>3</sub><sup> $\Theta$ </sup> is sp<sup>2</sup> & trigonal planar.





vot. con

27.  $O = \overset{\oplus}{N} = O$  Bond order = 2  $^{\Theta}O - N = O$  Bond order = 1.5



- 33. The incorrect Lewis diagram are (A) and (C) because octet of O and S are incomplete respectively .
- (b) If X-axis is internuclear axis, then it will result in π bond.
  (c) It will result in σ bond.
  (d) & (e) It shows zero overlap with no bond formation.
- **37.**  $C^* \rightarrow 1s^2 2s^1 2p^3$  4 unpaired electron  $\therefore$  4 bonds  $B^* \rightarrow 1s^2 2s^1 2p^2$  3 unpaired electron  $\therefore$  3 bonds  $I^* \rightarrow 5s^2 5p^4 5d^1$  3 unpaired electron  $\therefore$  3 bonds  $P^* \rightarrow 3s^2 3p^3$  3 unpaired electron  $\therefore$  3 bonds \* represent excited state
- **38.** It is the orbital that undergo hybridisation and not the electrons. For example , for orbitals of nitrogen atom  $(2s^2 2p_x^1 2p_y^1 2p_z^1)$  belonging to valency shell when hybridise 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 take part in hybridisation.

# **40.** $H-C=C-CH_3$

The two  $\pi$  bonds are in mutually perpendicular plane. The terminal C-atom is sp<sup>3</sup> hybridised.



44. 
$$0 - N = 0$$
  $\int_{a}^{b} \int_{a}^{b} \int_{a}^{b$ 



Number of all strange points. Consumbles of the and points f is the point of the point of the point of the points of the poin

2. Number of electrons pairs = 6; number of bond pairs = 5; number of lone pairs =1. According to VSEPR theory geometry of the molecule is square bipyramidal. As all positions are equivalent the lone pair of electrons can occupy any position in octahedral geometry as given below.



1.

Valence shell electron configuration of CI, 3s<sup>2</sup> 3p<sup>5</sup>



To obtain effective  $p\pi - d\pi$  overlap the size of the d orbital must be similar to size of the p orbital. Hence in chlorine,  $p\pi - d\pi$  bonding is so strong that no polymerization of oxoanions occurs.

(A) With hydrogen sulphur does not undergo sp<sup>3</sup>d<sup>2</sup> hybridisation because of larger difference in energies between s, p and d-orbitals. Sulphur show +6 oxidation state with highly electronegative elements like O and F.
 (B) As fluorine is smaller and more electronegative than oxygen.

(C) I being large in size, cannot get accomodated around S.





 $\sim$ CIO<sub>3</sub><sup>-</sup>, XeF<sub>4</sub> and SF<sub>4</sub> have 1, 2 and 1 lone pair of electrons respectively.

**11.** The spatial arrangement of six electron clouds (five bond pairs and one lone pair) round the central Br-atom is octahedral. Due to the presence of one lone pair of electrons in the axial hybrid orbital, the shape of  $BrF_5$  gets distorted and becomes square pyramidal. Basal F-atoms are slightly displaced upwards from the base of the square pyramid.

 $\begin{array}{ll} Br-F(b) & \mbox{distance} = 1.79 \mbox{ Å} \\ Br-F(a) & \mbox{distance} = 1.68 \mbox{ Å} \\ F(b)-Br-F(b) & \mbox{angle} = 89^{\circ} \, 48' \\ F(b)-Br-F(a) & \mbox{angle} = 86^{\circ} \, 30' \\ F(b)-Br-e & \mbox{angle} = 93^{\circ} \, 30' \\ \end{array}$ 



12. XeO<sub>2</sub>F<sub>2</sub> has trigonal bipyramidal geometry. Due to presence of lone pair on equitorial position, the shape is seesaw.



(C) It is believed that pure p atomic orbitals participate in bonding and due to Ip-Ip repulsion the bond angle decreases to 92.5°.

(D) The nitrogen is in sp<sup>3</sup> hybridisation but due to lp-bp repulsion the bond angle decreases to 107°.

	SO <sub>2</sub>	OH <sub>2</sub>	SH <sub>2</sub>	$NH_{3}$
Bond angle :	119.5°	104.5°	92.5°	107°

**6.** (A)  $CF_4$  is tetrahedral where as  $SF_4$  is see-saw shaped.

(B) 
$$\bigcirc_{F}$$
  $\downarrow_{F}$   $\downarrow_{F}$   $\bigcirc_{F}$   $O = C = O$  both linear according to VSEPR.

- (C)  $\mathsf{BF}_{_3}$  is trigonal planar and  $\mathsf{PCI}_{_3}$  is pyramidal.
- (D)  $PF_5$  is trigonal bipyramidal and  $IF_5$  is square pyramidal.

7. 
$$X \xrightarrow{X} X$$

Maximum 12 bond angles are of 90°.

8. The correct order of bond angle (smallest first) is



pot. off

- **12.** Calcium carbide is ionic carbide having  $[: C \equiv C :]^{2-}$
- **13.**  $NO_2^+$  Number of electron pairs = 2 Number of bond pairs = 2 Number of lone pair = 0

So, the species is linear with sp hybridisation.

 $NO_{3}^{-}$  Number of electron pairs = 3 Number of bond pairs = 3 Number of lone pair = 0

So, the species is trigonal planar with sp<sup>2</sup> hybridisation.

 $\operatorname{Ca}^{2+}\left[:C_{2\pi}^{1\sigma}C:\right]^{2-}$ 

 $O = N_{sp} = O$ 

sp<sup>2</sup>

sp<sup>3</sup>

- $NH_4^+$  Number of electron pairs = 4 Number of bond pairs = 4 Number of lone pair = 0 So, the species is tetrahedral with sp<sup>3</sup> hybridisation.
- 14. The structure is pentagonal bipyramid having sp<sup>3</sup>d<sup>3</sup> hybridisation as given below :



18. Silicon exists as covalent crystal in solid state. (Network like structure, like diamond).

15.

16.

17.

# **ALP Solutions**

# PART-I

- 2. Electronegativity difference between two combining elements must be larger for ionic compound and it is the essential condition for the formation of ionic compounds. It is ionic because electronegativity difference between two combining elements is 1.8.
- 4. (A)  $BrF_5$  contains 10 electrons inplace of eight. (B)  $SF_6$  contains 12 electrons inplace of eight. (C)  $IF_7$  contains 14 electrons inplace of eight.

9.

5. The maximum covalency of an element is equal to the number of s & p electrons in valence shell.

Bond energ	Bond energy $\infty$ Bond order		
Species	Bond order		
CO	3		
CO <sub>2</sub>	2		
CO_3^2-	1.33		

6.

8.

7.  $H - N^* - N^* = N^{2-}$ ; there is positive charge on two adjacent nitrogen atoms. This leads to repulsion and thus (II)

increases the energy of the molecule.





(B)  $N \equiv C = C = C = C = N$ (C) In diamond each carbon atom is in sp<sup>3</sup> hybridisation.

(D) O = C = C = C = O

sp sp

sp

12.  $CH_2 = CH$ steric No. = 2  $\therefore$  Hybridisation sp.

- **13.** A fact, to be remembered.
- 14. The cation should be  $[H C \equiv N Xe F]^{+}$  Hybridisations sp sp sp<sup>3</sup>d



**16.** Generally lone pair causes more distortion than a double bond so equitorial  $/FSF_{4}$  in SOF<sub>4</sub> > equitorial  $/FSF_{4}$  in SF<sub>4</sub>

$$OCF_2: \qquad F \\ F \\ 108^{\circ} C = O \\ F \\ 126^{\circ}$$

due to low bond pair bond pair repulsion because of flourine & large repulsion due to double bond.

SF<sub>4</sub> 
$$F$$
 axial FSF < 180° due to lone pair.

Similar orbitals on hybridisation can not decrease their energy due to energy conservation law



- **18.** (a) According to VSEPR as electonegativity of central atom decreases, bond angle decreases. So bond angle of  $H_2O > H_2S > H_2S = H_2Te$ 
  - (b)  $\dot{C}_2 H_2 > \dot{C}_2 H_4 > \dot{C} H_4 > N\dot{H}_3$  with bond pair- lone pair repulsion sp sp<sup>2</sup> sp<sup>3</sup> sp<sup>3</sup>

(c)  $SF_6 < NH_3 < H_2O < OF_2$  in this case bond angle of  $NH_3$  is highest because lp - lp repulsion is absent in. it. (d)  $CIO_2 > H_2O > H_2S > SF_6$ 

 $CIO_2$  bond angle is highest due to its sp<sup>2</sup> hybridisation, rest all are sp<sup>3</sup> or sp<sup>3</sup>d<sup>2</sup> hybridised more repulsion in double bond electrons.

19.

Hydrogen atoms are in a vertical plane with axial fluorine atoms,  $\pi$ -bond involving a p-orbital of carbon atom must lie in equatorial plane of the molecule.

Six atoms, i.e. 2 H-atoms, C,S. and both axial F-atoms lie in one plane.

- **20.** Due to more polarising power of Li against other members of the family.
- **21.** Oxidation no. of N in  $N_2O_5$  is + 5 Anhydride of HOCI is  $Cl_2O_5$ .

The bond length decreases with increase in difference of electronegativity.

22\*. (A) is incorrect, as ionic compounds have higher melting points as well as higher boiling points due to strong electrostatic force of attraction between the ions. (B), (C) and (D) are properties of ionic compounds.

### PART - II

7. Two terminal carbons can be assumed to be at A and B, while the central carbon at O. Then, AB = 2AP





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.

- **B-2.** In SOCl<sub>2</sub>, sulphur atom is sp<sup>3</sup> hybridised. Due to the presence of one lone pair of electrons on 'S' atom, the molecule has distorted tetrahedral shape. i.e., trigonal pyramidal shape. This shape contains two chlorine and one oxygen atom in a triangle. The S O pi bond is  $d\pi p\pi$  pi bond.
- **C-1.** The electron density is zero in the nodal plane during the formation of a molecular orbital from atomic orbitals of the same atom.
- **C-4.** (A) Bond order of  $N_2^+ = 2.5$ ; The bond order of  $O_2^+ 1/2(10-5) = 2.5$ .
  - (B) Bond order of  $F_2 = 1$ , The bond order of  $Ne_2 = 0$ .
  - (C) Bond order of  $O_2 = 2$ ; The bond order of  $B_2 = 1$ .
  - (D) Bond order of  $C_2 = 2$ ; The bond order of  $N_2 = 3$ .
- **C-6.**  $N_2^{2-}$ :  $\sigma 1s^2 \sigma 1s^2 \sigma 2s^2 \sigma 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2 \pi 2p_x^1 \pi^* 2p_y^1$ .

**B.O.** 
$$N_2^{2-} = \frac{10-6}{2} = 2.$$
; **B.O.**  $O_2 = \frac{10-6}{2} = 2$ 

NOt isoelectronic with  $O_2$  so B.O. =  $\frac{10-6}{2}$  = 2.

All have same number of electrons (i.e. 16) so isoelectronic.

**D-1.** 
$$B_2$$
 bond order = 1 ;  $C_2$  bond order = 2 ;  $F_2$  bond order = 1 ;  $O_2^-$  bond order = 1.5 bond order  $\propto$  1/bond length.

D-2. (A) NO<sup>-</sup> is derivative of O<sub>2</sub> and isoelectronic with O<sub>2</sub>. So  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_z^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$  and 2 unpaired electrons. (B)  $O_2^{2-}$ :  $(\sigma^*1s)^2 (\sigma^*2s)^2 (\sigma^*2s)^2 (\sigma^2p_z)^2 (\pi^2p_z^2 = \pi^2p_y^2) (\pi^*2p_z^2 = \pi^*2p_z^2)$  and no unpaired electrons. (C)  $CN^-$  is derivative of and isoelectronic with  $N_2$ :  $(\sigma^*1s)^2 (\sigma^*1s)^2 (\sigma^*2s)^2 (\pi^*2p_z^2 = \pi^2p_y^2) (\sigma^2p_z)^2$  and no unpaired electron. (D) CO is derivative of and isoelectronic with N<sub>2</sub>:  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$  and no unpaired electron. D-4. (A) Stability  $O_2^+ > O_2^- > O_2^-$ 2.5 2 1.5 Bond order (C) In all these molecules all electrons are paired in molecular orbitals. D-7. (C)  $O_2: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1) O_2^{-1}: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$ (I)  $O_2^+$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\sigma^2 p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$ D-9. Bond order = 1/2(10 - 5) = 2.5. (II) NO is derivative of O<sub>2</sub> and isoelectronic with O<sub>2</sub><sup>+</sup>: so  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_z^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p^0)$ Bond order = 1/2(10-5) = 2.5. (III)  $N_2^+$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$ Bond order = 1/2(9-4) = 2.5.  $O_2^+$ , NO and  $N_2^+$  have same bond order i.e. 2.5 and have same magnetic property having one unpaired electron. E-1. (A) N<sub>2</sub>O<sub>3</sub> Dinitrogen trioxide (B) N<sub>2</sub>O<sub>2</sub><sup>2-</sup> Hyponitrite ion  $(C) N_2 O_5$ Dinitrogen pentoxide Dinitrogen tetroxide  $(D) N_2 O_4$ (pπ – pπ)  $\pi$  bond O=



general formula of cyclic silicates is [Si, O3,]2n-

PART - III

- 1. Order of acidic character is HCIO > HBrO > H IO as the order of the stability of their conjugate base is  $CIO^- > IO^-$ ; because CI being small size atom can form effective  $\pi$ -bond with oxygen.
- **3.** Both are correct and Statement-2 is the correct explanation of Statement-1. In  $[A|(H_2O)_6]^{3+}$ , aluminium is in +3 oxidation state. So,



5. Both statements are true and the Statement-2 is the true explanation of Statement-1.

**Fullerenes :** It contains twenty 'six -membered rings' and twelve 'five membered rings'. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C - C distance of 143.5 pm and 138.3 pm respectively.

8. Both are true statements and the Statement-2 in the correct explanation of Statement-1.  $C_2$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$  or KK  $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ 

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

**10.** Both the statements are true and the Statement-2 is the correct answer for the Statement-1.



 $(CH_3)_2$ ;  $C: + B(CH_3)_3 \longrightarrow (CH_3)_2$ ;  $C: \longrightarrow B(CH_3)_3$ In H<sub>3</sub>Si – O – H<sub>3</sub>Si, due to  $p\pi - d\pi$  delocalisation, availability of lone pairs on O – atom is decreased and thus disilyl ether does not the react with B(CH<sub>3</sub>)<sub>3</sub>.

11.

					E	XERCISE # 2
						PART - I
5.	*σЗр	_	_	_	_	
	*π Зр	$\downarrow$	$\downarrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	
	πЗр	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	$\downarrow\uparrow$	
	σЗр	$\downarrow\uparrow$		$\downarrow\uparrow$		
	*σ <b>3</b> s	$\downarrow\uparrow$		$\downarrow \uparrow$		
	σ <b>3s</b>	$\downarrow\uparrow$		$\downarrow \uparrow$		× •
		$S_2$		S2 <sup>2-</sup>		
	Bond o	order S	$_{2} = \frac{8-4}{2}$	=2 (pa	ramagneti	c with two unpaired electrons)
	$S \stackrel{\pi}{=} S.$			_		S
	Bond o	order S	$_{2}^{2^{-}} = \frac{8^{-}}{2}$	<sup>6</sup> = 1 (d	iamagneti	c, as all electrons are paired).
6.	Compl	lex exis	sts as NC	)⁺ and [B	F <sub>4</sub> ]⁻ . NO⁺	is isoelectronic with N <sub>2</sub> ; so $\sigma$ 1s <sup>2</sup> , $\sigma$ *1s <sup>2</sup> , $\sigma$ 2s <sup>2</sup> , $\sigma$ *2s <sup>2</sup> , $\pi$ 2p <sup>2</sup> <sub>x</sub> = $\pi$ 2p <sup>2</sup> <sub>y</sub> ,
	$\sigma 2p_z^2$ ,	then it	s bond o	rder is <sup>1</sup>	$\frac{0-4}{2} = 3$	N°.
9.	(a) (Si0	O <sub>3</sub> <sup>2−</sup> ) <sub>n</sub>				(b) $\overline{a}$ $\overline{a}$ $\overline{a}$ $\overline{a}$ $\overline{a}$ $((Si_4O_{11})^{6-})_n$
	(c) <sub>O-</sub>	O <sup>−</sup> I Si O <sup>−</sup>		0-   Si, 0-	= (Si <sub>3</sub>	(d) (SiO <sub>3</sub> <sup>2−</sup> ) <sub>3</sub>
	(e) (Na	a+ (PO <sub>3</sub> -	$())_{6} = Na_{6}($	(PO <sub>3</sub> ) <sub>6</sub>	$\langle \cdot \rangle$	
12.	Phosp Di met Pyro p <b>Ans.</b>	horous a phos hospho 224	acid $(H_3)$ sphoric a pric acid	PO <sub>3</sub> ) Dik cid (H <sub>2</sub> P (H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> )	$pasic : x = {}_{2}O_{6}$ Dibas tetrabasio	z = 2 ic $\therefore y = 2$ c $\therefore y = 4$
	Dener	44:00 - 11			الداءم مرار	
1.	Boron	trimeth	yi is a we	aker Lev	vis acid tha	an the boron trinalides or monoborane. The electron donating effect of

the methyl groups hinders the complex formation with trimethyl amine. Hence the bond  $N \rightarrow B$  is weakest in  $[(CH_3)_3 N \rightarrow B(CH_3)_3]$ . Me<sub>3</sub>N as donor (capacity). BBr<sub>3</sub> > BCl<sub>3</sub> > BF<sub>3</sub> ~ BH<sub>3</sub> > BMe<sub>3</sub>. **3.** Partial double bond character is developed in B–F bond of BF<sub>3</sub> (due to formation of dative  $\pi$  bond)

In other case B is sp<sup>3</sup> hybridised (tetrahedral molecule or ion) and the possibility for  $\pi$  bonding no longer exists.

**4.** There is  $p\pi$ -d $\pi$  delocalization of lone pair of electron on nitrogen atom and empty d-orbital of silicon but not  $p\pi$  –  $p\pi$ , one of the 2s-orbital electrons jumps to the last  $P_{\tau}$  orbital and does not participate in sp<sup>2</sup> hybridisation.



7.  $S_1$ : as it does not have d-orbitals.

$$S_2: CIF_3 \bigcirc I_F^F C\ell - F$$

of con

 $S_3$ : In  $B_2$  mixing of the  $\sigma_g(2s)$  orbital with the  $\sigma_g(2p)$  orbital lowers the energy of the  $\sigma_g(2s)$  orbital and increases the energy of the  $\sigma_g(2p)$  orbital to a higher level than the  $\pi$  orbitals. As a result, the last two electrons are unpaired in the degenerate (having the same energy)  $\pi$  orbitals, and the molecule is paramagnetic. In  $N_2$  the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  levels of  $N_2$  interact (mix) less than the  $B_2$  and  $C_2$  levels, and the  $\sigma_g(2p)$  and  $\pi_u(2p)$  are very close in energy.

8. M.O for 
$$C_2 = \sigma_1 s^2 < \sigma_1 s^2 < \sigma_2 s^2 < \sigma_2 s^2 < \frac{\pi_2 p^2 y}{\mu_0 m_0} = \frac{\pi_2 p^2 z}{\mu_0 m_0} < \frac{\sigma_2 p_x}{\mu_0 m_0}$$

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  $C_2^{2-} \left[ C \stackrel{\text{def}}{=} C \right]^{2-}$ .

12.		NO⁻ >	NO	>	NO <sup>+</sup>	(bond length)
	Bond order	2.0	2.5		3	
		H_ >	H_+	>	He_+	(bond energy)
	Bond order	1	0.5	U	0.5	( <b>C</b> , )
	(In He <sub>2</sub> <sup>+</sup> more electron ir	n antibon	ding N	ЛO	's)	
	` Z	NQ_+ >	NO <sub>2</sub>	>	NO_	(bond angle)
	Bond angle	180	1330		115 <sup>0</sup>	
	Ū.	0,2- <	$O_{2}^{+}$	<	O <sub>2</sub>	(paramagnetic moment)
	No. of unpaired e⁻	0	1		2	
		1			10	_7
13.	$\text{He}_2^+$ bond order = $\frac{2}{2}$	$=\frac{1}{2}; O_2^{-1}$	bond	oro	der = $\frac{10}{2}$	$\frac{1}{2} = 1.5$
	$C_2$ bond order = $\frac{8-4}{2}$ =	<sup>2</sup> ; NO	bond	oro	der = $\frac{10}{2}$	$\frac{-5}{2} = 2.5$
	Bond order $\infty$ bond dise	sociation	energ	gy.		
14.	diamond (1.54 Å)					
	graphite (1.42 Å) . ( $\perp$ r te	o the she	ets th	nere	e is no co	ovalent bonding)
	C <sub>60</sub> (1.45 Å and 1.38 Å)					
	benzene (1.36 Å).					

17. (I)  $[PCI_{\downarrow}]^{+} \rightarrow sp^{3}$ 

> $has \approx 102^\circ$  bond angle due to Ip–Ip repulsion, as bond pairs are closer to F-atoms. (II) pot. of

(III) All have sp<sup>3</sup> hybridisation and one lone pair.





18.

19. Hybridisation is sp<sup>3</sup>.



- $(CH_3)_2$  O: can act as lewis base but  $(SiH_3)_2$  O&  $(SiH_3)_3$  N can not, as one pairs on O & N are deloecalised in to 21. empty orbitals of Si.
- 23. (A) Nitrogen is more electronegative than phosphorus.



So, dipole moment of trimethylamine is greater than trimethy phosphine.

$$(B) H_3Si \stackrel{\checkmark}{\longleftarrow} O \stackrel{\uparrow}{\longrightarrow} SiH_3 \longleftrightarrow H_3Si = O \stackrel{\uparrow}{\longrightarrow} SiH_3$$

In trisilyl ether the lone pair of electron on oxygen atom is less easily available for donation because of  $p\pi$ -d $\pi$ delocalisation due to presence of the vacant d-orbital with Si. This however is not possible with carbon in  $CH_2$ -O - CH, due to the absence of d-orbital making it more basic.

(C) Bond order of C<sub>2</sub> and O<sub>2</sub> are same i.e., 2. In C<sub>2</sub> molecules both bonds are  $\pi$ -bonds whereas, there is one  $\sigma$  and one  $\pi$ -bond in O<sub>2</sub> molecule

$$C_{2} = 131 \text{ pm}^{2}; O_{2} = 121 \text{ pm}.$$

$$Si(Me)_{3} = 121 \text{ pm}.$$

$$F = B = Sp^{2}(\text{trigonal planar})$$

$$B = Sp^{2}(\text{trigonal planar})$$

$$F = F$$

26.

$$(D) \bigcup_{O}^{O_{\overline{V}}} N - N \bigcup_{O}^{PO}$$

**25.** In FO<sup>+</sup> total no. of electrons = 16, so bond order will be 2. In FO<sup>-</sup> total number of electrons = 18, so bond order will be 1.

$$P_4O_{10} \qquad O \qquad p\pi - d\pi \\ (\pi - bond) \\ O = P \qquad O \qquad P = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O \qquad O = O \\ O = P \qquad O = O \\ O = P \qquad O = O \\ O$$

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  $p\pi - d\pi$  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.

27. Fullerene are cage like molecules.  $C_{60}$  molecule has a shape like soccer ball and called **Buckminsterfullerene**. It contains twenty 'six -membered rings' and twelve 'five membered rings'. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp<sup>2</sup> hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively.



5. (A)  $N_2^+$ : BO = 2.5 (4 electron in antibonding MO) 1 unpaired electron (Paramagnetic)

 $N_2^{-1}$ : BO = 2.5 (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic)

(B) NO : BO = 2.5 (5 electron in antibonding MO) 1 unpaired electron (Paramagnetic).Last electron in antibonding MO.So, easily removed.

 $N_2$ : BO = 3 (4 electron in antibonding MO) 0 unpaired electron (diamagnetic).Last electron in bonding MO.So, not easily removed.

(C) NO<sup>+</sup> : BO = 3 (0 unpaired electron) diamagnetic [BO  $\uparrow \Rightarrow$  BL  $\downarrow$  ].

(D)  $He_2^+$ : BO = 0.5 (1 unpaired electron) paramagnetic [1 electron in antibonding MO].

 $H_2^+$ : BO = 0.5 (1 unpaired electron) paramagnetic [0 electron in antibonding MO].



1.

(A)		Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons /Magnetic property
	$O_2^+$ (dioxygenyl)	2.5	112.3	1 (paramagnetic)
	$O_2$ (dioxygen)	2.0	120.07	2 (paramagnetic)
	$O_2^{-}$ (superoxide)	1.5	128	1(paramagnetic)
	$O_2^{2-}$ (peroxide)	1.0	149	0 (diamagnetic)

Bond order  $\propto$  stability (i.e., bond strength)

(B) Helium molecule (He<sub>2</sub>): He<sub>2</sub>:  $(\sigma 1s)^2 (\sigma^* 1s)^2$ 

Bond order of He<sub>2</sub> is  $\frac{1}{2}(2-2) = 0$ 

The molecular orbital description of  $He_2$  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. 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.

(C) Carbon molecule (C<sub>2</sub>) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$  or KK  $(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ Lithium molecule (Li<sub>2</sub>) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2$ 

**Peroxide**  $(O_2^{2-})$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^2 s)^2 (\sigma^2 p_2)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$ As all electrons are paired so  $C_2$ ,  $Li_2$  and  $O_2^{2-}$  are diamagnetic. (D) **Fluorine molecule**  $(F_2)$ :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^2 s)^2 (\sigma^2 2p_y^2) (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$ 

3. **(B)** Oxygen molecule  $(O_2) : O_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$ Bond order = 1/2(10-6) = 2.0,  $O_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$ Bond order = 1/2(10-5) = 2.5. Nitrogen molecule  $(N_2) : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$ The bond order of  $N_2$  is 1/2(10-4) = 3.  $N_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$ Bond order = 1/2(9-4) = 2.5.

# EXERCISE # 3

PART - I

HO

1.

According to the structure of cyclic metaphosphoric acid,  $(HPO_3)_3$ , three are there P – O – P bonds.



There is no S-S bond in  $S_3O_9$ .

4.  $CN^{-}$ , CO and NO<sup>+</sup> all have same number of electrons i.e. 14. So all are isoelectronic species. Further all the species are isoelectronic with N<sub>2</sub> which have molecular orbital electronic configuration as follows

$$\sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2}^* \sigma_{2s^2}^* \pi_{2p_x^2} \pi_{2p_y^2} \sigma_{2p_z^2}^*;$$

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

Hence all will have same bond order and that is three.

5. Here ammonia acts as a lewis base and boron trifluoride as lewis acid as represented below. Hence in this complex both N and B acquire tetrahedral geometry and sp<sup>3</sup> hybridisation.

$$H \xrightarrow{H} \bigcup_{i=1}^{n} \bigcup_{i=1}^{$$

6.  $O_2^{-}$  is derivative of  $O_2$  and has 17 electrons. So its molecular orbital electronic configuration is

$$\sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2}^* \sigma_{2s^2}^* \sigma_{2p_z^2}^* \pi_{2p_x^2} \pi_{2p_y^2} \pi_{2p_x^2}^* \pi_{2p_x^2}^* \pi_{2p_y^1}^*$$

As it contains one unpaired electron in  $\pi^* 2p_y^1$  molecular orbital so it is paramagnetic. Rest all species have paired electrons so diamagnetic.

8. It is peroxodisulphuric acid, the Marshall's acid and contains one – O – O – linkage as given in structure



- 9. Molecular orbital electronic configuration is  $\sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2}^* \sigma_{2s^2}^* \sigma_{2p_z^2}^* \pi_{2p_x^2} \pi_{2p_y^2}^* \pi_{2p_x^1}^* \pi_{2p_y^0}^*$ As it contains one unpaired electron it is paramagnetic and bond order = (10-5)/2 = 2.5 ( $O_2 = 2.0$ ).
- (A) In two dimensional sheet silicates, three oxygen atoms of [SiO₄]<sup>4−</sup> are shared with adjacent tetrahedral [SiO₄]<sup>4−</sup> units,
  - (B) One oxygen atom is shared between two adjacent tetrahedra,  $[SiO_4]^4$ .
  - (C) All four oxygen atoms are shared between adjacent tetrahedra,  $[SiO_4]^4$ .
  - (D) Two oxygen atoms are shared between adjacent tetrahedra,  $[SiO_4]^{4-}$  forming a linear chain.

**15.** Bond order = 
$$\frac{N_b - N_a}{2}$$

$$CO = \sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2}^* \sigma_{2s^2}^* \pi_{2p_x^2} \pi_{2p_y^2}^* \sigma_{2p_z^2}^*$$
  
Bond order of CO = 10 - 4 / 2 = 3

$$\mathbf{O}^{-} \equiv \sigma_{1s^{2}} \sigma_{1s^{2}} \sigma_{2s^{2}} \sigma_{2s^{2}} \sigma_{2p_{z}^{2}} \sigma_{2p_{x}^{2}} \sigma_{2p_{x}^{2}} \sigma_{2p_{y}^{2}} \sigma_{2p_{x}^{1}} \sigma_{2p_{x}^{1}} \sigma_{2p_{y}^{1}}$$

	Bond c	order of N	NO <sup>-</sup> = 10 − 6 / 2 = 2	
	NO⁺ ≡	σ <sub>1s²</sub> σ'	$*_{1s^2} \sigma_{2s^2} \sigma_{2s^2}^* \sigma_{2p_z^2} \pi_{2p_x^2} \pi_{2p_y^2}$	
	Bond c	order of N	$10^{+} = 10 - 4 / 2 = 3$	
	CN⁻ ≡	σ <sub>1s²</sub> σ'	$*_{1s^2} \sigma_{2s^2} \sigma_{2s^2}^* \pi_{2p_x^2} \pi_{2p_y^2} \sigma_{2p_z^2}$	
	Bond c	order of C	$CN^{-} = 10 - 4 / 2 = 3$	
	$N_2 \equiv$	σ <sub>1s²</sub> σ'	$*_{1s^2} \sigma_{2s^2} \sigma_{2s^2} \sigma_{2s^2} \pi_{2p_x^2} \sigma_{2p_y^2} \sigma_{2p_z^2}$	
	Bond c	order of N	$J_2 = 10 - 4 / 2 = 3.$	
16.	KO <sub>2</sub> ex In O <sub>2</sub> -,	tists as K superoxi	$C^* \& O_2^-$ . de ion there are total number of e	electrons = $16 + 1 = 17$ .
	MOT c	onfigurat	$tion = \sigma_{1s^2} \sigma_{1s^2}^* \sigma_{2s^2} \sigma_{2s^2}^* \sigma_{2p_2}^*$	$\pi_{2p_{x}^{2}}\pi_{2p_{y}^{2}}\pi_{2p_{x}^{2}}^{*}\pi_{2p_{x}^{1}}^{*}$
	$O_2^-$ has	s one unp	paired electron in antibonding $\pi^*2$	$p_{y}^{1}$ . So it is paramagnetic.
17.	Steric ı	number =	= 4 ; thus sp <sup>3</sup> hybridisation in $P_4$	. As each phosphorus is sp³, so
	% p ch	aracter v	will be = $\frac{3}{4} \times 100 = 75$ .	09
18.	(A)	$B_2$	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 = \pi 2$	2p <sub>y</sub> <sup>1</sup>
			Bond order = $\frac{6-4}{2} = 1$	Paramagnetic with two unpaired electrons.
			It undergoes oxidation as well a reactions.	as reduction which can be explained by taking the following
			$2B + 3Cl_2 \longrightarrow 2BCl_3;$	$2B + 3Ca \longrightarrow Ca_{3}B_{2}$ (boride)
	<b>(D)</b>	N	Mixing of 's' and 'p' orbitals take $-4a^2 - *4a^2 - 2a^2 - *2a^2 - 2a^2 - 2a^$	s place.
	(D)	IN <sub>2</sub>	10-4	Py-OZPz <sup>-</sup>
			Bond order = $\frac{10}{2}$ = 3	Diamagnetic
			It undergoes oxidation as well a reactions.	as reduction which can be explained by taking the following
			$N_2 + O_2 \longrightarrow 2NO;$	$6Li + N_2 \longrightarrow 2Li_3N$
		0	Mixing of 's' and 'p' orbitals take	
	(C)	$O_2^-$	$\sigma^{1}S^{2}\sigma^{-1}S^{2}\sigma^{2}S^{2}\sigma^{-2}S^{2}\sigma^{2}p_{z}^{2}\pi^{2}p_{z}$	$f_{x}^{2} = \pi 2 p_{x}^{2} \pi^{2} 2 p_{x}^{2} = \pi^{2} 2 p_{y}^{1}$
			Bond order = $\frac{10-7}{2}$ = 1.5	Paramagnetic with one unpaired electron.
			It undergoes oxidation as well a reactions.	as reduction which can be explained by taking the following
		•	$O_2^- \longrightarrow O_2^- + e^-;$	$O_2^- + e^- \longrightarrow O_2^{2-}$
		. 0	Mixing of 's' and 'p' orbitals does	s not take place.
	(D)	02	$\sigma$ 1s <sup>2</sup> $\sigma$ *1s <sup>2</sup> $\sigma$ 2s <sup>2</sup> $\sigma$ *2s <sup>2</sup> $\sigma$ 2p <sub>z</sub> <sup>2</sup> $\pi$ 2p	$r_{x}^{2} = \pi 2 p_{x}^{2} \pi^{*} 2 p_{x}^{\dagger} = \pi^{*} 2 p_{y}^{\dagger}$
		N	Bond order = $\frac{10-0}{2}$ = 2	Paramagnetic with two unpaired electrons.
	S		It undergoes oxidation as well a reactions.	as reduction which can be explained by taking the following
			$O_2 \longrightarrow O_2^+ + e^-;$	$O_2 + e^- \longrightarrow O_2^-$
5	3		Mixing of 's' and 'p' orbitals does	s not take place.

**19.** (A) 
$$N \xrightarrow{1.126 \text{ Å}} N \xrightarrow{1.186 \text{ Å}} O$$

N<sub>2</sub>O







1.864 Å

20. B<sub>2</sub>; total number of electrons = 10. The MOT electron configuration violating the Hund's rule will be thus :

 $\sigma_{1s}^{2} \sigma_{1s}^{*2} \sigma_{2s}^{2} \sigma_{2s}^{*2} \sigma_{2s}^{*2} \pi_{2p_{x}}^{2} = \pi_{2p_{y}}^{0} \sigma_{2p_{z}}^{0}$ So, bond order =  $\frac{6-4}{2} = 1$ 

As all electrons are paired, the molecule is diamagnetic.

## PART - II

(B)

- $O_2$  bond order = 2;  $O_2^-$  bond order = 1.5;  $O_2^{2-}$  bond order = 1.0;  $O_2^+$  bond order = 2.5. 1.
- 2. NO and NO<sup>+</sup> are derivative of  $O_2$ . NO(isoelectronic with  $O_2^+$ ) :  $(\sigma_1 s)^2 (\sigma_2 s)^2 (\sigma_2 s)^2 (\sigma_2 s)^2 (\sigma_2 p_2)^2 (\pi_2 p_2^- = \pi_2 p_2^-) (\pi_2 p_2^- = \pi_2 p_2^-)$ Bond order = 1/2(10 - 5) = 2.5. NO<sup>+</sup>(isoelectronic with  $O_2^{2+}$ ) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^2 2s)^2 (\sigma 2p_z)^2 (\pi 2p_z^2 = \pi 2p_v^2) (\pi^* 2p_x = \pi^* 2p_v)$ Bond order = 1/2(10 - 4) = 3. Bond order  $\propto$  1/bond length. So NO<sup>+</sup> has shorter bond length.

4.  $\text{He}_{2}^{+} \rightarrow \sigma (1s)^{2} \sigma^{*} (1s)^{1}$ , one unpaired electron.  $H_2 \rightarrow (1s)^2$ ,  $\sigma^* (1s)^0$ , no unpaired electron.  $H_2^+ \rightarrow \sigma (1s)^1$ ,  $\sigma^* (1s)^0$ , one unpaired electron.  $H_2^- \rightarrow \sigma$  (1s)<sup>2</sup>,  $\sigma^*$  (1s)<sup>1</sup>, one unpaired electron.

5. The electronic configuration of oxygen atom is 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>4</sup>. Each oxygen atom has 8 electrons. Hence in each  $O_2^{2-}$  ion there are 16 + 2 = 18 electrons. The electronic configuration of  $O_2^{2-}$  ion is K

$$(2s)^2 \sigma^* (2s)^2 \pi (2p_z)^2 \pi (2p_x) p (2p_y)^2 \pi^* (2p_x)^2 \pi^* (2p_y)^2$$

Here KK represents non-bonding molecular orbital of 1s orbital. O<sub>2</sub><sup>2-</sup> contains no unpaired electrons.

The electronic configuration of B<sub>2</sub> molecule is

K σ(2s)<sup>2</sup> σ\*(2s)<sup>2</sup> π(2p<sub>x</sub>)<sup>1</sup> π(2p<sub>y</sub>)<sup>1</sup>

it contains 2 unpaired electrons. The electronic configuration of N<sub>2</sub><sup>+</sup> ion is

KK  $\sigma(2s)^2 \sigma^*(2s)^2 \pi(2p_2)^2 \sigma(2p_2)^2 \sigma(2p_2)^1$ 

it contains one unpaired electron.

The electronic configuration of O<sub>2</sub> molecule is

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

It contains 2 unpaired electron.

- $O_{2}^{2-}(8+8+2=18): \sigma 1s^{2} \sigma^{*} 1s^{2} \sigma 2s^{2} \sigma^{*} 2s^{2} \sigma 2p_{z}^{2} \pi 2p_{x}^{2} \qquad \pi 2p_{y}^{2} \pi^{*} 2p_{x}^{2} \pi^{*} 2p_{y}^{2} \text{ ; all electrons are paired. So}$ 6. diamagnetic.
- 7. Molecular orbital configuration of

$$O_2 \qquad \Rightarrow \qquad \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$$

$$\Rightarrow$$
 Paramagnetic

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

$$\begin{array}{ccc} \mathsf{O}_2^+ & \Rightarrow & \sigma 1 \mathrm{s}^2 \sigma \, 2 \mathrm{s}^2 \sigma \, 2 \mathrm{s}^2 \sigma \, 2 \mathrm{p}^2_z \, \pi 2 \mathrm{p}_x^2 \, \pi 2 \mathrm{p}_y^2 \, \pi^* \, 2 \mathrm{p}^1 \\ \Rightarrow & \mathsf{Paramagnetic} \end{array}$$

Bond order = 
$$\frac{10-5}{2} = 2.5$$

$$\begin{array}{ccc} \mathsf{N}_{2} & \Rightarrow & \sigma 1 s^{2} \sigma^{*} 1 s^{2} \sigma 2 s^{2} \sigma^{*} 2 s^{2} \pi 2 p_{x}^{2} \pi 2 p_{y}^{2} \sigma 2 p_{z}^{2} \\ \Rightarrow & \text{paramagnetic} \end{array}$$

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

$$\begin{array}{ccc} \mathsf{N}_2^{\,*} & \Rightarrow & \sigma 1 s^2 \, \sigma^* \, 1 s^2 \, \sigma 2 s^2 \, \sigma^* \, 2 s^2 \, \pi 2 p_{\,_x}^2 \, \pi 2 p_{\,_y}^2 \, \sigma 2 p_{\,_z}^1 \\ \Rightarrow & \mathsf{Paramagnetic} \end{array}$$

Bond order = 
$$\frac{9-4}{2}$$
 = 2.5

$$\begin{array}{ccc} C_2 & \Rightarrow & \sigma 1 s^2 \, \sigma^* \, 1 s^2 \, \sigma 2 s^2 \, \sigma^* \, 2 s^2 \, \pi 2 p_x^2 \, \pi 2 p_y^1 \\ & \Rightarrow & \text{Paramagnetic} \end{array}$$

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

$$C_2^{\ *} \qquad \Rightarrow \qquad \sigma 1 s^2 \, \sigma^* \, 1 s^2 \, \sigma 2 s^2 \, \sigma^* \, 2 s^2 \, \pi 2 p_x^2 \, \pi 2 p_y^1$$

Bond order = 
$$\frac{7-7}{2}$$

NO 
$$\Rightarrow \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_y^1$$
  
 $\Rightarrow Paramagnetic$ 

Bond order = 
$$\frac{10-5}{2}$$
 = 2.5  
NO<sup>+</sup>  $\Rightarrow$   $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$   
 $\Rightarrow$  Diamagnetic  
Bond order =  $\frac{10-4}{2}$  = 3.

8. NO<sup>+</sup> is derivative of 
$$Q_2$$
; NO<sup>+</sup> (isoelectronic with  $Q_2^{2+}$ )  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$ 

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

 $CN^{-}$  is derivative of  $N_2$ ;  $CN^{-}$  (isoelectronic with  $N_2$ )  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$ 

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



Decrease in B – F bond length which results in the higher bond dissociation energy of B – F in BF, is due to delocalised  $p\pi$ – $p\pi$  bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

- Bond Order 10.
  - $\frac{10-5}{2} = 2.5$ (1)  $O_{2}^{+}$  $O_{2}^{-} \qquad \frac{10-7}{2} = 1.5$   $O_{2}^{2-} \qquad \frac{10-8}{2} = 1$   $O_{2}^{2+} \qquad \frac{10-4}{2} = 3$ (2)
  - (3) (4)

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

- So,  $O_2^{2+}$  has the shortest bond length.
- 11. N<sub>2</sub> and C<sub>2</sub> both are diamagnetic Ans is (1) and (2)
- $H_2^{2+}$ : Bond order = 0 12.
  - $He_2$ : Bond order =  $\frac{2-2}{2} = 0$

So, both  $H_2^{2+}$  & He<sub>2</sub> do not exist.

 $\begin{array}{ccccccc} \text{Li}_{_2} & \sigma 1 s^2 & \sigma^* 1 s^2 & \sigma 2 s^2 \\ \text{Li}_{_2}^{+} & \sigma 1 s^2 & \sigma^* 1 s^2 & \sigma 2 s^1 \\ \text{Li}_{_2}^{-} & \sigma 1 s^2 & \sigma^* 1 s^2 & \sigma 2 s^2 \sigma^* 2 s^1 \end{array}$ 13. Bond order = 1 Bond order = 0.5 Bond order = 0.5Stability order  $Li_2 > Li_2^+ > Li_2^-$ 

## **P Solutions** AL

PART-I







4. In BF<sub>3</sub> the B - F bond length is shorter than normal bond character on account of  $p\pi - p\pi$  back bonding (1.30 Å). In 1 : 1 complex there is no  $p\pi - p\pi$  back bonding and hence the B–F bond length is longer, (1.35 Å).



## Steric number 4 4 Hence both N and B have tetrahedrdal geometry with sp<sup>3</sup> hybridisation.

- 7.  $N_2: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^2$ The bond order of  $N_2$  is 1/2(10 - 4) = 3.  $N_2^*: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$ The bond order of  $N_2^+$  is 1/2(9 - 4) = 2.5.  $O_2: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$ The bond order of  $O_2 1/2(10 - 6) = 2$ .  $O_2^-: (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$ The bond order of  $O_2 1/2(10 - 7) = 1.5$ . NO<sup>+</sup> derivative of  $O_2$  and isoelectronic with  $O_2^{2+}$ ; so  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ The bond order of  $NO^+ 1/2(10 - 4) = 3$ . NO derivative of  $O_2$  and isoelectronic with  $O_2^+$ ;  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ ,  $(\pi^* 2p_x)^1$ The bond order of NO is 1/2(10 - 5) = 2.5. bond order  $\sigma$  1/bond length  $\infty$  bond dissociation energy.
- 9. Bond order of  $N_2 = 3$  bond order of  $N_2^+ = 2.5$ B.O. of  $O_2 = 2$ . B.O. of  $O_2^+ = 2.5$
- (A) H<sub>2</sub>O<sub>2</sub> = 1.48 Å due to repulsions between non-bonded pairs of electron on O-atoms and O<sub>2</sub>F<sub>2</sub> = 1.217 Å.
   (B) In O<sub>2</sub><sup>2-</sup> very slightly increases due to charge (-ve) on two O atoms.

C)	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
			4
O <sub>2</sub> (dioxygenyl)	2.5	112.3	
O <sub>2</sub> (dioxygen)	2.0	120.07	2
$O_2^-$ (superoxide)	1.5	128	1
O <sub>2</sub> <sup>2-</sup> (peroxide)	1.0	149	0

- **11.** OF is derivative of O<sub>2</sub> and isoelectronic with O<sub>2</sub><sup>-</sup>. So  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$ The bond order of OF 1/2(10-7) = 1.5.
- **13.** The correct formula of borax is  $Na_2[B_4O_5(OH)_4]$ .  $8H_2O$ . The structure of anion is :



16.

17.

$$(A) O = C = C = C = O$$
$$| | |$$
$$sp sp sp$$



**19.**  $Cl_2O > F_2O$  and  $F_2O < H_2O$ 111° 102° 102° 104°  $NO_2^+ > NO_2^$ sp sp<sup>2</sup>

 $Asl_3 > AsBr_3 > AsCl_3$  (due to size of halogen)

**20.** (A) 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.





(R) Number of  $\pi$  bonds in NO<sup>+</sup> are two.

(S) 
$$\begin{bmatrix} F \\ I \\ B \\ F \\ F \\ F \end{bmatrix}^{-}$$

Steric number of central atom boron is 4 + 0 = 4; so its hybridisation is sp<sup>3</sup> and thus the number of hybrid orbitals involved in sp<sup>3</sup> hybridisation is four.

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 $\pi$  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.

(i) P = O have bond length of 1.43 Å (8 covalent bonds) (ii) P - O have bond length of 1.60Å (12 covalent bonds)

(iii) Number of P - O - P linkage = 6.

(iv) Number of lone pair on each phosphorus atom is zero.

# **CHEMICAL BONDING - III**

# EXERCISE # 1

#### PART - I

**A-1.** According to Fajan's rule as size of anion increases and charge on anion increases polarisability of anions increases and thus covalent character increases. Hence they follow the following order.

(a) NaF < Na<sub>2</sub>O < Na<sub>3</sub>N (b) NaCl < MgCl<sub>2</sub> < AlCl<sub>3</sub> < SiCl<sub>4</sub> < PCl<sub>5</sub>

## PART - II

A-1. As charge on cations increases, their polarising power increases and thus covalent character increases.

$$\overset{+}{Li}\overset{2+}{Cl} \overset{3+}{<} \overset{3+}{BCl} \overset{4+}{_3} \overset{4+}{_3} \overset{+}{_2} \overset{+}{_2} \overset{+}{_2} \overset{+}{_3} \overset{+}{_$$
- A-2. Increase in oxidation state (Ni<sup>4+</sup>) increases the polarising power of cation and thus increases the polarisation of Br<sup>-</sup> ion.
- **A-4.** Because of high charge density on Sn<sup>4+</sup> it has high polarising power and thus leads to greater polarisation of anion i.e., greater distortion of electron clouds of the Cl<sup>-</sup> ions. So SnCl<sub>4</sub> is most covalent.
- **B-1.** The strength of metallic bonds depends upon the number of mobile electron(s) per atom. Sodium has only one mobile electron per atom where as iron has 8 mobile electrons per atom.
- **B-3.** Cu, Ag, Zn are solids at room temperature where as mercury is liquid.

## PART - III

- 1. LiBr has more solubility being more ionic than LiI. Lattice energy as well as hydration energy of LiBr are more than for LiI due to small size of Br.
- 2. Due to poor shielding by d-electrons in Ga<sup>3+</sup>, its Z<sub>eff</sub> is more. So its polarising power is more and hence it forms compound with higher covalent character.

# EXERCISE # 2

## PART - I

2. A monoatomic anion is more stable with more polarising cation but a polyatomic anion is more stable with less polarising anion.

so, the order of thermal stability are :

(i)  $\text{Li}_2\text{O} > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{Cs}_2\text{O}$  (ii)  $\text{LiO}_2 < \text{NaO}_2 < \text{KO}_2 < \text{CsO}_2$  (iii) LiOH < NaOH < KOH < RbOH < CsOH

**3.** (a) Agl < AgBr < AgCl < AgF - size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.

(b)  $Bel_2 < BeBr_2 < BeCl_2 < BeF_2$  – size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.

(c)  $PbI_2 < PbBr_2 < PbCI_2 < PbF_2 - size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.$ 

(d)  $AI_2(SO_4)_3 < MgSO_4 < Na_2SO_4$  – charge on cation increases, polarisation increases, covalent character increases and so solubility in water decreases.

(e)  $BCl_3 < BeCl_2 < LiCl - charge on cation increases, polarisation increases, covalent character increases and so solubility in water decreases.$ 

# PART - II

- 1. As size of cations increase, their polarising power decrease and thus ionic character increase.
- 3. Sn<sup>4+</sup> has highest polarising power amongst Na<sup>+</sup>, Pb<sup>2+</sup>, Sn<sup>4+</sup> and Al<sup>3+</sup> because of smaller size and higher charge. So SnCl<sub>4</sub> is most covalent and thus has least melting point.
- 5. AgI is less soluble than AgF due to covalent nature. LiI is more soluble then LiF due to high size difference of ions more ionic nature, more melting point. Higher the charge density, larger will be the hydrated radii.
- 6. Metallic bond results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.
- **10.**\* (A) It results from the electrical attractions among positively charged metal ions and mobile, delocalised electrons belonging to the crystal as a whole.
  - (B) In general, greater the number of (n-1)d and ns electrons, stronger is the resultant bonding.
  - (C) Strength of metallic bond depend on the type of hybrid orbitals participating in metallic bonding.

(D) As the size of atom increases the attraction between the positive part of the atom and delocalised electrons decreases and thus the strength of the metallic bond decreases.

## PART - III

(D) For more covalent character, small cation and large anion are favourable factors. In MgS, Mg<sup>2+</sup> will have higher polarising power and S<sup>2-</sup> will have higher polarisability. Hence there will be higher polarisation of anion resulting in higher covalent character.

- 2. Due to smaller size of  $Be^{2+}$  and largest size of  $I^-$  amongst all anions i.e.  $F^-$ ,  $CI^-$ ,  $Br^-$  and  $I^-$ , there will be greater polarisation of anion. Thus  $BeI_2$  will be most covalent i.e. least ionic.
- 3. As the size of the cations increases in the order  $Si^{4+} < Sn^{4+} < Sn^{2+}$ and for size of anions  $F^- < Cl^$ so the order of increasing ionic character is  $SiCl_a < SnCl_a < SnF_a < SnCl_2 < SnF_2$ .
- 4. As polarizability of anion increases covalent character increases.

# EXERCISE # 3

#### PART - I

- 1. Statement-1 : Germanium is a semiconductor, where the energy gap between adjacent bands is sufficiently small for thermal energy to be able to promote a small number of electrons from the full valence band to the empty conduction band. This leaves both bands partially filled, so the material can conduct electricity. Statement-2 : Incorrect statement.
- 2. Due to small size of B, it is very difficult to remove the electrons from boron to form ionic bond as it will require very high energy. On the other hand, due to its very small size having high polarising power causes greater polarisation and eventually significant covalent character according to Fajan's rule.

#### PART - II

- 1. The elements of group 14 show an oxidation state of +4 and +2. The compounds showing an oxidation state of +4 forms covalent compound and have tetrahedral structures, e.g. SnCl<sub>4</sub>, PbCl<sub>4</sub>, SiCl<sub>4</sub>, etc. whereas those which show +2 oxidation state are ionic in nature and behave as reducing agent. e.g. SnCl<sub>2</sub>, PbCl<sub>2</sub> etc. Further as we move down the group the tendency of the element to form covalent compound decreases but the tendency to form ionic compound increases.
- High charge and small size of the cations increases polarisation.
   As the size of the given cations decreases as : K<sup>+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > Be<sup>2+</sup>
   Hence, polarising power increases as : K<sup>+</sup> < Ca<sup>2+</sup> < Mg<sup>2+</sup> < Be<sup>2+</sup>
- **3.** Covalent character in ionic compounds is governed by Fazan's Rule. AICl<sub>3</sub> will show Maximum covalent character on account of higher polarising power of AI<sup>3+</sup> because of its having higher positive charge and smaller size.

# **ALP Solutions**

## PART-I

- **1.** Polarisation of the I<sup>-</sup> by the Cu<sup>2+</sup> results in the transference of an electron towards  $Cu^{2+}$  makes it as oxidising agent and I<sup>-</sup> as a reducing agent, reduces  $Cu^{2+}$  to  $Cu^{+}$  and itself oxidised to I<sub>2</sub>.
- 2. (A)  $N_2$  contains one  $\sigma$  and two  $\pi$  bonds but  $C_2$  contains only two  $\pi$  bonds as four electrons are present in bonding  $\pi$  molecular orbitals.

(B)  $Cu^{2+}$  has higher hydration energy then  $Cu^+$  so  $Cu^{2+}$  is more stable than  $Cu^+$ . Moreover,  $Cu^+$  undergoes disproportionation.  $2Cu^+ \rightarrow 2Cu^{2+} + Cu$ . (a fact)

(C) Can be explained by electron sea model as it is due to the presence of mobile electrons.

- **3.** Larger anion has higher polarisability.
- 5. Refer notes.

#### PART-II

For cations of nearly same radii and same charge, polarising power of cation is decided by their electronic configuration. Inert gas configuration < Non-inert gas configuration < pseudo inert gas configuration So , (i) Mg<sup>2+</sup>< Fe<sup>2+</sup> < Ni<sup>2+</sup> < Zn<sup>2+</sup> (ii) Al<sup>3+</sup> < Fe<sup>3+</sup> < Ga<sup>3+</sup>

# **CHEMICAL BONDING - IV**

## EXERCISE # 1

#### PART - I

- A-4.  $BF_3$ ,  $\mu = 0$  (trigonal planar);  $H_2S$ ,  $\mu = 0.95$  (bent with 2 lone pair);  $H_2O$ ,  $\mu = 1.85$  (bent with 2 lone pair). So the  $BF_{3} < H_{2}S < H_{2}O.$ increasing order of dipole moment is . Pot.
- % ionic character =  $\frac{6.32 \times 10^{-18}}{4.8 \times 10^{-10} \times 156 \times 10^{-10}} \times 100 = 84.5 \%$ A-5.

#### PART - II

- Dipole moment  $\propto \frac{1}{\text{bond angle}}$ A-1.
- $\mu \neq 0$ ; SiF<sub>4</sub>, BF<sub>3</sub> and PF<sub>5</sub> are symmetrical molecules thus  $\mu = 0$ . A-2.
- O = C = O. The values of C=O bond dipoles are same but acting in opposite direction; so cancel out. Thus A-3. dipole moment of CO<sub>2</sub> is zero.
- Symmetrical molecules have zero dipole moment. A-4.

planar, 
$$\theta = 120^{\circ}$$
,  $\mu = 0$ . Cl Cl Cl F  
 $\mu = 0$   
 $\mu = 0$   
 $\mu = 0$ 

A-6. Number of electron pairs = 4 Number of bond pairs = 2Number of lone pairs =  $2^{4}$ So, according to VSEPR theory to have minimum repulsions it acquires bent shape as shown below.

It is unsymmetrical molecule thus it will have some dipole moment.

A-7. Dipole moment depends on the electronegativity of the elements as it is the product of charge on one of the ions and the distance between them. Dipole moment of  $CH_3CI$  is greater than  $CH_3F$  due to more charge separation. (a fact)

A-5.

**π** – dτ

**A-8.** Dipole moment of compound if it would have been completely ionic =  $(4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-8} \text{ cm}) = 12.8 \text{ D}$ 

so % ionic character =  $\frac{4.0}{12.8} \times 100\% = 31.25\%$ 

**B-1.** All molecules have London dispersion force because of number of polarizable electrons. Non polar molecules have only London dispersion force because of polarisable electron. Benzene is non polar molecule.

Polar molecules have dipole-dipole attraction in addition to London dispersion force.

$$\begin{pmatrix} \delta^+ & \delta^- & \delta^+ & \delta^- \\ (H-CI) & (H-CI) \end{pmatrix}$$
 and so on

Molecules with, O–H, N–H, or F – H bond have hydrogen bonding in addition to London dispersion force. Molecule IC $\ell$  is polar, so in addition to London dispersion force it has dipole-dipole attraction also.

- **B-2.** Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C C bond length within the layer is 141.5 pm Each carbon atom in hexagonal ring undergoes sp<sup>2</sup> hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a  $\pi$  bond. The electrons are delocalised over the whole sheet.
- **B-4.** London forces are extremely short range in action and the weakest of all attractive forces. The order of strength of bonds/ forces is ionic bond > covalent bond > hydrogen bond > London force.
- **B-6.** Nitrogen is less electronegative than oxygen so electron pair is easily available for bonding, thus P has stronger H-bonding than Q. As oxygen is more electronegative so H-bond strength of Q is greater than S. The same explanation is given for R and S as that of P and Q.

**C-1.** As molecular weight increases, magnitude of Van der Waal's force of attraction increases. Therefore, boiling point increases. Though  $NH_3$  has strong H-bonding but boiling point of  $SbH_3$  is highest due to highest molecular weight. Boiling point  $NH_3 = 238.5$  K and  $SbH_3 = 254.6$  K.

#### **C-2.** (A) A fact

(B) In the solid state and in liquid HF, the HF<sub>2</sub><sup>-</sup> ion is held together by hydrogen bonding. In aqueous solutions there is hydrogen bonding but each HF molecule forms hydrogen bonds with the much more prevalent H<sub>2</sub>O present, instead of with other HF molecules and H<sub>3</sub>O<sup>+</sup> and F<sup>-</sup> are much more likely to be formed. (C) H<sub>3</sub>BO<sub>3</sub> (solid) has intermolecular hydrogen bonding.



(B) structure of anions are different 
$$CO_3^{2-}$$
 – trigonal planar (sp<sup>2</sup>)  $\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}^{2-}$   
 $SO_3^{2-}$  – trigonal pyramidal (sp<sup>3</sup>)  $\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}^{2-}$  (false)  
(C)  $O = \sum_{k=0}^{k} e \bigotimes_{0}^{0}$  no lone pair of electrons (false)  
(D) True.  $D_2O = 374.4 \text{ K}$ ;  $H_2O = 373.0 \text{ K}$   
(i)  $H_2O$  has highest boiling point because of H-bonding.  
(ii) Boiling point also depends on the magnitude of van der Waal's force of attraction, which in turns depends on molecular weight of the compounds. Thus the correct order is  $H_2O > H_2Te > H_2Se > H_2S$ .  
**PART - III**

1. F<sup>™</sup>

C-4.

Bond dipoles of N—F bonds are counter balanced to some extent by the dipole moment of

lone pair of electron acting in opposite direction. This reduces both the dipole moment and its donor powers.

- 4. Within the  $Ca^{2+}/SO_4^{2-}$  layers the ions are held together by strong electrovalent bonds. But these separated  $Ca^{2+}/SO_4^{2-}$  layers are linked by relative weak H bond. The weaker H bonds link  $SO_4^{2-}$  ions in the intermediate region. Consequently, the gypsum can be readily cleaved and stretched along the layer of water molecules. Anhydride has a completely ionic structure involving only  $Ca^{2+}$  and  $SO_4^{2-}$  ions.
- In the solid state, the B(OH)<sub>3</sub> units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.



London dispersion force exists among the non-polar molecules like F<sub>2</sub>, O<sub>2</sub>, I<sub>2</sub>, Cl<sub>2</sub> 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 distribution. 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.



atoms (covalently bonded) ; due to more charge separation in CH<sub>3</sub>Cl, it has higher dipole moment.

- **9.**  $\mathbf{S}_1 : \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$  Due to resonance , both bonds are equal.
  - $S_2$ : Hydration of ions due to force of attraction between ion and water molecule. Which is a dipole.
  - $\mathbf{S}_{3}$ : Due to intermolecular H-bonding, boiling point increases.
  - $\mathbf{S}_{4}$ : A symmetrical molecule with identical bonds have zero dipole moment.
- 11. (A) As  $\delta^+$  charge on central atom increases, the attraction between  $\delta^+$  and  $\delta^-$  increases and thus Xe-F bond length decreases. The correct order is XeF<sub>2</sub> > XeF<sub>4</sub> > XeF<sub>6</sub>

(B)  $PH_5$  can not undergo sp<sup>3</sup>d hybridisation as there is much large difference in size of s, p and d orbitals.  $PH_5$  does not exist as no partial positive charge develops on P atom.

(C) Dipole moment of  $CH_3CI$  is greater than  $CH_3F$  due to greater charge sepration on carbon and chlorine atoms in  $CH_3CI$ .

(D) it is a correct order.

The strength of hydrogen bond depends upon :

(i) size (ii) electronegativity and (iii) ease of donation of electron pair by electronegative element.

Higher the value of electronegativity and smaller the size of the covalently bonded atom to H atom stronger is the hydrogen bonding.

- 13. It has intramolecular H-bonding
- **14.** Strength of H-bond depends on following factors.
  - (i) Electronegativity of element covalently bonded to hydrogen atom.
  - (ii) Size of electronegative element.
  - (iii) Ease of donation of lone pair of electrons by electronegative element.
- 15. S<sub>1</sub>: Due to intermolecular H-bonding in HF it boils at higher temperature than HCI
  - $S_2$ : Mol. wt. of HBr < Mol. wt. of HI
  - $S_3$ : Bond order of N<sub>2</sub> is more than N<sub>2</sub><sup>+</sup>.
  - S<sub>4</sub>: Molecular mass of F<sub>2</sub> is less than that of Cl<sub>2</sub>
- **16.**  $S_1$ : Polarising power of a cation is inversely proportional to its size.

B.O. = 2

He<sub>2</sub><sup>+</sup> : σ1s<sup>2</sup>σ\*1s<sup>1</sup>

But He<sub>2</sub><sup>+</sup> has electron in antibonding molecular orbital so its is unstable.

- **S**<sub>3</sub>: H-bond formation requires the availability of lone pair of electron.
- $\mathbf{S}_{\mathbf{A}}^{2}$ : In Cl<sub>2</sub>O, the bond angle is more than 109°28' due to steric repulsion.
- **18.** (A) in  $S_8$  hybridisation of each S-atom is sp<sup>3</sup>, in  $P_4$  hybridisation of each P-atom is sp<sup>3</sup>

(B)  $(B) = \sum_{F}^{177^{\circ}} \sum_{F}^{F} \sum_{F}^{104^{\circ}} due to bp-lp repulsions$ 

(C) Inter molecular H-bonding (PO<sub>4</sub><sup>3-</sup> groups are bonded by many H-bonds)



D)

C

19.

22.\*

As a result of H-bonding, number of sulphuric acid molecules are associated to form cluster. Hence it has high boiling point and viscosity.

(II) All S — O bond lengths are equal due to resonance.



21.\* (A) I – CI, linear and polar because of the difference in the electronegativities of iodine and chlorine.



(B) Dipole moment is a vector quantity as it depends on the magnitude and the direction.

 $(C) \begin{array}{c} \leftarrow I & I \rightarrow \\ O = C = O & \mu = 0. \end{array}$ 

(D) As a result of polarisation in covalent bond which arises due to the difference in the electronegativities of combining atoms, the molecule possesses the **dipole moment**.



Greater the size of the halogen atom greater will be bond angle.





4. (A)  $CuSO_4$ .  $5H_2O$   $SO_4^{2-}$  is resonance stablized. (B)  $Ca^{2+}/SO_4^{2-}$  are held together by electrostatic force of attraction i.e., ionic bond but alternate layers by H-bonds with water molecules.

5. (A) Br<sub>2</sub> is non-polar in nature. All molecules experience London dispersion forces which results from the motion of electrons.

(B) HF has hydrogen bonding in liquid as well as in solid state. HF molecules also experience dispersion forces. (C) Ion-dipole forces are found in the solutions of ionic compounds in polar solvent where solvated species such as  $Na(OH_2)_x^+$  and  $F(H_2O)_y^-$  exist. Hydrogen bond exist between water molecules. In addition they also experience dispersion London forces.

(D) CH<sub>3</sub>NH<sub>2</sub> is a polar molecule that can form hydrogen bonds. In addition, it has dispersion forces.

(E) Induced dipole-dipole interaction exists between non-polar molecules and polar molecules such as clathrate compound of Xe gas with water, when water is frozen under a high pressure of the gas. They have formulae approximating to  $6H_2O$ : 1 gas atom (i.e. Xe. $6H_2O$ ).

In addition, Xe.6H, O has H-bonding and dispersion forces.

#### PART - IV

2. Vector addition of dipole moment cancels the dipole moment due to three C–Cl bonds. Only one remains.

→polar

$$\begin{array}{c} CI \ F \\ (B) \ CI \ I \ F \\ F \end{array} \rightarrow \text{polar}$$



F P−CI → polar

4. 
$$X = \sqrt{a^2 + a^2 + 2a.a\cos 120^\circ}$$
Net dipole moment

$$=\sqrt{2a^2-a^2} = a$$

6.

- 7. o-nitrophenol has intramolecular H-bonding so it will be vaporised first.
- 8. D<sub>2</sub>O has different physical properties than H<sub>2</sub>O max. density of D<sub>2</sub>O is at approximately 10°C.

# EXERCISE # 3

## PART - I

- 1. Intermolecular forces between  $H_2S$ ,  $H_2Se$  and  $H_2Te$  molecules are purely Van der Waal's force of attraction while in water there is stronger H-bonding between the water molecules. H-bond is stronger than Van der Waal's force of attraction and thus more energy is required for converting  $H_2O(\ell)$  to  $(H_2O)(g)$ .
- 2. (i) In carboxylic acid H-bonding is stronger than that in alcohol.
  - (ii) In aldehyde there is dipole-dipole attraction
  - (iii) H-bonding is stronger than dipole-dipole attraction.
  - (iv) Boiling point  $\infty$  strength of intermolecular force of attraction.



1. The reason for the lesser volatility of alcohol than ethers is the intermolecular association of a large number of molecules due to hydrogen bonding as – OH group is highly polarised.

hydrogen bonding

No such hydrogen bonding is present in ethers.



ot.on



5.  $O^{2-}$  (base) + H<sub>2</sub>O (acid)  $\longrightarrow$  OH<sup>-</sup> (C.B) + OH<sup>-</sup> (C.A.) O<sup>2-</sup> acts as Lewis base.



- 4. This is based on the decreasing electronegativity difference between H (2.1) and Sb (1.9), As (2.0), P (2.1) and N (3.0).
- 5. van der Waal's forces  $\infty$  molecular weight. So AgBr will have maximum van der Waals forces.
- 6. (C) Both compounds have intermolecular H-bonding amongst themselves and with water.
- 7. In  $CH_4$ ,  $H_2Se$  and  $H_2S$  the central atoms are not more electronegative; hence do not form hydrogen bonds with itself and other molecule. In  $N_2H_4$  the nitrogen is more electronegative and thus is able to form hydrogen bond with itself and other molecules like water.
- **10.** (A) Like hydrated copper sulphate (CuSO<sub>4</sub>.5H<sub>2</sub>O) in which one water molecule is hydrogen bonded to coordinated water molecule, one water molecule is coordinated to lone pair of electrons on SnCl<sub>2</sub> and the other is hydrogen bonded to coordinated water molecule.
- **13.** In pure phosphoric acid the  $PO_4^{3-}$  groups are bonded together through many hydrogen bonds.
- 14. HF is least volatile (i.e. high boiling point) due to strong intermolecular hydrogen bonding.
- **15.** Boiling point of  $SbH_3$  is greater than  $NH_3$ . The higher boiling point of  $SbH_3$  is attributed to higher van der Waal forces because of its higher molecular weight. (a fact)
- S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ion : Individual O.N. of S atoms = +6 and -2. Average O.N. = +2 SbH<sub>3</sub> has higher bp than NH<sub>3</sub>, due to vander waal forces. In hydracids, the acidity increases down the group while for oxyacids, the acidity decreases down the group.
- 17. Polarity depend on net dipole moment. If diple moment  $\mu = 0$  it is nonpolar.



**18.** (A) Ethyne being non-polar is more soluble in acetone.

(B)  $CD_{3}F$  is more polar than  $CH_{3}F$ . In  $CD_{3}F$ , C–D bond is more polar as deuterium is more electropositive than hydrogen.

(C) Silyl isocyanate (SiH<sub>3</sub>NCO) is linear in shape because of  $p\pi$ -d $\pi$  delocalisation of lone pair of electrons on nitrogen. While in methyl isocyanate (CH<sub>3</sub>NCO) there is no  $p\pi$ -d $\pi$  delocalisation of electron as carbon does not have empty d-orbital and thus is bent in shape.

In  $CH_2 = C = C = C = CH_2$ , the 2H-atoms on one C-atom lie in a plane perpendicular to the plane in which 2H-atoms on other C-atom lie.

**19.** H=O 
$$H=O$$
  $H=O$   $H=O$ 

The P = O contain one  $p\pi$ -d $\pi$  bond. The PO<sub>4</sub><sup>3-</sup> ion show resonance. Due to the presence of H-bonded to O, it show intermolecular H-bonding due to which it is syrupy.

20. The critical temperature depends on the magnitude (of strength) of intermolecular force of attraction between the molecules. If a molecule has dipole moment it means there is dipole dipole attraction between the molecules and thus it will affect the critical temperature.

#### **PART-II**

- **1.**  $CO_2$  :O = C = O: and  $BF_3$
- 2. C–F bond is most polar due to maximum difference in electronegativity.
- H−C≡ C−H sp Hybridisation.
   Due to sp hybridisation of C atom, the electronegativity of C is more and hence can form H-bond with HF.
- 4. The structure of chloral hydrate is a follows



Its stability is due to intermolecular H-bonding.

5. Thio-ethers have higher boiling points due to their higher molecular weights than that of ethers.

 $\mu_{Th} = 4.8 D$ 

6.  $\Delta EN = 1.4$ % ionic character = 29.26  $\mu_{obser} = 1.4 D$ 

d = 1 Å

- 7. Percentage of IC =  $\frac{6 \times 10^{-18}}{4.8 \times 10^{-10} \times 2.5 \times 10^{-8}} \times 100 = 50\%$
- 8. Dipole moment of compound would have been completely ionic =  $(4.8 \times 10^{-10} \text{ esu}) (2.25 \times 10^{-8} \text{ cm}) = 4.8 \times 2.25 \text{ D}$

so % ionic character = 
$$4.8 \times 2.25$$
 × 100% = 83.33 %

9. H  

$$\mu_{R} = \sqrt{2\mu_{S-H}^{2} + 2\mu_{S-H}^{2} \times \cos 97^{\circ}}$$
  
 $\mu_{R} = \sqrt{2} \times \mu_{S-H} \times \sqrt{1-0.12}$   
 $\mu_{R} = \sqrt{2} \times \mu_{S-H} \times \sqrt{0.88}$   
 $\mu_{S-H} = \frac{1.5}{\sqrt{2} \times 0.94} D$ 

$$(\mu_{\text{S-H}})_{\text{Cal}} = \frac{0.15 \times 10^{-9} \times 1.6 \times 10^{-19}}{\frac{10}{3} \times 10^{-30}}$$

 $(\mu_{S-H})_{Cal} = 3 \times 0.15 \times 1.6 \times 10 \text{ D}$ 

So % lonic character =  $\frac{1.5}{\sqrt{2} \times 0.94} \times \left[\frac{1}{0.15 \times 16 \times 3}\right] \times 100 = 16 \%$ 



No of  $p\pi$ -d $\pi$  bonds = 6.

(Q) NOHSO<sub>4</sub> exists as NO<sup>+</sup> and HSO<sub>4</sub><sup>-</sup>; NO<sup>+</sup> is derivative of oxygen and isoelectronic with  $O_2^{2+}$ . Bond order is 1/2 (10 - 4) = 3.



No of vacant sp<sup>3</sup> hybrid orbitals participating in the formation of banana bonds are 2.



**12.** Theoretical value of dipole moment of a 100% ionic character =  $e \times d$ = (1.60 × 10<sup>-19</sup> C) (1.41 × 10<sup>-10</sup> m) = 2.26 × 10<sup>-29</sup> Cm Observed value of dipole moment = 2.60 × 10<sup>-30</sup> Cm

Percent ionic character =  $\frac{\text{observed value}}{\text{theoretical value}} \times 100 = \frac{2.60 \times 10^{-30}}{2.26 \times 10^{-29}} \times 100 = 11.5\%$  Ans.

**13.** For a diatomic molecule dipole moment  $\mu = e \times d$ 

Electronic charge =  $\frac{\mu}{d} = \frac{1.2 \times 10^{-18} \text{ esu cm}}{1.0 \times 10^{-8} \text{ cm}}$ Actual value of electronic charge =  $4.8 \times 10^{-10}$  esu Fraction of the electronic charge =  $\frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = 0.25$  **14.** (i) Bond order of  $N_2 = 1/2 (10 - 4) = 3$ 

Bond order of  $O_2 = 1/2 (10 - 6) = 2$ Bond order of  $F_2 = 1/2 (10 - 8) = 1$ 

Bond order of  $O_2^{+} = 1/2 (10 - 5) = 2.5$ 

Bond order is directly proportional to the bond strength and so, the increasing order of their bond dissociation energies is :  $F_2 < O_2 < O_2^+ < N_2$ .

(ii) The strength of H – bond mainly depends on the electronegativity of the atom attached to the H atom and it increases with increasing electronegativity of the atom attached to polar H atom. So the increasing order of strength of hydrogen bonding (X - H - - - X) is : S < CI < N < O < F

