

CHEMICAL BONDING

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JEE(Advanced) Syllabus

Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

JEE(Main) Syllabus

Chemical Bonding and Molecular Structure
Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, valence bond theory, resonance, geometry of molecules, VSEPR theory, concept of hybridization involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only). Hydrogen bond.



Chemical Bonding-I

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

Covalent Bond :

A chemical bond formed by sharing of electrons between two elements is called as covalent bond.

$A-A$ (*Single bond*) : When 2 electrons are shared between the two combining elements.

$A=A$ (*Double bond*) : When 4 electrons are shared between the two combining elements.

$A\equiv A$ (*Triple bond*) : When 6 electrons are shared between the two combining elements.

To explain nature of chemical bond, different theories are given

(i) *Octet rule*

(ii) *Valence bond theory*

(iii) *Valence shell electron pair repulsion theory*

(iv) *Molecular orbital theory*.

Section (A) : Octet rule, Lewis dot structures

Octet rule : "Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

- (i) It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.
- (ii) It means that these atoms must have a stable electronic configuration.
- (iii) These elements (noble gases) have 8 electrons ($ns^2 np^6$) except helium which has 2 electrons ($1s^2$) in their outer most shell.

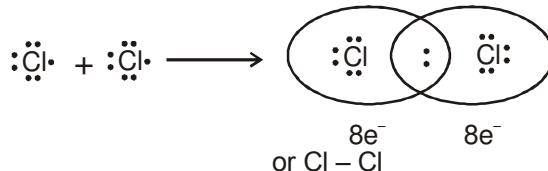
Element	Ne	Ar	Kr	Xe	Rn
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Outer most shell configuration

2s ² 2p ⁶	3s ² 3p ⁶	4s ² 4p ⁶	5s ² 5p ⁶	6s ² 6p ⁶
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- (iv) It is therefore concluded that $ns^2 np^6$ configuration in the outer energy level constitutes a structure of maximum stability or minimum energy.

The **Octet rule** 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



Covalent bond between two Cl atoms

Figure

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

Lewis Dot Structures :

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

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

- (i) The total number of electrons are obtained by adding the valence electrons of combining atoms.
- (ii) For Anions, we need to add one electron for each negative charge.
- (iii) For cations, we need to subtract one electron for each positive charge.
- (iv) After then the central atom is decided.



To decide, Central atom, following steps are followed :

- (1) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-} , 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

Molecule/ion	H_2	O_2	O_3	NF_3	CO_3^{2-}	HNO_3	CH_4	HCHO
Lewis Representation	$\text{H}-\text{H}$	$:\ddot{\text{O}}=\ddot{\text{O}}:$						

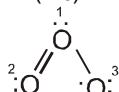
Each H-atom attains the configuration of helium (a duplet of electrons)

Section (B) : Formal charge & limitations of octet rule

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

Formal charge (F.C.) On an atom in a Lewis structure	$= \left[\begin{matrix} \text{Total number of valence} \\ \text{electron in the free atom} \end{matrix} \right] - \left[\begin{matrix} \text{Total number of non bonding} \\ (\text{lone pair}) \text{ electrons} \end{matrix} \right] - \left(\frac{1}{2} \right) \left[\begin{matrix} \text{Total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{matrix} \right]$
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Let us consider the ozone molecule (O_3). The Lewis structure of O_3 , may be drawn as :



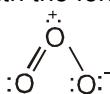
The atoms have been numbered as 1, 2 and 3. The formal charge on :

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

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

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

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 :** (i) The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.
(ii) Pair of +1 and -1 formal charge on adjacent atoms is considered a coordinate bond.
 $\text{:}\bar{\text{C}}\equiv\ddot{\text{O}}:\Rightarrow\text{:}\ddot{\text{C}}\leq\text{O}:$
(iii) Lewis dot structure with minimum formal charges is most stable.

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, BeH₂ and BCl₃.

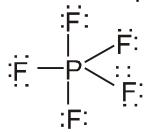


2. **Odd-electron molecules :** In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide (NO₂), the octet rule is not satisfied for all the atoms.
e.g. NO, ClO₂, ClO₃

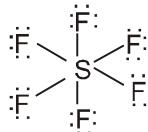


3. **The expanded octet :** Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the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

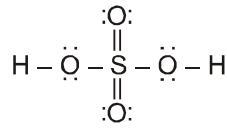
Some of the examples of such compounds are: PF₅, SF₆, PCl₅, HNO₃, SO₃, SO₂, H₂SO₄ and a number of coordination compounds.



PF₅



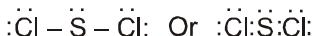
SF₆



H₂SO₄

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

- O 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.



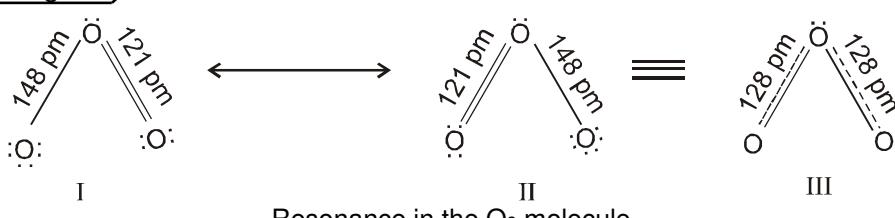
4. **Other drawbacks of the octet theory :**

- (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 XeF₂, KrF₂, XeOF₂ 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.

Section (C) : Resonance and bond order calculation

Resonance :

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O₃ molecule can be equally represented by the structures I and II shown below :



Structures I and II represent the two canonical forms.

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.

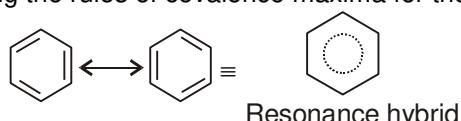
Obviously, this cannot be represented by either of the two Lewis structures shown above.

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.

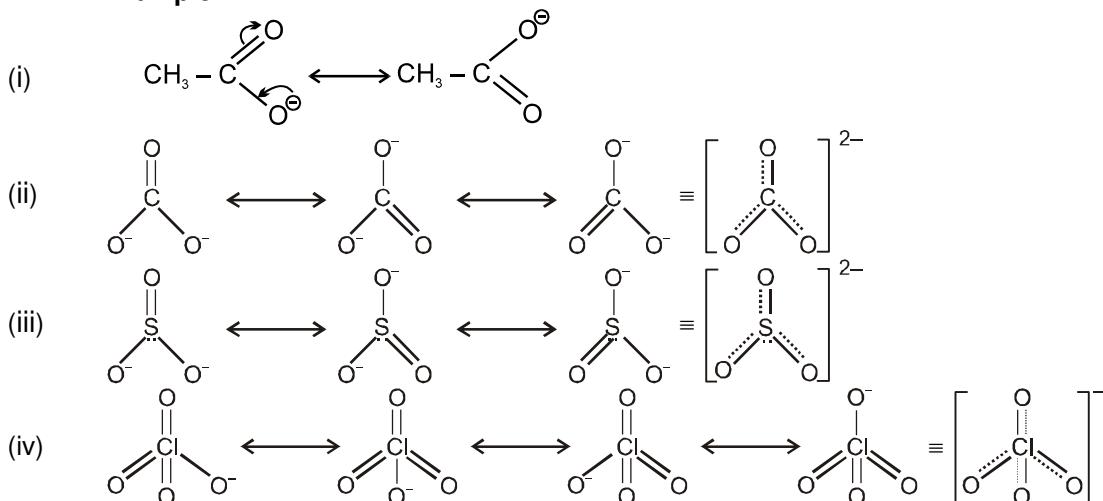
Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 , more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

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.



Example :

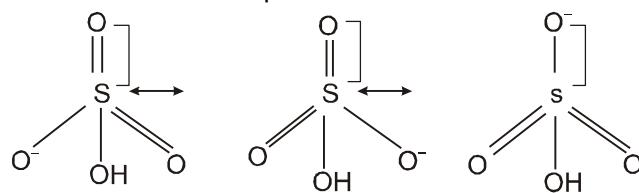


- Resonance energy = Actual bond energy – Energy of most stable resonating structure.
- Stability of molecule \propto resonance energy.
- More is the number of covalent bonds in molecule more will be its resonance energy.
- Resonance energy \propto number of resonating structures.



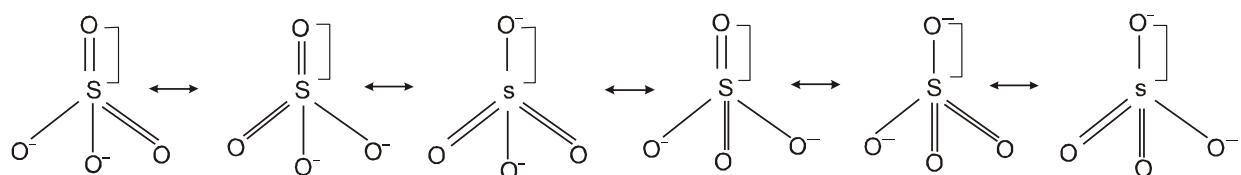
Bond order in oxoanions and corresponding acids :

Let's start with example of HSO_4^-



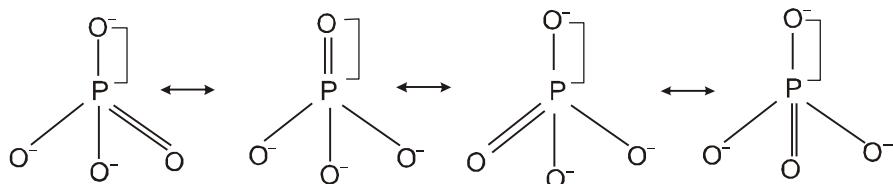
○ Bond order = $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1}{3} = 5/3$

Consider another example of SO_4^{2-} :



○ Bond order = $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1+2+1+1}{6} = 1.5$

Consider another example of PO_4^{3-} :



○ Bond order = $\frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{1+2+1+1}{4} = 5/4$

Section (D) : VBT, overlapping of orbitals

Modern Concept of Covalent Bond (VBT) :

- (i) Introduced by Heitler and London.
- (ii) This theory is based on the knowledge of Atomic orbitals electronic configuration of electrons, the overlap criterion 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 H_A and H_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.

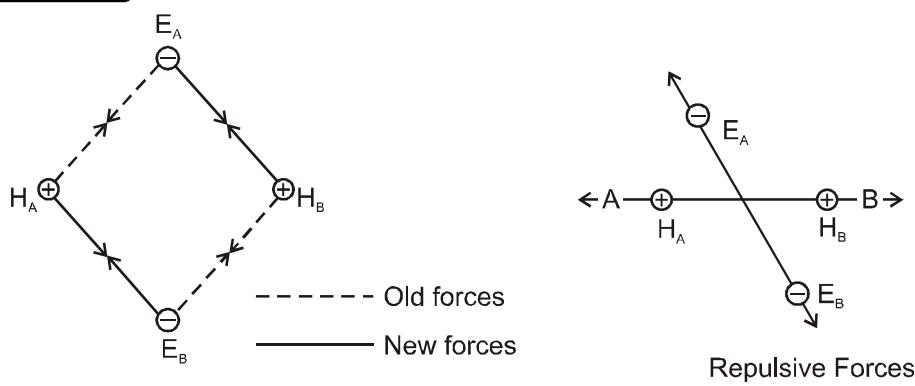
Attractive forces arise between :

- (i) nucleus of one atom and its own electron that is $H_A - E_A$ and $H_B - E_B$.
- (ii) nucleus of one atom and electron of other atom i.e., $H_A - E_B$, $H_B - E_A$.

Similarly repulsive forces arise between :

- (i) electrons of two atoms like $E_A - E_B$, (ii) nuclei of two atoms $H_A - H_B$.

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

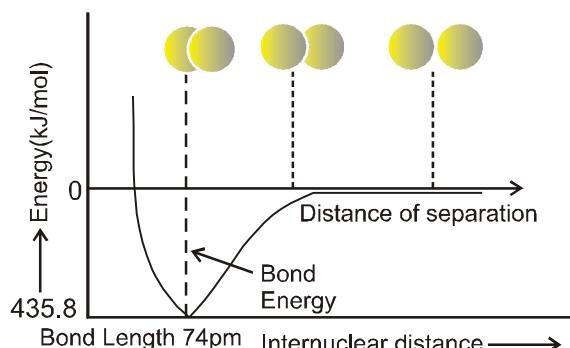
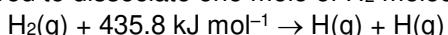


Attractive Forces

Figure : Forces of attraction and repulsion during the formation of H_2 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 minima in the curve depicted in Fig. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

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

Orbital Overlap Concept

- In the formation of H_2 Molecule, In the minimum energy state when two H atoms are so near that their atomic orbitals undergoes partial interpenetration. This partial merging is called overlapping.
- Acc. 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.
- The extent of overlap decides the strength of a covalent bond.
- Greater the overlap, stronger is the bond formed between two atoms.

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.

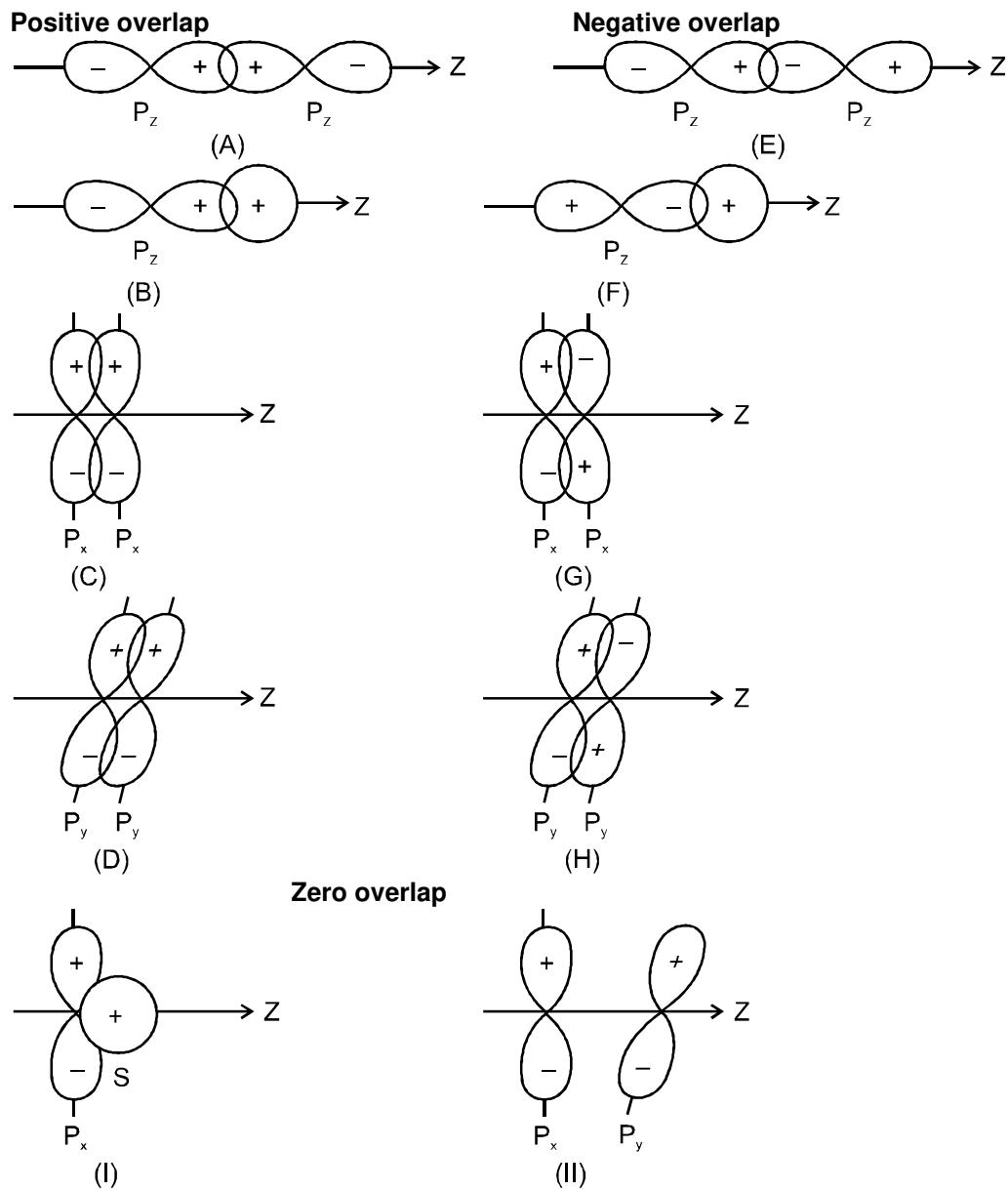


Figure : Positive, negative and zero overlaps of s and p atomic orbitals

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 (σ) bond, and (ii) pi (π) bond

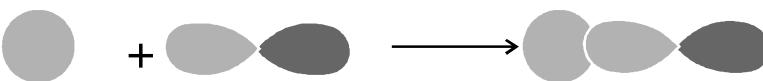
(i) **Sigma (σ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

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

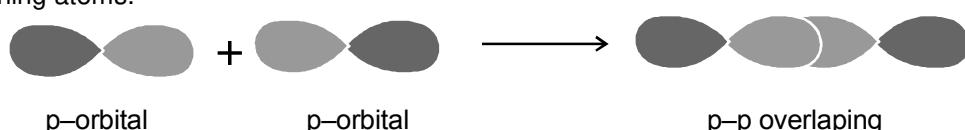




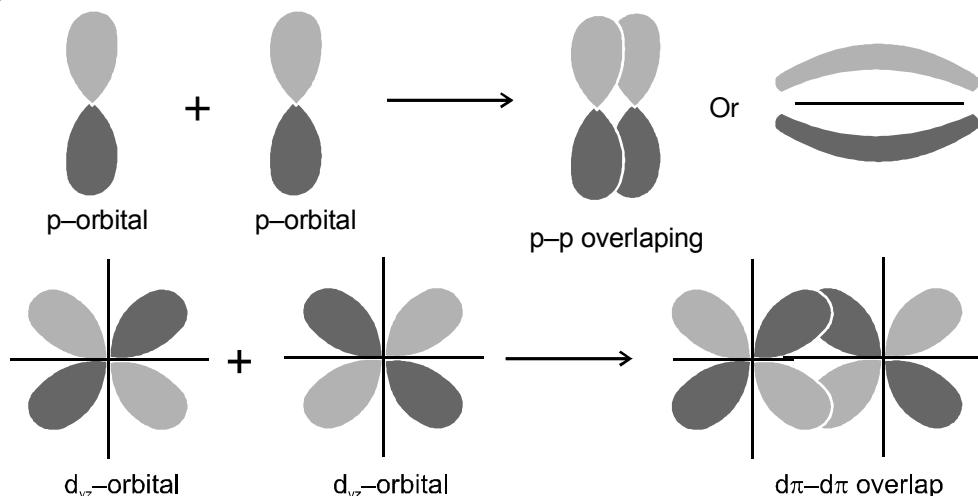
- **s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.



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



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

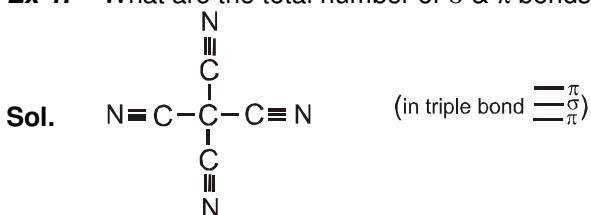


Strength of Sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the 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

- Ex-1.** What are the total number of σ & π bonds in tetracyanomethane.



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



MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Ex-1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :

- | | |
|---|---|
| (a) SiSi bond in $\text{Cl}_3\text{SiSiCl}_3$ | (b) SiCl bond in $\text{Cl}_3\text{SiSiCl}_3$ |
| (c) CaF bond in CaF_2 | (d) NH bond in NH_3 |

Sol. (a) Covalent, due to identical electronegativity.

(b) Polar covalent, due to less electronegativity difference.

(c) Ionic, due to more electronegativity difference.

(d) Polar covalent, due to different electronegativity.

Ex-2. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?

Sol. 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.



Exercise-1

 Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Octet rule, Lewis dot structures

- A-1.** 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 , C_3^{4-} , S_3^{2-} , NOCl , SOBr_2 , SO_2Cl_2

A-2. With the help of Lewis dot structure find the number of total covalent bonds formed in the following species.
(i) CO_3^{2-} , (ii) CCl_4 , (iii) NF_3

A-3. Indicate what is wrong with each of the following Lewis structures? Replace each with a more acceptable structure.
(a) $[\ddot{\text{S}}-\text{C}=\ddot{\text{N}}:]^-$ (b) $[\ddot{\text{Cl}}]^+[\ddot{\text{O}}]^{2-}[\ddot{\text{Cl}}]^+$ (c) $\ddot{\text{O}}=\text{N}=\ddot{\text{O}}$ (d) $\begin{array}{c} \ddot{\text{Cl}} & \ddot{\text{N}} = \ddot{\text{Cl}} \\ | \\ : \ddot{\text{Cl}} : \end{array}$

A-4. In how many of the following species, the central atoms have two lone pairs of electrons ?
(i) XeF_4 (ii) XeF_5^- (iii) Fe_2SeO_6 (iv) XeF_6^+ (v) XeOF_4

Section (B) : Formal charge & limitations of octet rule

Section (C) : Resonance and Bond order Calculation

- C-1.** Write down the resonance structure(s) for :

 - SO_4^{2-}
 - CH_3COO^-
 - HCO_3^-
 - NO_3^-
 - PO_4^{3-}

Also calculate average bond order of M–O bond in these compounds.
Where M is central atom (And M–O bonds considered are the one which involve delocalization)

C-2. How many types of N–O bondlengths are present in (a) HNO_3 (b) NO_3^- ?

C-3. Explain the following :
C–O bond lengths in formic acid are 1.23 \AA & 1.36 \AA and both the C–O bond lengths in sodium formate have same value 1.27 \AA .

C-4. 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 $\text{CH}_2=\text{C}=\text{C}=\text{CH}_2$.

D-2. Draw the type of overlaps between

 - (a) s and p_x
 - (b) p_x and p_x
 - (c) p_y and p_y
 - (d) p_z and p_z
 - (e) s and d_{z^2}
 - (f) s and $d_{x^2-y^2}$
 - (g) s and d_{yz}
 - (h) p_z and d_{z^2}
 - (i) p_z and d_{xy}
 - (j) p_x and d_{xy}
 - (k) p_x and d_{z^2}
 - (l) p_x and $d_{x^2-y^2}$
 - (m) $d_{x^2-y^2}$ and $d_{x^2-y^2}$
 - (n) d_{xy} and d_{xy}
 - (o) d_{xy} and d_{yz}

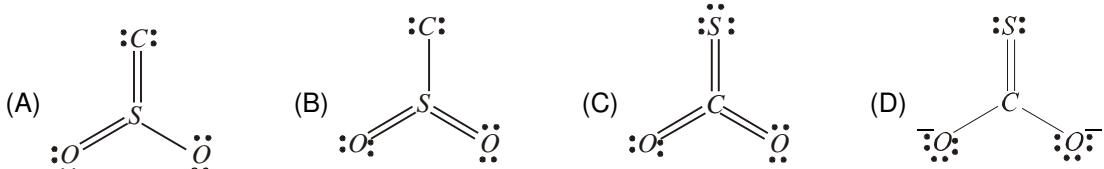
if internuclear axis is z-axis. Identify them as σ , π , δ bond wherever bond is formed.



PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Octet rule, Lewis dot structures

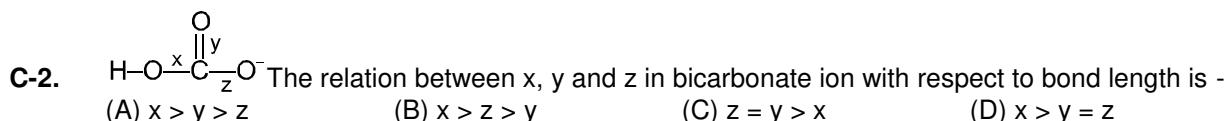
- A-2.** The possible structure of monothiocarbonate ion is :



Section (B) : Formal charge & limitations of octet rule

Section (C) : Resonance and Bond order Calculation

- C-1.** The average charge on each O atom and average bond order of I-O bond in IO_6^{5-} is :
 (A) -1 and 1.67 (B) -5/6 and 1.67 (C) -5/6 and 1.33 (D) -5/6 and 1.167



Section (D) : VBT, Overlapping of orbitals

- D-1. Which of the following overlaps is incorrect [assuming z-axis to be the internuclear axis] ?

(a) $2p_y + 2p_y \rightarrow \pi 2p_y$ (b) $2p_z + 2p_z \rightarrow \sigma 2p_z$ (c) $2p_x + 2p_x \rightarrow \pi 2p_x$ (d) $1s + 2p_y \rightarrow \pi(1s - 2p_y)$
 (A) 'a' & 'b' (B) 'b' & 'd' (C) only 'd' (D) None of these

- D-2.** Effective overlapping will be shown by :

(A) $\oplus\ominus + \oplus\ominus$ (B) $\overset{+}{\ominus} + \overset{-}{\oplus}$ (C) $\oplus\ominus + \ominus\oplus$ (D) All the above

- D-3.** Indicate the wrong statement according to Valence bond theory :

 - (A) A sigma bond is stronger than π -bond
 - (B) p-orbitals always have only sidewise overlapping
 - (C) s-orbitals never form π -bonds
 - (D) There can be only one sigma bond between two atoms

- D-4.** C_3^{4-} has :

(A) two σ and two π -bond
(B) three σ and one π -bond
(C) two σ and one π -bond
(D) two σ and three π -bond



- D-5.** Which of the following is not correct _____

 - (A) A sigma bond is weaker than π -bond
 - (B) A sigma bond is stronger than π -bond
 - (C) A double bond is stronger than a single bond
 - (D) A double bond is shorter than a single bond

PART - III : MATCH THE COLUMN

- 1. Match the column**

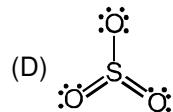
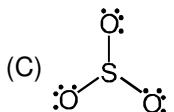
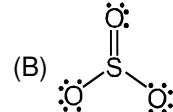
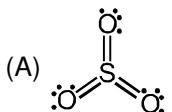
	Column-I		Column-II
	Molecule/ion		Number of σ bonds
(A)	C_2^{-2}	(p)	5
(B)	C_2H_2	(q)	1
(C)	CH_3OH	(r)	3
(D)	HNO_3	(s)	4

Exercise-2

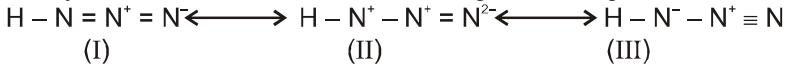
 Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

5. Which of the following structure is the most preferred structure for SO_3 ?



6. For hydrazoic acid, which of the following resonating structure will be least stable?



7. What is correct order of bond order of Cl–O bond.

- (A) $\text{ClO}_4^- > \text{ClO}_3^- > \text{ClO}_2^- > \text{ClO}^-$ (B) $\text{ClO}^- < \text{ClO}_2^- > \text{ClO}_3^- < \text{ClO}_4^-$
 (C) $\text{ClO}_3^- < \text{ClO}_2^- < \text{ClO}_4^- < \text{ClO}^-$ (D) $\text{ClO}_2^- < \text{ClP}_3^- < \text{ClO}_4^- < \text{ClO}^-$

8. Which of the following statements is not correct for sigma and pi bond formed between two carbon atoms?

- (A) Free rotation of atoms about a sigma - bond is allowed but not in case of a pi-bond
 - (B) Sigma -bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard
 - (C) Sigma-bond is stronger than a pi-bond
 - (D) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol. respectively.



9. Number and type of bonds between two carbon atoms in CaC_2 are :
 (A) one sigma (σ) and one pi (π) bond (B) one σ and two π bonds
 (C) one σ and one and a half π bond (D) one σ bond
10. The number of σ and π bonds in dicyanogen (CN_2) are :
 (A) $2\sigma + 3\pi$ (B) $3\sigma + 2\pi$ (C) $3\sigma + 4\pi$ (D) $4\sigma + 3\pi$

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. In OF_2 number of bond pairs of electrons are :
2. How many of the following molecules the central atom is surrounded by atleast 10 electrons.
 (i) ClO_2 (ii) NO_3^- (iii) O_3 (iv) PCl_5
 (v) SO_3 (vi) SO_4^{2-} (vii) CO_2 (viii) N_3^-
 (ix) I_3^-
3. Number of molecule or ions having lone pairs ≥ 2 for central atom are :
 (i) HClO_4 (ii) HClO_3 (iii) HClO_2 (iv) H_2O
 (v) NH_2^- (vi) ClF_3 (vii) XeF_2 (viii) XeF_4
 (ix) XeF_6 (x) I_3^- (xi) N_3^- (xii) O_3
 (xiii) ICl_4^- (xiv) ICl_2^+ (xv) XeO_3 (xvi) XeF_5^-
4. Total no. of resonating structure in CO_3^{2-} are :
5. Compound SO_3 has x bond pairs and y lone pairs. Calculate value of $x + y$.
6. Find the number of molecule having two lone pairs on central atom.
 (i) I_3^+ (ii) XeF_2 (iii) XeF_4 (iv) H_2O
 (v) NH_2^- (vi) H_2S (vii) H_2SO_4 (viii) NF_3
7. Consider y-axis as internuclear axis, how many of following will lead to π bond formation :
 (i) $\text{p}_y - \text{p}_y$ (ii) $\text{p}_x - \text{p}_x$ (iii) $\text{p}_z - \text{p}_z$ (iv) $\text{d}_{xy} - \text{d}_{xy}$
 (v) $\text{d}_{yz} - \text{d}_{yz}$ (vi) $\text{p}_x - \text{d}_{xy}$ (vii) $\text{d}_{xy} - \text{p}_z$ (viii) $\text{d}_{xz} - \text{d}_{xz}$

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Find the correct statements regarding SO_4^{2-} .
 (A) Bond order of S–O bond is 1.5 (B) Bond order of S–O bond is 2.5
 (C) It violates Octet Rule. (D) All S–O bonds are equivalent.
2. Which of the following Lewis diagram is/are incorrect ?
- (A) $\text{Na}^+ \ddot{\text{O}}-\ddot{\text{C}}\text{l}^-$
- (B) $\begin{array}{c} :\ddot{\text{C}}\text{l}: \\ | \\ :\ddot{\text{C}}\text{l}-\text{C}-\ddot{\text{C}}\text{l}: \\ | \\ :\ddot{\text{C}}\text{l}: \end{array}$
- (C) $\left[\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \\ | \\ \text{H} \end{array} \right]_2^+ \quad [\ddot{\text{S}}]^{2-}$
- (D) $\begin{array}{ccccc} & \text{H} & \text{H} & & \\ & | & | & & \\ \text{H} & -\text{N} & -\text{N}-\text{H} & & \\ & \cdot\cdot & \cdot\cdot & & \end{array}$
3. Which are the exceptions of the lewis octet rule.
 (A) NO_3^- and N_2O (B) BeH_2 and NO
 (C) KrF_2 and ClF_3 (D) All of these
4. Which species have same bond order ?
 (A) CO_3^{2-} (B) NO_3^- (C) NO_2 (D) NO



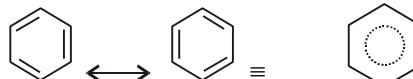
PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

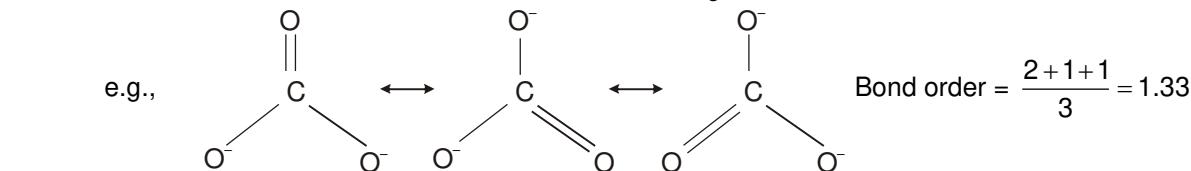
Definition: Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound.

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



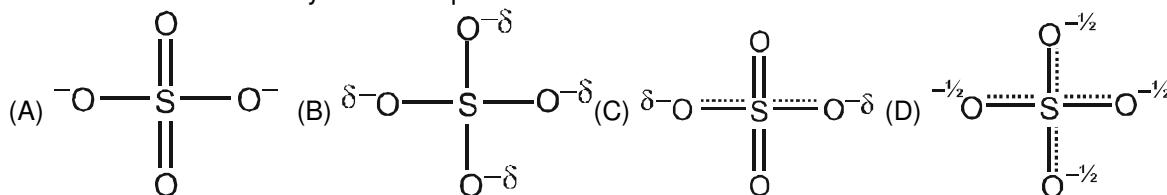
Resonance hybrid

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



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

1. Which is the resonance hybrid of sulphate ion :



2. The correct order of increasing C–O bond length of CO, CO₃²⁻, CO₂ is :

(A) CO₃²⁻ < CO₂ < CO (B) CO₂ < CO₃²⁻ < CO (C) CO < CO₃²⁻ < CO₂ (D) CO < CO₂ < CO₃²⁻

Comprehension # 2

Answer Q.3, Q.4 and Q.5 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents ions, column-2 represents number of equal contributing resonating structure while column-3 represents bond order.

Column-1		Column-2		Column-3	
(I)	SO ₄ ²⁻	(i)	4	(P)	1.66
(II)	CO ₃ ²⁻	(ii)	6	(Q)	1.25
(III)	NO ₂ ⁻	(iii)	3	(R)	1.33
(IV)	PO ₄ ³⁻	(iv)	2	(S)	1.5

3. In which of the following combination are correct for hypervalent ion.

(A) (I) (ii) (R) (B) (II) (i) (R) (C) (IV) (i) (Q) (D) (III) (iv) (S)

4. In which of the following combination octet is not violated.

(A) (IV) (i) (Q) (B) (II) (iii) (R) (C) (II) (i) (R) (D) (III) (iii) (P)

5. In which of the following combination the sum of oxidation state of central atom and number of π -bonds is maximum.

(A) (I) (ii) (S) (B) (II) (iii) (R) (C) (IV) (i) (Q) (D) (III) (iv) (R)



Exercise-3

* Marked Questions may have more than one correct options.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Molecular shapes of SF_4 , CF_4 and XeF_4 are respectively : [JEE-2000(S), 1/135]
 - (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.

2. The number of lone pair(s) of electrons in XeOF_4 is : [JEE-2004(S), 3/144]
 - (A) 3
 - (B) 2
 - (C) 1
 - (D) 4

3. In which of the following the maximum number of lone pairs is present on the central atom ? [JEE-2005(S), 3/144]
 - (A) $[\text{ClO}_3]^-$
 - (B) XeF_4
 - (C) SF_4
 - (D) I_3^-

- 4.* The compound(s) with TWO lone pairs of electrons on the central atom is(are). [JEE(Advanced) 2016, 4/124]
 - (A) BrF_5
 - (B) ClF_3
 - (C) XeF_4
 - (D) SF_4

5. The sum of the number of lone pairs of electrons on each central atom in the following species is $[\text{TeBr}_6]^{2-}$, $[\text{BrF}_2]^+$, SNF_3 , and $[\text{XeF}_3]^-$ [Atomic numbers: N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54] [JEE Advanced 2017, 3/122]

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. The number of lone pairs on Xe in XeF_2 , XeF_4 and XeF_6 respectively are : [AIEEE-2002, 3/225]
 - (1) 3, 2, 1
 - (2) 2, 4, 6
 - (3) 1, 2, 3
 - (4) 6, 4, 2

2. In the anion HCOO^- the two C–O bonds are found to be of equal length. What is the reason for it ? [AIEEE-2003, 3/225]
 - (1) Electronic orbits of carbon atom are hybridised.
 - (2) The C=O bond is weaker than the C–O bond.
 - (3) The anion HCOO^- has two resonating structures.
 - (4) The anion is obtained by removal of a proton from the acid molecule.

3. Which of the following has maximum number of lone pairs associated with Xe ? [AIEEE-2011, 4/120]
 - (1) XeF_4
 - (2) XeF_6
 - (3) XeF_2
 - (4) XeO_3

4. Which of the following exists as covalent crystals in the solid state ? [AIEEE-2013, 4/120]
 - (1) Iodine
 - (2) Silicon
 - (3) Sulphur
 - (4) Phosphorus

5. The correct statement for the molecule, CsI_3 , is : [JEE(Main)-2014, 4/120]
 - (1) it is a covalent molecule.
 - (2) it contains Cs^+ and I_3^-
 - (3) it contains Cs^{3+} and I^- ions.
 - (4) it contains Cs^+ , I^- and lattice I_2 molecule.

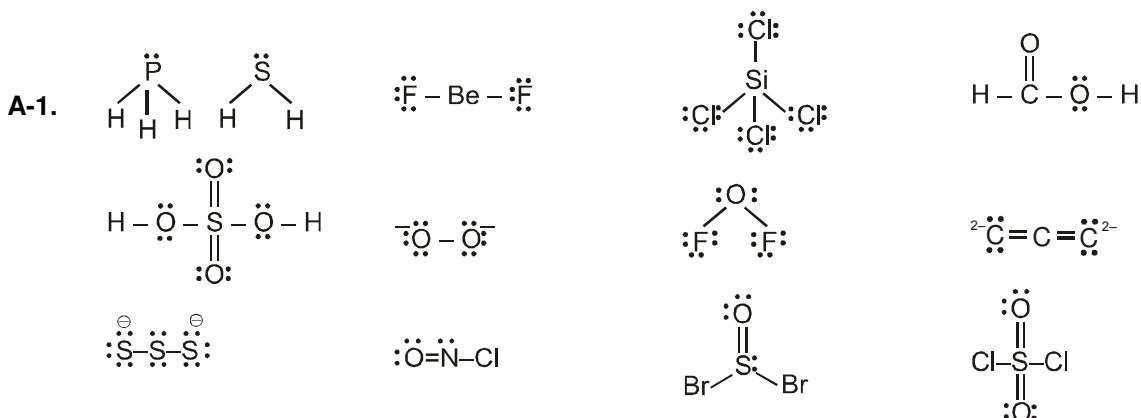
6. Total number of lone pair of electrons in I_3^- ion is : [JEE(Main)-2018, 4/120]
 - (1) 9
 - (2) 12
 - (3) 3
 - (4) 6



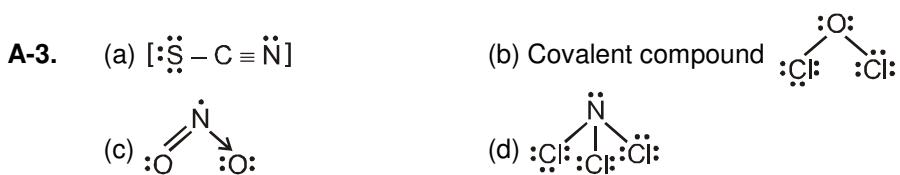
Answers

EXERCISE - 1

PART - I



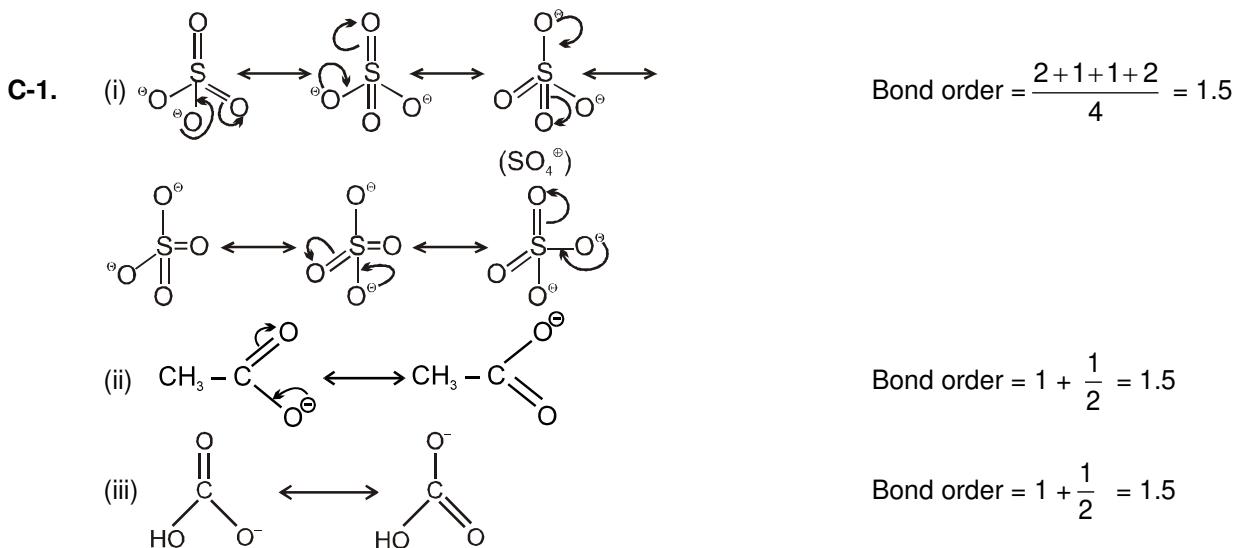
- A-2.** (i) 4 (ii) 4 (iii) 3

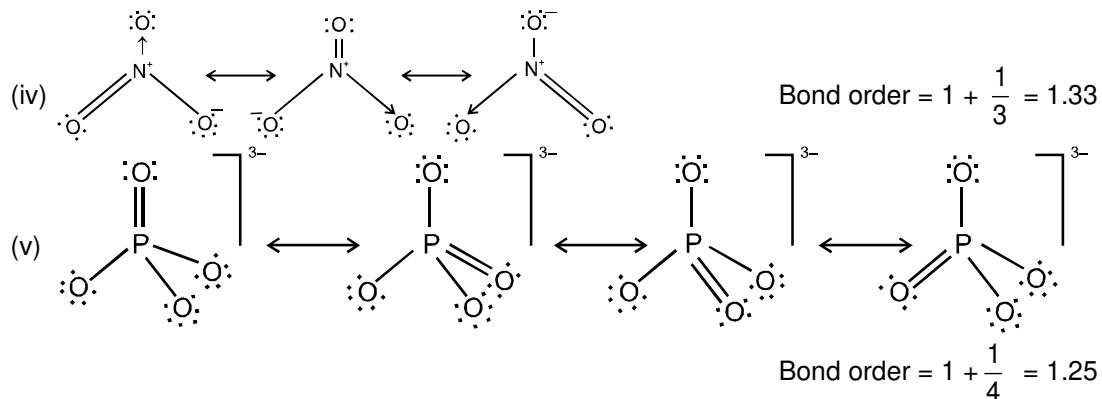


- A-4.** 5 (i, ii, iv, vii, viii)

- B-1.** 5 (ii, iv, v, vii, viii)

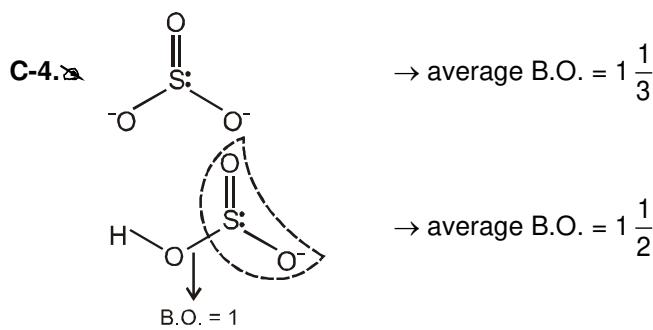
B-2.	BCl_3	Electron deficient molecule	;	XeF_2	Super octet molecule
	NO	Odd electron	;	IF_7	Super octet molecule
	NO_2	Odd electron	;	ClF_3	Super octet molecule
	ClO_2	Odd electron			





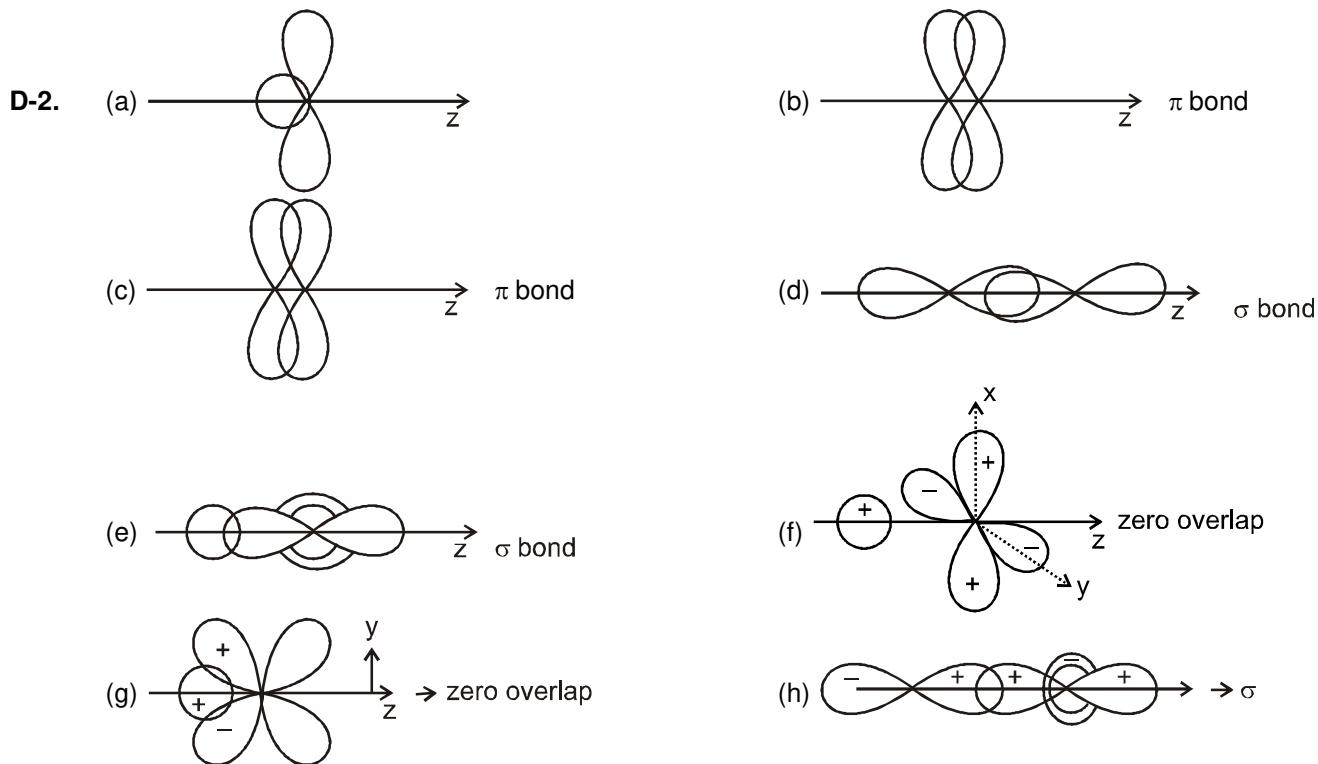
C-2. (a) 2 (b) 1

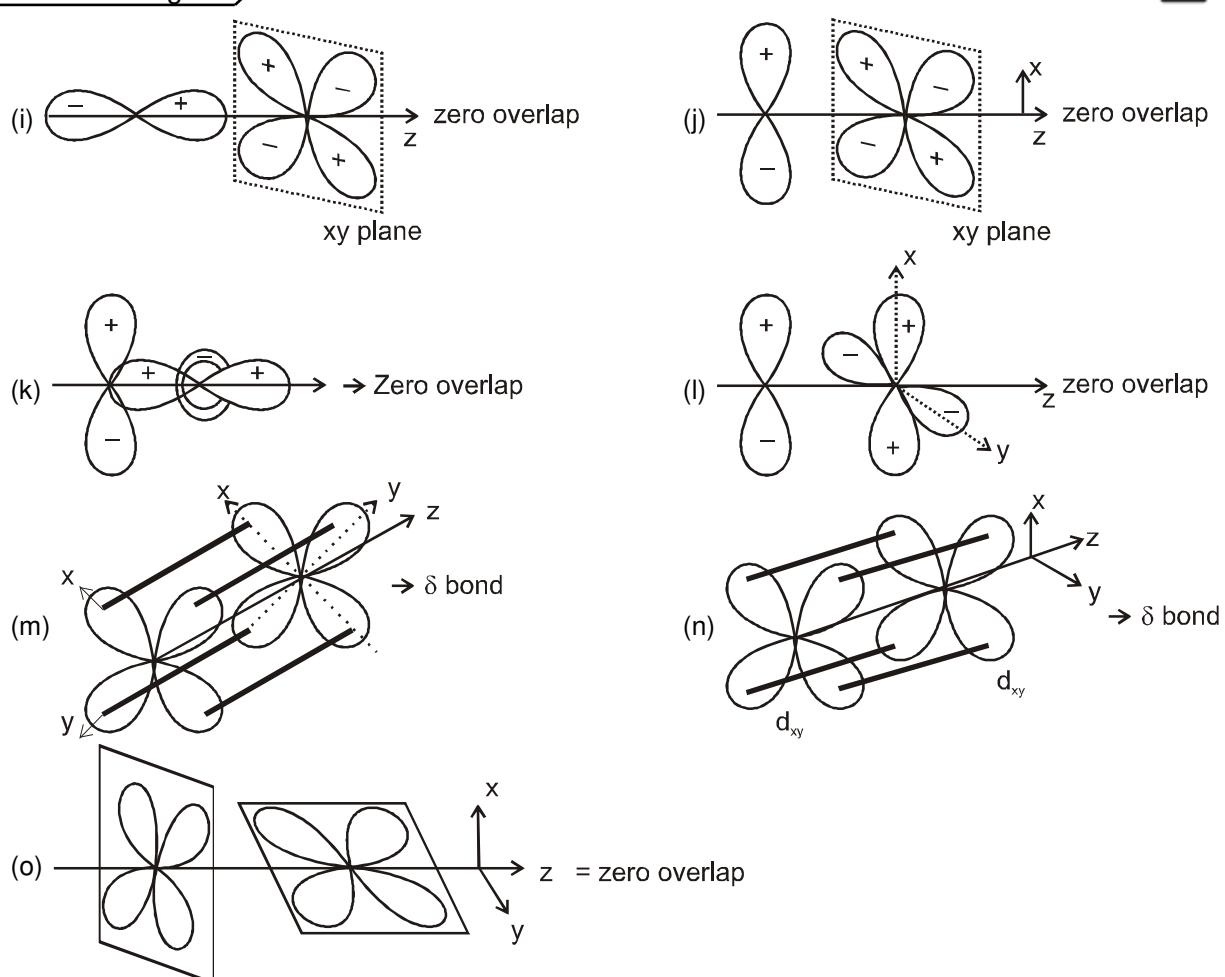
C-3. Sodium formate exists as $\text{HCOO}^- \text{Na}^+$



Hence one bond in HSO_3^- is longer than S–O bond in SO_3^{2-} . But other two S–O bond in HSO_3^- are shorter bonds.

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



**PART - II**

A-1. (C)

A-2. (D)

A-3. (C)

B-1. (D)

B-2. (D)

B-3. (D)

C-1. (D)

C-2. (D)

C-3. (C)

C-4. (D)

D-1. (C)

D-2. (C)

D-3. (B)

D-4. (A)

D-5. (A)

PART - III

1. (A) \rightarrow q, (B) \rightarrow r, (C) \rightarrow p, (D) \rightarrow s

EXERCISE - 2**PART - I**

1. (D)

2. (B)

3. (D)

4. (B)

5. (A)

6. (B)

7. (A)

8. (D)

9. (B)

10. (C)

PART - II

1. 2

2. 5 (i, iv, v, vi, ix)

3. 10 (iii, iv, v, vi, vii, viii, x, xiii, xiv, xvi)

4. 3

5. 12 ($x = 6, y = 6$)

6. 5 (i, iii, iv, v, vi)

7. 5 (ii, iii, iv, v, vi)

**PART - III**

1. (ACD) 2. (AC) 3. (BC) 4. (AB)

PART - IV

1. (D) 2. (D) 3. (C) 4. (B) 5. (A)

EXERCISE - 3

PART - I

1. (D) 2. (C) 3. (D) 4.* (BC) 5. 6

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (1) 2. (3) 3. (3) 4. (2) 5. (2)
6. (1)



Chemical Bonding-II

Section (A) : VSEPR theory

Valence shell electron pair repulsion (VSEPR) theory :

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

The main postulates of VSEPR theory are as follows :

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

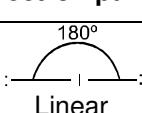
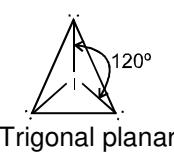
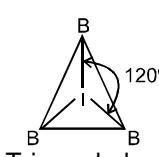
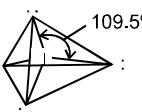
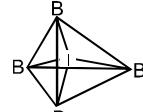
lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) - bond pair (bp)

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

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

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

Table-1

Number of electron pairs	General formula type	Arrangement of electron pairs	Molecular Geometry	Example
2	AB_2	 Linear	B-A-B Linear	$BeCl_2, HgCl_2$
3	AB_3	 Trigonal planar	 Trigonal planar	BF_3
4	AB_4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+





5	AB_5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	AB_6	 Octahedral	 Octahedral	SF_6
7	AB_7	 Pentagonal bipyramidal	 Pentagonal bipyramidal	IF_7

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

Table-2

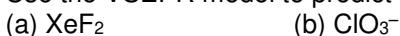
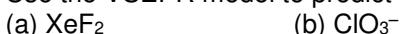
General formula type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples	
AB_2E	2	1		Bent	SO_2, O_3	
AB_3E	3	1		Trigonal Pyramidal	NH_3	
AB_2E_2	2	2		Bent	H_2O	
AB_4E	4	1		See saw	SF_4	
AB_3E_2	3	2		T-shape	ClF_3	
AB_5E	5	1		Square Pyramidal	$XeOF_4$	
AB_4E_2	4	2		Square Planar	XeF_4	
AB_5E_2	5	2		Pentagonal Planar	XeF_5^-	

Shapes of Molecules containing Bond Pair and Lone Pair



Solved Examples

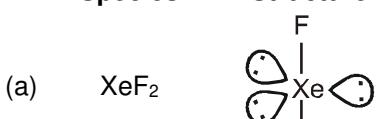
Ex-1. Use the VSEPR model to predict the geometry of the following :



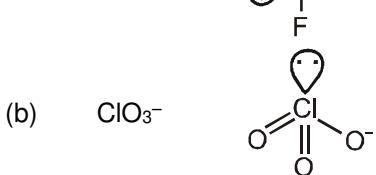
Sol.

Species

Structure



lone pairs occupy the equatorial positions to have minimum repulsion. Thus it is linear.



To minimize the repulsion between lone pair and double bond, species acquires trigonal pyramidal.

Section (B) : Hybridisation

Hybridisation :

- Hypothetical concept introduced by Pauling and Slater.
- Atomic orbitals of same atom combine to form new set of equivalent orbitals known as hybrid orbitals.
- This phenomenon is known as hybridization.
- Process of intermixing of the atomic orbitals of equal or slightly different energies in the formation of new set of orbitals of equivalent energies and shape is known as hybridization.

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

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

- (i) The orbitals present in the valence shell (and sometimes penultimate shell also) 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 undergoes 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 hybridized 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 atoms 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_2 , NO , NO_2), free radicals and compounds like B_2H_6 which involve 3 centre 2e- bond (banana bond).

For example :

$$\text{O}=\text{C}=\text{O} \quad \text{S.No.} = 2 + 0 = 2$$

$$\begin{array}{c} \text{O} \\ | \\ \text{S} \\ || \\ \text{O} \end{array} \quad \text{S.No.} = 2 + 1 = 3$$

$$\begin{array}{c} \text{O} \\ | \\ \text{N} \\ | \\ \text{O} \end{array} \quad \text{S.No.} = 3 + 0 = 3$$

$$\begin{array}{c} \text{O} \\ | \\ \text{Cl} \\ || \\ \text{O} \end{array} \quad \text{S.No.} = 3 + 1 = 4$$



Table-3

Steric number	Types of Hybridisation	Geometry	Involving orbitals
2	sp	Linear	ns, np _x / p _z / p _y
3	sp ²	Trigonal planar	ns, np _x , p _z / p _y , p _z /p _x , p _y
4	sp ³	Tetrahedral	ns, np _x , p _z , p _y
5	sp ³ d	Trigonal bipyramidal	ns, np _x , p _z , p _y , d _z ²
6	sp ³ d ²	Octahedral	ns, np _x , p _z , p _y , d _z ² d _{x²-y²}
7	sp ³ d ³	Pentagonal bipyramidal	ns, np _x , p _z , p _y , d _z ² d _{x²-y²} , d _{xy}

sp hybridisation :

- This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.
- Each sp hybrid orbital 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

BeCl₂ : The ground state electronic configuration of Be is 1s²2s². 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.

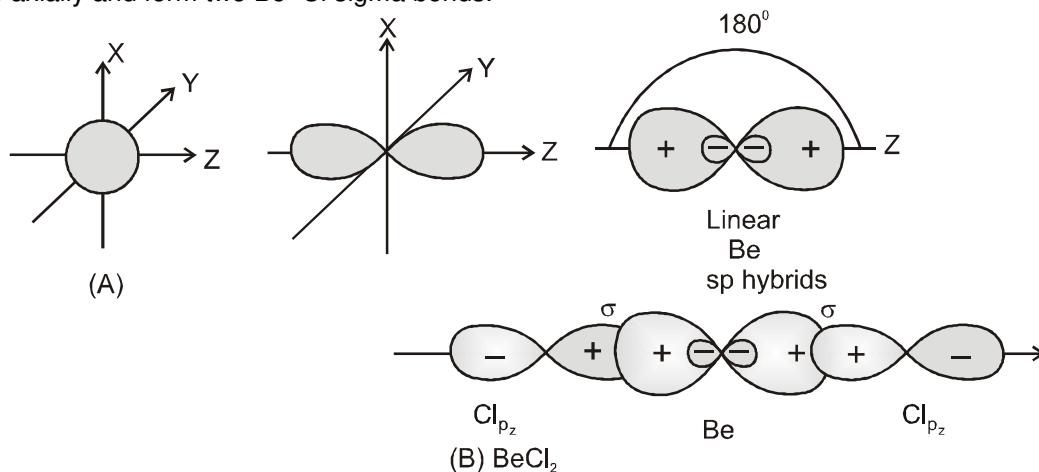


Figure : (A) Formation of sp hybrids from s and p orbitals ; (B) Formation of the linear BeCl₂ molecule.

Examples of sp hybridisation.**Species**

H–C≡N

H–C≡C–H

O=C=O

H₂C=C=CH₂N₃[−] (azide ion)

N=N=N

HgCl₂NO₂⁺ (nitronium ion), N₂O

Hydrazoic acid

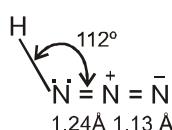
Important characteristic

Linear, highly poisonous, weak acid

Linear, π bond planes are perpendicular

Linear, both π bond are perpendicular to each other

Non planar both hydrogen are perpendicular to each other

Iso electronic with CO₂ and linear in shape. Both N–N bonds are similar

sp² hybridisation :

Mixing of one s and two p orbitals to form 3 equivalent sp² hybridized orbitals.

For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as a result boron has three unpaired electrons.

These three orbitals (one 2s and two 2p) hybridise to form three sp² 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 $\text{B}-\text{Cl}$ bonds.

Therefore, in BCl_3 , the geometry is trigonal planar with $\text{Cl}-\text{B}-\text{Cl}$ bond angle of 120° .

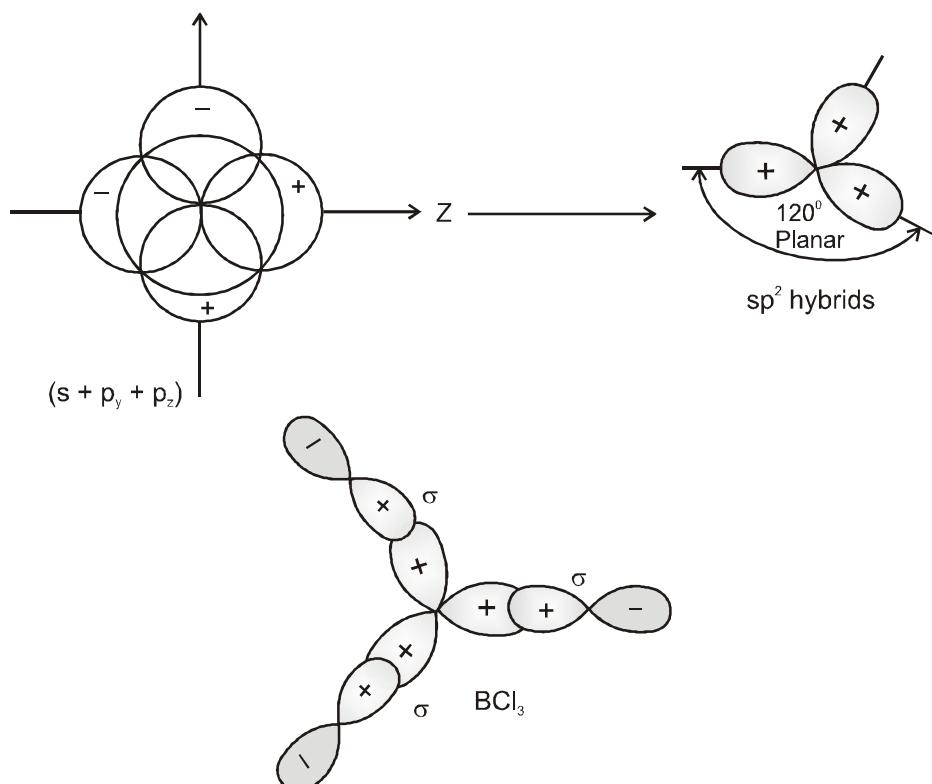


Figure : Formation of sp² hybrids and the BCl_3 molecule

Steric No. = 3

Geometry = Trigonal planar

Ideal bond angle = 120°

Table-4

Type	AB_3	AB_2L
Shape	Trigonal	V-shape (bent)
Example	C_6H_6 , CO_3^{2-} , HCO_3^- , H_2CO_3 , graphite, BF_3 , $\text{B}(\text{OH})_3$, SO_3 , NO_3^- , C_{60} (Fullerene)	NOCl , O_3 , NO_2 , NO_2^-

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

Molecule	Structure	Statements
SO_3		All three S–O bonds are equivalent. Out of 3p bond one pπ-pπ other two are pπ-dπ.
O_3		V shaped molecule. Both O–O bond length are equal.

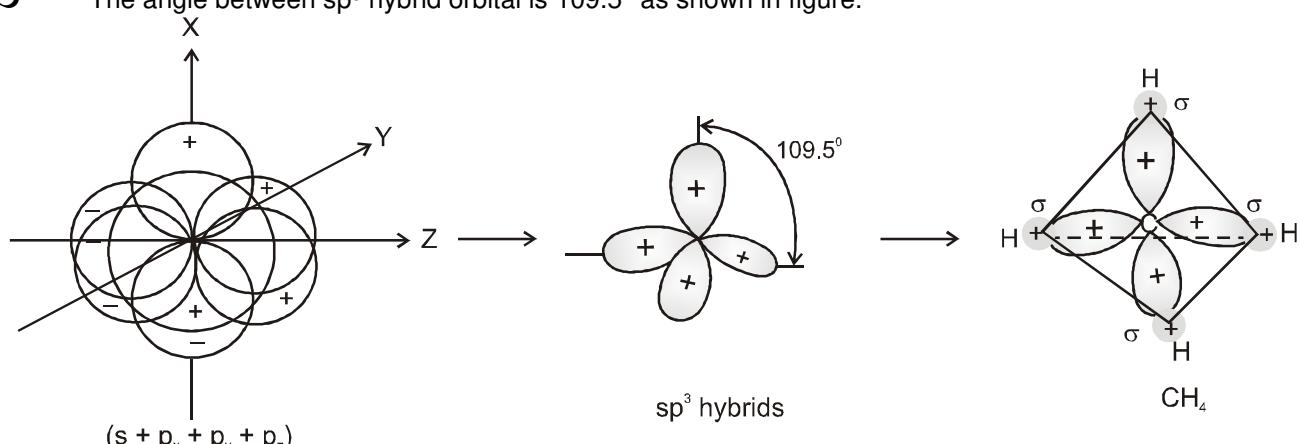


CO_3^{2-}		All three C–O bonds are equivalent. Bond lengths are shorter than single bond length but longer than double bond length.
NO_2^-		Bond order of N–O bond is 1.5, planar molecule.

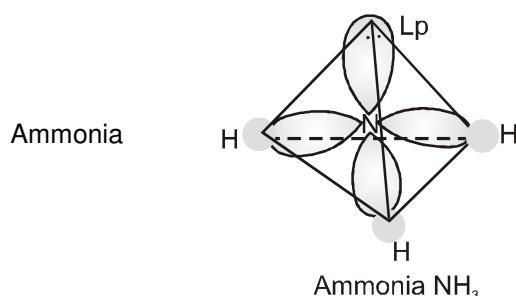
Note : In N_2O_5 , N is sp^2 hybridised but in solid, N_2O_5 exist in NO_2^+ (N is sp hybridised) and NO_3^- (N is sp^2 hybridised) ions.

sp^3 hybridisation :

- mixing of one s and three p orbitals to form 4 equivalent sp^3 hybridized orbitals.
- 4 sp^3 orbitals are directed towards four corner of tetrahedron.
- 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^3 hybrid orbital of equivalent energies and shape.
- There is 25% s-character and 75% p-character in each sp^3 hybrid orbital. The four sp^3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron.
- The angle between sp^3 hybrid orbital is 109.5° as shown in figure.



Figure



Three hybrid orbitals overlap with H atoms. One hybrid orbital contains lone pair. Geometry gets distorted and bond angle is reduced to 107° from 109.5° .

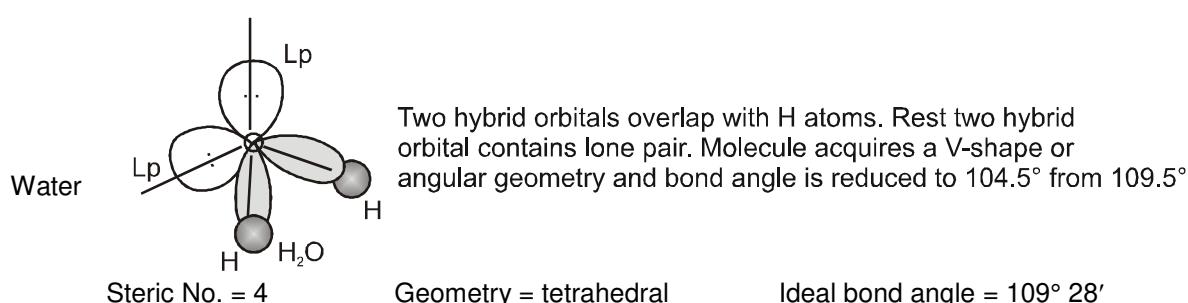
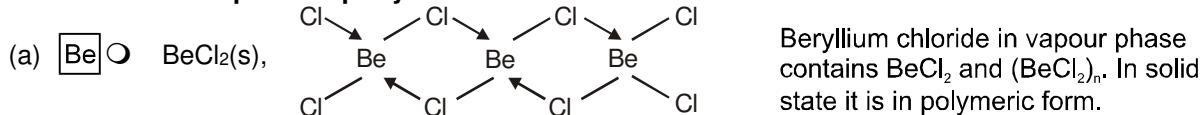




Table-5

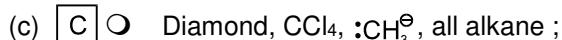
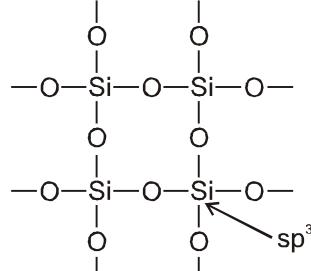
Type	AB_4	AB_3L	AB_2L_2	ABL_3
Shape	tetrahedral	pyramidal	V-shape or bent	Linear
Example	CH_4	XeO_3	OBr_2	$-\text{OCl}$

Some other Examples of sp^3 hybridisation

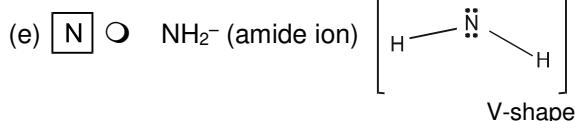
Beryllium chloride in vapour phase contains BeCl_2 and $(\text{BeCl}_2)_n$. In solid state it is in polymeric form.



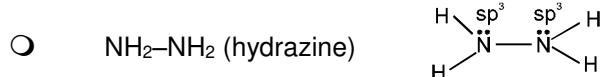
BF_4^- ions have a very low tendency to form complexes in aqueous solutions.

Structure of SiO_2 

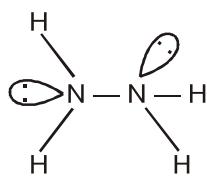
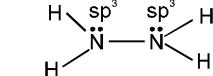
SiO_2 is a covalent network solid like diamond



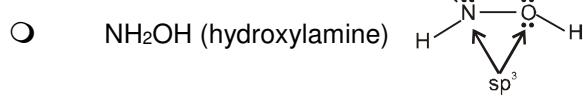
V-shape



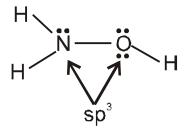
Each N atom is tetrahedrally surrounded by one N, two H and a lone pair.



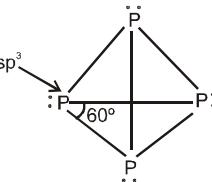
Structure is similar to that of ethane. The two halves of the molecules are rotated 95° about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å. The bond length is not greater or less than expected bond length of N–N.



Ip-Ip repulsion increases the N–O bond length.

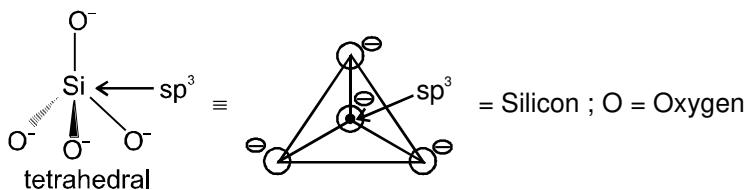


All phosphorus atoms occupy all four vertices of tetrahedron. There are six P–P bonds and $\angle \text{P–P–P} = 60^\circ$. Since bond angle is 60° (against normal tetrahedral bond angle, 109.5°) so, P_4 molecule is a strained molecule. So it is chemically very reactive.

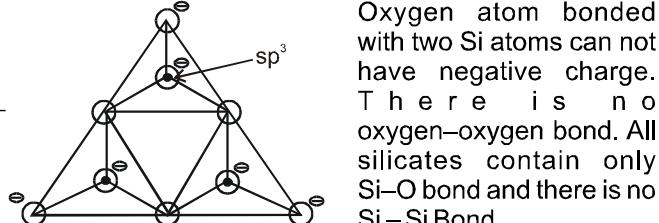




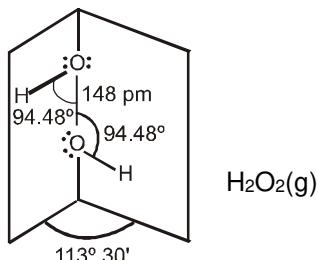
- Structures of silicate ion : $[\text{SiO}_4]^{4-}$



- Structures of cyclic silicates : $[\text{Si}_3\text{O}_9]^{6-}$



- H_2O_2

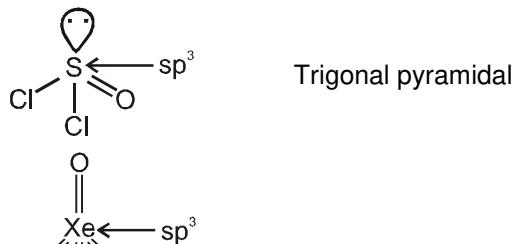


$\text{H}_2\text{O}_2(\text{g})$

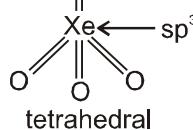
O – O bond length (148 pm) is larger than the expected due to the repulsions between the lone pairs on the two oxygen atoms.

It has book like structure (angle between the two pages of the book 113°30'). 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.

- SOCl_2 (Thionyl chloride)



- XeO_4



• sp^3d hybridisation :

Steric number = 5

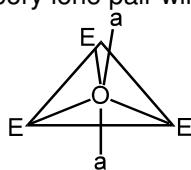
Geometry = trigonal bipyramidal

Table-6

Type	AB_5	AB_4L	AB_3L_2	AB_2L_3
Shape	Trigonal bipyramidal	See-saw	T-shape	Linear
Example	PCl_5 , PBr_5 , PF_5 etc.	SF_4 , XeO_2F_2	ClF_3 , $[\text{XeF}_3]^+$	XeF_2 , I_3^- , $[\text{ICl}_2]^-$

Important points regarding sp^3d :

- According to VSEPR theory lone pair will occupy equatorial (E) positions but not axial (a).



- More electronegative atoms will prefer to occupy axial positions.

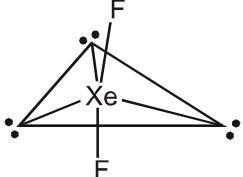
- Since, double bonds occupy more space. Therefore, they will also prefer equatorial positions.



AB₅	PCl ₅ (g)		It is covalent in the gas but in solid state exists as ionic solid consisting of [PCl ₄] ⁺ (tetrahedral) and [PCl ₆] ⁻ (octahedral). All P-Cl bonds are not of equal lengths. Here axial bonds are longer and weaker than equatorial bonds.
	PF ₅ (g)		PF ₅ (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. PF ₅ remains covalent and is trigonal bipyramidal in the solid state.
	PBr ₅ (g)		PBr ₅ exist as (PBr ₄) ⁺ Br ⁻ in solid state.
	PCl ₃ F ₂		PCl ₃ F ₂ is non polar molecule as all three Cl atoms are at equatorial position and both F atoms in axial position.
	PCl ₂ F ₃		PCl ₂ F ₃ is polar molecule as both Cl atoms and one F atom are at equatorial position and both F atoms in axial position.
AB₄L	SF ₄		SF ₄ molecule have T-shape geometry.
	XeO ₂ F ₂		Both F atoms will be at equatorial position.
AB₃L₂	ClF ₃		T-shape (It is planar molecule)
	I ₃ ⁻		I ₃ ⁻ has linear shape as both I atoms are at axial position.





	XeF ₂		XeF ₂ has linear shape as both F atoms are at axial position.
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sp³d² hybridization :

Steric number = 6

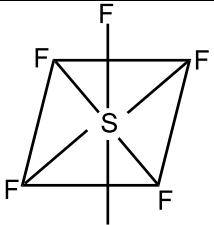
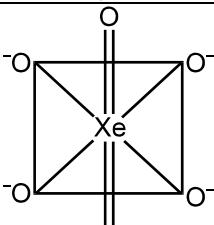
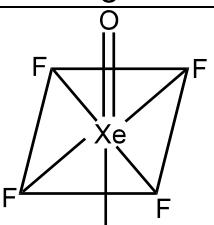
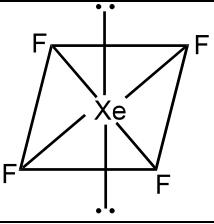
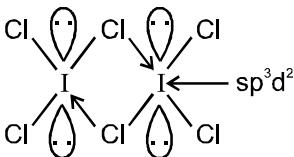
Geometry = octahedral

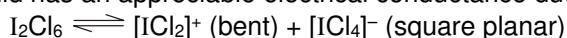
Table-7

Type	AB ₆	AB ₅ L	AB ₄ L ₂
Shape	Octahedral	Square Pyramidal	Square Planar
Example	SF ₆ , PF ₆ ⁻ , [SiF ₆] ²⁻ , [AlF ₆] ³⁻ , [XeO ₆] ⁴⁻	BrF ₅ , IF ₅ , XeOF ₄	ICl ₄ ⁻ , XeF ₄

Important : Since, octahedral is a symmetrical figure hence

- (a) positions of a lone pair can be anywhere
 (b) but if there are two lone pairs (max.) then these must be in the trans position.

AB ₆	SF ₆		Bond angle = 90° Due to over-crowding and maximum valency of S, SF ₆ is much less active (almost inert) than SF ₄ .
	[XeO ₆] ⁴⁻		[XeO ₆] ⁴⁻ is perxenate ion & H ₄ XeO ₆ is called perxenic acid. But H ₂ [XeO ₄] is called xenic acid.
AB ₅ L	XeOF ₄		Molecule has square pyramidal geometry.
AB ₄ L ₂	XeF ₄		Molecule has square planar geometry.
	I ₂ Cl ₆		ICl ₃ does not exist, but the dimer I ₂ Cl ₆ is 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 ₂ to I.

Note : The liquid has an appreciable electrical conductance due to self ionization.

sp^3d^3 Hybridization :

Steric number = 7

Geometry = Pentagonal bi-pyramidal

Table-8

Type	AB_7	AB_6L
Shape	Pentagonal bi-pyramidal	Distorted octahedral
Example	IF_7	XeF_6

AB_7	IF_7		Bond angle = 72° & 90°
AB_6L	$XeF_6(g)$		Distorted octahedron with a nonbonding electron pair either at the centre of a face or the midpoint of an edge.
	$XeF_6(s)$		$XeF_6(s)$ is found to be ionic solid consisting of $[XeF_5]^+$ and F^- ions. It is found that F^- is forming a bridge between two XeF_5^+ ions.
	$[XeF_5]^-$		Pentagonal planar ion with two nonbonding electron pairs above and below the plane of the pentagon.



Section (C) : Bond angle, bond length comparison

- (i) Size of atom (see along the group) \propto bond length
 $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$
 $\text{F}-\text{F} < \text{Cl}-\text{Cl} < \text{Br}-\text{Br} < \text{I}-\text{I}$
 $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$
- (ii) Multiplicity of bond (nearly same period element)
single bond > double bond > triple bond
 $\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C}$
 $\text{F}-\text{F} > \text{O}=\text{O} > \text{N}=\text{N}$
- (iii) Electronegativity difference (See along the period)
 $\text{H}-\text{C} > \text{H}-\text{N} > \text{H}-\text{O} > \text{H}-\text{F}$

HOW TO COMPARE BOND ANGLES

Bond angle depends on the following factor

- I. Hybridisation
- II. No. of lone pair
- III. Size or electronegativity of central atom
- IV. Size or electronegativity of terminal atom

1. **Hybridisation :**

$$\begin{array}{cccccc} \text{sp} & > & \text{sp}^2 & > & \text{sp}^3 & > \text{sp}^3\text{d}^2 \\ 180^\circ & & 120^\circ & & 109^\circ 28' & & 90^\circ \end{array}$$

2. **Number of lone pair :** If hybridisation of the central atom is same but number of lone pair is different then more is the number of lone pair less is the bond angle.

e.g.	CH_4	NH_3	H_2O
Hybridisation	sp^3	sp^3	sp^3
lone pair	$\ell.P. = 0$	$\ell.P. = 1$	$\ell.P. = 2$
B.A.	$109^\circ 28'$	107°	104°

3. **Size or electronegativity of central atom :** When hybridisation is same and no. of lone pair is same but central atom is different then see the electronegativity of central atom. More is the electronegativity more is the bond angle.

e.g.	NH_3	PH_3	AsH_3	SbH_3
Hybridisation	sp^3	no	no	no
lone pair	$\ell.P. = 1$	$\ell.P. = 1$	$\ell.P. = 1$	$\ell.P. = 1$
B.A.	107°	93°	92°	91°

4. **Size or electronegativity of terminal atom :**

Hybridisation same, lone pair same, central atom same but terminal atom is different then greater is the size of the terminal atom greater will be the bond angle. Only in case of fluorine the electronegativity factor is considered, due to greater electronegativity of the fluorine atom the bond angle for it comes out to be smallest (due to smaller bond pair repulsions)

e.g.	PF_3	PCl_3	PBr_3	PI_3
Hybridisation	sp^3	sp^3	sp^3	sp^3
lone pair	$\ell.P. = 1$	$\ell.P. = 1$	$\ell.P. = 1$	$\ell.P. = 1$
B.A.	98°	100°	101°	102°

Reason : As the E.N. of $x \uparrow$, b.p.-b.p. repulsion will less but l.p. compression will work as usual

Drago rule : Element of 3rd and higher period (4, 5) (p-Block) does not allow hybridisation in molecule when they form bond if they have lone pair on them with less electronegative elements such as hydrogen.

eg : PH_3 , $(\text{CH}_3)_2\text{S}$, AsH_3 , H_2S not have hybridisation.

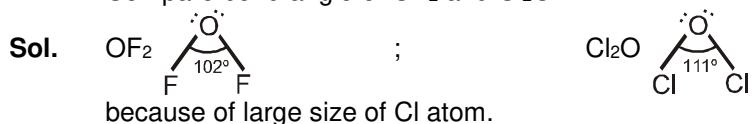
Bent rule : According to Bent's rule, more electronegative atoms prefer hybrid orbitals having less S character and more electropositive atoms prefer hybrid orbitals having more S character.

eg : In CH_2F_2 , $\text{F}-\text{C}-\text{F}$ bond angle less than 109.5° indicating less than 25% S character.
 $\text{H}-\text{C}-\text{H}$ bond angle more than 109.5° indicating more than 25% S character.

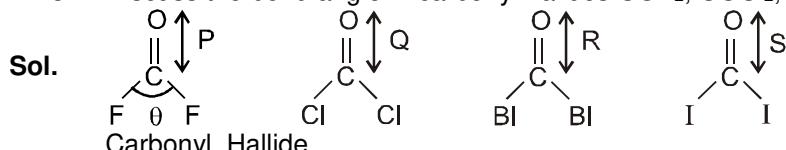


Solved Examples

Ex-2. Compare bond angle of OF_2 and Cl_2O .



Ex-3. Discuss the bond angle in carbonyl halides COF_2 , COCl_2 , COBr_2 , COI_2 .



Carbonyl Halide

B.A. $\theta \Rightarrow \text{COF}_2 < \text{COCl}_2 < \text{COBr}_2 < \text{COI}_2$

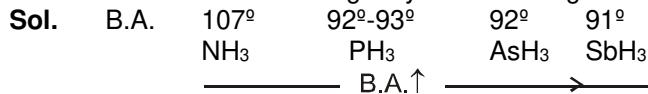
Explanation \Rightarrow

(A) double bonds require more room than single bonds. Hence C=O group compresses the molecule and bond angle \downarrow max. in COF_2 . Later on halogen atom becomes bigger and less (-ve) also so

\therefore Inter atomic repulsion between the halogens causes \uparrow in B.L.

As X(halogen) becomes less and less (-ve) b.p.-b.p. repulsion also becomes imp and therefore $\theta \uparrow$

Ex-4. Discuss the bond angle hydride of nitrogen family.



Section (D) : Multicentered species

O	P_4O_6		P-O bond length shows that the bridging bonds on the edges are 1.65 \AA and are normal single bonds. There is no P-P bonds.
O	P_4O_{10}		The P-O bond lengths shows that the bridging bonds on the edges are 1.60 \AA but the P=O bonds on the corners are 1.43 \AA and this P=O is formed by pp-dp back bonding. A full p-orbital on the oxygen atom overlaps sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P-P bonds. Total L.P. = 20. Total no. of p-d bonds = 4



Exercise-1

 **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : VSEPR theory

- A-1.** Why NO_2^+ and I_3^- are linear species ?

A-2. PCl_5 has the shape of a trigonal bipyramidal whereas IF_5 has the shape of square pyramidal. Explain.

A-3. Write the geometry of XeF_4 and OSF_4 using VSEPR theory and clearly indicate the position of lone pair of electrons.

A-4. Explain the structure of ClF_3 on the basis of VSEPR theory.

Section (B) : Hybridisation

- B-1.** Explain hybridisation of central atom in :

(1) XeF ₂	(2) XeF ₄	(3) PCl ₃	(4) PCl ₅ (g)
(5) SF ₆	(6) IF ₃	(7) IF ₅	(8) IF ₇
(9) CH ₄	(10) CCl ₄	(11) SiCl ₄	(12) SiH ₄
(13) H ₂ O	(14) NH ₃	(15) PO ₄ ³⁻	(16) BrF ₅
(17) NO ₃ ⁻	(18) CO ₃ ²⁻	(19) NH ₄ ⁺	(20) ClO ₃ ⁻

- B-2.** The order of size of the hybrid orbitals is as follows $sp < sp^2 < sp^3$. Explain.

B-3. 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_4 (b) $XeOF_4$

Section (C) : Bond angle, bond length comparison

- C-1.** Draw an electron dot structure for Br_3^- . Deduce an approximate value of the bond angle.

C-2. Which compound has the smallest bond angle in each series ?

(a) SbCl_3	SbBr_3	SbI_3
(b) PI_3	AsI_3	SbI_3

C-3. Compare the C–H bond strength in C_2H_6 , C_2H_4 and C_2H_2 .

C-4. The POCl_3 molecule has the shape of an irregular tetrahedron with the P atom located centrally. The Cl–P–Cl angle is found to be 103.5° . Give a qualitative explanation for the deviation of this structure from a regular tetrahedron.

C-5. Which one has highest and least bond angle in the following ?

(1) CH_4 PH_3 AsH_3 SbH_3	(2) H_2O H_2S H_2Te CO_2
(3) PH_3 H_2O	(4) Cl_2O ClO_2
(5) PF_3 PH_3	(6) BF_3 NF_3
(7) NH_3 NF_3	(8) PF_3 PCl_3

C-6. Write the Increasing order of Bond length of each :

(1) $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$	(2) $\text{C}=\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{F}$	(3) $\text{H}-\text{Cl}$, $\text{H}-\text{Br}$, $\text{H}-\text{I}$, HF
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Section (D) : Multicentered species



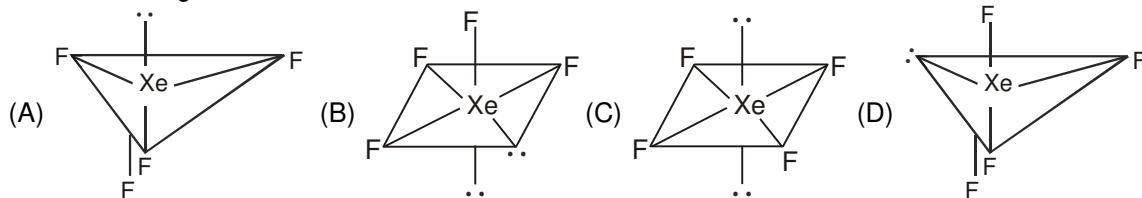
D-3. Calculate individual and average oxidation number (if required) of the marked element and also draw the structure of the following compounds or molecules.

- (1) $\text{Na}_2\text{S}_2\text{O}_3$ (2) $\text{Na}_2\text{S}_4\text{O}_6$ (3) $\text{H}_2\text{S}\text{O}_5$ (4) $\text{H}_2\text{S}_2\text{O}_8$ (5) $\text{H}_2\text{S}_2\text{O}_7$ (6) S_8
 (7) HNO_4 (8) C_3O_2 (9) OsO_4 (10) PH_3 (11) CrO_4^{2-} (12) $\text{Cr}_2\text{O}_7^{2-}$
 (13) $\text{Cr O}_2\text{Cl}_2$ (14) CrO_5 (15) $\text{Na}_2\text{H PO}_4$ (16) FeS_2 (17) $\text{C}_6\text{H}_{12}\text{O}_6$ (18) $\text{NH}_4 \text{NO}_3$

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : VSEPR theory

A-1. Which is the right structure of XeF_4 ?



A-2. Identify the correct match.

(i)	XeF_2	(a)	Central atom has sp^3 hybridisation and bent geometry.
(ii)	N_3^-	(b)	Central atom has sp^3d^2 hybridisation and octahedral.
(iii)	PCl_6^- (PCl_5 (s) anion)	(c)	Central atom has sp hybridisation and linear geometry.
(iv)	ICl_2^+ (I_2Cl_6 (ℓ) cation)	(d)	Central atom has sp^3d hybridisation and linear geometry.
(A) (i – a), (ii – b), (iii – c), (iv – d)		(B) (i – d), (ii – b), (iii – d), (iv – c)	
(C) (i – b), (ii – c), (iii – a), (iv – d)		(D) (i – d), (ii – c), (iii – b), (iv – a)	

A-3. Which of the following statement is true for IO_2F_2^- ?

- (A) The electrons are located at the corners of a trigonal bipyramidal but one of the equatorial pairs is unshared.
 (B) It has sp^3d hybridisation and is T-shaped.
 (C) Its structure is analogous to SF_4 .
 (D) (A) and (C) both

A-4. Which reaction involves a change in the electron-pair geometry for the underlined element ?

- (A) $\underline{\text{BF}}_3 + \text{F}^- \longrightarrow \underline{\text{BF}}_4^-$ (B) $\underline{\text{NH}}_3 + \text{H}^+ \longrightarrow \underline{\text{NH}}_4^+$
 (C) $2\underline{\text{SO}}_2 + \text{O}_2 \longrightarrow 2\underline{\text{SO}}_3$ (D) $\text{H}_2\underline{\text{O}} + \text{H}^+ \longrightarrow \text{H}_3\underline{\text{O}}^+$

A-5. In which of the following molecules number of lone pairs and bond pairs on central atom are not equal ?

- (A) H_2O (B) I_3^- (C) O_2F_2 (D) SCl_2

A-6. Which of the following species given below have shape similar to XeOF_4 ?

- (A) XeO_3 (B) IOF_4^+ (C) PCl_5 (D) XeF_5^\oplus

Section (B) : Hybridisation

B-1. The hybridization of carbon atoms in C_2-C_3 single bond of $\text{HC} \equiv \text{C}-\text{CH}=\text{CH}_2$ is :

- (A) sp^3-sp^3 (B) sp^2-sp (C) $\text{sp}-\text{sp}^2$ (D) sp^3-sp

B-2. Specify the hybridisations of central atom in the following species respectively $\{\text{N}_3^-, \text{NOCl}, \text{N}_2\text{O}\}$

- (A) sp, sp^2 , sp (B) sp, sp, sp^3 (C) sp^2 , sp, sp (D) sp^2 , sp^2 , sp.

B-3. In pent-3-en-1-yne the terminal carbon-atoms have following hybridisation

- (A) sp & sp^2 (B) sp^2 & sp^3 (C) sp^2 & sp (D) sp & sp^3

B-4. S_1 : $[\text{XeF}_7]^+$ has sp^3d^3 hybridisation

S_2 : $[\text{PCl}_4]^+$ has sp^3d^2 hybridisation

S_3 : $[\text{SF}_6]$ has sp^3d^2 hybridisation

S_4 : $[\text{PF}_4]^+$ has sp^3 hybridisation

- (A) T F F T (B) T T F T (C) T F T T (D) F F F T



B-5. $\text{BF}_3 + \text{F}^- \rightarrow \text{BF}_4^-$

What is the hybridization state of B in BF_3 and BF_4^- :

- (A) sp^2, sp^3 (B) sp^3, sp^3 (C) sp^2, sp^2 (D) $\text{sp}^3, \text{sp}^3\text{d}$

Section (C) : Bond angle, bond length comparison

C-1. The ONO angle is maximum in :

- (A) HNO_3 (B) NO_2^+ (C) HNO_2 (D) NO_2

C-2. Which statement is correct for N_3^- ion.

- (A) It is bent molecule (B) Bond angle is $< 120^\circ$
 (C) Central atom is sp^2 hybridized (D) None of these

C-3. Consider the following molecules ; $\begin{array}{cccc} \text{H}_2\text{O} & \text{H}_2\text{S} & \text{H}_2\text{Se} & \text{H}_2\text{Te} \\ \text{I} & \text{II} & \text{III} & \text{IV} \end{array}$

Arrange these molecules in increasing order of bond angles.

- (A) I < II < III < IV (B) IV < III < II < I (C) I < II < IV < III (D) II < IV < III < I

C-4. In which of the following bond angle is maximum

- (A) NH_3 (B) NH_4^+ (C) PCl_3 (D) SCl_2

C-5. In which of the following central atom is unhybridised?

- (A) $\text{S}(\text{CH}_3)_2$ (B) SO_2 (C) SiH_4 (D) PCl_3

Section (D) : Multicentered species

D-1. The no. of S-O-S bonds in the trimer of SO_3 is

- (A) 1 (B) 2 (C) 3 (D) None

D-2. Which of the following species do not contain S-S linkage?

- (A) $\text{H}_2\text{S}_2\text{O}_5$ (B) $\text{H}_2\text{S}_2\text{O}_7$ (C) $\text{H}_2\text{S}_2\text{O}_3$ (D) $\text{H}_2\text{S}_4\text{O}_6$

D-3. Which statement is **incorrect** about pyrosilicate ion.

- (A) sp^3 hybridisation
 (B) One oxygen atom is shared between two tetrahedron
 (C) there are eight Si-O bond
 (D) There is one Si-Si bond

D-4. Which is correct about the cyclic silicate $[\text{Si}_6\text{O}_{18}]^{n-}$:

- (A) The value of n is 12
 (B) each Si atom is bonded with three oxygen atoms
 (C) each oxygen atom is bonded with two Si atoms
 (D) all the above are correct.

PART - III : MATCH THE COLUMN

1. Match the following :

	Column-I		Column-II
(A)	SF_2	(p)	sp^3 and bent
(B)	KrF_4	(q)	two lone pairs on central atom
(C)	NOCl	(r)	bond angle $< 109^\circ 28'$
(D)	NF_3	(s)	sp^2 and bent
		(t)	sp^3d^2 and square planar

2. Match the compounds listed in column-I with characteristic(s) listed in column-II.

	Column - I		Column - II
(A)	$\text{ClF}_2^-, \text{ClF}_2^+$	(p)	Square pyramidal.
(B)	$\text{IO}_2\text{F}_2^-, \text{F}_2\text{SeO}$	(q)	See-saw and pyramidal shaped respectively.
(C)	$\text{IOF}_4^-, \text{XeOF}_2$	(r)	Linear and bent shaped respectively.
(D)	$\text{BrF}_5, \text{XeOF}_4$	(s)	Square pyramidal and T-shaped respectively.
		(t)	Both sp^3d^2 .



3. Match the following :

	Column-I	Column-II
(A)	$\text{H}_3\text{P}_3\text{O}_9$	(p) S–O–S bond is present
(B)	$\text{H}_2\text{S}_2\text{O}_7$	(q) Di-basic acid
(C)	$\text{H}_2\text{S}_4\text{O}_6$	(r) P–O–P bond is present
(D)	$\text{H}_4\text{P}_2\text{O}_5$	(s) Central atom (S or P) in maximum oxidation state.

Exercise-2

☞ Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

- The hybridisation of P in phosphate ion (PO_4^{3-}) is the same as :
(A) I in ICl_4^- (B) S in SO_3 (C) N in NO_3^- (D) S in SO_3^{2-}
- Choose the molecules in which hybridisation occurs in the ground state ?
(a) BCl_3 (b) NH_3 (c) PCl_3 (d) BeF_2
The correct answer is -
(A) a, b, d (B) a, b, c (C) b, c (D) c, d
- The bent or V-shape of the molecule can be resulted from which of the following hybridization.
(A) sp^3 (B) sp^2 (C) Both (A) and (B) (D) None of these
- sp^3d hybridization is considered to be a combination of two hybridization. They are
(A) $\text{p}^3 + \text{sd}$ (B) $\text{sp}^2 + \text{pd}$ (C) $\text{spd} + \text{p}^2$ (D) none of these
- If the equatorial plane is x–y plane in sp^3d hybridisation then the orbital used in pd hybridisation are -
(A) p_z and d_{z_2} (B) p_x and d_{xy} (C) p_y and d_{yz} (D) none of these
- A σ -bonded molecule MX_3 is T-shaped. The number of lone pairs of electrons can be
(A) 0 (B) 2 (C) 1 (D) none of these
- Which of the following should have pyramidal shape :
(A) $[\text{ClOF}_2]^+$ (B) ICl_3 (C) $[\text{BrICl}]^-$ (D) All of these
- Which of the following molecules has two lone pairs and bond angle (need not be all bond angles) < 109.5°?
(A) SF_2 (B) KrF_4 (C) ICl_4^- (D) All of these
- The correct order of bond angle is :
(A) $\text{H}_2\text{S} < \text{NH}_3 < \text{BF}_3 < \text{CH}_4$ (B) $\text{NH}_3 < \text{H}_2\text{S} < \text{CH}_4 < \text{BF}_3$
(C) $\text{H}_2\text{S} < \text{NH}_3 < \text{CH}_4 < \text{BF}_3$ (D) $\text{H}_2\text{S} < \text{CH}_4 < \text{NH}_3 < \text{BF}_3$
- In which of the following molecules are all the bonds not equal?
(A) NF_3 (B) ClF_3 (C) BF_3 (D) AlF_3
- Which of the following is correct order of bond length ?
(A) $\text{BF}_4^- < \text{BF}_3$ (B) $\text{NO}_2^+ < \text{NO}_2^-$ (C) $\text{CCl}_4 < \text{CF}_4$ (D) ${}^+\text{CH}_3 > \text{CH}_4$
- Identify the correct statement :
(A) single N–N bond is stronger than single P–P bond
(B) single N–N bond is weaker than single P–P bond
(C) $\text{N} \equiv \text{N}$ is weaker than $\text{P} \equiv \text{P}$
(D) None of these
- In which of the following species peroxide group is not present :
(A) $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ (B) $[\text{S}_2\text{O}_8]^{2-}$ (C) CrO_5 (D) HNO_4



PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. Find the number of planar molecule.

(a) BF_3 (b) BCl_3 (c) CO_3^{2-} (d) SO_3
(e) NH_3 (f) NCl_3 (g) PCl_3 (h) XeF_4

2. Find the number of species having bond angle less than $109^\circ 28'$.

(a) H_2S (b) SO_4^{2-} (c) CCl_4 (d) NH_3
(e) PH_3 (f) SiH_4 (g) NH_4^+ (h) PF_3
(i) NH_2^- (j) SO_3 (k) H_2O

3. Find out total number of π bond in following xenon oxyfluorides.
 XeOF_2 , XeO_2F_4 , XeO_3 , XeO_4 , XeO_3F_2 , XeOF_4 , XeO_2F_2

4. P_4O_{10} has two different types of P–O bonds. Find the no. of P–O bonds with shorter bond length.

5. Difference in the oxidation number of sulphur atom is in $\text{Na}_2\text{S}_4\text{O}_6$ is x, that of $\text{H}_2\text{S}_2\text{O}_5$ is y. Find value of $x \times y$ is :

6. In a P_4O_6 molecule, the total number of P–O–P bonds is :

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE



4. Which is true about NH_2^- , NH_3 , NH_4^+ ?
 (A) Hybridization of N is same. (B) No. of lone pair of electron on N are same.
 (C) Molecular geometry (i.e. shape) is different. (D) Bond angle is same.
5. Which of the following molecule (s) has/have bond angle close to 90° ?
 (A) NH_3 (B) H_2S (C) PH_3 (D) ICl_3
6. Which of the following statements are true about borax :
 (A) Boron atoms are present in 2 different oxidation state and it different by 1
 (B) the average oxidation state of boron is same that in B_2H_6 .
 (C) Boron atoms are present in different hybridization
 (D) 2 boron atoms are connected with 4 oxygen each and 2 boron atoms are connected with 3 oxygen atom each.
7. Identify the correct statement
 (A) $\text{H}_2\text{S}_2\text{O}_7$ has peroxy linkage
 (B) $\text{H}_2\text{S}_2\text{O}_6$ has S-S linkage
 (C) $\text{H}_2\text{S}_2\text{O}_8$ has peroxy linkage
 (D) H_2SO_3 (Sulphurous acid) has S in +4 oxidation state
8. In which of the following compound(s) oxidation number of one central atom is/are ≥ 6 ?
 (A) N_2O_6 (B) CrO_5 (C) H_3PO_5 (D) $\text{H}_2\text{S}_2\text{O}_8$

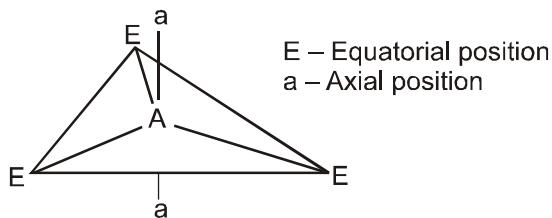
PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

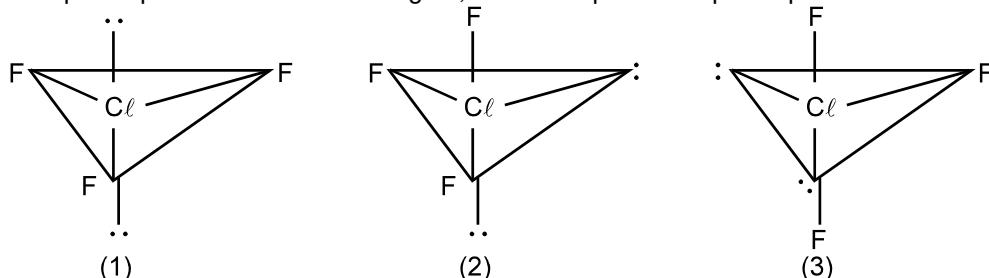
Comprehension # 1

VSEPR THEORY

The trigonal bipyramidal is not a regular shape since the bond angles are not all the same. It therefore follows that the corners are not equivalent in ClF_3 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 are the weakest.



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.





Comprehension # 2

Answer Q.5, Q.6 and Q.7 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 : compound, column-2 : shape while in column-3 : Hybridisation are given.

Observe the three columns in which column-1 : compound, column-2 : shape while in column-3 : Hybridisation are given.					
Column-1 (Compound)		Column-2 (Shape)		Column-3 (Hybridisation)	
(I)	XeF ₄	(i)	Tetrahedral	(P)	sp ³
(II)	ClF ₃	(ii)	Square planar	(Q)	sp ²
(III)	SiF ₄	(iii)	Bent	(R)	sp ³ d
(IV)	CH ₃ OCH ₃	(iv)	T-shape	(S)	sp ³ d ²

5. Which of the following combination is true for compound which have 2 lone pair of electrons on central atom?
(A) (I), (ii), (S) (B) (I), (ii), (R) (C) (I), (i), (P) (D) (II), (iv), (Q)

6. Which combination is correct for the compound having bond angle $> 109^{\circ}28'$?
(A) (III), (i), (P) (B) (IV), (iii), (P) (C) (IV), (ii), (P) (D) (I), (ii), (S)

7. Which of the following is true for a planar compound?
(A) (III), (i), (P) (B) (I), (iv), (P) (C) (II), (iv), (R) (D) (II), (i), (P)

Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Marked Questions may have more than one correct options.



4. The correct order of hybridisation of the central atom in the following species; NH₃, PCl₅ and BCl₃ is : [JEE-2001(S), 1/135]
 (A) dsp², sp², sp³ (B) sp³, dsp³, sp² (C) dsp², sp³, dsp³ (D) dsp², sp², dsp³
5. The number of S–S bonds, in sulphur trioxide trimer (S₃O₉) is : [JEE-2001(S), 1/135]
 (A) three (B) two (C) one (D) Zero
6. Which of the following are isoelectronic and isostructural ? [JEE-2003(S), 3/144]
 NO₃⁻, CO₃²⁻, ClO₃⁻, SO₃
 (A) NO₃⁻, CO₃²⁻ (B) SO₃, NO₃⁻ (C) ClO₃⁻, CO₃²⁻ (D) CO₃²⁻, SO₃.
7. Which of the following represent the given mode of hybridisation sp²–sp²–sp–sp from left to right. [JEE-2003(S), 3/144]
 (A) H₂C=CH–C≡N (B) HC≡C–C≡CH (C) H₂C=C=C=CH₂ (D)
8. Using VSEPR theory, draw the shape of PCl₅ and BrF₅. [JEE-2003(M), 2/144]
9. Amongst the following the acid having –O–O– bond is : [JEE-2004(S), 3/144]
 (A) H₂S₂O₃ (B) H₂S₂O₅ (C) H₂S₂O₆ (D) H₂S₂O₈
10. Use VSEPR model to draw the structures of OSF₄ and XeF₄ (indicate the lone pair(s) on central atom) and specify their geometry. [JEE-2004(M), 2/144]
11. Write the structure of P₄O₁₀. [JEE-2005(M), 1/144]
12. The percentage of p-character in the orbitals forming P–P bonds in P₄ is : [JEE-2007, 3/162]
 (A) 25 (B) 33 (C) 50 (D) 75
- 13.* The nitrogen oxide(s) that contain(s) N—N bond(s) is(are) : [JEE-2009, 4/160]
 (A) N₂O (B) N₂O₃ (C) N₂O₄ (D) N₂O₅
14. Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF₅ is : [JEE-2010, 3/163]
15. The shape of XeO₂F₂ molecule is [JEE-2012, 3/136]
 (A) trigonal bipyramidal (B) square planar
 (C) tetrahedral (D) see-saw
16. The total number of lone pairs of electrons in N₂O₃ is : [JEE(Advanced) 2015, 4/168]
17. Among the triatomic molecules/ions, BeCl₂, N₃⁻, N₂O, NO₂⁺, O₃, SCl₂, ICl₂⁻, I₃⁻ and XeF₂, the total number of linear molecules(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is [JEE(Advanced) 2015, 4/168]
 [Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54]
- 18.* The crystalline form of borax has [JEE Advanced 2016, 4/124]
 (A) tetrานuclear [B₄O₅(OH)₄]²⁻ unit
 (B) all boron atoms in the same plane
 (C) equal number of sp² and sp³ hybridized boron atoms
 (D) one terminal hydroxide per boron atom
19. The total number of compounds having at least one bridging oxo group among the molecules given below is _____. [JEE Advanced 2018, 3/120]
 N₂O₃, N₂O₅, P₄O₆, P₄O₇, H₄P₂O₅, H₅P₃O₁₀, H₂S₂O₃, H₂S₂O₅

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. The hybridisation of the underline atom changes in : [AIEEE-2002, 3/225]
 (1) AlH₃ changes to AlH₄⁻ (2) H₂O changes to H₃O⁺
 (3) NH₃ changes to NH₄⁺ (4) in all cases



2. Bond angle of $109^\circ 28'$ is found in : [AIEEE-2002, 3/225]
 (1) NH_3 (2) H_2O (3) CH_3^+ (4) NH_4^+
3. Which of the following compounds has the smallest bond angle in its molecule ? [AIEEE-2003, 3/225]
 (1) SO_2 (2) H_2O (3) H_2S (4) NH_3
4. The pair of species having identical shapes for molecules of both species is : [AIEEE-2003, 3/225]
 (1) CF_4 , SF_4 (2) XeF_2 , CO_2 (3) BF_3 , PCl_3 (4) PF_5 , IF_5 .
5. The maximum number of 90° angles between bond pair–bond pair of electrons is observed in : [AIEEE-2004, 3/225]
 (1) dsp^3 (2) sp^3d (3) dsp^2 (4) sp^3d^2
6. The correct order of bond angles (smallest first) in H_2S , NH_3 , BF_3 and SiH_4 is : [AIEEE-2004, 3/225]
 (1) $\text{H}_2\text{S} < \text{SiH}_4 < \text{NH}_3 < \text{BF}_3$ (2) $\text{NH}_3 < \text{H}_2\text{S} < \text{SiH}_4 < \text{BF}_3$
 (3) $\text{H}_2\text{S} < \text{NH}_3 < \text{SiH}_4 < \text{BF}_3$ (4) $\text{H}_2\text{S} < \text{NH}_3 < \text{BF}_3 < \text{SiH}_4$
7. Which one of the following does not have sp^2 hybridized carbon? [AIEEE-2004, 3/225]
 (1) Acetone (2) Acetic acid (3) Acetonitrile (4) Acetamide
8. The molecular shapes of SF_4 , CF_4 and XeF_4 are : [AIEEE-2005, 3/225]
 (1) the same with 2, 0 and 1 lone pairs of electrons on the central atom, respectively.
 (2) the same with 1, 1 and 1 lone pair of electrons on the central atom, respectively.
 (3) different with 0, 1 and 2 lone pairs of electrons on the central atom, respectively.
 (4) different with 1, 0 and 2 lone pairs of electrons on the central atom, respectively.
9. The number and type of bonds between two carbon atoms in calcium carbide are : [AIEEE-2005 (3/225), 2011 (4/120)]
 (1) one sigma, one pi (2) one sigma, two pi (3) two sigma, one pi (4) two sigma, two pi
10. The hybridisation of orbitals of N atom in NO_3^- , NO_2^+ and NH_4^+ are respectively : [AIEEE-2011, 4/120]
 (1) sp, sp^2 , sp^3 (2) sp^2 , sp, sp^3 (3) sp, sp^3 , sp^2 (4) sp^2 , sp^3 , sp
11. The structure of IF_7 is : [AIEEE-2011, 4/120]
 (1) square pyramid (2) trigonal bipyramidal (3) octahedral (4) pentagonal bipyramidal
12. The molecule having smallest bond angle is : [AIEEE-2012, 4/120]
 (1) NCl_3 (2) AsCl_3 (3) SbCl_3 (4) PCl_3
13. In which of the following pairs the two species are not isostructural ? [AIEEE-2012, 4/120]
 (1) CO_3^{2-} and NO_3^- (2) PCl_4^+ and SiCl_4 (3) PF_5 and BrF_5
 (4) AlF_6^{3-} and SF_6
14. The species in which the N atom is in a state of sp hybridization is : [JEE(Main)-2016, 4/120]
 (1) NO_2^- (2) NO_3^- (3) NO_2 (4) NO_2^+

JEE(MAIN) ONLINE PROBLEMS

1. The number and type of bonds in C_2^{2-} ion in CaC_2 are : [JEE(Main) 2014 Online (09-04-14), 4/120]
 (1) One σ -bond and one π -bond (2) One σ -bond and two π -bonds
 (3) Two σ -bonds and two π -bonds (4) Two σ -bonds and one π -bonds
2. Which one of the following does not have a pyramidal shape? [JEE(Main) 2014 Online (11-04-14), 4/120]
 (1) $(\text{CH}_3)_3\text{N}$ (2) $(\text{SiH}_3)_3\text{N}$ (3) $\text{P}(\text{CH}_3)_3$ (4) $\text{P}(\text{SiH}_3)_3$
3. The geometry of XeOF_4 by VSEPR theory is : [JEE(Main) 2015 Online (10-04-15), 4/120]
 (1) pentagonal planar (2) octahedral (3) square pyramidal (4) trigonal bipyramidal
4. Which of the following compound has a P–P bond ? [JEE(Main) 2015 Online (11-04-15), 4/120]
 (1) $\text{H}_4\text{P}_2\text{O}_5$ (2) $(\text{HPO}_3)_3$ (3) $\text{H}_4\text{P}_2\text{O}_6$ (4) $\text{H}_4\text{P}_2\text{O}_7$
5. Choose the incorrect formula out of the four compounds for an element X below :
 (1) X_2O_3 (2) X_2Cl_3 (3) $\text{X}_2(\text{SO}_4)_3$ (4) XPO_4



6. The group of molecules having identical shape is : [JEE(Main) 2016 Online (09-04-16), 4/120]
 (1) PCl_5 , IF_5 , XeO_2F_2 (2) BF_3 , PCl_3 , XeO_3 (3) ClF_3 , XeOF_2 , XeF_3^+ (4) SF_4 , XeF_4 , CCl_4
7. **Assertion:** Among the carbon allotropes, diamond is an insulator, Whereas, graphite is a good conductor of electricity.
Reason: Hybridization of carbon in diamond and graphite are sp^3 and sp^2 , respectively.
 [JEE(Main) 2016 Online (10-04-16), 4/120]
 (1) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
 (2) Assertion is incorrect statement, but the reason is correct.
 (3) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
 (4) Both assertion and reason are incorrect.
8. The bond angle H–X–H is the greatest in the compound : [JEE(Main) 2016 Online (10-04-16), 4/120]
 (1) NH_3 (2) PH_3 (3) CH_4 (4) H_2O
9. Identify the pair in which the geometry of the species is T-shape and square-pyramidal, respectively :
 [JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) ICl_2^- and ICl_5 (2) IO_3^- and IO_2F_2^- (3) ClF_3 and IO_4^- (4) XeOF_2 and XeOF_4
10. $\begin{array}{c} \text{H} & \text{N}^{(\text{I})} & \text{N}^{(\text{II})} \\ | & & | \\ \text{H} & \cdots & \cdots \end{array}$
 In hydrogen azide (above) the bond orders of bonds (I) and (II) are :
 [JEE(Main) 2018 Online (15-04-18), 4/120]

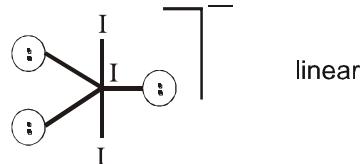
(I)	(II)	(I)	(II)
(1) < 2	> 2	(2) > 2	> 2
(3) > 2	< 2	(4) < 2	< 2
11. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridization are respectively : [JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) 33 and 25 (2) 67 and 75 (3) 50 and 75 (4) 33 and 75
12. The decreasing order of bond angles in BF_3 , NH_3 , PF_3 and I_3^- is :
 (1) $\text{I}_3^- > \text{BF}_3 > \text{NH}_3 > \text{PF}_3$ (2) $\text{BF}_3 > \text{I}_3^- > \text{PF}_3 > \text{NH}_3$
 (3) $\text{BF}_3 > \text{NH}_3 > \text{PF}_3 > \text{I}_3^-$ (4) $\text{I}_3^- > \text{NH}_3 > \text{PF}_3 > \text{BF}_3$
13. The number of P–O bonds in P_4O_6 is : [JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) 6 (2) 9 (3) 12 (4) 18
14. In XeO_3F_2 , the number of bond pair(s), π -bond(s) and lone pair(s) on Xe atom respectively are :
 [JEE(Main) 2018 Online (15-04-18), 4/120]
 (1) 5, 2, 0 (2) 4, 2, 2 (3) 5, 3, 0 (4) 4, 4, 0
15. Among the oxides of nitrogen : [JEE(Main) 2018 Online (16-04-18), 4/120]
 N_2O_3 , N_2O_4 and N_2O_5 ; the molecule(s) having nitrogen-nitrogen bond is/are :
 (1) N_2O_3 and N_2O_4 (2) N_2O_4 and N_2O_5 (3) N_2O_3 and N_2O_5 (4) Only N_2O_5
16. Which of the following conversions involves change in both shape and hybridisation ?
 [JEE(Main) 2018 Online (16-04-18), 4/120]
 (1) $\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$ (2) $\text{BF}_3 \rightarrow \text{BF}_4^-$ (3) $\text{CH}_4 \rightarrow \text{C}_2\text{H}_6$ (4) $\text{NH}_3 \rightarrow \text{NH}_4^+$
17. The **incorrect** geometry is represented by : [JEE(Main) 2018 Online (16-04-18), 4/120]
 (1) NF_3 – trigonal planar (2) BF_3 – trigonal planar
 (3) AsF_5 – trigonal bipyramidal (4) H_2O – bent
18. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF_4 , respectively, are :
 [JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) sp^3d^2 and 1 (2) sp^3d^2 and 2 (3) sp^3d and 1 (4) sp^3d and 2



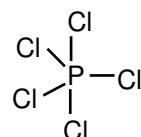
19. Two pi and half sigma bonds are present in : [JEE(Main) 2019 Online (10-01-19), 4/120]
(1) N_2^+ (2) O_2 (3) O_2^+ (4) N_2
20. The pair that contains two P–H bonds in each of the oxoacid is: [JEE(Main) 2019 Online (10-01-19), 4/120]
(1) $\text{H}_4\text{P}_2\text{O}_5$ and H_3PO_3 (2) $\text{H}_4\text{P}_2\text{O}_5$ and $\text{H}_4\text{P}_2\text{O}_6$ (3) H_3PO_2 and $\text{H}_4\text{P}_2\text{O}_5$ (4) H_3PO_3 and H_3PO_2
21. The element that shows greater ability to form $\text{p}\pi\text{-p}\pi$ multiple bonds, is: [JEE(Main) 2019 Online (12-01-19), 4/120]
(1) Ge (2) Sn (3) C (4) Si

**Answers****EXERCISE - 1****PART - I****A-1.**

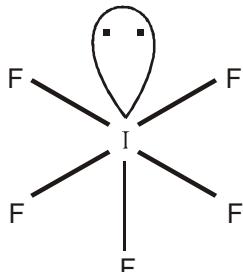
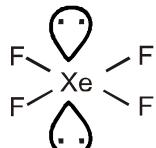
In NO_2^+ the N has sp hybridisation; so it is linear $\text{O}=\overset{+}{\text{N}}=\text{O}$
 In I_3^- there are 5 electron pairs around central iodine atom (3 lone pairs and 2 bond pairs). The hybridisation of iodine is thus sp^3d . To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.

**A-2.**

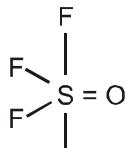
In PCl_5 there are 5 electron pairs around central phosphorus atom and all are bond pairs. The hybridisation of phosphorus is thus sp^3d . To have minimum repulsions between bp-bp it acquires trigonal bipyramidal shape as shown below.



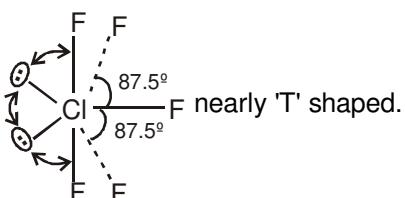
In IF_5 there are 6 electron pairs around central iodine atom. The hybridisation of iodine is thus sp^3d^2 . 6 electron pairs contain 5 bond pairs and one lone pair so it will be square pyramidal to have minimum repulsions between lp-bp and bp-bp.

**A-3.**

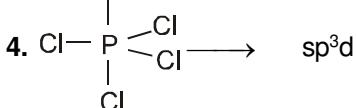
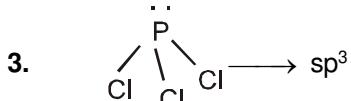
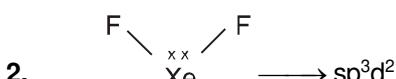
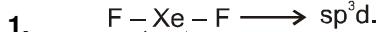
Square planar

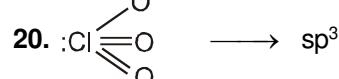
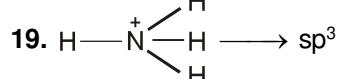
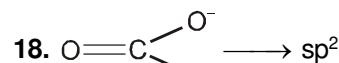
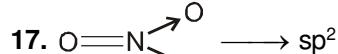
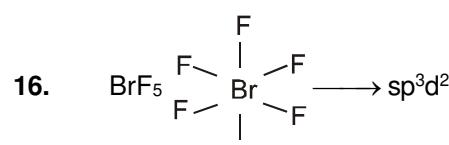
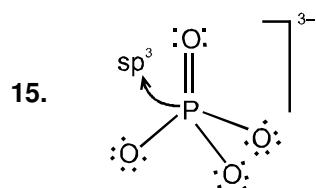
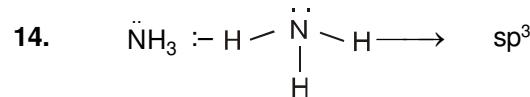
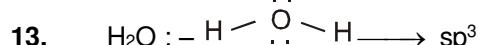
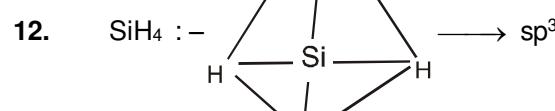
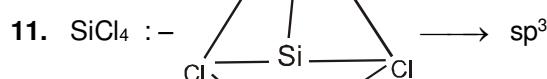
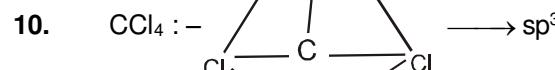
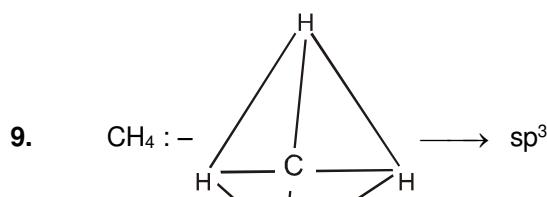
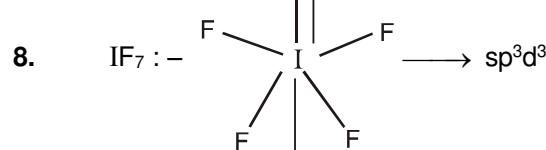
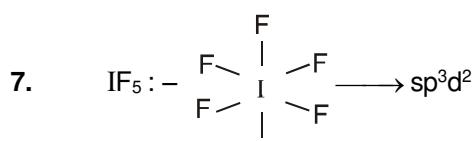
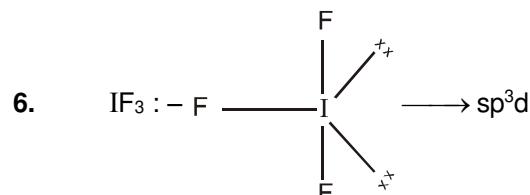
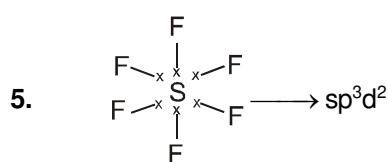


Trigonal bipyramidal

A-4.

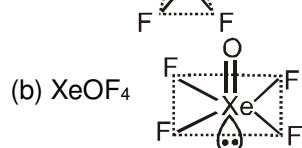
nearly 'T' shaped.

B-1.



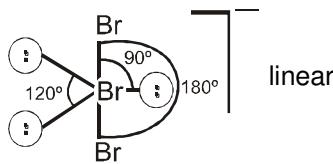
B-2. True, As the s character in hybrid orbital decrease, size of hybrid orbital increases.

B-3. (a) SF₄ 4 bond pair & 1 lone pair, Hybridization = sp³d Shape : see saw

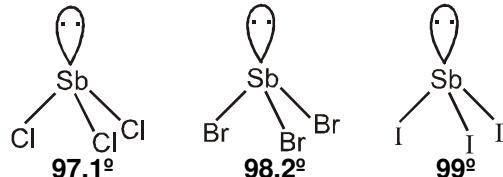


**C-1.**

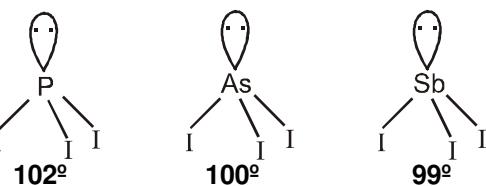
In Br_3^- there are 5 electron pairs around central bromine atom (3 lone pairs and 2 bond pairs). The hybridisation of bromine is thus sp^3d . To have minimum repulsions between lp-lp and lp-bp it acquires linear shape as shown below.

**C-2.**

(a) 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_3 .



(b) 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 Pb_3 . 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 SbI_3 , 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.

C-3. Order of C—H bond strength is $\text{C}_2\text{H}_2 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_6$ as %s character decreases in the same order.

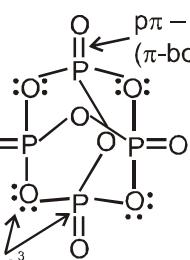
C-4.  double bond occupies large area and has large electron density. So there is intrinsic repulsion between P=O and P—Cl bond pairs. To minimize this repulsion bond angle decrease from 109.5° to 103.5° .

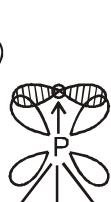
C-5. Highest bond angle

Lowest bond angle

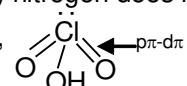
- | | |
|--|--|
| (1) CH_4 | SbH_3 |
| (2) CO_2 | H_2Te |
| (3) H_2O | PH_3 |
| (4) ClO_2 | Cl_2O |
| (5) PF_3 (sp^3 hybridisation) | PH_3 (no hybridisation) |
| (6) BF_3 (sp^2 hybridisation) | NF_3 (sp^3 hybridisation) |
| (7) NH_3 | NF_3 |
| (8) PCl_3 | PF_3 |

C-6. (1) $\text{C}\equiv\text{C} < \text{C}=\text{C} < \text{C}-\text{C}$ (2) $\text{C}-\text{F} < \text{C}-\text{O} < \text{C}-\text{N}$ (3) $\text{HF} < \text{H}-\text{Cl} < \text{H}-\text{Br} < \text{H}-\text{I}$ **D-1.** (a) 4 (b) 3 (c) 3 (d) 6 (e) 4 (f) 0

D-2. (a) P_4O_{10} , 



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

(d) HClO_3 , 



- D-3. (1) +2 (6, -2) (2) +5/2(5, 5, 0, 0) (3) +6 (4) +6 (+6, +6) (5) +6 (+6, +6)
 (6) 0 (7) +5 (8) 4/3 (+ 2, +2, 0) (9) +8 (10) -3
 (11) +6 (12) +6 (+6, +6) (13) +6 (14) +6 (15) +5
 (16) +2 (17) 0 (18) -3, +5

Note: Inside the bracket () answer for individual oxidation number is given.

PART - II

- | | | | | |
|----------|----------|----------|----------|----------|
| A-1. (C) | A-2. (D) | A-3. (D) | A-4. (A) | A-5. (B) |
| A-6. (D) | B-1. (B) | B-2. (A) | B-3. (D) | B-4. (C) |
| B-5. (A) | C-1. (B) | C-2. (D) | C-3. (B) | C-4. (B) |
| C-5. (A) | D-1. (C) | D-2. (B) | D-3. (D) | D-4. (A) |

PART - III

1. (A – p, q, r) ; (B – q, r, t) ; (C – s) ; (D – r) 2. (A – r) ; (B – q) ; (C – s) ; (D – p, t)
 3. (A – r,s); (B – p,q,s) ; (C – q); (D – q,r)

EXERCISE - 2

PART - I

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (D) | 2. (C) | 3. (C) | 4. (B) | 5. (A) |
| 6. (B) | 7. (A) | 8. (D) | 9. (C) | 10. (B) |
| 11. (B) | 12. (B) | 13. (A) | 14. (A) | 15. (A) |
| 16. (B) | 17. (A) | 18. (D) | | |

PART - II

1. 5 (a, b, c, d, h) 2. 6 (a, d, e, h, i, k) 3. 16
 4. 4 5. 10 6. 6

PART - III

- | | | | | |
|----------|----------|----------|---------|----------|
| 1. (AC) | 2. (CD) | 3. (ABC) | 4. (AC) | 5. (BCD) |
| 6. (BCD) | 7. (BCD) | 8. (BD) | | |

PART - IV

- | | | | | |
|--------|--------|--------|-----------|--------|
| 1. (C) | 2. (D) | 3. (D) | 4.* (ABC) | 5. (A) |
| 6. (B) | 7. (C) | | | |

EXERCISE - 3

PART - I

1. (B) 2. (C)

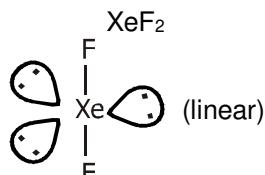
3. According to VSEPR theory

Number of electron pairs = 5,

Number of bond pairs = 2,

So, Number of lone pairs = 3.

Thus XeF_2 is linear with 3 lone pairs occupying 3 equatorial positions of trigonal bipyramidal so as to minimize the repulsions.



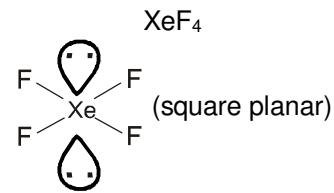


Number of electron pairs = 6,

Number of bond pairs = 4,

So, Number of lone pairs = 2.

Thus XeF_4 is linear with 2 lone pairs occupying 2 axial positions of octahedral pyramidal so as to minimize the repulsions.

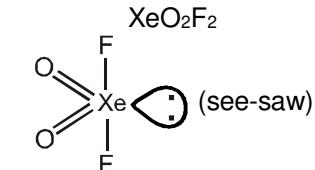


Number of electron pairs (including super electron pairs) = 5,

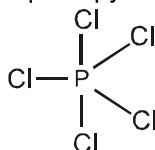
Number of bond pairs = 4,

So, Number of lone pairs = 1.

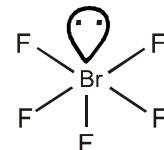
Thus XeO_2F_2 is see-saw with 1 lone pair occupying one equatorial position and two double bonds occupying other two equatorial positions of trigonal bipyramidal so as to minimize the repulsions.



4. (B) 5. (D) 6. (A) 7. (A)
8. There are 5 electron pairs and all are bond pairs in PCl_5 . So to have the minimum repulsions between bond pairs it acquires trigonal bipyramidal shape. In BrF_5 , there are 6 electron 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.



PCl_5 (trigonal bipyramidal),

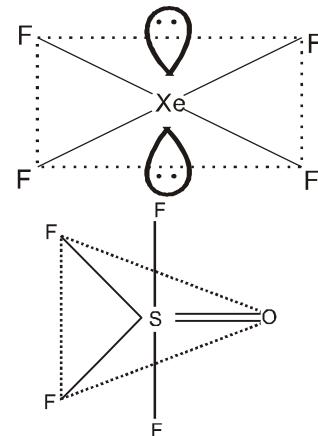


BrF_5 (square pyramidal)

9. (D)

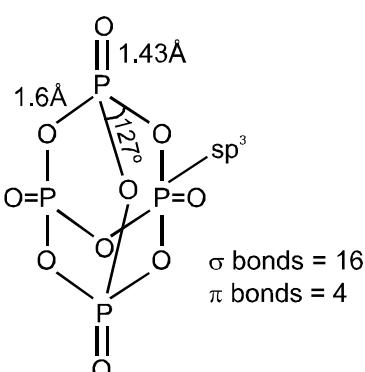
- 10.

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 :



In OSF_4 , 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:



11. Structure of P_4O_{10} .

12. (D) 13.* (ABC) 14. 0 or 8 15. (D) 16. 8
17. 4 18.* (ACD) 19. 6

PART - II**JEE(MAIN) OFFLINE PROBLEMS**

- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 1. (1) | 2. (4) | 3. (3) | 4. (2) | 5. (4) |
| 6. (3) | 7. (3) | 8. (4) | 9. (2) | 10. (2) |
| 11. (4) | 12. (3) | 13. (3) | 14. (4) | |

JEE(MAIN) ONLINE PROBLEMS

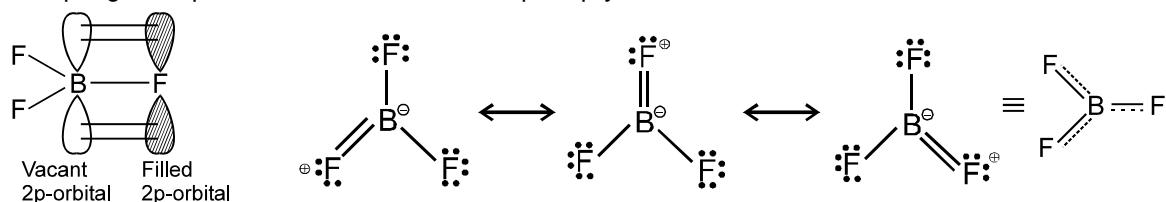
- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 1. (2) | 2. (2) | 3. (3) | 4. (3) | 5. (2) |
| 6. (3) | 7. (1) | 8. (3) | 9. (4) | 10. (1) |
| 11. (2) | 12. (1) | 13. (3) | 14. (3) | 15. (1) |
| 16. (2) | 17. (1) | 18. (1) | 19. (1) | 20. (3) |
| 21. (3) | | | | |



Chemical Bonding-III

Section (A) : 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.

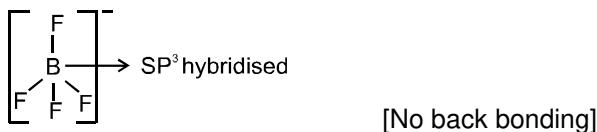


- Decrease in B-F bond length is due to delocalised $p\pi-p\pi$ bonding between filled p-orbital of F atom and vacant p-orbital of B atom.
 - The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows : $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$
 - There is $p\pi-p\pi$ back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to Bl_3 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 :
- $\text{Si} > \text{P} > \text{S} > \text{Cl}$
- The extent of $p\pi-p\pi$ overlapping $\propto \frac{1}{\text{Lewis acid character}}$

Solved Examples

Ex-1. Compare B-F bond length in BF_3 and $[\text{BF}_4]^-$.

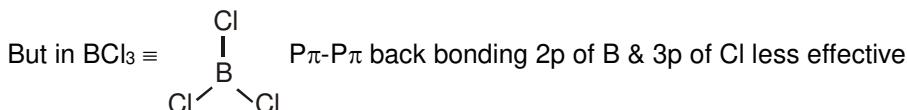
Sol. $\text{BF}_3 + \text{KF} \longrightarrow \text{K}^+ [\text{BF}_4]^-$



B-F Bond length (order) $[\text{BF}_4]^- > \text{BF}_3$

Ex-2. Explain all boron trihalides are lewis acids also explain their order.

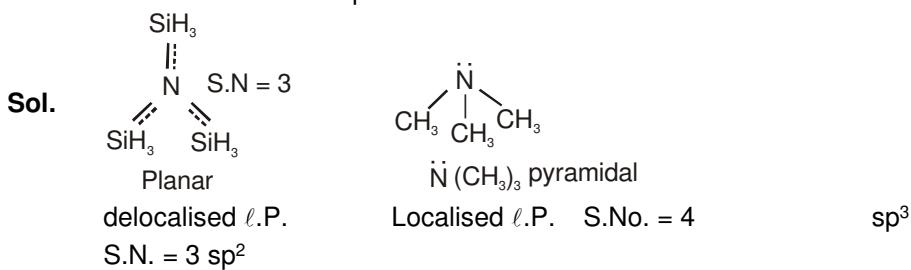
Sol. Boron trihalides are electron deficient molecules therefore act as a Lewis acids



tendency to accept L.P in $\text{BCl}_3 > \text{BF}_3$. Lewis acid strength $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.

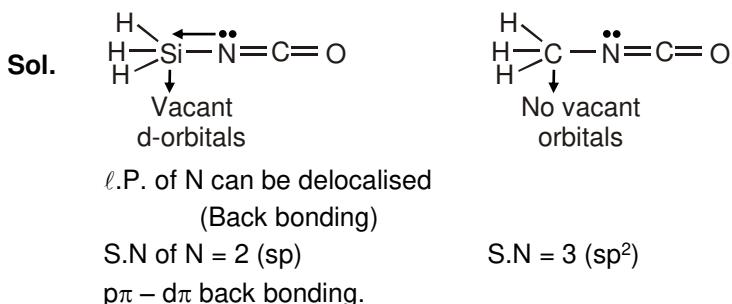


Ex-3. Trisilylamine is a planar molecular and does not act as a lewis base while trimethyl is a pyramidal and act as lewis base. Explain it :



* But in a similar compound $\text{N}(\text{PH}_3)_3$ the shape is found to be pyramidal, so N atom must be sp^3 hybridised due to much less extent of back bonding into the vacant orbitals of P.

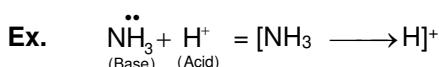
Ex-4. Silyl isocyanate (SiH_3NCO) is linear but methyl isocyanate (CH_3NCO) is bent explain !



Section (B) : Electron deficient bonding

Definition of Lewis acid and base :

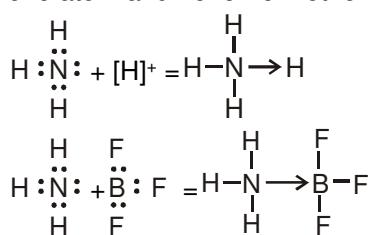
- A lewis acid is an electron pair acceptor and lewis base is electron pair donor.



Proton is a lewis acid and Ammonia is lewis base since the lone pair of electron of the nitrogen atom can be donated to a proton.

Coordinate Bond :

A bond in which sharing of a pair of electron between two atoms, where both electrons originate from one atom and none from other is called **coordinate bond**.



Electron deficient bonding :

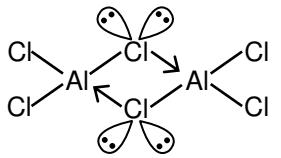
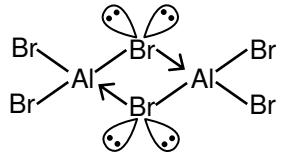
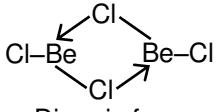
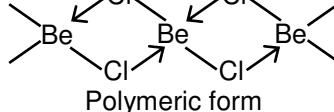
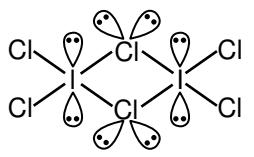
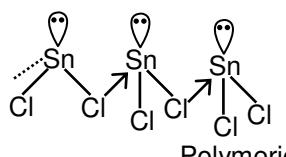
There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e bonds (two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds(3c-2e) present in diborane B_2H_6 , $Al_2(C_2H_5)_6$, $BeH_2(s)$, bridging metal carbonyls.

B_2H_6 (diborane) \Rightarrow It is having (3centre – 2electron bond) / (banana bond) / (electron deficient bond)



Compound	Bridge	Hybridisation	Planar/Non Planar	Structure
B_2H_6	$3c - 2e^-$	sp^3-s-sp^3	Non planar	
			<p>B_2H_6 have 4 2c-2e bonds and 2 3c-2e bonds. Bridging bonds have larger bond length than terminal bonds. Angle between terminal bonds is more than angle between bridging bonds if all 4 terminal bonds are in one plane then bridging bonds are in perpendicular plane.</p>	
Al_2H_6	$3c - 2e^-$	sp^3-s-sp^3	Non planar	
Be_2H_4	$3c - 2e^-$	sp^2-s-sp^2	planar	
$(BeH_2)_n$	$3c - 2e^-$	sp^3-s-sp^3	Non planar	
			All bonds except the extreme ends are 3C - 2e ⁻ bonds.	
$Al_2(CH_3)_6$	$3c - 2e^-$	$sp^3-sp^3-sp^3$	Non planar	
$Al_2(C_6H_5)_6$	$3c - 2e^-$	$sp^3-sp^2-sp^3$	Non planar	



Compound	Bridge	Hybridisation	Planar/ Non Planar	Structure
Al ₂ Cl ₆	3c – 4e ⁻	sp ³ –sp ³ –sp ³	Non Planar	 <p>(Driving force is to complete the octet) Only covalent bond, no electron deficient bond is present.</p>
Al ₂ Br ₆	3c – 4e ⁻	sp ³ –sp ³ –sp ³	Non Planar	 <p>Dimeric form</p>
Be ₂ Cl ₄	3c – 4e ⁻	sp ² –sp ³ –sp ²	Planar	 <p>Dimeric form</p>
(BeCl ₂) _n (solid)	3c – 4e ⁻	sp ³ –sp ³ –sp ³	Non Planar	 <p>Polymeric form</p>
I ₂ Cl ₆	3c – 4e ⁻	sp ³ d ² –sp ³ –sp ³ d ²	Planar	 <p>Dimeric form</p>
SnCl ₂ (Solid)	3c – 4e ⁻	sp ³ –sp ³ –sp ³	Non Planar	 <p>(Driving force is to complete the octet) Polymeric form</p>

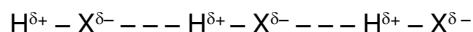


Section (C) : H-bonding & intermolecular force of attraction.

Hydrogen Bond :

Discovered by Huggins, Latimer and Rodbush.

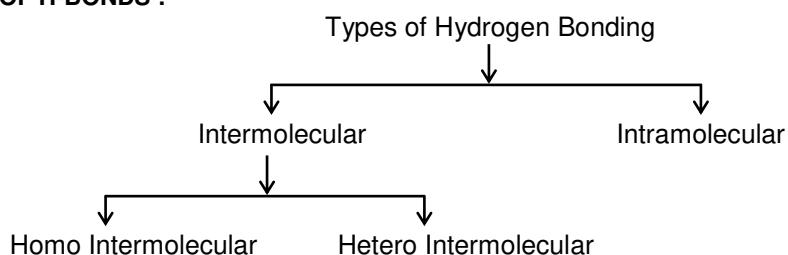
When hydrogen is bonded to strongly electronegative element 'X'. The electron pair shared between the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional positive charge (δ^+) while X' attain fractional negative charge (δ^-). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as :



Main condition for Hydrogen bonding :

- (i) Hydrogen should be covalently bonded with high electronegative element like F, O, N.
- (ii) Atomic size of electronegative element should be small
Decreasing order of atomic size is : N > O > F
Decreasing order of electronegativity is : F (4.0) > O (3.5) > N (3.0)
- (iii) Strength of Hydrogen bond \propto Electronegativity of element $\propto \frac{1}{\text{atomic size of element}}$
- (iv) Hydrogen bonding occurs in HCN, due to ($-\text{C}\equiv\text{N}$) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.
 $\text{H}-\text{C}\equiv\text{N}^{-\delta} \dots \dots +\delta\text{H}-\text{C}\equiv\text{N}^{-\delta} \dots \dots +\delta\text{H}-\text{C}\equiv\text{N}$

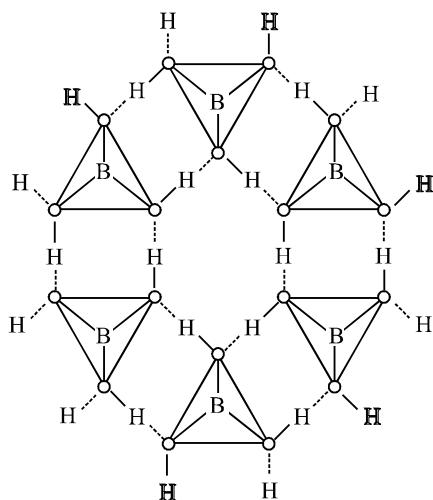
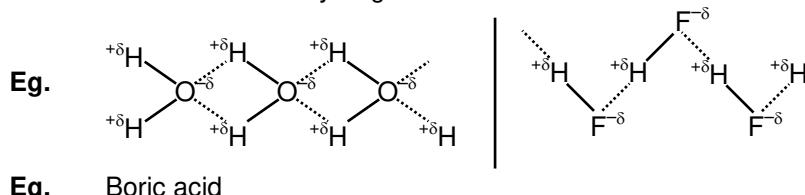
TYPES OF H-BONDS :



(A) Intermolecular Hydrogen bond :

Hydrogen bond formation between two or more molecules of either the same or different compounds known as **Inter molecular Hydrogen bonding**.

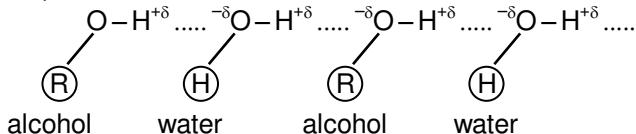
- (i) **Homo intermolecular** : Hydrogen bond between molecules of same compounds.





In the solid state, the $\text{B}(\text{OH})_3$ units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 \AA).

- (ii) **Hetro intermolecular** : Hydrogen bond between molecules of different compounds.
Eg. alcohol, water

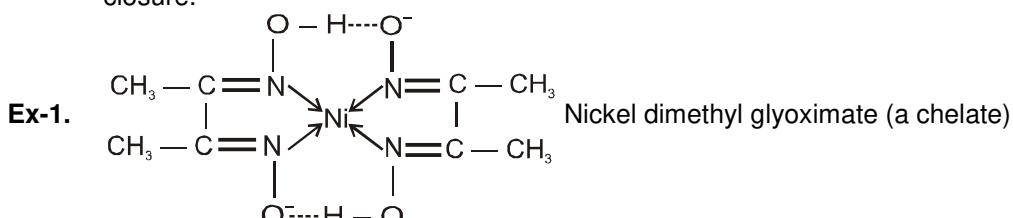


- (B) **Intra molecular Hydrogen bond** : It takes place within the molecule.

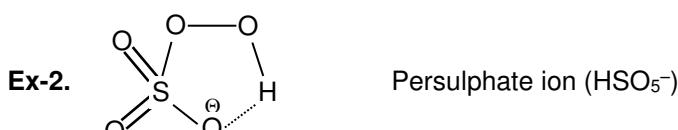
- (i) Hydrogen bonded with electronegative elements of a functional group, form Hydrogen bond with another electronegative element present on nearest position on the same molecule.
(ii) This type of Hydrogen bond is mostly occurred in organic compounds.
(iii) It results in ring formation (Chelation).

Necessary conditions for the formation of intramolecular hydrogen-bonding :

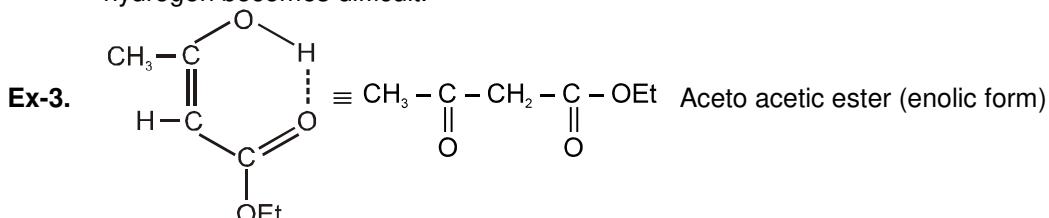
- the ring formed as a result of hydrogen bonding should be planar.
- a 5- or 6-membered ring should be formed.
- interacting atoms should be placed in such a way that there is minimum strain during the ring closure.



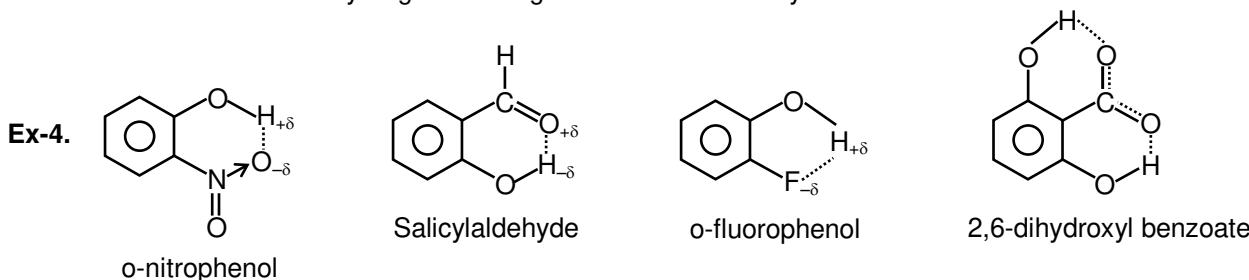
Extra stability of the complex is because of intramolecular hydrogen bonding in addition to the chelating effect.

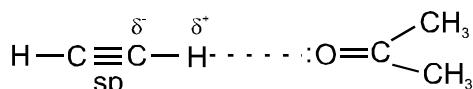


K_1 of peroxomono sulphuric acid (i.e., caros acid) is greater than K_2 . After the loss of one hydrogen, the persulphate ion gets stabilised due to intramolecular hydrogen bonding and thus the removal of second hydrogen becomes difficult.



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





None of the above 2 has H-bonding individually.

But C_2H_2 is not soluble in water because water molecules already so much associated through H-bond that it is almost impossible for C_2H_2 molecules to break that association.

So, it is not soluble in H_2O (l)

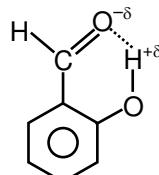
(c) Solubility order- $CH_3OCH_3 < CH_3OH$

Primary amine > secondary amine > tertiary amine

(B) Intra molecular Hydrogen bonding :

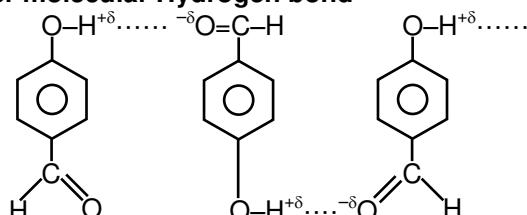
(a) It decreases solubility as it form chelate by Hydrogen bonding, so hydrogen is not free for other molecule.

(b) It can't form H-bond with water molecule so can't dissolves.



Salicylaldehyde

(C) Inter molecular Hydrogen bond

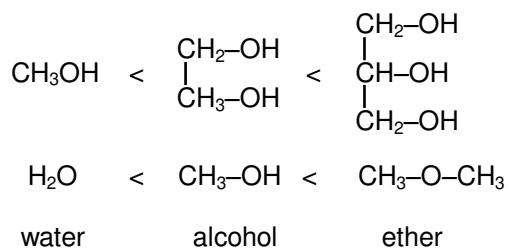


p-hydroxy benzaldehyde

It can form hydrogen bond with water molecule so it can dissolved

(ii) Viscosity:

Hydrogen bond associates molecules together, so viscosity increases



(iii) Melting point and boiling point

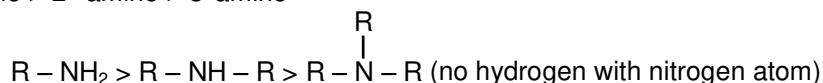
(a) Due to intermolecular hydrogen bond melting point & boiling point of compounds increases.

$H_2O > CH_3OH > CH_3-O-CH_3$

(b) Trihydric alcohol > dihydric alcohol > monohydric alcohol

Monocarboxylic acid form stronger hydrogen bond than alcohol of comparable molecular weight. Therefore boiling point of carboxylic acid is higher than alcohol.

(c) Decreasing order of melting point & boiling point isomer amines-
 $1^\circ\text{-amine} > 2^\circ\text{-amine} > 3^\circ\text{amine}$



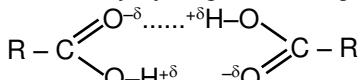


(d)	Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.				
VA	VIA	VIIA			
NH ₃	H ₂ O	HF	boiling point	HF > HI > HBr > HCl	
PH ₃	H ₂ S	HCl		H ₂ O > TeH ₂ > SeH ₂ > H ₂ S	
AsH ₃	SeH ₂	HBr		NH ₃ > SbH ₃ > AsH ₃ > PH ₃	
SbH ₃	TeH ₂	HI			

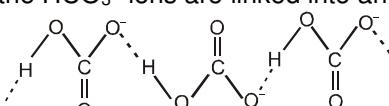
But sudden increase in boiling point of NH₃, H₂O and HF is due to hydrogen bonding
H₂O > HF > NH₃

- (e) Intramolecular hydrogen bonding gives rise to ring formation, so the force of attraction among these molecules are vander waal's force. So, melting point and boiling point are low.

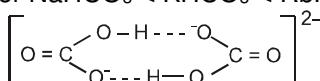
- (iv) **Molecular weight:** Molecular weight of CH₃COOH is double of its molecular formula, due to dimer formation occur by hydrogen bonding.



The crystal structures of NaHCO₃ and KHCO₃ both show hydrogen bonding, but are different.
(a) In NaHCO₃, the HCO₃⁻ ions are linked into an infinite chain.



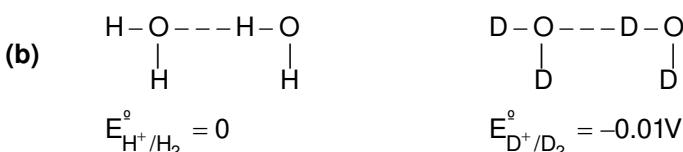
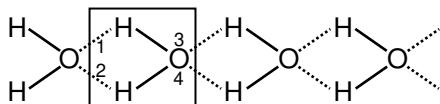
(b) in KHCO₃, RbHCO₃, CsHCO₃, HCO₃⁻ forms a dimeric anion.
Solubility in water NaHCO₃ < KHCO₃ < RbHCO₃ < CsHCO₃



- (v) **Physical state:** H₂O is liquid while H₂S is gas.

(a) **Water and Ice :** Both have hydrogen bonding even then density of ice is less than water. Volume of ice is more because of open cage like crystal structure, from by association of water molecules with the help of hydrogen bond.

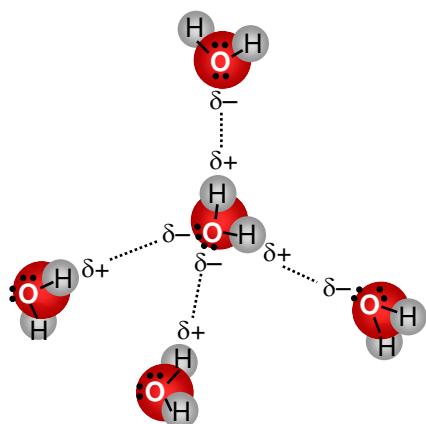
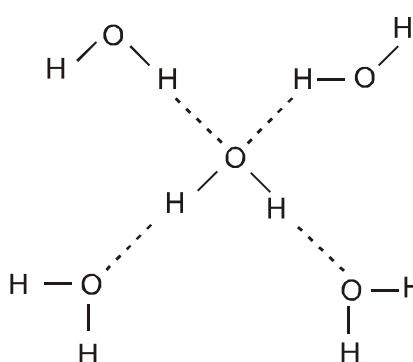
H₂O becomes solid (Ice) due to four hydrogen bond among water molecule are formed in tetrahedral manner.

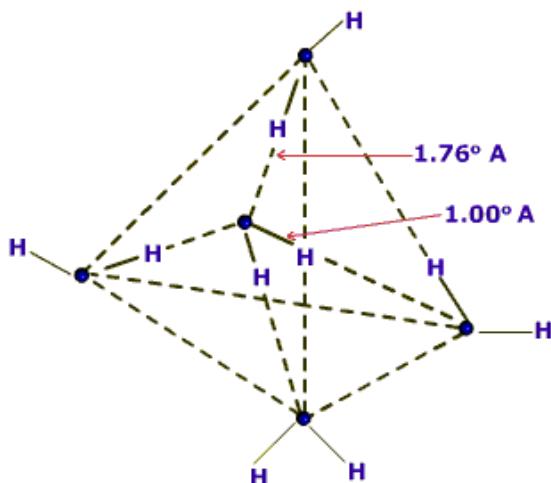


D is more electro positive than H

So, it is capable of forming slightly more H bond than H that why D₂O molecule are more associated and its boiling point is more than the boiling point of H₂O liquid.

- (c) **Ice floats on water**





No. of water molecule attached to 1 H_2O molecule = 4

No. of H bonds in a molecule = 2

One H_2O is tetrahedrally bonded with 4 H_2O molecules.

Intermolecular spacing increases

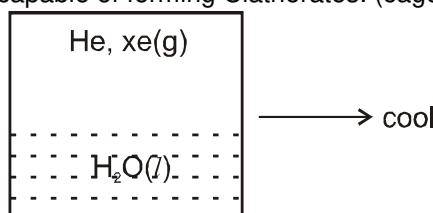
So, density of ice decreases

(d) $\text{D}_2\text{O}(\text{s})$

Density of $\text{D}_2\text{O}(\text{s})$ > density of $\text{H}_2\text{O}(\text{l})$

So, it sinks in $\text{H}_2\text{O}(\text{l})$ but floats on $\text{D}_2\text{O}(\text{l})$

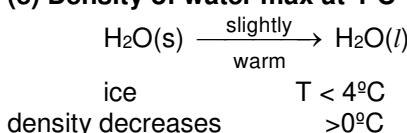
Due to open structure, ice is capable of forming Clathrates. (cage like compounds)



Xe will be captured by ice.

Xe(g) because of its bigger atomic size is trapped in the cages formed by H_2O molecules in the structures of ice. He cannot be trapped due to smaller size. Such compounds are called clathrates compounds.

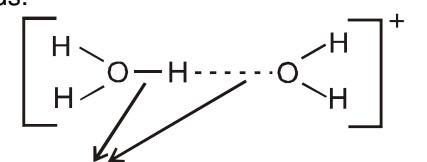
(e) Density of water max at 4°C



In this temperature region some of the ice melts and hence some H_2O molecule go into the cages of remaining ice structure.

So, volume decreases density increases becoming max at 4°C but beyond this temp thermal effects become dominating volume increases then density decreases.

(f) An interesting hydrate of Hydronium ion with the formula $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ in which H_2O molecules are hydrogen bonded. Some lower species like H_5O_2^+ have also been observed where the 2 water molecules are linked three H bonds.

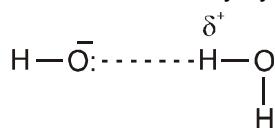


Bond strength 100-150 kJ/mole

(Proton transfer takes place)

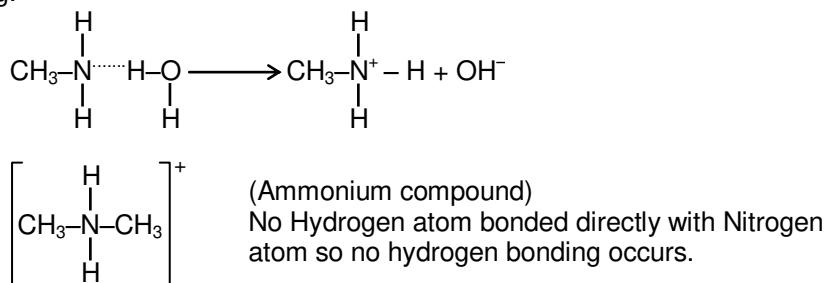


Similarly H_3O_2^- ions are also observed which is actually hydrate OH^- ion.



(vi) Base strength

CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, form hydrogen bond with water. So, less hydrolysis i.e. it gives OH^- ions. While $(\text{CH}_3)_4\text{N}^+$ OH^- (ammonium compound) will give OH^- ion in large amount due to no hydrogen bonding.



Ex. Which is a stronger base why?

- (a) Trimethyl ammonium hydroxide $[\text{N}(\text{CH}_3)_3]\text{OH}$
- (b) Tetramethyl ammonium hydroxide $[\text{N}(\text{CH}_3)_4]^+\text{OH}^-$

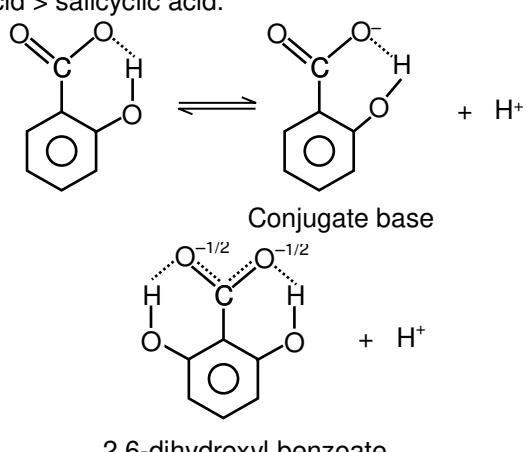
b is more basic

$(\text{CH}_3)_3\text{N}: \cdots\cdots \text{H}-\text{O}$
Due to nitramolecular H bonding, release of OH^- ion become difficult \therefore it is a weaker base.

Effect of intramolecular H-bonding

(i) Strength of acid :

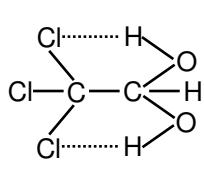
(a) The formation of intramolecular H-bonding in the conjugate bas of an acid gives extra stability to conjugate base and hence acid strength increases eg. Salicylic acid is stronger than benzoic acid and 2, 6-dihydroxy benzoic acid $>$ salicylic acid.



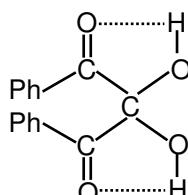
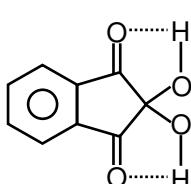
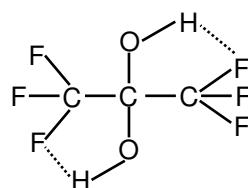
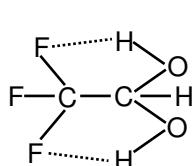
- (b) $\text{C}_2\text{H}_5\text{SH}$ is more acidic than $\text{C}_2\text{H}_5\text{OH}$. In $\text{C}_2\text{H}_5\text{OH}$, hydrogen bonds forms, so H^+ is not free
- (c) HF is weaker acid than HI, due to hydrogen bond in $\text{H}-\text{F}$, H^+ is not free.

(ii) Stability of chloral hydrate :

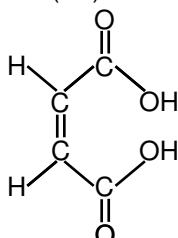
If two or more OH group on the same atom are present it will be unstable, but chloral hydrate is stable (due to Hydrogen bonding)



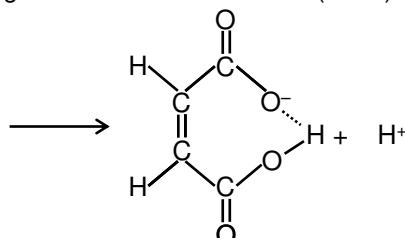
Chloral hydrate



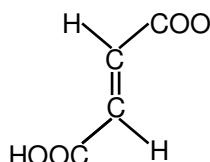
(iii) Maleic acid (cis) is stronger acid than fumaric acid (trans).



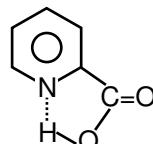
(Maleic acid)



Stable conjugate base of maleic acid



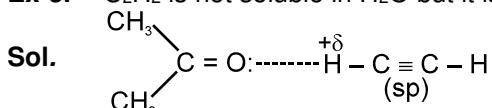
Fumaric (No-intramolecular hydrogen bonding)



Note : The relative strength of various bonds is as follows
Ionic bond > covalent bond > Metallic bond > Hydrogen bond > Vander waal's bond.

Solved Examples

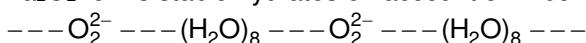
Ex-5. C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.



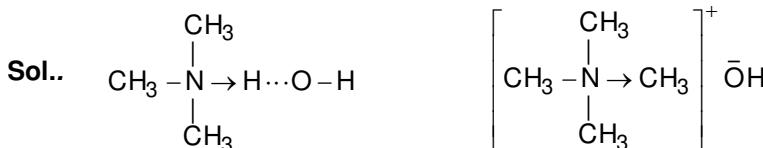
In hybridisation as %s character increase, electronegativity increase hence C_2H_2 forms H-bonds with O-atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O .

Ex-6. Why crystalline sodium peroxide is highly hygroscopic in nature.

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



Ex-7. Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.





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 cannot occur, so the OH^- group ionizes easily and thus it is a much stronger base.

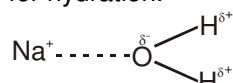
Intermolecular forces (Van der Waal's Forces) :

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 (Keesom forces)
- (c) Ion-induced dipole attraction (Debye force)
- (d) Dipole-induced dipole attraction
- (e) Instantaneous dipole- Instantaneous induced dipole attraction (Dispersion force or London forces)

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

- (a) **Ion-dipole attraction** : Exists between an ion and a polar molecule. Its strength depends on (i) size of ion (ii) charge on the ion (iii) dipole moment of the polar molecule. It is thought to be directional. Ion-dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as $\text{Na}(\text{OH}_2)_x^+$ and $\text{F}(\text{H}_2\text{O})_y^-$ (for solution of NaF in H_2O) are found. Hence this force is responsible for hydration.



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



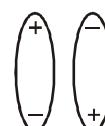
- (c) **Ion-induced dipole attraction** : Exists between ion and non-polar molecules (e.g., an atom of a noble gas such as Xenon).



- (d) **Dipole-induced dipole attraction** : Exists between polar and non-polar molecules.



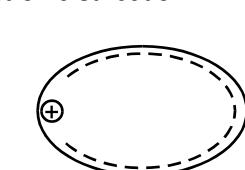
Head to tail arrangement of dipoles



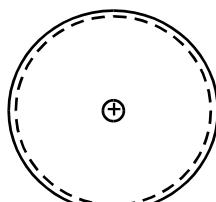
Antiparallel arrangement of dipoles

- (e) **Instantaneous dipole- Instantaneous induced dipole attraction** :

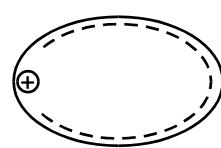
Exists among the non-polar molecules like H_2 , O_2 , Cl_2 etc. in solid or liquid states. Even in atoms in molecules which have no permanent dipole, instantaneous dipoles will arise as a result of momentary unbalances in electron distribution.



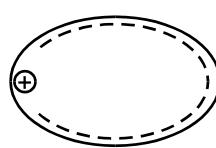
instantaneous dipole
due to motion of
electrons



symmetrical distribution
of electron cloud



instantaneous dipole



instantaneous induced dipole



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.



Note : Fluoro carbon have usually low boiling points because tightly held electrons in the fluorine atoms have a small polarizability.

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

Solved Examples

Ex-8. Give the order of boiling point of following
 Cl_2 , HCl

Sol. $\text{Cl}_2\text{-Cl}_2$ < $\text{HCl}\text{-HCl}$ (boiling point)
 dispersion force dipole-dipole attraction
 As dipole-dipole attraction is stronger than dispersion force.

Ex-9 Arrange the inert gases, according to their increasing order of boiling points

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

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



Exercise-1

 **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Back bonding

Section (B) : Electron deficient bonding

- B-1.** Explain why
(i) NH_3 is better e⁻ pair donor than PH_3 .
(ii) NH_3 is a better base than CH_3CN ?

B-2. Why BCl_3 and SiF_4 act as Lewis acids ? Explain.

B-3. BF_3 exists but BH_3 does not. explain Why.

B-4. Which orbitals are involved in banana bonding in $\text{Al}_2(\text{CH}_3)_6$?

Section (C) : H-bonding & intermolecular force of attraction.

- C-1.** In which of the following the hydrogen bonding is strongest. Explain briefly ?
(a) O – H – – – S (ℓ) (b) S – H – – – O (ℓ) (c) F – H – – – F⁻ (s) (d) F – H – – – O (ℓ)

C-2. Why D₂O has higher viscosity than H₂O ?

C-3. Why glucose, fructose, sucrose etc. are soluble in water though they are covalent compounds ?

C-4. Ethanol has higher boiling point than diethyl ether. Why ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Back bonding

- A-1.** For BF_3 molecule which of the following is true ?
(A) B-atom is sp^2 hybridised.
(B) There is a $\text{p}\pi-\text{p}\pi$ 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

A-2. Which of the following statements regarding the structure of SOCl_2 is not correct ?
(A) The sulphur is sp^3 hybridised and it has a tetrahedral shape.
(B) The sulphur is sp^3 hybridised and it has a trigonal pyramid shape.
(C) The oxygen-sulphur bond is $\text{p}\pi-\text{d}\pi$ bond.
(D) It contain one lone pair of electrons in the sp^3 hybrid orbital of sulphur.

A-3. Respective order of strength of back-bonding and Lewis acidic strength in boron trihalides is :
(A) $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ and $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ (B) $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ and $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$
(C) $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$ and $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ (D) $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$ and $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$

Section (B) : Electron deficient bonding



Section (C) : H-bonding & intermolecular force of attraction.

- C-1.** Which of the following is not correctly matched with respect to the intermolecular forces existing amongst the molecules (Hydrogen bonding is not taken as dipole-dipole attraction) ?
(A) Benzene – London dispersion forces
(B) Orthophosphoric acid – London dispersion force, hydrogen bonding.
(C) Hydrochloric acid – London dispersion force, dipole-dipole attraction
(D) Iodine monochloride – London dispersion force

C-2. Which of the following factor is responsible for van der Waals forces ?
(A) Instantaneous dipole-induced dipole interaction.
(B) Dipole-induced dipole interaction and ion-induced dipole interaction.
(C) Dipole-dipole interaction and ion-induced dipole interaction.
(D) All of these.

C-3. Which of the following bonds/forces is weakest ?
(A) Covalent bond (B) Ionic bond (C) Hydrogen bond (D) London force

C-4. In which of the following compound, intra (A) carbonyl oxygen attack



The correct order of H-bond strengths is :

- C-6.** Amongst NH_3 , PH_3 , AsH_3 and SbH_3 the one with highest boiling point is :
 (A) NH_3 because of lower molecular weight (B) SbH_3 because of higher molecular weight
 (C) PH_3 because of H-bonding (D) AsH_3 because of lower molecular weight

C-7. The correct order of boiling point is :
 (A) $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ (B) $\text{H}_2\text{O} > \text{H}_2\text{Se} > \text{H}_2\text{Te} > \text{H}_2\text{S}$
 (C) $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$ (D) $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$

C-8. Which of the following compounds has the highest boiling point
 (A) HCl (B) HBr (C) H_2SO_4 (D) HNO_3

**PART - III : MATCH THE COLUMN****1. Match the following :**

	Column-I		Column-II
(A)	BF_3	(p)	sp^3 hybridization
(B)	$(\text{SiH}_3)_3\text{N}$	(q)	$\text{p}\pi-\text{p}\pi$ back bond
(C)	B_2H_6	(r)	$\text{p}\pi-\text{d}\pi$ back bond
(D)	SiO_2	(s)	3c-2e bond

2. Match the following :

	Column-I		Column-II
(A)	$\text{HCl} < \text{HF}$	(p)	Strength of hydrogen bonding
(B)	$\text{PH}_3 < \text{NH}_3$	(q)	Dipole moment
(C)	$\text{H}_2\text{O} < \text{D}_2\text{O}$	(r)	Boiling point
(D)	$\text{F}_2 < \text{Cl}_2$	(s)	Bond energy

3. Match the column:

Column-I	Column-II
(A) Liquid bromine	(p) Hydrogen bond
(B) Solid hydrogen fluoride	(q) Ion-dipole force
(C) Solution of sodium fluoride in water	(r) Dispersion force.
(D) Liquid methylamine	(s) Dipole induced dipole interaction.
(E) Noble gas clathrate in ice.	

Exercise-2**Marked questions are recommended for Revision.****PART - I : ONLY ONE OPTION CORRECT TYPE**

- In which of the following compounds B–F bond length is shortest ?

(A) BF_4^- (B) $\text{BF}_3 \leftarrow \text{NH}_3$ (C) BF_3 (D) $\text{BF}_3 \leftarrow \text{N}(\text{CH}_3)_3$
- Which of the following statement is false for trisilylamine ?

(A) Three sp^2 orbitals are used for σ bonding, giving a plane triangular structure.
 (B) The lone pair of electrons occupy a p-orbital at right angles to the plane triangle and this overlaps with empty p-orbitals on each of the three silicon atoms resulting in π bonding.
 (C) The N–Si bond length is shorter than the expected N–Si bond length.
 (D) It is a weaker Lewis base than trimethyl amine.
- In which of the following molecules/species all following characteristics are found ?

(a) Tetrahedral hybridisation
 (b) Hybridisation can be considered to have taken place with the help of empty orbital(s).
 (c) All bond lengths are identical i.e. all A–B bond lengths are identical.
 (A) B_2H_6 (B) Al_2Cl_6 (C) BeCl_2 (g) (D) BF_4^-
- H-bonding is maximum in

(A) $\text{C}_6\text{H}_5\text{OH}$ (B) $\text{C}_6\text{H}_5\text{COOH}$ (C) $\text{CH}_3\text{CH}_2\text{OH}$ (D) CH_3COCH_3
- Which one of the following does not have intermolecular H-bonding ?

(A) H_2O (B) o-nitro phenol (C) HF (D) CH_3COOH
- Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.

S₁ : HF boils at a higher temperature than HCl.
 S₂ : HBr boils at lower temperature than HI.
 S₃ : Bond length of N_2 is less than N_2^+ .
 S₄ : F_2 has higher boiling point than Cl_2 .

(A) T F T T (B) T T F F (C) T T T F (D) T T T T



7. Select the correct statement for the sulphuric acid.
- It has high boiling point and viscosity.
 - There are two types of bond lengths in its bivalent anion.
 - $p\pi-d\pi$ bonding between sulphur and oxygen is observed.
 - Sulphur has the same hybridisation that is of boron in diborane.
- (A) II and III only (B) II, III and IV only (C) I, III and IV only (D) III and IV only
8. Which of the following is least volatile ?
- (A) HF (B) HCl (C) HBr (D) HI

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following has hydrogen bonding
- | | | | |
|---------------------------------------|---------------------|------------------------|--------------------------|
| (a) NH ₃ | (b) CH ₄ | (c) H ₂ O | (d) HI |
| (e) HF | (f) HCOOH | (g) B(OH) ₃ | (h) CH ₃ COOH |
| (i) HCO ₃ ⁻ ion | | | |

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which compounds are lewis acids ?
- (A) AlCl₃ (B) BCl₃ (C) H₂O (D) NH₃
2. Which of the following is/are electron deficient compounds ?
- (A) NaBH₄ (B) B₂H₆ (C) AlCl₃ (D) LiAlH₄
3. Which of the following have coordinate bonds ?
- (A) NH₄Cl (B) NaCl (C) O₃ (D) Cl₂
4. Which of the following is/are correct.
- (A) Boiling point of alcohol is higher than than of diethyl ether
(B) Density of water is higher than ice.
(C) Glycerol is more viscous than ethanol
(D) Ammonia is more easily liquified than HCl due to H-bonding in NH₃
5. Which of the following statements is **correct** regarding phosphoric acid ?
- (A) $p\pi-d\pi$ back bonding exist between O and P.
(B) The anion is resonance stabilized.
(C) It is a dibasic acid.
(D) Inter molecular H bonding between molecules make it a syrupy (viscous) liquid.
6. Which of the following is correct order of strength of hydrogen bonding?
- (A) N—H- - -N > N—H- - -O (B) F—H- - -N > O—H- - -N
(C) N—H- - -Cl > N—H- - -N (D) O—H- - -F > O—H- - -O

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Bridge bonding is a specific kind of bonding in pages of chemistry. In general σ -bond pair delocalisation is very difficult. But electron deficiency of the central atom forces to delocalised and forms this kind of bond.

1. The state of hybridisation of central atom in dimer form of both BH₃ and BeH₂ is
- (A) sp², sp (B) sp³, sp² (C) sp³, sp³ (D) sp², sp³
2. Which of the following molecule has complete octet
- (A) B₂H₆ (B) Al₂Cl₆ (C) Be₂Cl₄ (D) BeH₂
3. The B₂H₆ molecule is dissolved in tetrahydrofuran. Which atom(s) is/are having changes of hybridisation with respect to reactant and final product of the process given.
- (A) B only (B) B and O (C) B, O and C (D) None of these



4. In which of the dimerisation process, the achievement of the octet is not the driving force.
 (A) $2\text{AlCl}_3 \longrightarrow \text{Al}_2\text{Cl}_6$ (B) $\text{BeCl}_2 \longrightarrow \text{BeCl}_2$ (solid)
 (C) $2\text{ICl}_3 \longrightarrow \text{I}_2\text{Cl}_6$ (D) $2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$
5. The molecule is not having $3c - 2e$ bond.
 (A) BeH_2 (dimer) (B) BeH_2 (solid) (C) C_2H_6 (D) B_2H_6

Comprehension # 2

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents species, column-2 represents hybridization and shape while column-3 represents properties.					
Column-1		Column-2		Column-3	
Species		Hybridization & shape		Properties	
(I)	O_2	(i)	sp^3	(P)	Paramagnetic
(II)	XeF_2	(ii)	sp^3d	(Q)	Diamagnetic
(III)	H_2O	(iii)	Linear	(R)	H-bond formation
(IV)	ICl_2^+	(iv)	Angular (V-shape)	(S)	Polar nature

6. Correct combination is/are :
 (A) (I) (iii) (q) (B) (II) (i) (p) (C) (I) (iii) (q) (D) (IV) (iii) (p)
7. Correct combination is/are :
 (A) (I) (iii) (q) (B) (II) (iii) (s) (C) (III) (iv) (p) (D) (IV) (i) (s)
8. Incorrect combination is/are :
 (A) (I) (iii) (p) (B) (II) (ii) (q) (C) (III) (i) (r) (D) (IV) (ii) (p)

Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Amongst H_2O , H_2S , H_2Se and H_2Te the one with highest boiling point is : [JEE-2000, 1/135]
 (A) H_2O because of H-bonding. (B) H_2Te because of higher molecular weight.
 (C) H_2S because of H-bonding. (D) H_2Se because of lower molecular weight.
2. Identify the correct order of boiling points of the following compounds : [JEE-2002, 3/150]
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 1 2 3
 (A) $1 > 2 > 3$ (B) $3 > 1 > 2$ (C) $1 > 3 > 2$ (D) $3 > 2 > 1$
3. Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of BCl_3 & NH_3 . [JEE-2002(S), 3/150]
 (A) N : tetrahedral sp^3 , B : tetrahedral sp^3 (B) N : pyramidal sp^3 , B : pyramidal sp^3
 (C) N : pyramidal sp^3 , B : planar sp^2 (D) N : pyramidal sp^3 , B : tetrahedral sp^3
4. Which one is more soluble in diethyl ether anhydrous AlCl_3 or hydrous AlCl_3 ? Explain in terms of bonding. [JEE-2003(M), 2/144]
5. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3 , AlF_3 is precipitated. Write the balanced chemical equations. [JEE-2004(M), 2/144]
6. Predict whether the following molecules are iso-structural or not. Justify your answer. [JEE-2005(M), 2/144]
 (i) NMe_3 (ii) $\text{N}(\text{SiMe}_3)_3$
7. The number of water molecule (s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is [JEE-2009, 4/160]

**PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)****JEE(MAIN) OFFLNE PROBLEMS**

1. An ether is more volatile than an alcohol having the same molecular formula. This is due to:
 (1) dipolar character of ethers
 (2) alcohols having resonance structures.
 (3) inter-molecular hydrogen bonding in ethers
 (4) inter-molecular hydrogen bonding in alcohols. [AIEEE-2003, 3/225]
2. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively :
 (1) sp^2 and sp^2 (2) sp^2 and sp^3 (3) sp^3 and sp^2 (4) sp^3 and sp^3 [AIEEE-2004, 3/225]
3. The structure of diborane (B_2H_6) contains :
 (1) four 2c–2e bonds and four 3c–2e bonds
 (2) two 2c–2e bonds and two 3c–3e bonds
 (3) two 2c–2e bonds and four 3c–2e bonds
 (4) four 2c–2e bonds and two 3c–2e bonds [AIEEE-2005, 4½/225]
4. A metal, M forms chlorides in +2 and +4 oxidation states. Which of the following statements about these chlorides is correct ?
 (1) MCl_2 is more volatile than MCl_4
 (2) MCl_2 is more soluble in anhydrous ethanol than MCl_4
 (3) MCl_2 is more ionic than MCl_4
 (4) MCl_2 is more easily hydrolysed than MCl_4 [AIEEE-2006, 3/165]
5. Among the following mixtures, dipole-dipole as the major interaction, is present in ? [AIEEE 2006, 3/165]
 (1) Benzene and carbon tetrachloride
 (2) Benzene and ethanol
 (3) Acetonitrile and acetone
 (4) KCl and water
6. Which of the following hydrogen bonds is the strongest ?
 (1) O – H ... O (2) O – H ... F (3) F – H ... H (4) F – H ... F [AIEEE-2007, 3/120]
7. The bond dissociation energy of B–F in BF_3 is 646 kJ mol⁻¹ whereas that of C–F in CF_4 is 515 kJ mol⁻¹. The correct reason for higher B–F bond dissociation energy as compared to that of C–F is :
[AIEEE-2009, 4/144]
 (1) stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4 .
 (2) significant p π –p π interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4 .
 (3) lower degree of p π –p π interaction between B and F in BF_3 than that between C and F in CF_4 .
 (4) smaller size of B-atom as compared to that of C-atom.
8. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water ?
 (1) Oxide ion accepts sharing in a pair of electrons
 (2) Oxide ion donates a pair of electrons
 (3) Oxidation number of oxygen increases
 (4) Oxidation number of sodium decreases [AIEEE-2011, 4/120]
9. Which one has the highest boiling point ?
 (1) He (2) Ne (3) Kr (4) Xe [JEE(Main)-2015, 4/120]
10. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is:
 (1) ion-ion interaction (2) ion-dipole interaction (3) London force (4) hydrogen bond [JEE(Main)-2015, 4/120]

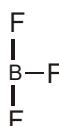


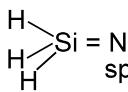
11. Which one of the following statements about water is **FALSE** ? [JEE(Main)-2016, 4/120]
 (1) Water can act both as an acid and as a base.
 (2) There is extensive intramolecular hydrogen bonding in the condensed phase.
 (3) Ice formed by heavy water sinks in normal water.
 (4) Water is oxidized to oxygen during photosynthesis.
- 12.* Which of the following are Lewis acids ? [JEE(Main)-2018, 4/120]
 (1) PH₃ and SiCl₄ (2) BCl₃ and AlCl₃ (3) PH₃ and BCl₃ (4) AlCl₃ and SiCl₄

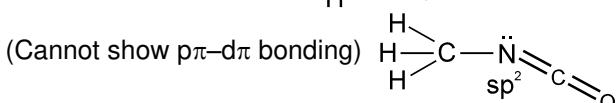
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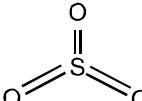
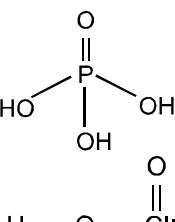
1. The number of 2-centre-2-electron and 3-centre-2-electron bonds in B₂H₆, respectively, are: [JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) 2 and 4 (2) 2 and 2 (3*) 4 and 2 (4) 2 and 1
2. The hydride that is NOT electron different is : [JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) GaH₃ (2*) SiH₄ (3) AlH₃ (4) B₂H₆

**Answers****EXERCISE - 1****PART - I**

- A-1.** In $\text{Me}_3\text{N} \longrightarrow$  , the electron deficiency of boron is compensated by the lone pair of electron donated by nitrogen atom. Whereas 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.

- A-2.** (Shows $p\pi-d\pi$ bonding) 



- A-3.** (i)  two $p\pi-d\pi$ bond and one $p\pi-p\pi$ bond. (ii)  one $p\pi-d\pi$ bond
 (iii) $\text{N}\equiv\text{N}$ two $p\pi-p\pi$ bond. (iv)  three $p\pi-d\pi$ bond.

- B-1.** (i) In NH_3 molecule N atom has lone pair in sp^3 hybrid orbital while in PH_3 as suggested by its bond angle (92°) the lone pair must be present in 'S' orbital which is much more contracted than sp^3 . Hence PH_3 becomes a poor donor than NH_3 .
 (ii) CH_3CN has lone pair on sp hybridized nitrogen atom while NH_3 has lone pair on sp^3 hybridized nitrogen atom.
- B-2.** In BCl_3 , octet of Boron is incomplete. In SiF_4 , silicon has vacant d-orbitals, by which it can accept electron pair.
- B-3.** BF_3 molecule being electron deficient gets stabilised through $p\pi-p\pi$ back bonding. whereas BH_3 removes its electron deficiency through dimerisation and thus exists as B_2H_6 .
- B-4.** sp^3 hybridised orbital of both aluminium and sp^3 hybridised orbital of carbon.
- C-1.** Very strong hydrogen bonding occurs in the alkali metal hydrogen fluorides of formula $\text{M}[\text{HF}_2]$; there is a linear symmetrical anion having an overall, F-H-F distance of 2.26 \AA .
- $[\text{F}-\text{H}-\text{F}]^- \longleftrightarrow [\text{F}-\text{H}-\text{F}]^-$
 $\text{F}^- + \text{HF} \longrightarrow [\text{FHF}]^- ; \Delta H = -161 \pm 8 \text{ kJ mol}^{-1}$
- C-2.** Deuterium is more electropositive than hydrogen. Therefore, stronger H-bonding is found in D_2O than in H_2O . D_2O is also denser than H_2O .
- C-3.** These compounds contain polar-OH groups which can form H-bonds with water.
- C-4.** In ethanol, there is H-bonding but in diethyl ether, there is no H-bonding (because O-atom is attached to C-atom) but there exists weak dipole-dipole attraction in diethyl ether.

**PART – II**

- | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| A-1. (D) | A-2. (A) | A-3. (C) | B-1. (A) | B-2. (C) |
| B-3. (B) | B-4. (B) | B-5. (B) | C-1. (D) | C-2. (D) |
| C-3. (D) | C-4. (D) | C-5. (D) | C-6. (B) | C-7. (D) |
| C-8. (C) | | | | |

PART – III

1. (A - q) ; (B - r) ; (C - s,p) ; (D - p, r)
2. (A - p, q, r, s) ; (B - p, q, r, s) ; (C - p, q, r, s) ; (D - r, s)
3. (A - r) ; (B - p, r) ; (C - p, q, r) ; (D - p, r) ; (E - p, r, s).

EXERCISE - 2**PART – I**

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (C) | 2. (B) | 3. (D) | 4. (B) | 5. (B) |
| 6. (C) | 7. (C) | 8. (A) | | |

PART – II

1. 7 (Except (b, d)

PART – III

- | | | | | |
|----------------|----------------|----------------|------------------|-----------------|
| 1. (AB) | 2. (BC) | 3. (AC) | 4. (ABCD) | 5. (ABD) |
| 6. (AB) | | | | |

PART – IV

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (B) | 2. (B) | 3. (D) | 4. (C) | 5. (C) |
| 6. (C) | 7. (D) | 8. (D) | | |

EXERCISE – 3**PART – I**

- | | | |
|---------------|---------------|---------------|
| 1. (A) | 2. (B) | 3. (A) |
|---------------|---------------|---------------|

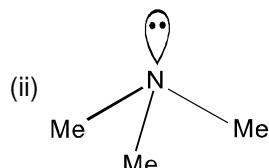
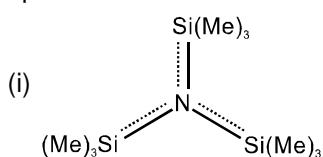
- 4.** In diethyl ether ($\text{C}_2\text{H}_5-\ddot{\text{O}}-\text{C}_2\text{H}_5$) oxygen atom has two lone pairs of electrons, thus acts as Lewis base while in anhydrous AlCl_3 aluminium has vacant 3p-orbital of valence shell and thus acts as Lewis acid. AlCl_3 accepts a lone pair of electrons from diethyl ether to complete its octet forming a complex $\text{C}_2\text{H}_5-\ddot{\text{O}}:\rightarrow \text{AlCl}_3$. Hence, anhydrous AlCl_3 is more soluble in diethyl ether by means of solvolysis in comparison to hydrous AlCl_3 (i.e., $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). Hydrous AlCl_3 is a polar compound, while ether is non-polar, so on basis of Thumb's rule, like dissolve in like solvents. Hence hydrous AlCl_3 is least soluble in ether.



5. There is inter molecular hydrogen bonding in HF and because of this it is weakly dissociated. So AlF_3 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^- ion which leads to the formation of a colourless soluble complex,
 $\text{AlF}_3 + \text{KF} \longrightarrow \text{K}_3[\text{AlF}_6]$.

BF_3 is more acidic than AlF_3 because of the small size of B than that of Al. Thus BF_3 pulls out F^- from $[\text{AlF}_6]^{3-}$ forming $[\text{BF}_4]^-$ and AlF_3 . Hence AlF_3 is precipitated on adding BF_3 to $[\text{AlF}_6]^{3-}$.
 $\text{K}_3[\text{AlF}_6] + 3\text{BF}_3 \longrightarrow 3\text{K}[\text{BF}_4] + \text{AlF}_3 \downarrow$.

6. (i) $\text{N}(\text{SiMe}_3)_3$ 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, $\text{N}(\text{SiMe}_3)_3$ with steric number three is trigonal planar.
(ii) In $\text{N}(\text{Me})_3$, 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 $\text{N}(\text{Me})_3$ with steric number four is trigonal pyramidal with a lone pair at the apex.



Hence both are not isostructural.

7. 4

PART – II

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- | | | | | |
|---------|------------|--------|--------|---------|
| 1. (4) | 2. (1) | 3. (4) | 4. (3) | 5. (3) |
| 6. (4) | 7. (2) | 8. (2) | 9. (4) | 10. (2) |
| 11. (2) | 12.* (2,4) | | | |

JEE(MAIN) OFFLINE PROBLEMS

- | | |
|--------|--------|
| 1. (3) | 2. (2) |
|--------|--------|



Chemical Bonding-IV

Section (A) : Molecular Orbital Theory (MOT)

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

- (i) Just as electrons of any atom are present in various atomic orbitals, electrons of the molecule are present in various molecular orbitals.
- (ii) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.
- (iii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**
- (iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.
- (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- (vi) Just as the electron probability distribution around a 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)

- Consider the example of H₂ molecule and label both nucleis as H_A and H_B.
- Both nucleus will have a wave function Ψ_A & Ψ_B associated to it.
- Bonding molecular orbital will be formed when both wave functions will combine in same phase.
 $\psi_m = [\Psi_A + \Psi_B]$
- Antibonding molecular orbital will be formed when both wave functions will combine in opposite phase.
 $\psi_m^* = [\Psi_A - \Psi_B]$

Note: The above equation should be regarded as the summation of the wave functions not as the mathematical addition or subtraction of wave function.

The molecular wave functions ψ_m and ψ_m^* are bonding and antibonding molecular orbitals; orbitals of this type, in which the line joining the two nuclei is a symmetry axis for the electron distribution, are known as σ orbitals if bonding and σ^* orbitals if antibonding, so we may alternatively denote them σ_{1s} and σ^*_{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.

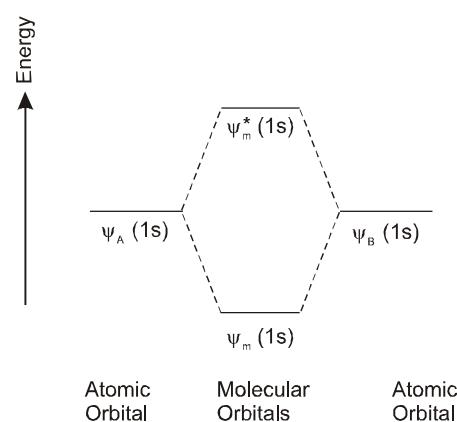


Figure: The relative energy levels of molecular orbitals and their constituent atomic orbitals for H₂.

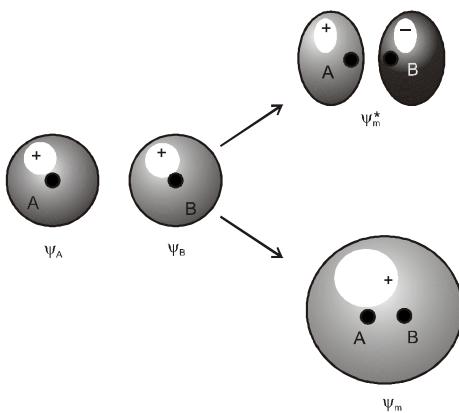


Figure : Another representation of the formation of molecular orbitals for H_2 . Since the σ and σ^* orbitals are respectively centrosymmetric and non-centrosymmetric these orbitals may also be denoted by the symbols σ_g and σ_u^* .

Molecular orbital wave functions are designated as ψ_g and ψ_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 σ and π^* molecular orbitals are gerade and σ^* and π 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 σ (sigma), π (pie), δ (delta) etc.

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

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

Difference between π molecular orbitals and the σ orbitals.

- (1) For π overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, while for σ overlap the lobes point along the line joining the two nuclei.



- (2) For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.
- (3) The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the inter nuclear line a change in the sign of lobe occurs. The π bonding orbitals are therefore ungerade, whereas all σ bonding MO's are gerade. Conversely the antibonding π MO's are gerade while all σ antibonding MO's are ungerade.

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

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

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

The increasing order of energies of various molecular orbitals for Be_2 , B_2 , C_2 , N_2 etc., is :

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

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

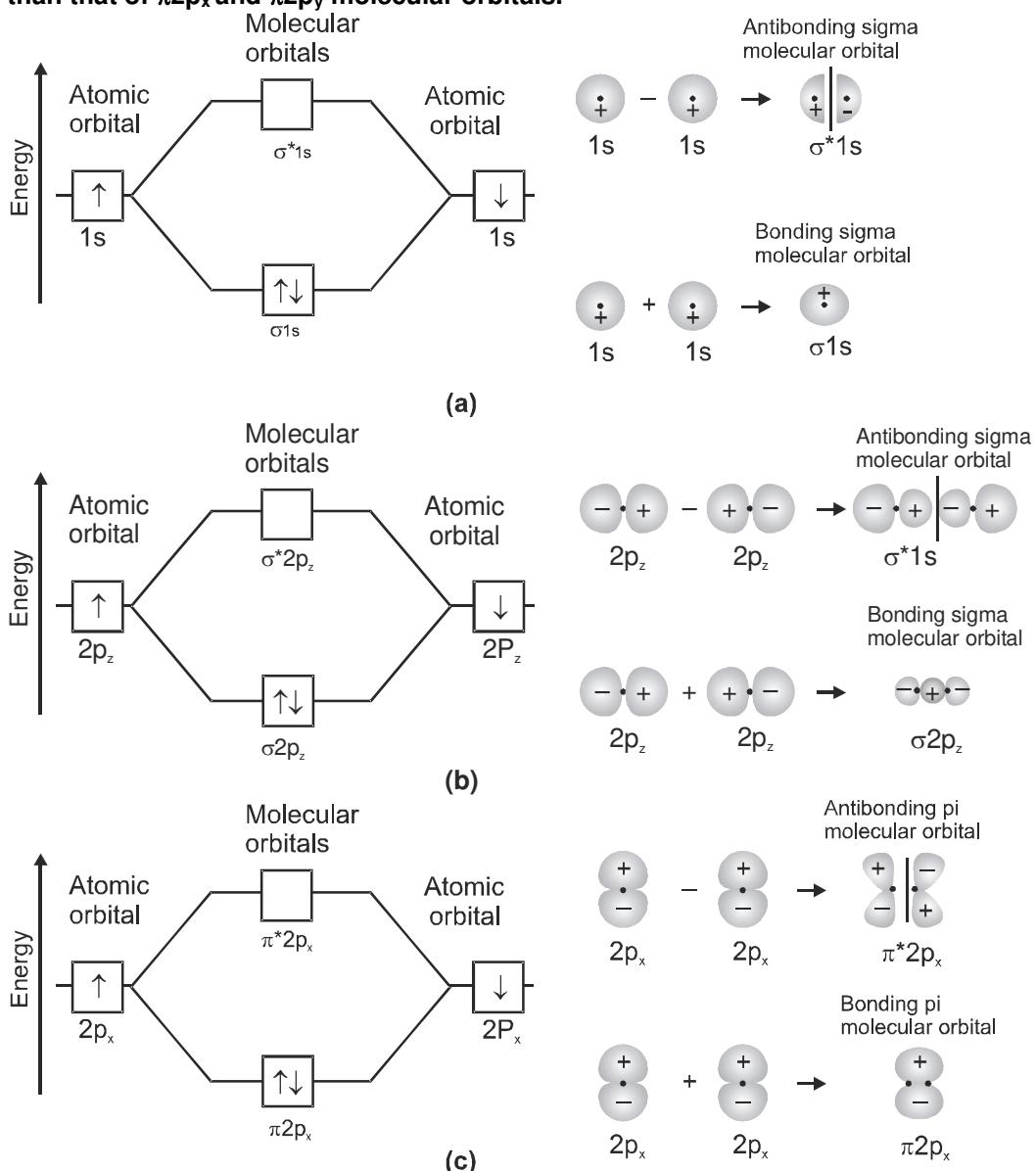


Figure : Bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) $2p_z$ atomic orbitals and (c) $2p_x$ atomic orbitals.



Section (B) : Application of MOT

ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR

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

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

BOND ORDER

$$\text{Bond order (B.O.)} = \frac{1}{2}(N_b - N_a)$$

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

BOND-LENGTH

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

MAGNETIC NATURE

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule. However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O_2 molecule.

BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

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

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

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

2. Helium molecule (He_2) : $(\sigma 1s)^2 (\sigma^*1s)^2$

$$\text{Bond order of } He_2 \text{ is } \frac{1}{2}(2 - 2) = 0$$

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. 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_2 has a very low binding energy, approximately 0.01J/mol ; for comparison, H_2 has a bond energy of 436 kJ/mol.

3. Lithium molecule (Li_2) : $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2$

Its bond order, therefore, is $1/2(4 - 2) = 1$. It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic Li_2 , the molecules are known to exist in the vapour phase. The MO model predicts a single Li-Li bond in Li_2 , in agreement with gas phase observations of the molecule.

Beryllium (Be_2) : $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2$

Be_2 has the same number of antibonding and bonding electrons and consequently a bond order of zero. Hence, like He_2 , Be_2 is not a stable chemical species.

Boron (B_2) : $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2 (\pi 2p_{1x}^1 = \pi 2p_{1y}^1) (\sigma p_z)^0$

Here is an example in which the Molecular orbital model has distinct advantage over the Lewis dot picture, B_2 is found only in the gas phase; solid boron is found in several very hard forms with complex bonding, primarily involving B_{12} icosahedra. B_2 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 σ_g (2p) orbital is expected to be lower in energy than the π_u (2p) orbitals and the resulting molecule would be diamagnetic. However, mixing of the σ_g (2s) orbital with the σ_g (2p) orbital lowers the energy of the σ_g (2s) orbital and increases the energy of the σ_g (2p) orbital to a higher level than the π orbitals, giving the order of energies shown above. As a result, the last two electrons are unpaired in the degenerate (having the same energy) π 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_2):** $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2 (\pi 2p_{x}^2 = \pi 2p_{y}^2)$ or KK $(\sigma 2s)^2 (\sigma^*2s)^2 (\pi 2p_{x}^2 = \pi 2p_{y}^2)$
 The simple MO picture of C_2 predicts a doubly bonded molecule with all electrons paired, but with both highest occupied molecular orbitals (HOMOs) having π symmetry. It is unusual because it has two π bonds and no σ bond. The bond dissociation energies of B_2 , C_2 and N_2 increase steadily, indicating single, double, and triple bonds with increasing atomic number. Although C_2 is not a commonly encountered chemical species (carbon is more stable as diamond, graphite, and the fullerenes), the acetylidate ion, C_2^{2-} , is well known, particularly in compounds with alkali metals, alkaline earths, and lanthanides. According to the molecular orbital model, C_2^{2-} 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 (acetylidate) :

Table-1

C – C Distance (pm)	
C = C (gas phase)	132
H – C ≡ C – H	120.5
CaC ₂	119.1

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 π 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 (942 kJ/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 $\sigma_g(2p)$ and $\pi_u(2p)$ are very close in energy.

The bond order of N_2 is $1/2(10 - 4) = 3$. It contains one sigma and two π bonds.

6. **Anionic nitrogen species (N_2^-):** Though 15 electrons but derived from N_2 , hence electronic configuration will be according to N_2
 Electronic configuration : $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2 (\pi 2p_{x}^2 = \pi 2p_{y}^2) (\sigma 2p_z)^2, (\pi^*2p_x)^1$

The bond order of N_2^- 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):** $(\sigma 1s)^2 (\sigma^*1s)^2 (\sigma 2s)^2 (\sigma^*2s)^2 (\sigma 2p_z)^2 (\pi 2p_{x}^2 = \pi 2p_{y}^2) (\pi^*2p_x^1 = \pi^*2p_y^1)$
 O_2 is paramagnetic. This property, as for B_2 , cannot be explained by the traditional Lewis dot structure ($\cdot\ddot{O} = \ddot{O}\cdot$), but is evident from the molecular orbital picture, which assigns two electrons to the degenerate π_g^* orbitals. The paramagnetism can be demonstrated by pouring liquid O_2 between the poles of a strong magnet; some of the O_2 will be held between the pole faces until it evaporates. The bond order of O_2 is $\frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$. So in oxygen molecule, atoms are held by a double bond.

Moreover, it may be noted that it contains two unpaired electrons in π^*2p_x and π^*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-2

	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
O_2^+ (dioxygenyl)	2.5	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 unusually long bond distance.



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 unusually long bond distance.

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

Fluorine molecule (F_2) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2)$

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_2 , O_2 , and F_2 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 $\sigma_g(2p)$ 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_2 and F_2 . The higher σ_g orbital is seen again in CO .

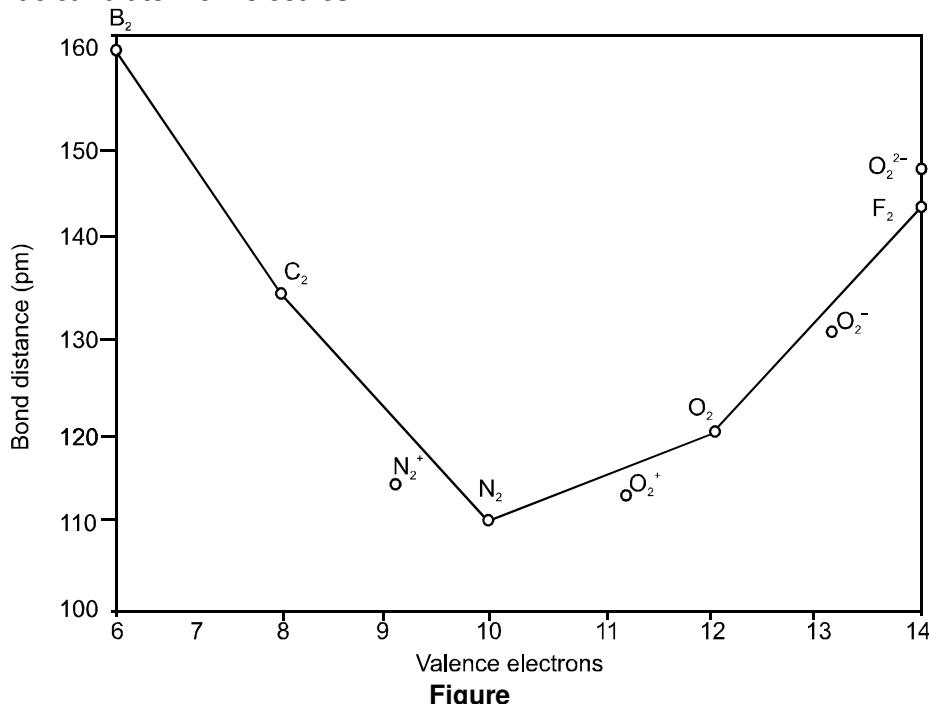
Neon molecule (Ne_2) : $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^2) (\sigma^* 2p_z)^2$

All the molecular orbitals are filled, there are equal numbers of bonding and antibonding electrons and the bond order is therefore zero. The Ne_2 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^+ , O_2^{2+} are also shown in the figure and follow a similar trend.



Figure

Solved Examples

Ex-1. Though O_2 molecule is paramagnetic yet it is a colourless gas. Why ?

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

Ex-2. Correct order of bond energy is:

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

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

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

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

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

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



Sol. (A,B,C) Species CO, CN⁻, NO⁺ are isoelectronic with 14 electrons to N₂ which has bond order of 3 (i.e. $\frac{10 - 4}{3} = 3$), so their bond order will be equal to three.

Ex-4. Which of the following are diamagnetic?

- (A) C₂ (B) O₂²⁻ (C) Li₂ (D) N₂⁺

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

Section (C) : Metallic bonding

Most metals crystallise in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electron 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 :

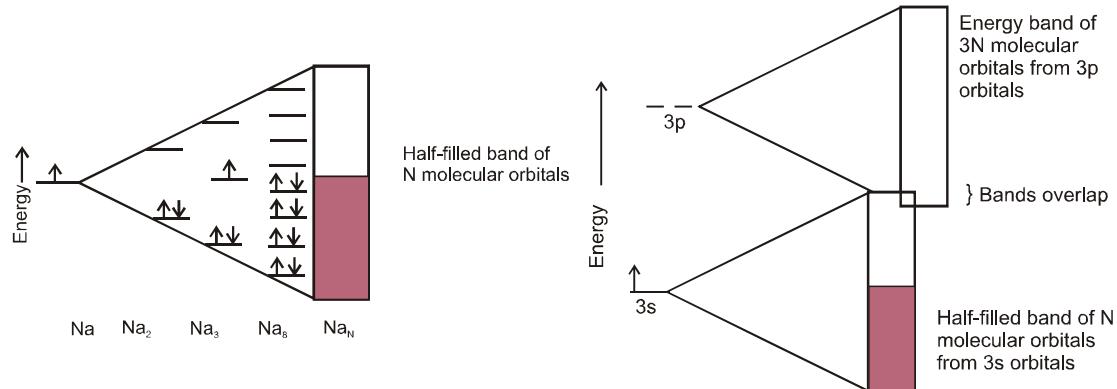


Figure : Band of orbital in crystal of sodium and overlapping of a half-filled "3s" band with an empty "3p" band of Na_n crystal

- According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band.
- A band within which (or into which) electrons must move to allow electrical conduction is called a conduction band.
- The electrical conductivity of a metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.
- Crystalline non-metals, such as diamond and phosphorus, are insulators, they do not conduct electricity. It is due to the fact that their highest-energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty band (conduction band) by an energy difference called the band gap.
- In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band.

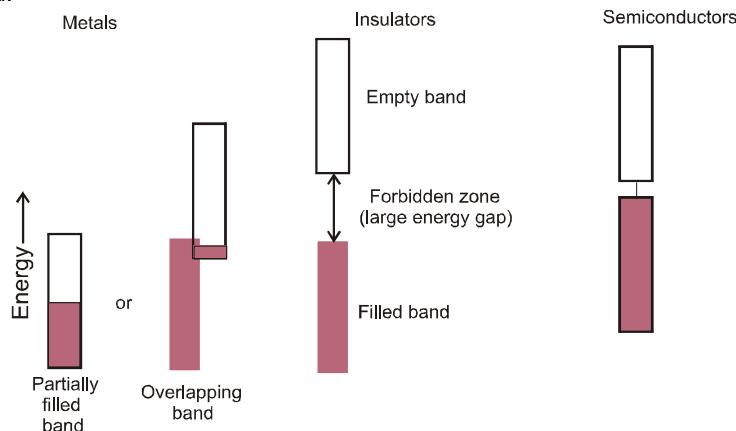




Figure : Distinction among metals, insulators and semiconductors. In each case an unshaded area represents a conduction band.

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

(B) Electron-Sea Model

- In lithium the ions would be Li^+ and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties.
- If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.
- In thermal conductivity no electrons leave or enter the metal but those in the region being heated gain kinetic energy and transfer this to other electrons.
- According to the electron-sea model, the case of deformation of metals can be thought of in this way: If one layer of metal ions is forced across another, perhaps by hammering, the internal structure remains unchanged as the sea of electrons rapidly adjusts to the new situation.

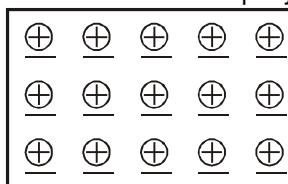


Fig. Metallic Bonding
in Electron-Sea Model

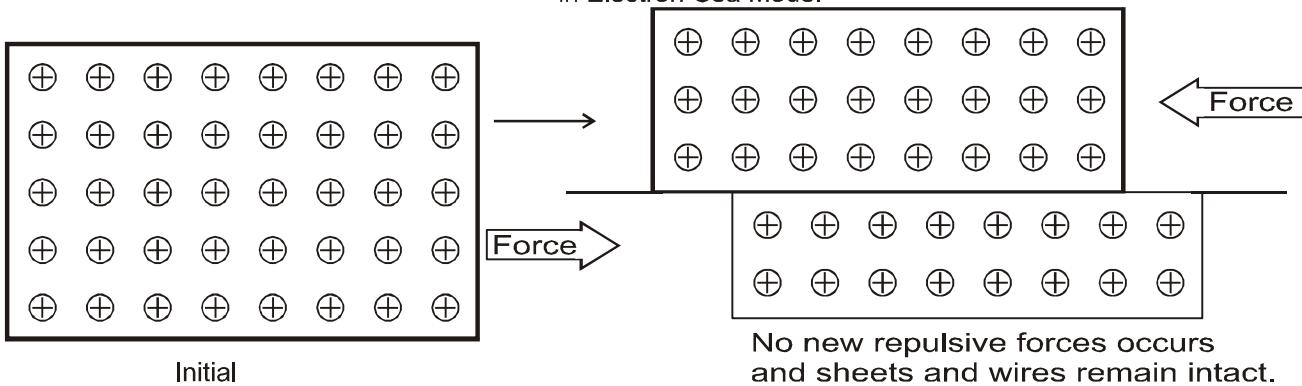


Figure : Effect of Distortion (by hammering) on Metal Sheet (assuming Electron Sea Model)

Solved Examples

Ex-5. Why transition element have high heat of atomization.

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

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Ex-1. Super oxides are coloured and paramagnetic why ?

Sol. Super oxides contain one unpaired electron in anti bonding molecular orbital and are coloured due to transition of HOMO orbital electron within visible region.

Ex-2. Of the species O_2^+ , O_2^- , O_2 and O_2^{2-} which would have the maximum bond strength ?

Sol. O_2^+ has higher bond order i.e. 2.5 than $\text{O}_2(2)$ and $\text{O}_2^-(1.5)$ and bond strength is directly proportional to bond order.



Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : MOT

A-1. Find out the bond order of :

- (a) H₂ (b) H₂⁺ (c) He₂ (d) Li₂ (e) Be₂ (f) B₂

A-2. Identify the molecules or atoms or ions from the following molecular orbital energy level formulations. The species should be selected from (B₂, C₂, O₂²⁺, O₂, F₂, N₂)

- (a) KK σ (2s)² σ^{*} (2s)² π(2p_x)¹ π(2p_y)¹
 (b) KK σ (2s)² σ^{*} (2s)² π(2p_x)² π(2p_y)²
 (c) KK σ (2s)² σ^{*} (2s)² σ(2p_z)² π(2p_x)² π(2p_y)²
 (d) KK σ (2s)² σ^{*} (2s) σ(2p_z)² π(2p_x)² π(2p_y)² π(2p_x)¹ π^{*} (2p_y)¹
 (e) KK σ (2s)² σ^{*} (2s)² σ(2p_z)² π(2p_x)² π(2p_y)² π^{*}(2p_x)² π^{*}(2p_y)²
 (f) KK σ (2s)² σ^{*} (2s)² π(2p_y)² π(2p_x)² σ(2p_z)²

A-3. What is the bond order of underlined species in NO [BF₄]?

Section (B) : Application of MOT

B-1. How would you explain that B₂ molecule is not diamagnetic?

B-2. Explain why NO⁺ is more stable towards dissociation into its atoms than NO ?

B-3. Which of the following are gerade molecular orbitals?

- (i) σ^{*}2s (ii) σ2p_z (iii) π2p_y (iv) π^{*}2p_x

B-4. Arrange following compounds in the order of increasing order of O–O bond length.

- (i) O₂ (ii) O₂[BF₄] (iii) KO₂

Section (C) : Metallic bonding

C-1. Zinc has lowest melting point in 3d-series elements. Why ?

C-2. Among Be and Li, which should have higher melting point and why ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : MOT

A-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 (B) maximum in the nodal plane
 (C) zero in the nodal plane (D) zero on the surface of the lobe

A-2. If Z-axis is the molecular axis, then π-molecular orbitals are formed by the overlap of

- (A) s + p_z (B) p_x + p_y (C) p_z + p_z (D) p_x + p_x

A-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

A-4. Which of the following pairs have identical values of bond order ?

- (A) N₂⁺ and O₂⁺ (B) F₂ and Ne₂ (C) O₂ and B₂ (D) C₂ and N₂



Section (B) : Application of MOT

Section (C) : Metallic bonding

- C-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.

C-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.

C-3. In the following metals which one has lowest probable interatomic forces
(A) Copper (B) Silver (C) Zinc (D) Mercury

PART - III : MATCH THE COLUMN

- 1. Match the following :**

	Column – I	Column – II
(A)	O_2 and NO^-	(p) Same magnetic property and bond order as that in N_2^+
(B)	O_2^+ and NO	(q) Same bond order but not same magnetic property as that in O_2
(C)	CO and CN^-	(r) Same magnetic property and bond order as that N_2^{2-}
(D)	C_2 and CN^+	(s) Same magnetic property and bond order as that in NO^+



Exercise-2

 **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

PART - II : SINGLE OR DOUBLE INTEGER TYPE



4. Which of the following have bond order less than two ?
- | | | | |
|-----------------------|------------------------|---------------------|--------------------|
| (a) NO_3^- | (b) CO_3^{2-} | (c) F_2 | (d) Cl_2 |
| (e) Br_2 | (f) O_2^{2-} | (g) O_2^- | (h) N_2^- |
| (i) O_2^{2+} | (j) Li_2^+ | (k) He_2^+ | |

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following have bond order three ?
(A) O_2^{2+} (B) NO^+ (C) CN^- (D) CN^+
2. The species which are paramagnetic is/are :
(A) NO (B) NO_2 (C) ClO_2 (D) N_2O_4
3. Which of the statement(s) are correct ?
(A) There is a single bond in FO^+
(B) The F and O are further apart in FO^- than in FO^+ .
(C) There is a double bond in FO^- .
(D) It would take more energy to break F–O bond in FO^+ than in FO^- .
4. Among the following, the species with one unpaired electron are :
(A) O_2^+ (B) NO (C) O_2^- (D) B_2
5. Identify correct statements
(A) Down the group strength of metallic bond increases nearly all in transition elements.
(B) Down the group strength of metallic bond increases in alkali metals.
(C) Down the group strength of metallic bond decreases in alkali metals.
(D) Down the group strength of metallic bond decreases in transition metals.
6. Which of the following statements are correct for band theory of metallic bond.
(A) Valence band is empty or half filled in metal.
(B) Conduction band is empty in metal
(C) Energy gap between conduction and valence band is very large in non-conductors.
(D) Overlapping of conduction & valence band occurs in semi-conductors
7. The force that binds a metal atom to a number of electrons with in its sphere of influence is known as a metallic bond. Now, which of these is /are true for this found.
(A) Metallic bond is non-directional in nature.
(B) Metallic bonds are weaker than covalent bond.
(C) Energy required to vapourise a mole of metal (say, copper) to the vapour state is larger than the energy required to vapourise a mole of a covalent substance (say, graphite)
(D) The valency electrons in a metallic bond are mobile.

PART - IV : COMPREHENSION

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_b) is greater than the number of antibonding molecular orbital electrons (N_a) 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_2 molecule does not exist 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 $\pi 2 p_x$ and $\pi 2 p_y$

2. The bromine (Br_2) is coloured because:
 - (A) the difference in energy (ΔE) between HOMO and LUMO is large and the electronic excitation takes place by absorption of light which falls in ultra violet region.
 - (B) the difference in energy (ΔE) between HOMO and LUMO is small and the electronic excitation takes place by absorption of light which falls in infrared region.
 - (C) the bromine molecule is paramagnetic and the difference in energy (ΔE) is such that the electronic excitation takes place in visible light.
 - (D) the difference in energy (ΔE) between HOMO and LUMO is such that the electronic excitation takes place by absorption of light which falls in visible region and bromine molecule is diamagnetic.

3. N_2 has greater bond dissociation energy than N_2^+ , whereas O_2 has a lower bond dissociation energy than O_2^+ 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.

Comprehension # 2

In a molten metal, the metallic bond is still present, although the order structure has been broken down. The metallic bond isn't fully broken until the metal boils. That means boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting the bond is loosened, not broken.

4. Order of boiling point of K, Ca, Sc is
 - (A) K > Ca > Sc
 - (B) Ca > K > Sc
 - (C) Sc > Ca > K
 - (D) K > Sc > Ca

5. Order of boiling point & melting point of Zn, Cd, Hg, respectively is :
 - (A) Zn > Cd > Hg & Zn > Cd > Hg
 - (B) Hg > Cd > Zn & Zn > Cd > Hg
 - (C) Hg > Cd > Zn & Hg > Cd > Zn
 - (D) Zn > Cd > Hg & Hg > Cd > Zn

Comprehension # 3

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 σ s and 3 σ^* s). This consists of a nearly continuous band of orbitals belonging to the crystal as a whole. One mole of Na atoms contributes one mole (6.02×10^{23}) of valence electrons thus, 6.02×10^{23} orbitals in the band are half-filled.

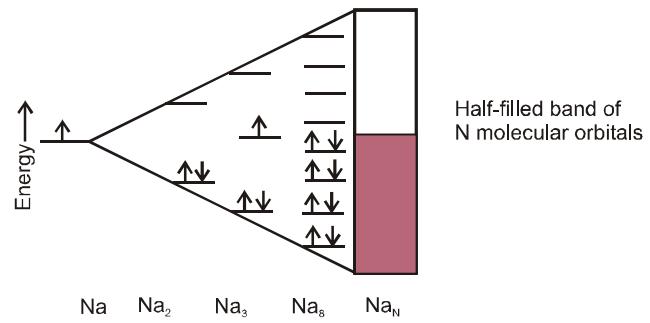


Figure-1. The band of orbitals resulting from interaction of the 3s-orbitals in a crystal of sodium



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.

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

(B)

Electron-Sea Model :

Metals have ability to conduct electricity, ability to conduct heat, ease of deformation [that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility)] and lustrous appearance. One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a "sea of electrons". In lithium the ions would be Li^+ and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

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

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

6.

Considering band model, select the incorrect statement :

- (A) Li metal should have partially filled valence band and empty conduction band.
- (B) Mg metal should have fully filled valence band and overlapping conduction band.
- (C) Electrical conductivity of a metal decreases as temperature increases.
- (D) The energy spread of each atomic energy level of an element behaving like a semiconductor is infinitesimally small.

7.

All metal written below have usually low melting points except :

- (A) Caesium
- (B) Gallium
- (C) Gold
- (D) Mercury

8.

Which of the following physical properties can be explained by electron sea model :

- (A) Electrical conduction
- (B) Thermal conduction
- (C) Malleability
- (D) All of these

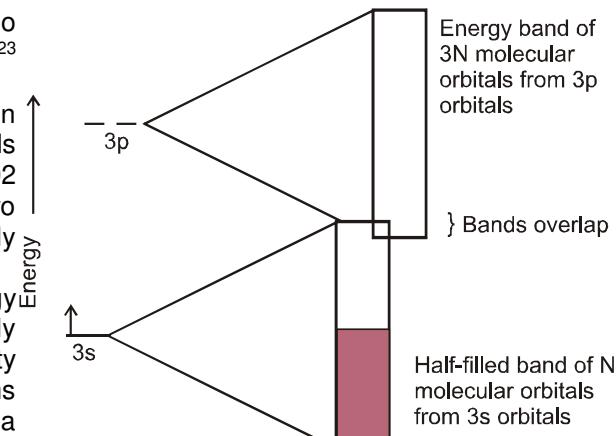


Figure-2. Overlapping of a half-filled "3s" band with an empty "3p" band of Na_N crystal

**Comprehension # 4**

Answer Q.9, Q.10 and Q.11 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents molecule, column-2 represents bond orders while column-3 represents molecule properties. Properties of molecule explained by molecular orbital theory. Like magnetic nature, orbital mixing etc.

Column 1	Column 2	Column 3
(I) B_2	(i) Bond Order = 2	(P) Diamagnetic in Nature
(II) O_2^+	(ii) Bond Order = 2.5	(Q) SP Mixing Occur
(III) F_2	(iii) Bond Order = 1	(R) Paramagnetic in Nature
(IV) C_2	(iv) Bond Order = 3	(S) Highest Occupied Molecular orbital (HOMO) is Bonding Molecular orbital (BMO)

9. Which is incorrect combination?
 (A) (I) (iii) (Q) (B) (II) (ii) (P) (C) (III) (iii) (P) (D) (IV) (i) (P)
10. Which is correct combination for Diamagnetic species ?
 (A) (III) (i) (P) (B) (IV) (ii) (R) (C) (IV) (i) (S) (D) (III) (iii) (Q)
11. Which is correct combination?
 (A) (III) (ii) (S) (B) (III) (iii) (Q) (C) (II) (ii) (P) (D) (I) (iii) (R)

Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Write the Molecular orbital electron distribution of O_2 . Specify its bond order and magnetic property.
 [JEE-2000(M), 3/135]
2. Which of the following molecular species has unpaired electron(s) ?
 (A) N_2 (B) F_2 (C) O_2^- (D) O_2^{2-}
 [JEE-2002(S), 3/150]
3. According to molecular orbital theory, which one of the following statements about the molecular species O_2^+ is correct ?
 (A) It is paramagnetic and has less bond order than O_2
 (B) It is paramagnetic and more bond order than O_2
 (C) It is diamagnetic and has less bond order than O_2
 (D) It is diamagnetic and has more bond order than O_2
 [JEE-2004(S), 3/144]
4. Arrange the following three compounds in terms of increasing O—O bond length :
 O_2 , O_2 [AsF_6], K [O_2]
 Justify your answer based on the ground state electronic configuration of the dioxygen species in these three compounds.
 [JEE-2004(M), 2/144]
5. The species having bond order different from that in CO is :
 (A) NO^- (B) NO^+ (C) CN^- (D) N_2
 [JEE-2007, 3/162]
6. Among the following, the paramagnetic compound is :
 (A) Na_2O_2 (B) O_3 (C) N_2O (D) KO_2
 [JEE-2007, 3/162]
7. **Statement-1 :** Band gap in germanium is small, because
Statement-2 : The energy spread of each germanium atomic energy level is infinitesimally small.
 (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.
 [JEE-2007, 3/162]



8. **Statement-1 :** Boron always forms covalent bond, **because**
Statement-2 : The small size of B^{3+} 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.
9. Match each of the diatomic molecules in **Column I** with its property/properties in **Column II**. [JEE-2009, 8/160]
- | Column I | Column II | [JEE-2009, 8/160] |
|-----------------|------------------------------------|-------------------|
| (A) B_2 | (p) Paramagnetic | |
| (B) N_2 | (q) Undergoes oxidation | |
| (C) O_2^- | (r) Undergoes reduction | |
| (D) O_2 | (s) Bond order ≥ 2 | |
| | (t) Mixing of 's' and 'p' orbitals | |
10. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is : [JEE-2010, 5/163]
- (A) 1 and diamagnetic
(C) 1 and paramagnetic
- (B) 0 and diamagnetic
(D) 0 and paramagnetic
11. Assuming $2s$ - $2p$ mixing is **NOT** operative, the paramagnetic species among the following is : [JEE(Advanced) 2014, 3/120]
- (A) Be_2 (B) B_2 (C) C_2 (D) N_2
12. Match the orbital overlap figures shown in List-I with the description given in List-II and select the correct answer using the code given below the lists. [JEE(Advanced) 2014, 3/120]
- | | List-I | | List-II |
|----|---------------|----|--------------------------|
| P. | | 1. | $p-d \pi$ antibonding |
| Q. | | 2. | $d-d \sigma$ bonding |
| R. | | 3. | $p-d \pi$ bonding |
| S. | | 4. | $d-d \sigma$ antibonding |
- Code :
- | | | | | | | | |
|-------|---|---|---|-------|---|---|---|
| P | Q | R | S | P | Q | R | S |
| (A) 2 | 1 | 3 | 4 | (B) 4 | 3 | 1 | 2 |
| (C) 2 | 3 | 1 | 4 | (D) 4 | 1 | 3 | 2 |
- 13.* According to Molecular orbital Theory, [JEE(Advanced) 2016, 4/124]
- (A) C_2^{2-} is expected to be diamagnetic
(B) O_2^{2+} is expected to have a longer bond length than O_2
(C) N_2^+ and N_2^- have the same bond order
(D) He_2^+ has the same energy as two isolated He atoms

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) ONLINE PROBLEMS

1. Increasing order of bond strength of O_2 , O_2^- , O_2^{2-} and O_2^+ is : [AIEEE-2002, 3/225]
- (1) $O_2^+ < O_2 < O_2^- < O_2^{2-}$
(2) $O_2 < O_2^+ < O_2^- < O_2^{2-}$
(3) $O_2^- < O_2^{2-} < O_2^+ < O_2$
(4) $O_2^{2-} < O_2^- < O_2 < O_2^+$
2. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species? [AIEEE-2004, 3/225]
- (1) Bond length in NO^+ is greater than in NO (2) Bond length in NO is greater than in NO^+
(3) Bond length in NO^+ is equal to that in NO (4) Bond length is unpredictable



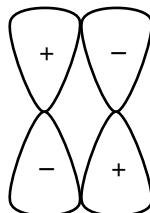
3. Which one of the following species is diamagnetic in nature ? [AIEEE-2005, 1½/225]
 (1) He_2^+ (2) H_2 (3) H_2^+ (4) H_2^-
4. Which of the following molecules/ions does not contain unpaired electrons? [AIEEE-2006, 3/165]
 (1) O_2^{2-} (2) B_2 (3) N_2^+ (4) O_2
5. Which of the following species exhibits the diamagnetic behaviour? [AIEEE-2007, 3/120]
 (1) O_2^{2-} (2) O_2^+ (3) O_2 (4) NO
6. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed ? [AIEEE-2007, 3/120]
 (1) $\text{O}_2 \longrightarrow \text{O}_2^+$ (2) $\text{N}_2 \longrightarrow \text{N}_2^+$ (3) $\text{C}_2 \longrightarrow \text{C}_2^+$ (4) $\text{NO} \longrightarrow \text{NO}^+$
7. Which one of the following pairs of species has the same bond order? [AIEEE-2008, 3/105]
 (1) CN^- and CN^+ (2) O_2^- and CN^- (3) NO^+ and CN^+ (4) CN^- and NO^+
8. Using MO theory predict which of the following species has the shortest bond length ? [AIEEE-2009, 4/144]
 (1) O_2^+ (2) O_2^- (3) O_2^{2-} (4) O_2^{2+}
- 9.* Which one of the following molecules is expected to exhibit diamagnetic behaviour ? [JEE(Main)-2013, 4/120]
 (1) C_2 (2) N_2 (3) O_2 (4) S_2
10. In which of the following pairs of molecules/ions, both the species are not likely to exist ? [JEE(Main)-2013, 4/120]
 (1) $\text{H}_2^+, \text{He}_2^{2-}$ (2) $\text{H}_2^-, \text{He}_2^{2-}$ (3) $\text{H}_2^{2+}, \text{He}_2$ (4) $\text{H}_2^-, \text{He}_2^{2+}$
11. Stability of the species Li_2 , Li_2^- and Li_2^+ increases in the order of : [JEE(Main)-2013, 4/120]
 (1) $\text{Li}_2 < \text{Li}_2^+ < \text{Li}_2^-$ (2) $\text{Li}_2^- < \text{Li}_2^+ < \text{Li}_2$ (3) $\text{Li}_2 < \text{Li}_2^- < \text{Li}_2^+$ (4) $\text{Li}_2^- < \text{Li}_2 < \text{Li}_2^+$
12. Which of the following species is not paramagnetic? [JEE(Main)-2017, 4/120]
 (1) CO (2) O₂ (3) B₂ (4) NO
13. According to molecular orbital theory, which of the following will **not** be a viable molecule ? [JEE(Main)-2018, 4/120]
 (1) H_2^- (2) H_2^{2-} (3) He_2^{2+} (4) He_2^+

JEE(MAIN) ONLINE PROBLEMS

1. Which of the following has unpaired electron(s) ? [JEE(Main) 2014 Online (09-04-14), 4/120]
 (1) N_2 (2) O_2^- (3) N_2^{2+} (4) O_2^{2-}
2. The correct order of bond dissociation energy among N_2 , O_2 , O_2^- is shown in which of the following arrangements? [JEE(Main) 2014 Online (11-04-14), 4/120]
 (1) $\text{N}_2 > \text{O}_2^- > \text{O}_2$ (2) $\text{O}_2^- > \text{O}_2 > \text{N}_2$ (3) $\text{N}_2 > \text{O}_2 > \text{O}_2^-$ (4) $\text{O}_2 > \text{O}_2^- > \text{N}_2$
3. Which one of the following molecules is paramagnetic ? [JEE(Main) 2014 Online (19-04-14), 4/120]
 (1) N_2 (2) NO (3) CO (4) O₃
4. After understanding the assertion and reason, choose the correct option.
Assertion : In the bonding molecular orbital (MO) of H₂, electron density is increased between the nuclei.
Reason : The bonding MO is $\psi_A + \psi_B$, which shows destructive interference of the combining electron waves. [JEE(Main) 2015 Online (10-04-15), 4/120]
 (1) Assertion is correct, reason is incorrect.
 (2) Assertion is incorrect, reason is correct.
 (3) Assertion and reason are correct, but reason is not the correct explanation for the assertion.
 (4) Assertion and reason are correct and reason is the correct and reason is the correct explanation for the assertion.



5. In the molecular orbital diagram for the molecular ion, N_2^+ , the number of electrons in the σ_{2p} molecular orbital is :
 (1) 0 (2) 2 (3) 3 (4) 1
 [JEE(Main) 2018 Online (15-04-18), 4/120]
6. Which of the following best describes the diagram below of a molecular orbital ?
 [JEE(Main) 2018 Online (15-04-18), 4/120]



- (1) A non-bonding orbital (2) An antibonding σ orbital
 (3) A bonding π orbital (4) An antibonding π orbital
7. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ?
 [JEE(Main) 2019 Online (09-01-19), 4/120]
 (1) Li_2^+ is unstable and Li_2^- is stable (2) Li_2^+ is stable and Li_2^- is unstable
 (3) Both are stable (4) Both are unstable
8. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic?
 [JEE(Main) 2019 Online (09-01-19), 4/120]
 (1) $\text{NO} \longrightarrow \text{NO}^+$ (2) $\text{O}_2 \longrightarrow \text{O}_2^{2-}$ (3) $\text{O}_2 \longrightarrow \text{O}_2^+$ (4) $\text{N}_2 \longrightarrow \text{N}_2^+$

**Answers****EXERCISE - 1****PART – I**

A-1. (a) 1 (b) 1/2 (c) 0 (d) 1 (e) 0 (f) 1

A-2. (a) B_2 (b) C_2 (c) O_2^{2+} (d) O_2 , (e) F_2 (f) N_2

A-3. 3

B-1. **Boron (B_2) :** B_2 is a good example of the energy level shift caused by the mixing of s and p orbitals. In the absence of mixing, the σ_g (2p) orbital is expected to be lower in energy than the π_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 π orbitals, giving the order of energies shown below. As a result, the last two electrons are unpaired in the degenerate (having the same energy) π orbitals, and the molecule is paramagnetic.
 $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_{1x} = \pi 2p_{1y}) (\sigma p_z)^0$.

B-2. NO^+ and NO are derivative of N_2 ; so NO^+ bond order = 3 and NO bond order = 2.5; B.O. \propto bond strength.

B-3. (ii) & (iv)

B-4. O–O bond length order is ii < i < iii

C-1. Weakest metallic bonding amongst the 3d-series elements \rightarrow no unpaired electrons available for metallic bonding in case of zinc.

C-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

A-1. (C)

A-2. (D)

A-3. (C)

A-4. (A)

A-5. (D)

A-6. (B)

A-7. (C)

B-1. (B)

B-2. (A)

B-3. (A)

B-4. (C)

B-5. (D)

B-6. (D)

C-1. (D)

C-2. (D)

C-3. (D)

PART – III

1. $(A - r) ; (B - p) ; (C - s) ; (D - q)$



EXERCISE – 2

PART – I

- | | | | | |
|----------------|--------|--------|--------|---------|
| 1. (A) | 2. (A) | 3. (C) | 4. (A) | 5. (D) |
| 6. (C) | 7. (A) | 8. (D) | 9. (C) | 10. (D) |
| 11. (A) | | | | |

PART – II

- | | |
|------------------------|----------------------------------|
| 1. 4 (a, b, d, g) | 2. 6 (a, b, c, d, e, f) |
| 3. 4 (ii, iv, vi, vii) | 4. 9 (a, b, c, d, e, f, g, j, k) |

PART – III

- | | | | | |
|----------|----------|---------|----------|---------|
| 1. (ABC) | 2. (ABC) | 3. (BD) | 4. (ABC) | 5. (AC) |
| 6. (BC) | 7. (ABD) | | | |

PART – IV

- | | | | | |
|----------------|--------|--------|--------|---------|
| 1. (D) | 2. (D) | 3. (B) | 4. (C) | 5. (A) |
| 6. (D) | 7. (C) | 8. (D) | 9. (B) | 10. (C) |
| 11. (D) | | | | |

EXERCISE – 3

PART – I

1. Molecular orbital electronic configuration of O₂ is as follows (Z is taken as molecular axis).

$$\sigma_{1s^2} \sigma^*_{1s^2} \sigma_{2s^2} \sigma^*_{2s^2} \sigma_{2p_z^2} \pi_{2p_x^2} = \pi_{2p_y^2} \pi^*_{2p_x^1} = \pi^*_{2p_y^1}.$$

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

As it contains two unpaired electrons in bonding π molecular orbitals O₂ is paramagnetic.

$$\text{So, Magnetic moment} = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2.83 \text{ B.M.}$$

2. (C) 3. (B)

4. The electronic configuration of O₂ will be:

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

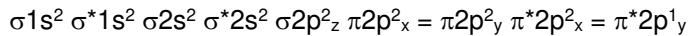
$$\text{Now bond order} = \frac{N_b - N_a}{2}$$

Where, N_b = Number of electrons in bonding orbitals

N_a = Number of electrons in antibonding orbitals

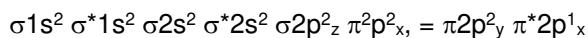
$$\text{bond order} = \frac{10 - 6}{2} = 2$$

Similarly electronic configuration of O_2^- (in KO_2) will be



$$\text{Bond order} = \frac{10 - 7}{2} = \frac{3}{2} = 1.5 \quad \text{In } O_2 [AsF_4]^- \text{, } O_2 \text{ is } O_2^+.$$

The electronic configuration of O_2^+ will be



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

Hence bond length order will be $O_2^+ < O_2 < O_2^-$ because Bond order $\propto \frac{1}{\text{Bond length}}$.

- | | | | |
|---|---------|---------|-----------|
| 5. (A) | 6. (D) | 7. (C) | 8. (A) |
| 9. (A) - p, q, r, t ; (B) - q, r, s, t ; (C) - p, q, r ; (D) - p, q, r, s | | | |
| 10. (A) | 11. (C) | 12. (C) | 13.* (AC) |

PART – II

JEE(MAIN) OFFLINE PROBLEMS

- | | | | | |
|---------|---------|---------|------------|---------|
| 1. (4) | 2. (2) | 3. (2) | 4. (1) | 5. (1) |
| 6. (4) | 7. (4) | 8. (4) | 9.* (1, 2) | 10. (3) |
| 11. (2) | 12. (1) | 13. (2) | | |

JEE(MAIN) ONLINE PROBLEMS

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (2) | 2. (3) | 3. (2) | 4. (1) | 5. (4) |
| 6. (4) | 7. (3) | 8. (1) | | |



Chemical Bonding-V

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.

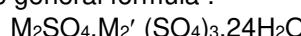
General properties of ionic compounds :

- (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.



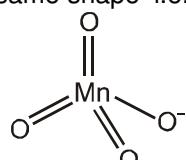
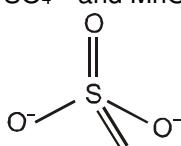
Conditions for isomorphism

- (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 :

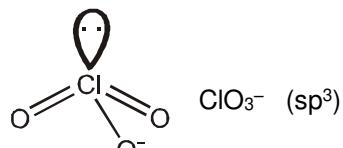
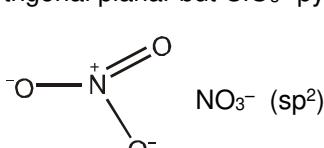


M = monovalent ; M' = trivalent

- (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_3 & NaClO_3 they have same formula type yet they are not isomorphous because NO_3^- is trigonal planar but ClO_3^- pyramidal.



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

- (c) **Electrical conductivity :** Ionic 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.



Solved Examples

Ex-1. Arrange in order of increasing ionic radii in water and their mobility : Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} .

Sol. (i) Size \propto 1/degree of hydration (i.e. with increase in size, number of water molecules around central metal ions decrease). So order of increasing radii is $\text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$.

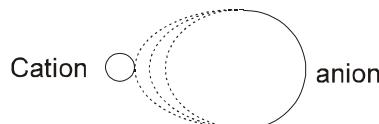
(ii) Heavily hydrated ions move slowly so the order of increasing mobility is

$$\text{Be}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}.$$

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

Covalent character in ionic compounds (Fajan's rule) :

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



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

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

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

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

Size of cation α 1 / polarisation.

$$\text{e.g., } \text{BeCl}_2 \quad \text{MgCl}_2 \quad \text{CaCl}_2 \quad \text{SrCl}_2 \quad \text{BaCl}_2$$

→ Size of cation increases Polarisation decreases Covalent character decreases

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

Size of anion α polarisation

$$\text{e.g., } \text{LiF} \quad \text{LiCl} \quad \text{LiBr} \quad \text{LiI}$$

→ – Size of anion increases
– Polarisation increases
– Covalent character increases

(iii) **Charge on cation :** Higher is the oxidation state of cation, more will be the deformation of anion and thus, more will be covalent character in compound.

Charge on cation α polarisation.

$$\text{e.g., } \text{NaCl} \quad \text{MgCl}_2 \quad \text{AlCl}_3$$

→ – Charge of cation increases
– Polarisation increases
– Covalent character increases

(iv) **Charge on anion :** Higher is the charge on anion more will be the polarisation of anion and thus more will be covalent character in the compound.

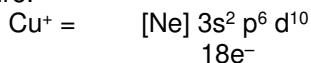
Charge on anion α polarisation.

$$\text{e.g., } \text{AlF}_3 \quad \text{Al}_2\text{O}_3 \quad \text{AlN}$$

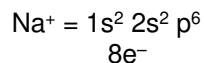
→ – Charge on anion increases
– Polarisation increases
– Covalent character increases



- (v) **Pseudo inert gas configuration of cation :** Cation having pseudo inert gas configuration has more polarizing power than the cation that has inert gas configuration. Thus NaCl having inert gas configuration will be more ionic whereas CuCl having pseudo inert gas configuration will be more covalent in nature.



Pseudo inert gas configuration
(poor shielding of d-electrons)



Inert gas configuration
(more shielding of s and p electrons)

Application & Exceptions of Fajan's Rules :

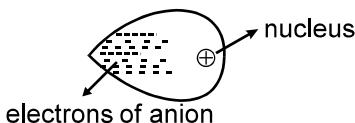
- (i) Ag_2S is less soluble than Ag_2O in H_2O because Ag_2S is more covalent due to bigger S^{2-} ion.
- (ii) $\text{Fe}(\text{OH})_3$ is less soluble than $\text{Fe}(\text{OH})_2$ in water because Fe^{3+} is smaller than Fe^{2+} and thus charge is more.
- (iii) Therefore, $\text{Fe}(\text{OH})_3$ is more covalent than $\text{Fe}(\text{OH})_2$.

The colour of some compounds can be explained on the basis of polarisation of their bigger negative ions.

For example :

AgCl is white AgBr , AgI , Ag_2CO_3 are yellow. Similarly, SnCl_2 is white but SnI_2 is black. PbCl_2 is white but PbI_2 is yellow.

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



Figure

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

BeCl_2 , MgCl_2 , CaCl_2 , SrCl_2 , BaCl_2

—————>—————>

Ionic character increases, melting point increases ; since size of cation increases & size of anions is constant.

CaF_2 , CaCl_2 , CaBr_2 , CaI_2

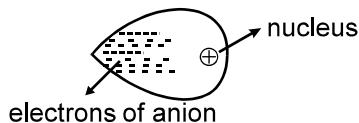
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Covalent character increase, melting point decrease ; since size of anions increase & size of cations is constant.

Solved Examples

- Ex-2.** AgCl is colourless whereas AgI is yellow, because of :

- (A) Ag^+ have 18 electron shell to screen the nuclear charge.
- (B) Ag^+ shows pseudo inert gas configuration.
- (C) distortion of I^- is more pronounced than Cl^- ion.
- (D) existence of d-d transition.



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

Section (B) : Dipole moment.

Polarity of bonds :

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

When a covalent bond is formed between two similar atoms, for example in H_2 , O_2 , Cl_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.

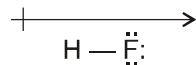
As a result of polarisation, the molecule possesses the **dipole moment** which can be defined as the product of magnitude of the partial charge (δ^+ or δ^-) developed on any of the covalently bonded atoms and the distance between two atoms.

Dipole moment (μ) = Magnitude of charge (q) \times distance of separation (d)

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

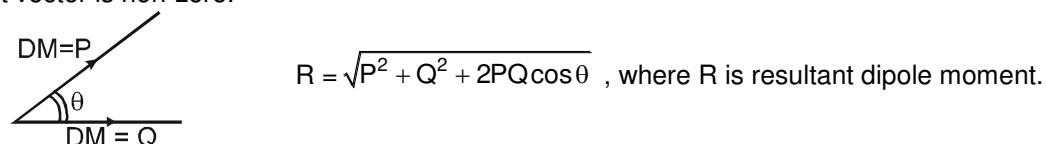
- $1 \text{ D} = 3.33564 \times 10^{-30} \text{ Cm}$, where C is coulomb and m is meter.
- $1 \text{ Debye} = 10^{-18} \text{ e.s.u. cm}$.

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

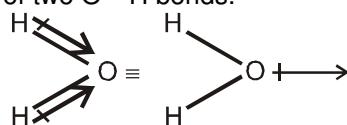


The shift in electron density is represented by crossed arrow ($\overrightarrow{\text{+}}$) above the Lewis structure to indicate the direction of the shift.

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.



For example of H_2O molecule, which has a bent structure, the two O—H bonds are oriented at an angle of 104.5° . Net dipole moment of $6.17 \times 10^{-30} \text{ Cm}$ ($1 \text{ D} = 3.33564 \times 10^{-30} \text{ Cm}$) is the resultant of the dipole moments of two O—H bonds.



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

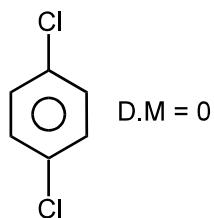
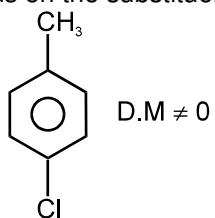
○ **Following compounds have zero dipole moment :**

$\text{BF}_3, \text{CO}_2, \text{SO}_3, \text{CF}_4, \text{PF}_5(\text{g}), \text{SF}_6, \text{XeF}_2, \text{CS}_2, \text{CCl}_4, \text{PCl}_5(\text{g}), \text{XeF}_4$

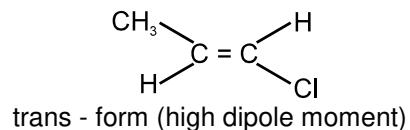
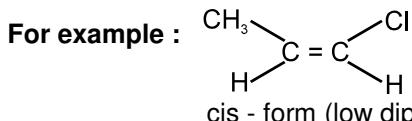
○ **Some important orders**

HF	$>$	HCl	$>$	HBr	$>$	HI
1.92 D		1.08		0.78		0.38
CH_3Cl	$>$	CH_2Cl_2	$>$	CHCl_3	$>$	CCl_4
1.86		1.6		1.0		0

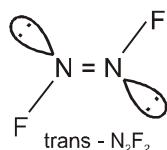
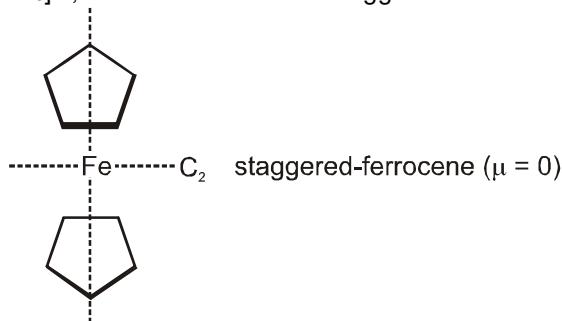
○ Usually for disubstituted Benzene order is o > m > p
But it all depends on the substituents



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



- 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 $[\text{CoF}_6]^{3-}$, 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.
- If molecule have $\mu = 0$, then it should be linear or having symmetrical geometry.
e.g. linear – CO_2 , CS_2 , $\text{BeCl}_2(\text{g})$; symmetrical geometry – BF_3 , CH_4 , PCl_5 , SF_6 , IF_7 , XeF_4 .
- If molecule has $\mu \neq 0$ then it should be angular or having unsymmetrical geometry.
 SnCl_2 , PbCl_2 , SO_2 , angular molecular geometry.
 NH_3 , H_2O , NF_3 , SF_4 , H_2S , unsymmetrical molecular geometry.
- % Ionic character =
$$\frac{\mu_{\text{Experimental}}}{\mu_{\text{Theoretical}}} \times 100 = \frac{\mu_{\text{Observed}}}{\mu_{(100\% \text{ ionic compound})}} \times 100$$

Solved Examples

Ex-3. The resultant dipole moment of water is 1.85 D ignoring the effects of lone pair. Calculate, the dipole moment of each OH bond (given that bond angle in $\text{H}_2\text{O} = 104^\circ$, $\cos 104^\circ = -0.25$).

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

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

$$(1.85)^2 = 2x^2 - \frac{x^2}{2} \Rightarrow \frac{3x^2}{2} \therefore x = 1.51 \text{ D}$$

Ex-4. For HCl molecule observed dipole moment is 1.03 D and bond length is 1.275 Å. Calculate % ionic character.

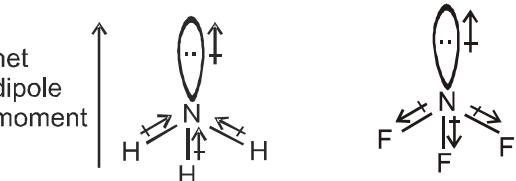
Sol. Dipole moment = $4.8 \times 10^{-18} \times 1.275 \times 10^{-8} = 4.8 \times 1.275$

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

Ex-5. Why NH_3 is having more dipole moment than NF_3 .

Sol. In NH_3 molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards Nitrogen atom but in NF_3 molecule.

Fluorine is more electronegative than Nitrogen so the net dipole moment is towards fluorine atoms. In NH_3 the bond pair moments and lone pair moments are in the same direction while in NF_3 the lone pair moment and bond pair moments are in opposite direction.

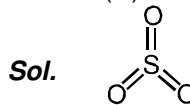




Ex-6. The geometry of SO_3 and its dipole moment are :

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

Ans. (C)



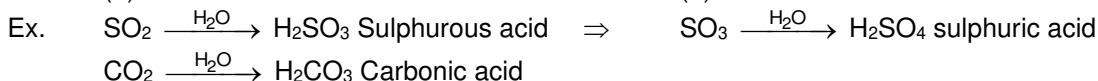
Sol. The steric number of sulphur = 3; so hybridisation is sp^2 . There is no lone pair on sulphur atom, therefore, according to VSEPR theory, the repulsions between the bond pairs of electrons will be similar. Hence the molecule will be symmetrical (trigonal planar) with zero dipole moment.

Section (C) : Acidic and basic character

Types of Oxides and acidic / basic nature of oxyacids and hydronium acid :

(a) Acidic oxides

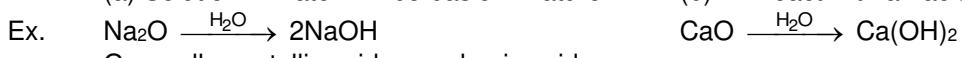
- (a) Solution in water will be acidic in nature



Generally non-metallic oxides are acidic oxides

(b) Basic oxides

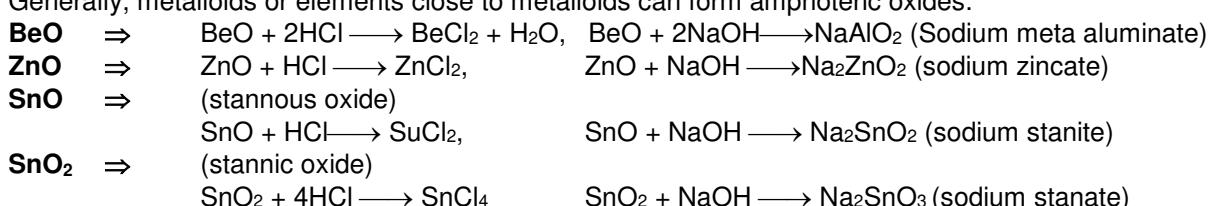
- (a) Solution in water will be basic in nature



(c) Amphoteric oxides

Can react with an acid as well as with a base.

Ex. Generally, metalloids or elements close to metalloids can form amphoteric oxides.



(d) Neutral oxides : will not react with acids or bases



(e) Amphiprotic oxide : which can accept and release H^+ ions

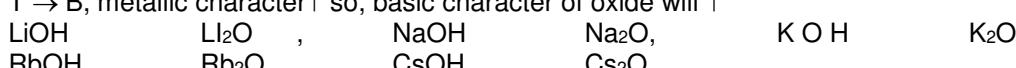
Ex. $\Rightarrow \text{H}_2\text{O}$

Periodicity in nature of oxides

(a) L \rightarrow R, metallic character \downarrow and non-metallic character \uparrow . So, basic character of oxides \downarrow and acidic character \uparrow

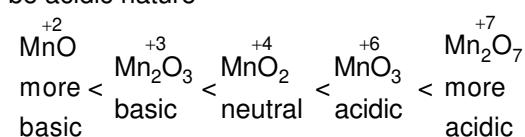
	Na_2O strongly basic	MgO basic	Al_2O_3 Amph	SiO_2 weakly acidic	P_2O_5 acidic	SO_3 strongly acidic	Cl_2O_7 strongly acidic
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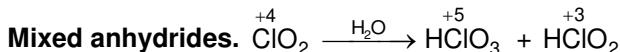
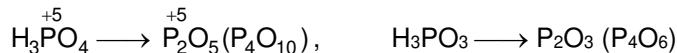
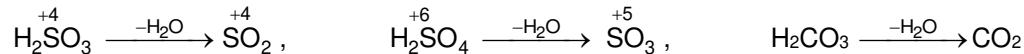
(b) T \rightarrow B, metallic character \uparrow so, basic character of oxide will \uparrow



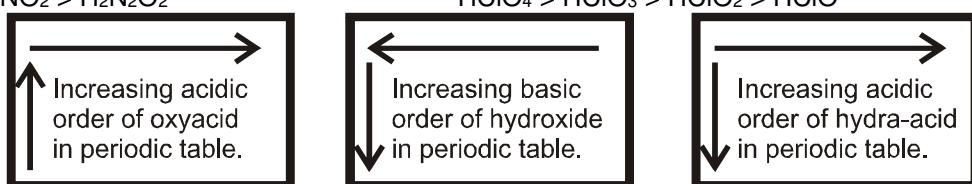
Basic character increases down the group

(c) If the same element is forming oxides in diff oxidation states, then greater the oxidation no greater will be acidic nature



**oxides are anhydrides of oxyacid or hydroxides****For oxy acids**

- (a) On moving **L → R** non-metallic character ↑ acidic strength↑
 $\text{H}_3\text{BO}_3 < \text{H}_2\text{CO}_3 < \text{HNO}_3 < \text{H}_2\text{SiO}_3 < \text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4$
- (b) On moving **T → B**, non-metallic character ↓ acidic strength ↓
 $\text{HNO}_3 > \text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4 > \text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$
- (c) If same element is forming oxycids in different oxidation states then, Greater the oxidation no. of the element greater will be the acidic strength
 $\text{HNO}_3 > \text{HNO}_2 > \text{H}_2\text{N}_2\text{O}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

**MISCELLANEOUS SOLVED PROBLEMS (MSPS)**

Ex-1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :

- (a) SiSi bond in $\text{Cl}_3\text{SiSiCl}_3$ (b) SiCl bond in $\text{Cl}_3\text{SiSiCl}_3$
 (c) CaF bond in CaF_2 (d) NH bond in NH_3

Sol. (a) Covalent, due to identical electronegativity.

(b) Polar covalent, due to less electronegativity difference.

(c) Ionic, due to more electronegativity difference.

(d) Polar covalent, due to different electronegativity.

Ex-2. (a) Which one has highest and lowest melting point and why?

NaCl KCl RbCl CsCl

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

$\text{CsF} > \text{CsCl} > \text{CsBr} > \text{CsI}$.

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

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

Ex-3. Which of the compounds MgCO_3 and ZnCO_3 is thermally more stable ? Explain.

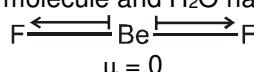
Sol. Mg^{+2} has less polarising power due to inert gas configuration while Zn^{+2} has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn^{+2} with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the CO_3^{2-} ion and as such the metal carbonate (ZnCO_3) gets readily decomposed into CO_2 and the oxide of the metal, ZnO . Thus ZnCO_3 is less stable than MgCO_3 .

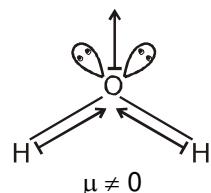
Ex-4. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?

Sol. 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.

Ex-5. Why BeF_2 has zero dipole moment whereas H_2O has some dipole moment ?

Sol. BeF_2 has linear molecule and H_2O has bent molecule.





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Ex-6. Why crystals of hydrated calcium sulphate are soft and easily cleaved whereas anhydrous calcium sulphate are very hard and difficult to cleave ?

Sol. With in the Ca^{2+} / SO_4^{2-} layer 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 weak H-bonds link SO_4^{2-} ion in the intermediate region.

Ex-7. A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is equal to 1.0 Å then the fraction of an electronic charge on each atom is :

Ans. (A)

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

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

Ex-8. The dipole moment of KCl is 3.336×10^{-29} Coulomb meter. The interionic distance in KCl is 2.6\AA . Find the % ionic character in KCl.

Sol. 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

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

Ex-9. The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67×10^{-8} cm. Calculate the percentage ionic character in KCl molecule.

Sol. Dipole moment of compound would have been completely ionic

$$= (4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-8} \text{ cm}) = 12.8 \text{ D}$$

$$\text{so \% ionic character} = \frac{10.0}{12.8} \times 100\% = 78.125\% \approx 78\% \text{ Ans.}$$



Exercise-1

Marked questions are recommended for Revision.

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, Na₃N and Na₂O (b) NaCl, MgCl₂, AlCl₃, SiCl₄ and PCl₅

A-2. SnCl₄ has melting point - 15°C where as SnCl₂ has melting point 535°C. Why?

A-3. SnCl₂ is white but SnI₂ is red. Why ?

Section (B) : Dipole moment

B-1. Inorganic benzene is more reactive than organic benzene. Why?

B-2. trans-1, 2 dichloro ethene have zero dipole moment while its cis- form has some dipole moment. Explain.

B-3. Why CCl₄ have zero dipole moment but CHCl₃ have some dipole moment ?

B-4. Arrange in increasing order of dipole moment ; H₂O, H₂S, BF₃.

B-5. Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character in LiF molecule Li—F bond length is 156 pm.

Section (C) : Acidic & basic character

C-1. (a) Write the formula of anhydride of the following acids :

- (i) Nitrous acid (HNO₂) (ii) Sulphuric acid (H₂SO₄)

- (b) What are amphoteric oxides ? Give 2 examples.

C-2. Arrange in the increasing order of acidic character : CO₂, N₂O₅, SiO₂, SO₃.

C-3. Arrange in the increasing order of basic character : MgO, SrO, K₂O, NiO, Cs₂O

PART - II : ONLY ONE OPTION CORRECT TYPE

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

A-1. Which of the following is in order of increasing covalent character ?

- (A) CCl₄ < BeCl₂ < BCl₃ < LiCl (B) LiCl < CCl₄ < BeCl₂ < BCl₃
 (C) LiCl < BeCl₂ < BCl₃ < CCl₄ (D) LiCl < BeCl₂ < CCl₄ < BCl₃

A-2. Which of the following combination of ion will have highest polarisation ?

- (A) Fe²⁺, Br⁻ (B) Ni⁴⁺, Br⁻ (C) Ni²⁺, Br⁻ (D) Fe, Br⁻

A-3. The correct order of decreasing polarizability of ion is :

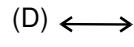
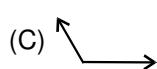
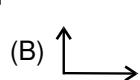
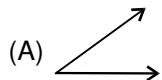
- (A) Cl⁻, Br⁻, I⁻, F⁻ (B) F⁻, I⁻, Br⁻, Cl⁻ (C) I⁻, Br⁻, Cl⁻, F⁻ (D) F⁻, Cl⁻, Br⁻, I⁻

A-4. SnCl₄ is a covalent liquid because :

- (A) electron clouds of the Cl⁻ ions are weakly polarized to envelop the cation.
 (B) electron clouds of the Cl⁻ 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.

Section (B) : Dipole moment

B-1. Which has maximum dipole moment ?





PART - III : MATCH THE COLUMN

- 1. Match the column:**

	Column-I		Column-II
(A)	CsCl, CsBr, CsI	(p)	Increasing order of covalent character
(B)	LiOH, NaOH, KOH	(q)	Decreasing order of thermal stability
(C)	LiH, NaH, KH	(r)	Decreasing order of lattice energy
(D)	Mg ₃ N ₂ , Ca ₃ N ₂ , Sr ₃ N ₂	(s)	Increasing order of thermal stability
		(t)	Increasing order of ionic character

Exercise-2

 Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Among the following compounds the one that is polar and has central atom with sp^3 hybridisation is :
(A) H_2CO_3 (B) SiF_4 (C) BF_3 (D) $HClO_2$

2. Which of the following are polar.
(A) XeF_4 (B) SO_3 (C) $XeOF_4$ (D) ICl_4^-



3. Which of the following statements is true?
 (A) The dipole moment of NF_3 is zero (B) The dipole moment of NF_3 is less than NH_3
 (C) The dipole moment of NF_3 is more than NH_3 (D) The dipole moment of NH_3 is zero
4. Which of the following would be expected to have a dipole moment of zero on the basis of symmetry?
 (A) SOCl_2 (B) OF_2 (C) SeF_6 (D) ClF_5
5. If molecule MX_3 has Zero dipole moment, the hybrid orbitals used by M (Atomic No. < 21) are
 (A) Pure p (B) sp hybrid (C) sp^2 hybrid (D) sp^3 hybrid
6. Which of the following are incorrect for dipole moment ?
 (A) Lone pair of elements present on central atom can give rise to dipole moment
 (B) Dipole moment is vector quantity
 (C) $\text{PF}_5(g)$ molecule has non zero dipole moment
 (D) Difference in electronegativities of combining atom can lead to dipole moment
7. Which of the following has minimum melting point
 (A) CsF (B) HCl (C) HF (D) LiF
8. Which of the following is false ?
 (A) Van der Waals forces are responsible for the formation of molecular crystals.
 (B) Branching lowers the boiling points of isomeric organic compounds due to reduction in the van der Waals force of attraction.
 (C) In graphite, van der Waals forces act between the carbon layers.
 (D) Boiling point of NH_3 is greater than SbH_3 .
9. Which of the following contains both electrovalent and covalent bonds ?
 (A) CH_4 (B) H_2O_2 (C) NH_4Cl (D) none
10. The correct order of the increasing ionic character is :
 (A) $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$ (B) $\text{BeCl}_2 < \text{MgCl}_2 < \text{BaCl}_2 < \text{CaCl}_2$
 (C) $\text{BeCl}_2 < \text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2$ (D) $\text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BeCl}_2$
11. Least melting point is shown by the compound :
 (A) PbCl_2 (B) SnCl_4 (C) NaCl (D) AlCl_3
12. CuI_2 is unstable even at ordinary temperature because :
 (A) the Cu^{2+} ion with a comparatively small radius has a strong polarising power.
 (B) the Cu^{2+} ion with a 17 electron outer shell has weak polarising power.
 (C) the I^- ion with a larger radius has a high polarisability.
 (D) both (A) and (C)

PART - II : SINGLE OR DOUBLE INTEGER TYPE

1. Find total no. of polar molecules.
 (a) PF_3Cl_2 (b) SF_4 (c) PCl_5 (d) PCl_3F_2
 (e) SF_6 (f) XeF_2 (g) NO_2^+ (h) BF_2Cl (i) BF_3
2. How many of the following compounds are planar as well as non polar compound :
 (a) C_3O_2 (b) $\text{CH}_2=\text{C}=\text{CH}_2$ (c) BF_3 (d) CCl_4
 (e) SF_6 (f) XeF_4 (g) IF_5 (h) IF_7
 (i) SF_4 (j) ClF_3
3. How many of the following are correct orders of property indicated against it ?
 (i) $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ (order of polarizability)
 (ii) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ (order of polarising power)
 (iii) $\text{Li}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$ (order of polarising power)
 (iv) $\text{LiI} > \text{NaI} > \text{KI}$ (order of ionic character)
 (v) $\text{Agl} > \text{AgBr} > \text{AgCl}$ (order of solubility in water)
 (vi) (Si-Si bond) Si > SiO_2 (Si-O bond) (order of % covalent character of bond).



4. How many of the following oxides are acidic ?
- | | | | |
|------------------------------------|------------------------------------|-----------------------|----------------------|
| (a) Mn ₂ O ₇ | (b) SO ₂ | (c) CO | (d) N ₂ O |
| (e) NO ₂ | (f) PbO ₂ | (g) Na ₂ O | (h) CrO ₃ |
| (i) ZnO | (j) Fe ₂ O ₃ | (k) SiO ₂ | (l) SnO |

PART - III : ONE OR MORE THAN ONE OPTION CORRECT TYPE

1. The halogen form compounds among themselves with formula XX', XX'₃, XX'₅ and XX'₇ where X is the heavier halogen. Which of the following pairs representing their structures and being polar and non-polar are correct?
- (A) XX' – Linear – polar
 - (B) XX'₃ – T-shaped – polar
 - (C) XX'₅ – square pyramidal – polar
 - (D) XX'₇ – Pentagonal bipyramidal – non-polar
2. Which of the following is/are correct statement(s) for dipole moment ?
- (A) Lone pair of electrons present on central atom can give rise to dipole moment.
 - (B) Dipole moment is vector quantity.
 - (C) CO₂ molecule has dipole moment.
 - (D) Difference in electronegativities of combining atoms can lead to dipole moment.
3. Which of the following are polar ?
- | | | | |
|----------------------|----------------------|-----------------------|-----------------------------------|
| (A) XeF ₄ | (B) XeF ₆ | (C) XeOF ₄ | (D) XeF ₅ ⁻ |
|----------------------|----------------------|-----------------------|-----------------------------------|
4. Which of the following compounds contain(s) both ionic and covalent bonds?
- | | | | |
|------------------------|---------|--|----------|
| (A) NH ₄ Cl | (B) KCN | (C) CuSO ₄ ·5H ₂ O | (D) NaOH |
|------------------------|---------|--|----------|
5. Which of the following factors do not favour electrovalency ?
- | | |
|----------------------------------|----------------------------------|
| (A) Low charge on ions | (B) High charge on ions |
| (C) Large cation and small anion | (D) Small cation and large anion |
6. 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.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

The degree of polarity of a covalent compound is measured by the dipole moment (μ_{bond}) of the bond defined as:

$$\mu_{\text{bond}} = \text{Charge on one of the poles} \times \text{bond length}$$

μ_{bond} is a vector quantity. The dipole moment of a molecule is the vector addition of all the bond dipole moments present in it. For a triatomic molecule, containing two bond's like H₂O, μ_{molecule} is given by

$$\mu^2_{\text{molecule}} = \mu^2_{\text{bond}} + \mu^2_{\text{bond}} + 2\mu_{\text{bond}} \cdot \mu_{\text{bond}} \cos \theta$$

θ = bond angle

The % ionic character of a bond is calculated using the equations

$$\% \text{ ionic character} = \frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100$$

μ_{ionic} = dipole moment when the molecule is assumed to be completely ionic.

1. Which of the following molecule has non-zero dipole moment -
- | | | | |
|----------------------|----------------------|-------------------------------------|----------------------|
| (A) XeF ₂ | (B) ClF ₃ | (C) XeO ₂ F ₄ | (D) XeF ₄ |
|----------------------|----------------------|-------------------------------------|----------------------|



Comprehension # 2

Molecular geometry is the general shape of a molecule as determined by the relative positions of the atomic nuclei. VSEPR model predicts the shape of the molecules & ions in which valence shell electron pairs are arranged about the atom as far away from one another as possible, thus minimizing pair repulsion information about the geometry of a molecule can sometimes be obtained from an experimental quantity called dipole moment.

Comprehension # 3

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^+ is more than K^+ .

8. Arrange the following compounds in increasing order of their ionic character :
 SnCl_2 , SnCl_4 , SiCl_4 , SnF_4 , SnF_2

- (A) $\text{SnF}_2 < \text{SnCl}_2 < \text{SnF}_4 < \text{SnCl}_4 < \text{SiCl}_4$ (B) $\text{SnF}_2 < \text{SnCl}_2 < \text{SnF}_4 < \text{SnCl}_4 < \text{SiCl}_4$

- (C) $\text{SiCl}_4 < \text{SnCl}_4 < \text{SnF}_4 < \text{SnCl}_2 < \text{SnF}_2$ (D) $\text{SnCl}_4 < \text{SnF}_4 < \text{SnCl}_2 < \text{SnF}_2 < \text{SiCl}_4$

- (A) $\text{BeF}_2 < \text{BeCl}_2 < \text{BeBr}_2 < \text{Bel}_2$
 (B) $\text{BeCl}_2 < \text{BeF}_2 < \text{Bel}_2 < \text{BeBr}_2$
 (C) $\text{Bel}_2 < \text{BeBr}_2 < \text{BeCl}_2 < \text{BeF}_2$
 (D) $\text{Bel}_2 < \text{BeCl}_2 < \text{BeBr}_2 < \text{BeF}_2$

- 10.** Which of the following combination of cation and anion has maximum covalent character.
(A) K^+ , Cl^- (B) Na^+ , Cl^- (C) Cs^+ , Cl^- (D) Mg^{+2} , Cl^-

**Comprehension # 4**

Answer 11, 12 and 13 by appropriately matching the information given in the three columns of the following table.

According to Fajan covalency is favoured by :

- (i) Small size of cation
- (ii) Large size of anion
- (iii) High charge on cation, anion or both
- (iv) Cation with non-noble gas configuration

Column-1		Column-2		Column-3	
(I)	NaF, NaCl, NaBr, NaI	(i)	Size of cation increases	(P)	Covalent character increases
(II)	NaCl, MgCl ₂ , AlCl ₃	(ii)	Size of anion increases	(Q)	Ionic character increases
(III)	MgCO ₃ , CaCO ₃ , SrCO ₃ , BaCO ₃	(iii)	Charge on anion increases	(R)	Melting point increases
(IV)	LiOH, NaOH, KOH, RbOH	(iv)	Charge density decreases (Magnitude)	(S)	Solubility increases

11. Which of the following combination is incorrect ?

(A) I, ii, P	(B) I, iv, P	(C) I, ii, R	(D) IV, i, S
--------------	--------------	--------------	--------------
12. Which of the following is correct combination ?

(A) II, i, P	(B) II, iv, Q	(C) III, iv, D	(D) III, i, Q
--------------	---------------	----------------	---------------
13. The incorrect combination is

(A) III, iv, Q	(B) IV, iv, S	(C) IV, iv, Q	(D) III, iv, P
----------------	---------------	---------------	----------------

Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Arrange the following compounds in order of increasing dipole moment toluene (I), m-dichlorobenzene (II), o-dichlorobenzene (III), p-dichlorobenzene (IV) :

(A) I < IV < II < III	(B) IV < I < II < III	(C) IV < I < III < II	(D) IV < II < I < III
-----------------------	-----------------------	-----------------------	-----------------------

[IIT JEE 1996]
2. Which contains both polar and non-polar bonds ?

(A) NH ₄ Cl	(B) HCN	(C) H ₂ O ₂	(D) CH ₄
------------------------	---------	-----------------------------------	---------------------

[IIT JEE 1997]
3. The geometry of H₂S and its dipole moment are :

(A) angular and non-zero	(B) angular and zero
(C) linear and non-zero	(D) linear and zero

[IIT JEE 1999]
- 4.* The molecules that will have dipole moment are

(A) 2, 2-dimethyl propane	(B) trans-2-pentene
(C) cis-3-hexene	(D) 2, 2, 3, 3-tetramethyl butane

[IIT JEE 1992]
5. The correct order of acidic strength is :

(A) Cl ₂ O ₇ > SO ₃ > P ₄ O ₁₀	(B) CO ₂ > N ₂ O ₅ > SO ₃
(C) Na ₂ O > MgO > Al ₂ O ₃	(D) K ₂ O > CaO > MgO

[JEE-2000, 1/135]



6. The set with correct order of acidity is : [JEE-2001, 1/135]
 (A) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 (B) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
 (C) $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$
 (D) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
7. Identify the correct order of acidic strengths of CO_2 , CuO , CaO , H_2O . [JEE-2002, 3/150]
 (A) $\text{CaO} < \text{CuO} < \text{H}_2\text{O} < \text{CO}_2$
 (B) $\text{H}_2\text{O} < \text{CuO} < \text{CaO} < \text{CO}_2$
 (C) $\text{CaO} < \text{H}_2\text{O} < \text{CuO} < \text{CO}_2$
 (D) $\text{H}_2\text{O} < \text{CO}_2 < \text{CaO} < \text{CuO}$
- 8.* The correct statement(s) regarding, (i) HClO , (ii) HClO_2 , (iii) HClO_3 and (iv) HClO_4 is(are)
 (A) The number of $\text{Cl}=\text{O}$ bonds in (ii) and (iii) together is two [JEE(Advanced) 2015, 4/168]
 (B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
 (C) The hybridization of Cl in (iv) is sp^3
 (D) Amongst (i) to (iv), the strongest acid is (i)

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Which one of the following is an amphoteric oxide? [AIEEE-2003, 3/225]
 (1) ZnO (2) Na_2O (3) SO_2 (4) B_2O_3 .
2. Which of the following pair of molecules will have permanent dipole moments for both members? [AIEEE-2003, 3/225]
 (1) SiF_4 and NO_2 (2) NO_2 and CO_2 (3) NO_2 and O_3 (4) SiF_4 and CO_2
3. Among Al_2O_3 , SiO_2 , P_2O_3 and SO_2 the correct order of acid strength is : [AIEEE-2004, 3/225]
 (1) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{SO}_2 < \text{P}_2\text{O}_3$ (2) $\text{SiO}_2 < \text{SO}_2 < \text{Al}_2\text{O}_3 < \text{P}_2\text{O}_3$
 (3) $\text{SO}_2 < \text{P}_2\text{O}_3 < \text{SiO}_2 < \text{Al}_2\text{O}_3$ (4) $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{P}_2\text{O}_3 < \text{SO}_2$
4. 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^+ , Ca^{2+} , Mg^{2+} , Be^{2+} ? [AIEEE-2007, 3/120]
 (1) $\text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+}$ (2) $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+$
 (3) $\text{Mg}^{2+} < \text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+}$ (4) $\text{Be}^{2+} < \text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$
5. Among the following the maximum covalent character is shown by the compound : [AIEEE-2011, 4/120]
 (1) FeCl_2 (2) SnCl_2 (3) AlCl_3 (4) MgCl_2
6. For which of the following molecule significant $\mu \neq 0$? [JEE(Main)-2014, 4/120]
 (i)
 (ii)
 (iii)
 (iv)
 (1) Only (i) (2) (i) and (ii) (3) Only (iii) (4) (iii) and (iv)
7. In the following reactions, ZnO is respectively acting as a/an : [JEE(Main)-2017, 4/120]
 (a) $\text{ZnO} + \text{Na}_2\text{O} \longrightarrow \text{Na}_2\text{ZnO}_2$ (b) $\text{ZnO} + \text{CO}_2 \longrightarrow \text{ZnCO}_3$
 (1) base and base (2) acid and acid (3) acid and base (4) base and acid



JEE(MAIN) ONLINE PROBLEMS

1. Amongst LiCl, RbCl, BeCl₂ and MgCl₂ the compounds with the greatest and the least ionic character respectively are : [JEE(Main) 2014 Online (19-04-14), 4/120]
(1) LiCl and RbCl (2) RbCl and BeCl₂ (3) MgCl₂ and BeCl₂ (4) RbCl and MgCl₂

2. Which of the alkaline earth metal halides given below is essentially covalent in nature ? [JEE(Main) 2015 Online (11-04-15), 4/120]
(1) SrCl₂ (2) CaCl₂ (3) BaCl₂ (4) MgCl₂

3. Molecular AB has a bond length of 1.61 Å and a dipole moment of 0.38 D. The fractional charge on each atom (absolute magnitude) is : ($e_0 = 4.802 \times 10^{-10}$ esu) [JEE(Main) 2015 Online (11-04-15), 4/120]
(1) 0.5 (2) 0.05 (3) 0 (4) 1.0

4. Which intermolecular force is most responsible in allowing xenon gas to liquefy? [JEE(Main) 2016 Online (09-04-16), 4/120]
(1) Instantaneous dipole-induced dipole (2) Ionic
(3) Ion-dipole (4) Dipole-dipole

5. Which of the following is a Lewis acid ? [JEE(Main) 2018 Online (15-04-18), 4/120]
(1) PH₃ (2) NF₃ (3) NaH (4) B(CH₃)₃

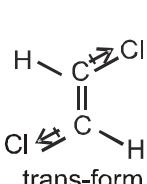


Answers

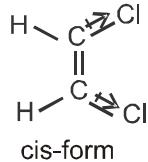
EXERCISE - 1

PART - I

- A-1.** (a) $\text{NaF} < \text{Na}_2\text{O} < \text{Na}_3\text{N}$ (b) $\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3 < \text{SiCl}_4 < \text{PCl}_5$
- 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.
- A-3.** Bigger anion has higher polarisability; more polarisation greater is the intensity of colour (valence shell electrons are loosely bound with the nucleus).
- B-1.** Inorganic benzene ($\text{N}_3\text{B}_3\text{H}_6$) contains polar covalent B –N bonds while benzene (C_6H_6) contains non-polar covalent C–C bonds.



B-2. Two chlorine atom lie opposite direction, so net dipole moment will be zero



Two chlorine atom lie on the same side of $\text{C} = \text{C}$. So there will be some net dipole moment

B-3. CCl_4 is a symmetrical and non polar molecule while CHCl_3 is an unsymmetrical and polar molecule.

B-4. $\text{BF}_3 < \text{H}_2\text{S} < \text{H}_2\text{O}$.

B-5. 84.5%

C-1. (a) (i) N_2O_3 (ii) SO_3

C-2. As ΔE_n (difference in electronegativities between element and oxygen) decreases, the acidic character increases. So, $\text{SiO}_2 < \text{CO}_2 < \text{N}_2\text{O}_5 < \text{SO}_3$.

C-3. Higher the metallic character, greater will be the basic character of its oxide as ΔE_n (difference in electronegativities between element and oxygen) increases.
So, $\text{NiO} < \text{MgO} < \text{SrO} < \text{K}_2\text{O} < \text{Cs}_2\text{O}$

PART - II

- | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| A-1. (C) | A-2. (B) | A-3. (C) | A-4. (B) | B-1. (A) |
| B-2. (C) | B-3. (B) | B-4. (D) | B-5. (A) | B-6. (A) |
| B-7. (B) | C-1. (C) | C-2. (C) | C-3. (A) | C-4. (D) |
| C-5. (A) | | | | |

PART - III

1. $(A - p, q, r) ; (B - s, t) ; (C - q, r, t) ; (D - s, t)$

EXERCISE - 2**PART - I**

- | | | | | |
|----------------|----------------|---------------|---------------|----------------|
| 1. (D) | 2. (C) | 3. (B) | 4. (C) | 5. (C) |
| 6. (C) | 7. (B) | 8. (D) | 9. (C) | 10. (A) |
| 11. (B) | 12. (D) | | | |

PART - II

- | | | | |
|-----------------------|-----------------------|-------------------------|-----------------------------|
| 1. 3 (a, b, h) | 2. 3 (a, c, f) | 3. 3 (i, ii, vi) | 4. 5 (a, b, e, h, k) |
|-----------------------|-----------------------|-------------------------|-----------------------------|

PART - III

- | | | | | |
|------------------|-----------------|----------------|------------------|----------------|
| 1. (ABCD) | 2. (ABD) | 3. (BC) | 4. (ABCD) | 5. (BD) |
| 6. (ABCD) | | | | |

PART - IV

- | | | | | |
|----------------|----------------|----------------|---------------|----------------|
| 1. (B) | 2. (B) | 3. (C) | 4. (C) | 5. (C) |
| 6. (D) | 7. (A) | 8. (C) | 9. (A) | 10. (D) |
| 11. (C) | 12. (D) | 13. (D) | | |

EXERCISE - 3**PART - I**

- | | | | | |
|---------------|---------------|-----------------|-----------------|---------------|
| 1. (B) | 2. (C) | 3. (A) | 4.* (BC) | 5. (A) |
| 6. (A) | 7. (A) | 8.* (BC) | | |

PART - II**JEE(MAIN) OFFLINE PROBLEMS**

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (1) | 2. (3) | 3. (4) | 4. (1) | 5. (3) |
| 6. (4) | 7. (3) | 8. (1) | | |

JEE(MAIN) ONLINE PROBLEMS

- | | | | | |
|---------------|---------------|---------------|---------------|---------------|
| 1. (2) | 2. (3) | 3. (2) | 4. (1) | 5. (4) |
|---------------|---------------|---------------|---------------|---------------|



Additional Problems for Self Practice (APSP)

 **Marked questions are recommended for Revision.**

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

1. The test is of **1 hour** duration.
 2. The Test Booklet consists of **30** questions. The maximum marks are **120**.
 3. Each question is allotted **4 (four)** marks for correct response.
 4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **$\frac{1}{4}$ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
 5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- 12.** Which of the following is non-polar :
 (1) NF_3 (2) BF_3 (3) PF_3 (4) SF_4

13. Strongest hydrogen bond present in :
 (1) O—H ----- S (2) S—H ----- O (3) F—H ----- F (4) F—H ----- O

14. Resonance structure of a molecule should not have
 (1) Identical bond position (2) Identical arrangements of atoms
 (3) Nearly the same energy content (4) The same number of paired electrons

15. The paramagnetic property of oxygen is well explained by :
 (1) Molecular orbital theory (2) Resonance theory
 (3) Valence bond theory (4) VSEPR theory

16. Which of the following statement is correct regarding molecular orbital theory (MOT) :
 (1) Energy of bonding orbital is less than anti-bonding orbital.
 (2) Energy of bonding orbital is more than anti-bonding orbital.
 (3) Bonding orbitals are monocentric.
 (4) Bonding orbital follow $n + \ell$ rule

17. PF_2Cl_3 is non polar because :
 (1) P—Cl bond is non-polar (2) Its dipole moment is zero
 (3) P—Cl bond is polar (4) P & Cl have equal electronegativity

18. The hybrid states of central atom in diborane, diamond and graphite are respectively :
 (1) sp^2 , sp^3 , sp^2 (2) sp^3 , sp^3 , sp^2 (3) sp^3 , sp^3 , sp^3 (4) sp , sp^2 , sp^3

19. Which of the set of species have same hybridization state but different shapes:-
 (1) NO_2^+ , NO_2 , NO_2^- (2) ClO_4^- , SF_4 , XeF_4
 (3) NH_4^+ , H_3O^+ , OF_2 (4) SO_4^{2-} , PO_4^{3-} , ClO_4^-

20. The bonds present in N_2O_5 are :
 (1) Only ionic (2) Covalent & coordinate
 (3) Only covalent (4) Covalent & ionic

21. The correct statement for the reaction:

$$\text{NH}_3 + \text{H}^+ \longrightarrow \text{NH}_4^+$$

 (1) Hybridisation state is changed (2) Bond angle increases
 (3) NH_3 act as a Lewis acid (4) Regular geometry becomes irregular

22. The correct order of decreasing polarisability of ions is :
 (1) $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{F}^-$ (2) $\text{F}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$
 (3) $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (4) $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

23. CCl_4 is more covalent than LiCl because :
 (1) There is more polarization of Cl in CCl_4 (2) There is more polarization of Cl in LiCl
 (3) CCl_4 has more weight (4) All of the above

24. An ionic compound $\text{A}^+ \text{B}^-$ is most likely to be formed when -
 (1) Ionization energy of A is low (2) Electron affinity of B is high
 (3) Electron affinity of B is low (4) Both (1) and (2)

25. Which of the following statements regarding HClO_3 is/are correct.
 (1) oxidation state of chlorine is +5 (2) it has two $\text{p}\pi\text{-d}\pi$ bonds
 (3) it has two type of Cl—O bond (4) all of these

26. The correct sequence of increasing covalent character is represented by -
 (1) $\text{BeCl}_2 < \text{NaCl} < \text{LiCl}$ (2) $\text{NaCl} < \text{LiCl} < \text{BeCl}_2$ (3) $\text{BeCl}_2 < \text{LiCl} < \text{NaCl}$ (4) $\text{LiCl} < \text{NaCl} < \text{BeCl}_2$

27. Correct order of bond length is :
 (1) N—H > P—H > Sb—H (2) N—H < P—H < Sb—H (3) P—H > N—H > Sb—H (4) Sb—H > N—H > P—H

28. Which of the following species contains three bond pairs and one lone pair around the central atom ?
 (1) NH_2^- (2) PCl_3 (3) H_2O (4) BF_3



Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I



12. Which of the following pairs has the strongest hydrogen bonding between themselves ? [NSEC-2002]
 (A) SiH₄ and SiF₄
 (B) CH₄ and CH₃OH
 (C) CH₃COCH₃ and CHCl₃
 (D) HCO₂H and CH₃CO₂H
13. SF₆ molecule hasgeometry. [NSEC-2002]
 (A) pyramidal
 (B) bi-pyramidal
 (C) tetrahedral
 (D) octahedral
14. Isosteres are compounds having similar geometry and isoelectronic species are species having the same number of electrons. The pair of species CO₂ and NO₂⁺ is [NSEC-2003]
 (A) isosteric and isoelectronic
 (B) isosteric, but not isoelectronic
 (C) isoelectronic, but not isosteric
 (D) neither isosteric nor isoelectronic.
15. Considering z-axis to be the internuclear axis, the combination of orbitals on Li and Cl atoms respectively, that can lead to a stable sigma bond [NSEC-2003]
 (A) 2s and 3p_y
 (B) 1s and 3p_y
 (C) 1s and 3p_z
 (D) 2s and 3p_z.
16. The number of hydrogen bonds formed by each H₂O molecule in an ice crystal is : [NSEC-2003]
 (A) 6
 (B) 4
 (C) 2
 (D) 3
17. The structures of AlCl₃ and PCl₃ can be described as [NSEC-2004]
 (A) both planar
 (B) both pyramidal
 (C) planar and pyramidal respectively
 (D) pyramidal and planar respectively.
18. Bond orders of NO and NO⁺ are respectively [NSEC-2004]
 (A) 2.5 and 3
 (B) 2 and 4
 (C) 3.5 and 2.5
 (D) 4 and 2
19. The molecule with non -zero dipole moment is [NSEC-2004]
 (A) BF₃
 (B) PCl₃
 (C) SiCl₄
 (D) XeF₄
20. The molecular orbital with highest energy in a nitrogen molecule is [NSEC-2004]
 (A) σ_{2p}
 (B) π_{2p}
 (C) σ^{*}_{2p}
 (D) π^{*}_{2p}
21. Which of the following has zero dipole moment ? [NSEC-2005]
 (A) NH₃
 (B) NF₃
 (C) BF₃
 (D) CHCl₃.
22. According to VSEPR theory the shape of SF₄ molecule is (atomic number of sulphur=16) [NSEC-2005]
 (A) squashed tetrahedral
 (B) square pyramidal
 (C) tetrahedral
 (D) square planar.
23. In which of the following cases, does breaking of the covalent bond take place? [NSEC-2005]
 (A) boiling of water
 (B) melting of KCN
 (C) boiling of CF₄
 (D) melting of SiO₂.
24. The hybrid orbitals used by chlorine in ClF₃ molecule are of the type [NSEC-2005]
 (A) sp³
 (B) sp²
 (C) sp²d
 (D) sp³d.
25. In solid CuSO₄. 5H₂O, copper is coordinated to [NSEC-2005]
 (A) one water molecule
 (B) three water molecules
 (C) five water molecules
 (D) four water molecules.
26. Which of the following contain maximum number of electrons in the antibonding molecular orbital? [NSEC-2005]
 (A) O₂²⁻
 (B) O₂
 (C) O₂⁻
 (D) O₂⁺.
27. Identify the molecule that has more covalent bond character. [NSEC-2005]
 (A) Na₂S
 (B) MgCl₂
 (C) NaH
 (D) SnCl₄
28. The non-linear molecule is [NSEC-2006]
 (A) SO₂
 (B) CO₂
 (C) HCN
 (D) C₂H₂.
29. In the ammonium ion,
 (A) the four hydrogens are at the corners of a square
 (B) all bonds are ionic
 (C) the nitrogen atom carries a formal charge
 (D) all bonds are co-ordinate ones. [NSEC-2006]



- 30.* Lewis dot structures of compounds of representative elements normally follow the octet rule.
Which of the following does not obey the octet rule ? [NSEC-2006]
 (A) CO_3^{2-} (B) O_3 (C) SO_2 (D) I_3^-
31. Trisilylamine N ($\text{Si}(\text{CH}_3)_3$)₃ is [NSEC-2006]
 (A) acidic (B) basic (C) neutral (D) amphoteric.
32. Which of the following compounds of phosphorus does not have resonating structures ? [NSEC-2006]
 (A) H_3PO_2 (B) H_3PO_3 (C) H_3PO_4 (D) $(\text{CH}_3)_2\text{HPO}_3$.
33. In thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$, the oxidation states of sulphur atoms are [NSEC-2006]
 (A) + II , + II (B) 0, + IV (C) + I , + III (D) -II , + VI.
34. Which type of bond exists between the two boron atoms in a diborane molecule ? [NSEC-2007]
 (A) 2-Center-2-electron (B) 3-Center-2-electron
 (C) 3-Center-3-electron (D) 4-Center-4-electron
35. According to Molecular Orbital Theory, the oxygen molecule is- [NSEC-2007]
 (A) Diamagnetic (B) Paramagnetic (C) Ferromagnetic (D) non magnetic
36. Which of the following has zero dipole moment? [NSEC-2007]
 (A) NH_3 (B) NF_3 (C) BF_3 (D) CHCl_3
37. Which of the following pairs is a Lewis acid & a Lewis base ? [NSEC-2007]
 (A) Cl^- & Ag^+ (B) NH_3 & BF_3 (C) SO_4^{2-} & HSO_4^- (D) H^+ & OH^-
38. Assuming a Lewis structure for SO_2 in which all the atoms obey the octet rule, the formal charge on S is: [NSEC-2007]
 (A) +1 (B) 0 (C) +2 (D) 2
39. In which of the following pairs are both molecules polar ? [NSEC-2008]
 (A) O_2 and H_2O (B) BF_3 and PCl_3 (C) SO_2 and SCl_2 (D) CS_2 and NO_2
40. The maximum possible number of hydrogen bonds a water molecule can form is [NSEC-2008]
 (A) 2 (B) 4 (C) 3 (D) 1
41. Which of the following has the highest bond order ? [NSEC-2008]
 (A) O_2 (B) O_2^+ (C) O_2 (D) O_2^{2-}
42. The hybridization of the atomic orbitals of sulphur in SO_3 , SO_4^{2-} and SF_4 are respectively: [NSEC-2009]
 (A) sp, sp³, sp² (B) sp, sp², sp³d (C) sp², sp, sp³ (D) sp², sp³, sp³d
43. The molecule which does not have a net dipole moment is – [NSEC-2009]
 (A) H_2O (B) NH_3 (C) BF_3 (D) BrF_5
44. The molecular geometry for ammonia is – [NSEC-2009]
 (A) saw horse (B) trigonal planar (C) tetrahedral (D) pyramidal
45. The sequence of molecular orbitals for the carbide ion (C_2^{2-}) is – [NSEC-2009]
 (A) $\sigma 1s^2$ σ^*1s^2 $\sigma 2s^2$ σ^*2s^2 $\pi 2p^4$
 (B) $\sigma 1s^2$ σ^*1s^2 $\sigma 2s^2$ σ^*2s^2 $\pi 2p^4$ $\sigma 2p^2$
 (C) $\sigma 1s^2$ σ^*1s^2 $\sigma 2s^2$ σ^*2s^2 $\pi 2p^4$ $\sigma 2p^2$ π^*2p^2
 (D) $\sigma 1s^2$ σ^*1s^2 $\sigma 2s^2$ σ^*2s^2 $\pi 2p^4$ $\sigma 2p^2$ π^*2p^4
46. The structure of SF_4 is [NSEC-2010]
 (A) Trigonal bipyramidal (B) Square planar
 (C) Squashed Tetrahedral (D) Octahedral
47. The pair which contains both molecules polar is [NSEC-2010]
 (A) O_2 & H_2O (B) CO_2 & PCl_3 (C) SO_2 & SCl_2 (D) CS_2 & NO_2
48. The species that contains maximum number of electrons in the antibonding molecular orbitals is : [NSEC-2010]
 (A) O_2^{2-} (B) O_2 (C) O_2^- (D) O_2^+



49. The compound that has the highest ionic character associated with the X-Cl bond is [NSEC-2010]
 (A) PCl_5 (B) BCl_3 (C) CCl_4 (D) SiCl_4
50. According to VSEPR theory the shape of IF_5 molecule will be [NSEC-2011]
 (A) tetrahedral (B) trigonal bipyramidal (C) square pyramid (D) trigonal planar
51. The formal charges on the atoms underlined are [NSEC-2011]
 $\text{C}_6\text{H}_5 - \underline{\text{C}}=\underline{\text{N}}-\underline{\text{O}}$
 (A) C = 0, N = -1, O = +1 (B) C = -1, N = +1, O = -1
 (C) C = 0, N = +1, O = -1 (D) C = +1, N = 0, O = -1
52. The compound that **does not** have a π bond is : [NSEC-2011]
 (A) SO_2 (B) SF_6 (C) O_2 (D) SO_3
53. The C–O–C bond angle in dimethylether is [NSEC-2011]
 (A) $109^\circ 28'$ (B) 110° (C) 120° (D) 180°
54. The relative basic strengths of NH_3 , CH_3NH_2 and NF_3 are in the order : [NSEC-2012]
 (A) $\text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{NF}_3$ (B) $\text{NH}_3 > \text{CH}_3\text{NH}_2 > \text{NF}_3$
 (C) $\text{NF}_3 > \text{CH}_3\text{NH}_2 > \text{NH}_3$ (D) $\text{CH}_3\text{NH}_2 > \text{NF}_3 > \text{NH}_3$
55. The molecule that has maximum covalent character : [NSEC-2012]
 (A) NaH (B) Na_2S (C) CaCl_2 (D) SnCl_4
56. Which of the following compounds has zero dipole moment ? [NSEC-2013]
 (A) NH_3 (B) NF_3 (C) BF_3 (D) CHCl_3
57. Which one of the following is not a valid structure for dinitrogen oxide ? [NSEC-2013]
- (I) $\begin{array}{c} \text{N} \equiv \text{N} \equiv \text{O} \\ \cdot \quad \cdot \end{array}$ (II) $\begin{array}{c} \text{N} \equiv \text{N} \equiv \text{O} \\ \cdot \quad \cdot \end{array}$
 (III) $\begin{array}{c} \text{N} \equiv \text{N} \equiv \text{O} \\ \cdot \quad \cdot \end{array}$ (IV) $\begin{array}{c} :\text{N} \quad \text{N} \equiv \text{O}: \\ \cdot \quad \cdot \end{array}$
- (A) I (B) II (C) III (D) IV
58. The bond order of NO^+ ion is : [NSEC-2013]
 (A) 1 (B) 2 (C) 2.5 (D) 3
59. Which of the following molecular structures is NOT possible ? [NSEC-2013]
 (A) OF_2 (B) SF_2 (C) OF_4 (D) SF_4
60. The molecule having the highest dipole moment is [NSEC-2014]
 (A) CO_2 (B) CH_4 (C) NH_3 (D) NF_3
- 61.* The species which has triangular planar geometry is [NSEC-2014]
 (A) NF_3 (B) NO_3^- (C) AlCl_3 (D) SbH_3
62. The correct order of stability for the following species is [NSEC-2014]
 (A) $\text{Li}_2 < \text{He}_2^+ < \text{O}_2^+ < \text{C}_2$ (B) $\text{C}_2 < \text{O}_2^+ < \text{Li}_2 < \text{He}_2^+$
 (C) $\text{He}_2^+ < \text{Li}_2 < \text{C}_2 < \text{O}_2^+$ (D) $\text{O}_2^+ < \text{C}_2 < \text{Li}_2 < \text{He}_2^+$
63. The hybridization of boron in the stable borane having the lowest molecular weight is – [NSEC-2014]
 (A) sp^2 (B) sp^3 (C) sp (D) sp^3d
64. For SF_4 , the molecular geometry and hybridization of the central atom respectively are: [NSEC-2014]
 (A) Square planar, dsp^2 (B) Tetrahedral, sp³
 (C) Seesaw, sp^3d (D) Square pyramid, sp^3d
65. The species that cannot exist is [NSEC-2014]
 (A) SiF_6^{2-} (B) BF_6^{3-} (C) SF_6 (D) AlF_6^{3-}
66. The species having highest bond energy is [NSEC-2015]
 (A) O_2 (B) O_2^+ (C) O_2^- (D) O_2^{2-}





- 67.** The structure of a molecule of $\text{N}(\text{SiMe}_3)_3$ is [NSEC-2015]
 (A) Pyramidal with angle close to 110°
 (B) T-shaped with angle 90°
 (C) Bent T-shaped with angle close to 89°
 (D) Trigonal planar with bond angle close to 120°
- 68.** The order of $p\pi$ - $d\pi$ interaction in the compounds containing bond between Si/P/S/Cl and oxygen is in the order [NSEC-2015]
 (A) $\text{P} > \text{Si} > \text{Cl} > \text{S}$ (B) $\text{Si} < \text{P} < \text{S} < \text{Cl}$ (C) $\text{S} < \text{Cl} < \text{P} < \text{Si}$ (D) $\text{Si} > \text{P} > \text{S} > \text{Cl}$
- 69.** Which one of the following information about the compounds is correct ? [NSEC-2016]
- | Compounds | Oxidation state of P | No. of P-OH bonds | No. of P-H bonds | No. of P=O bonds |
|--|----------------------|-------------------|------------------|------------------|
| [I] H_3PO_2 Hypophosphorous acid | 1+ | 2 | 1 | 0 |
| [II] $\text{H}_4\text{P}_2\text{O}_5$ pyrophosphorous acid | 3+ | 2 | 2 | 2 |
| [III] $\text{H}_4\text{P}_2\text{O}_6$ Hypophosphoric acid | 4+ | 2 | 2 | 2 |
| [IV] $\text{H}_4\text{P}_2\text{O}_7$ pyrophosphoric acid | 5+ | 3 | 1 | 4 |
- (A) I (B) III (C) IV (D) II
- 70.** The pair that is isostructural (i.e. having the same shape and hybridization) is [NSEC-2016]
 (A) NF_3 and BF_3 (B) BF_4^- and NH_4^+ (C) BCl_3 and BrCl_3 (D) NH_3 and NO_3^-
- 71.** Number of P-S single bonds and P-S double bonds ($\text{P}=\text{S}$) in P_4S_{10} are respectively [NSEC-2016]
 (A) 10, 6 (B) 16, 0 (C) 14, 2 (D) 12, 4
- 72.** Which of the following compounds contain 3-centered 2-electron bonding ? [NSEC-2016]
 (i) $[\text{BeF}_2]_n$ (ii) $[\text{Be}(\text{CH}_3)_3]_n$ (iii) $[\text{BeCl}_2]_n$ (iv) $[\text{BeH}_2]_n$
 (A) (i) and (ii) (B) (ii) and (iii) (C) (ii) and (iv) (D) (iii) and (iv)
- 73.** In ammonia the bond angle is $107^\circ 48'$ while in SbH_3 the bond angle is about $91^\circ 18'$. The correct explanation among the following is/are [NSEC-2016]
 (A) The orbitals of Sb used for the formation of Sb-H bond are almost pure p-orbitals.
 (B) Sb has larger size compared to N.
 (C) Sb has more metallic character than N.
 (D) All the statements are correct.
- 74.** Assuming that Hund's rule is violated by the diatomic molecule B_2 , its bond order and magnetic nature will be respectively [NSEC-2016]
 (A) 1, diamagnetic (B) 1, paramagnetic (C) 2, diamagnetic (D) 2, paramagnetic
- 75.** In the Lewis structure of ozone (O_3), the formal charge on the central oxygen atom is [NSEC-2017]
 (A) +1 (B) -1 (C) 0 (D) -2
- 76.** Which of the following represents the correct order of dipole moment? [NSEC-2017]
 (A) $\text{NH}_3 > \text{NF}_3 > \text{H}_3\text{O}$ (B) $\text{NH}_3 > \text{H}_2\text{O} > \text{NF}_3$ (C) $\text{H}_2\text{O} > \text{NH}_3 > \text{NF}_3$ (D) $\text{H}_2\text{O} > \text{NF}_3 > \text{NH}_3$
- 77.** Which of the following has the shortest bond length ? [NSEC-2017]
 (A) O_2 (B) O_2^- (C) O_2^+ (D) O_2^{-2}
- 78.*** Which of the following is not paramagnetic? [NSEC-2018]
 (A) S^{2-} (B) N^{2-} (C) O^{2-} (D) NO
- 79.** In which of the following, all the bond lengths are not the same ? [NSEC-2018]
 I. IF_4^+ II. BF_4^- III. SF_4 IV. TeCl_4
 (A) I, II, IV (B) II, III, IV (C) I, III, IV (D) I, II, III
- 80.** Among the following pairs, the one in which both the compounds as pure liquids can show significant auto ionization is [NSEC-2018]
 (A) H_2O and H_2S (B) BrF_3 and ICl_3 (C) PF_5 and PCl_5 (D) HF and HCl

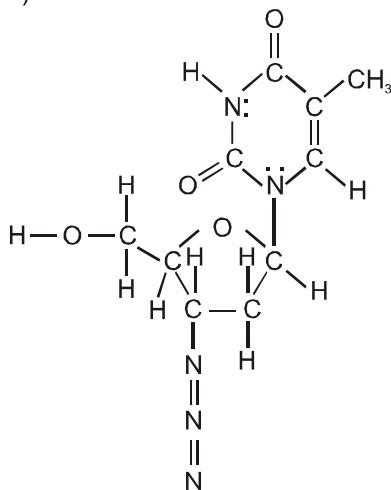


81. Which among the following is nonlinear ? [NSEC-2018]
 (A) N_3^- (B) ClF_2^- (C) Br_3^- (D) BrCl_2^+
82. The most stable Lewis structure of N_2O is [NSEC-2018]
 (A) $\ddot{\text{O}}=\ddot{\text{N}}=\ddot{\text{N}}:$ (B) $\ddot{\text{N}}=\text{O}=\ddot{\text{N}}:$ (C) $\ddot{\text{N}}-\text{N}=\text{O}:$ (D) $\ddot{\text{O}}-\text{N}=\text{N}:$

PART - III : HIGH LEVEL PROBLEMS (HLP)

SUBJECTIVE QUESTIONS

1. Draw the structure of the following compound and identify the hybridisation of the central atom, also count the Sigma and π -bond.
 (i) XeO_2F_2 (ii) PF_3Cl_2 (iii) NH_2OH (iv) Anion of $\text{PCl}_5(\text{s})$ (v) P_4
2. 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^3 hybridisation ?
 (b) How many carbon atoms have sp^2 hybridisation ?
 (c) How many nitrogen atoms (central atom not terminal) have sp hybridisation ?
 (d) How many π bonds are in the molecule ?

3. Draw structures for the polymeric $(\text{BeH}_2)_n$ and $(\text{BeCl}_2)_n$. Explain in brief why the hydride bridge in $(\text{BeH}_2)_n$ is considered to be electron deficient but not the halide bridge in $(\text{BeCl}_2)_n$?
4. Explain the structure, hybridisation and oxidation state of S in sulphuric acid, Marshall's acid, Caro's acid and oleum.
5. 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.

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P	Q	R	S

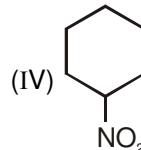
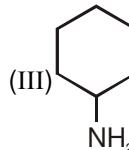
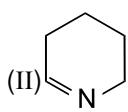
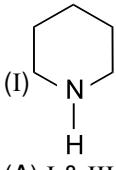
6. Draw the molecular orbital (both bonding and antibonding) and identify the number of nodal planes in the following combination of atomic orbitals with z as internuclear axis : d_{yz} and d_{yz}
7. Arrange the following cations in the order of increasing polarising power.
 (i) V^{3+} , Sc^{3+} , Ti^{3+} , Cr^{3+} (ii) Zn^{2+} , Cd^{2+} , Hg^{2+}

8. Why lithium salts are most hydrated amongst alkali metals salts ?

ONLY ONE OPTION CORRECT TYPE



23. In which of the following cyclic compound the nitrogen atom is sp^3 hybridised



(A) I & III

(B) I, II, III

(C) III & IV

(D) I, III & IV

24. Which of the statements is correct about SO_2 ?

- (A) two σ , two π and no lone pair of electrons (B) two σ and one π
 (C) two σ , two π and one lone pair (D) none of these

25. Arrange the following in the increasing order of deviation from normal tetrahedral angle :

- (A) $P_4 < PH_3 < H_2O$ (B) $PH_3 < H_2O < P_4$ (C) $P_4 < H_2O < PH_3$ (D) $H_2O < PH_3 < P_4$

26. In XeF_2 molecule the angle between two lone pair orbitals is α , the angle between lone pair orbital and bond pair orbital is β and the angle between bond pair orbitals is γ :

- (A) $\alpha = \beta = \gamma$ (B) $\alpha > \beta > \gamma$ (C) $\gamma > \beta > \alpha$ (D) $\gamma > \alpha > \beta$

27. In O_2F_2 , which of the following statement is incorrect.

- (A) O–F bond length in O_2F_2 is longer than O–F bond length in OF_2 .
 (B) The O.N. of oxygen in O_2F_2 is +1.
 (C) The O–O bond length in O_2F_2 is shorter than O–O bond length in H_2O_2 .
 (D) None of these

28. Identify the species containing Banana bonds

- (A) $(BeH_2)_n$ (B) BF_3 (C) $(AlCl_3)_2$ (D) $(BeCl_2)_n$

29. In the coordinate valency

- (A) Electrons are equally shared by the atoms
 (B) Electrons of one atom are shared between two atoms
 (C) Hydrogen bond is formed
 (D) Electrons are completely donated to other atom with no sharing

30. What is the nature of the bond between B and O in $(C_2H_5)_2OBH_3$.

- (A) Covalent (B) Co-ordinate covalent (C) Ionic bond (D) Banana shaped bond

31. Which of the following species does not contain N–N covalent bond?

- (A) N_2O_3 (B) $N_2O_2^{2-}$ (C) N_2O_5 (D) N_2O_4

32. Compounds in which oxidation state of at least one oxygen is (-1) :

- (1) H_2O_2 (2) O_2F_2 (3) H_2SO_5 (4) CrO_5
 (5) $H_2S_2O_8$ (6) $[Na_2B_2H_4O_8]$
 (A) 1,2,3,5 (B) 1,3,4,5,6 (C) 1,3,4,5 (D) 1,2,3,4,5,6

33. 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_2 molecule does not exist as the effect of bonding and anti-bonding orbitals cancel each other.
 (C) C_2, O_2^{2-} and Li_2 are diamagnetic
 (D) In F_2 molecule, the energy of σ_{2p_z} is more than π_{2p_x} and π_{2p_y}

34. Which of the following statement is incorrect?

- (A) During N_2^+ formation, one electron is removed from the bonding molecular orbital of N_2 .
 (B) During O_2^+ formation, one electron is removed from the antibonding molecular orbital of O_2 .
 (C) During O_2^- formation, one electron is added to the bonding molecular orbital of O_2 .
 (D) During CN^- formation, one electron is added to the bonding molecular orbital of CN .

35. Which the following molecules / species have identical bond order and same magnetic properties?

- (I) O_2^+ ; (II) NO ; (III) N_2^+
 (A) (I), (II) only (B) (I) and (III) only (C) (I), (II) and (III) (D) (II) and (III) only





- 47.** (a) There are only 12 bonding electrons available in one molecule of diborane.
 (b) $\text{B}_3\text{N}_3\text{H}_6$ is an electron deficient compound.
 (c) Al_2Cl_6 sublimes on heating and give AlCl_3 vapours at high temperature.
 (d) In $\text{Si}_2\text{O}_7^{6-}$ anion, one oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron.
 (A) T F T T (B) F T F F (C) T F T F (D) F T F T

48. The point of dissimilarity between $(\text{SO}_3)_3$ and (HPO_3) (cyclic trimers) is.
 (A) having six membered ring. (B) having central atom in same hybridization
 (C) having planar ring. (D) being isoelectronic.

49. Which of the following statements is/are true about hypophosphoric acid.
 (A) Oxidation state of phosphorus atoms present in hypophosphoric acid is +3
 (B) Phosphorous atom is present in 2 different oxidation state which are +3, +5
 (C) Oxidation state of phosphorous in hypophosphoric acid is +4
 (D) Oxidation state of phosphorus in hypophosphoric acid is + 5.

50. The gaseous HX molecule has a measured dipole moment of 4.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67×10^{-8} cm then the percentage ionic character in HX molecule is :
 (A) 78% (B) 31.25% (C) 50.25% (D) None of these

51. Which of the following models best describes the bonding within a layer of the graphite structure ?
 (A) metallic bonding (B) ionic bonding
 (C) non-metallic covalent bonding (D) van der Waals forces

52. Which of the following compounds would have significant intermolecular hydrogen bonding ?
 (A) HCl (B) H_2S (C) chloral hydrate (D) CH_3OH

53. Which of the following statement is not true ?
 (A) CCl_4 has higher boling point than CHCl_3 .
 (B) The HF_2^- ion exists in the solid state and in liquid HF solution , but not in dilute aqueous solutions.
 (C) Hydrogen bonding maintains the planar H_3BO_3 units in layers in solid state.
 (D) None of these.

54. **S₁** : In the solid $\text{B}(\text{OH})_3$ units are hydrogen bonded together into two-dimensional sheets with almost hexagonal symmetry.
S₂ : Na_2CO_3 is isomorphous with Na_2SO_3 as both have similar formula type.
S₃ : XeO_3F_2 has one lone pair of electron on central xenon atom.
S₄ : D_2O has higher boiling point than H_2O
 (A) T F T F (B) T F F T (C) T T F F (D) T T T T

55. Which is correct about D_2O
 (A) Its boiling point is higher than that of $\text{H}_2\text{O}(\ell)$ (B) O—D---O bond is stronger than O—H---O bond.
 (C) $\text{D}_2\text{O}(\text{s})$ sinks in $\text{H}_2\text{O}(\ell)$. (D) all the above are correct.

56. Among the following compounds, the correct order of the polarity of the bonds is :
 SbH_3 , AsH_3 , PH_3 , NH_3 .
 (A) $\text{SbH}_3 < \text{AsH}_3 < \text{PH}_3 < \text{NH}_3$ (B) $\text{AsH}_3 < \text{SbH}_3 = \text{PH}_3 < \text{NH}_3$
 (C) $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$ (D) $\text{AsH}_3 < \text{PH}_3 < \text{SbH}_3 < \text{NH}_3$

57. Given the species N_2 , CO , CN^- and NO^+ .Which of the following statement is incorrect .
 (A) All the species are diamagnetic
 (B) All the species are isoelectronic
 (C) All the species have dipole moment
 (D) All the species are linear

58. CH_3Cl has more dipole moment than CH_3F because :
 (A) electron affinity of chlorine is greater than that of fluorine.
 (B) the charge separation is larger in CH_3Cl compared to CH_3F .
 (C) the repulsion between the bond pairs and non-bonded pairs of electrons is greater in CH_3Cl than CH_3F .
 (D) chlorine has higher electronegativity than fluorine.

- 59.** Select the correct statement.
 (A) The order of Xe–F bond length in various fluorides of Xenon is $\text{XeF}_2 < \text{XeF}_4 < \text{XeF}_6$
 (B) PH_5 can undergo sp^3d hybridisation to have octahedral geometry.
 (C) Dipole moment of CH_3F is greater than that of CH_3Cl
 (D) Increasing strength of hydrogen bonding is $\text{Cl}-\text{H}----\text{Cl} < \text{N}-\text{H}----\text{N} < \text{O}-\text{H}----\text{O} < \text{F}-\text{H}----\text{F}$

60. The pairs of bases in DNA are held together by
 (A) Hydrogen bonds (B) Ionic bonds
 (C) Phosphate groups (D) Deoxyribose groups

61. The bond that determines the secondary structure of a protein is
 (A) Coordinate bond (B) Covalent bond (C) Hydrogen bond (D) Ionic bond

62. Which of the following has highest melting point according to Fajan's rule :
 (A) NaCl (B) MgCl_2 (C) AlCl_3 (D) LiCl

63. An element X occurs in short period having configuration ns^2np^1 . The formula and nature of its oxide is :
 (A) XO_3 , basic (B) XO_3 , acidic (C) X_2O_3 , amphoteric (D) X_2O_3 , basic

64. Which of the following compounds of elements in group IV is expected to be most ionic ?
 (A) PbCl_2 (B) PbCl_4 (C) CCl_4 (D) SiCl_4

65. Which of the following cannot be explained on the basis of Fajan's Rules ?
 (A) Ag_2S is much less soluble than Ag_2O
 (B) Fe(OH)_3 is much less soluble than Fe(OH)_2
 (C) BaCO_3 is much less soluble than MgCO_3
 (D) Melting point of AlCl_3 is much less than that of NaCl

66. S_1 : AgI is less soluble in water than AgF due to more polarisation of I^- ion in comparison to F^- ion.
 S_2 : Melting point of BaCl_2 is higher than the melting point of BeCl_2 due to greater ionic nature of BaCl_2 .
 S_3 : Order of hydrated radii is : $\text{Al}^{3+}(\text{aq}) > \text{Mg}^{2+}(\text{aq}) > \text{Na}^+(\text{aq})$
 (A) T T T (B) T T F (C) T F T (D) F T T

67. Correct order of strength of metallic bond in Li, K, Fe, W
 (A) $\text{W} > \text{Fe} > \text{Li} > \text{K}$ (B) $\text{Fe} > \text{W} > \text{K} > \text{Li}$ (C) $\text{Li} > \text{K} > \text{W} > \text{Fe}$ (D) $\text{K} > \text{Li} > \text{Fe} > \text{W}$

68. The ground state electronic configurations of some elements, P, Q, R, S, and T (these symbols represent the some of the known elements given in the periodic table) are as follows.
 P : $1s^2 2s^2 2p^6 3s^2 3p^2$
 Q : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
 R : $1s^2 2s^2 2p^6 3s^2 3p^1$
 S : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
 T : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.
 Match the electronic configurations of the elements with the properties given below and select the correct sequence by choosing the correct codes given.
 (i) Element forms a cation which is isoelectronic with P^{3-} .
 (ii) Element which in its compounds can show a maximum oxidation state of +6 and that is coloured too.
 (iii) Element has largest atomic radius and highest first ionisation energy in the respective period.
 (iv) Element which has intermediate value of electronegativity and its oxide forms salts with strong acids and bases.
 (A) Q R T P (B) Q S T R (C) Q R S T (D) P Q R S

69. Increasing order of extent of hydrolysis $\text{CCl}_4, \text{MgCl}_2, \text{AlCl}_3, \text{PCl}_5, \text{SiCl}_4$
 (A) $\text{MgCl}_2 < \text{AlCl}_3 < \text{CCl}_4 < \text{AlCl}_4 < \text{PCl}_5$
 (B) $\text{MgCl}_2 > \text{AlCl}_3 > \text{CCl}_4 > \text{AlCl}_4 > \text{PCl}_5$
 (C) $\text{CCl}_4 < \text{MgCl}_2 < \text{AlCl}_3 < \text{SiCl}_4 < \text{PCl}_5$
 (D) $\text{SiCl}_4 < \text{PCl}_5 < \text{CCl}_4 < \text{MgCl}_2 < \text{AlCl}_3$

MATCH THE COLUMN

- 70.** Match the species given in column-I with the type of hybridisation given in column-II.

	Column-I		Column-II
(A)	I_3^-	(p)	sp^3d
(B)	XeO_3	(q)	sp^3
(C)	ClOF_3	(r)	sp^2
(D)	XeF_5^+	(s)	sp^3d^2

- 71.** Match the column :

	Column – I	Column – II
(A)	SO_3 (gas)	(p) Polar with $\text{p}\pi-\text{d}\pi$ bonds and identical S–O bond lengths.
(B)	OSF_4	(q) One lone pair and $\text{p}\pi-\text{d}\pi$ bond.
(C)	SO_3F^-	(r) Non-polar with $\text{p}\pi-\text{p}\pi$ and $\text{p}\pi-\text{d}\pi$ bonds. Identical S–O bond lengths.
(D)	ClOF_3	(s) Polar with $\text{p}\pi-\text{d}\pi$ bond.

- 72.** Match the column :

	Column-I	Column-II
(A)	IF_2^-	(p) sp^3d
(B)	ClF_3	(q) polar
(C)	XeO_3F_2	(r) one of the bond angles is 180°
(D)	SF_4	(s) one lone pair

SINGLE AND DOUBLE VALUE INTEGER TYPE

- 73.** Number of hypervalent among following are :

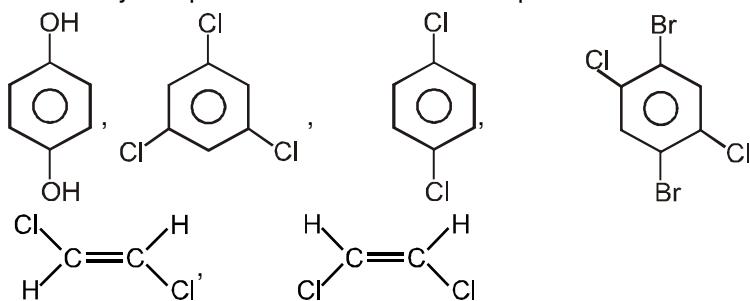
(i) H_2CO_3 , (ii) HNO_3 , (iii) HNO_2 , (iv) H_3PO_4 , (v) H_3PO_3 , (vi) H_3PO_2 , (vii) HClO_4 , (viii) HClO_3 , (ix) HClO_2 , (x) HClO , (xi) H_2SO_3 , (xii) H_2SO_4 , (xiii) $\text{H}_2\text{N}_2\text{O}_2$, (xiv) H_2SO_5 , (xv) $\text{H}_2\text{S}_2\text{O}_8$, (xvi) SO_3 , (xvii) SO_2 , (xviii) N_2O_5 , (xix) P_4O_{10}

- 74. Compound No. of peroxide linkage(s)**

- | | | | |
|----|-----------------------------------|---|---|
| 1. | HXeO_4^- | — | x |
| 2. | K_3CrO_8 | — | y |
| 3. | H_2TiO_4 | — | z |
| 4. | $\text{Na}_2\text{B}_4\text{O}_7$ | — | w |

The value of $x + y + z + w$ is/are

- 75.** How many compound which show \approx zero dipole moment.

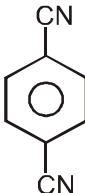


76. A bond X-Y has a dipole moment of 1.8×10^{-29} Cm and a bond length 150 pm. What will be the percentage of ionic character is given bond.



77. Number of non-polar molecule among the following is x and number of planar molecule is y. Give $x \times y$.

BF_3 , CO_2 , SO_2 , PCl_5 , ClF_3 , NH_3 , CH_4 ,



78. Among the following, give the number of correct order of boiling point or melting point.
- | | | | |
|---|---------------|---|---------------|
| (1) $\text{Zn} > \text{Cd} > \text{Hg}$ | Boiling point | (2) $\text{Zn} > \text{Cd} > \text{Hg}$ | Melting point |
| (3) $\text{K} > \text{Ca} > \text{Sc}$ | Boiling point | (4) $\text{Na} > \text{Mg} > \text{Al}$ | Boiling point |
| (5) $\text{Sc} > \text{Mn} > \text{Zn}$ | Melting point | (6) $\text{Pt} > \text{Pd} > \text{Ni}$ | Melting point |
| (7) $\text{Cr} > \text{Mn} < \text{Fe}$ | Melting point | (8) $\text{Ba} > \text{Li} > \text{Na}$ | Melting point |

79. Calculate total number of coordinate bonds in the following molecules.

(a) PCl_6^- (b) $\text{NH}_3 \cdot \text{BF}_3$ (c) HNO_3 (d) CO

80. Determine number of bonding electrons in H_3SiNCO .

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

81. Hypervalent compound is(are) :

(A) SO_3^{2-} (B) PO_4^{3-} (C) SO_4^{2-} (D) ClO_4^-

82. Which of the following overlaps is/are **incorrect** [assuming X-axis to be the internuclear axis] :

(a) $2p_y + 2p_y \rightarrow \pi$	(b) $2p_z + 2p_z \rightarrow \sigma$	(c) $2p_x + 2p_x \rightarrow \pi$
(d) $1s + 2p_y \rightarrow \pi$	(e) $2p_y + 2p_z \rightarrow \pi$	(f) $1s + 2s \rightarrow \sigma$
(A) 'a' & 'b'	(B) 'b' & 'd'	(C) 'd' & 'f'
(D) 'c' & 'e'		

83. In which of following, vacant orbital take part in hybridisation :

(A) BF_3 (B) PCl_6^- (C) BF_4^- (D) $\ddot{\text{N}}\text{H}_3$

84. Which is not true about VSEPR theory

(A) Lone pair-lone pair repulsion is maximum.
 (B) Lone pair and double bond occupy axial position in trigonal bipyramidal structure.
 (C) More electronegative atoms occupies axial position in trigonal bipyramidal structure.
 (D) Bigger atoms occupy axial positions in trigonal bipyramidal structure.

85. Select the **correct** statement.

(A) Peroxenate ion is $[\text{XeO}_6]^{4-}$ with octahedral geometry.
 (B) XeF_2 is linear molecule with 3 lone pairs (l.p)
 (C) XeOF_4 , XeF_4 , XeO_2F_2 all contains one lone pair only
 (D) None of these

86. Identify the **correct** option(s)

(A) $\text{NH}_4^+ > \text{NH}_3 > \text{NH}_2^-$ order of bond angle
 (B) $(\text{CH}_3)_3\text{B}$ is a trigonal planar molecule (not considering the H-atoms on 'C')
 (C) In NH_4Cl 'N' atom is in sp^3d hybridisation
 (D) In S_8 molecule a total of 16 electrons are left on all the 'S' atoms after bonding.

87. Which of the following statements is/are correct for ClO_4^- oxoanion ?

(A) It does not have any tendency of polymerisation.
 (B) It has strong $\pi\pi$ -bonding between chlorine and oxygen.
 (C) All Cl-O bonds are identical and chlorine atom is sp^3 hybridised.
 (D) The chemical bonding takes place in ground state and charge dispersion is more than ClO_3^- oxo anion.

88. Among the following back bonding is exhibited by

(A) BF_3 (B) $(\text{CH}_3)_3\text{N}$ (C) CH_3NCO (D) SiH_3NCO

89. Which of the following reactions is/are likely to be impossible.

(A) $(\text{CH}_3)_2\text{O} + \text{BF}_3 \rightarrow$ (B) $(\text{SiH}_3)_2\text{O} + \text{BF}_3 \rightarrow$ (C) $(\text{SiH}_3)_3\text{N} + \text{BF}_3 \rightarrow$ (D) All the above





- 101.** Select the correct statement(s) :

 - (A) In s-block elements, melting point generally decreases on moving down the group.
 - (B) Band model proposed to explain metallic bonding is based on molecular orbital theory.
 - (C) d-block elements get a dip at/near middle of series in enthalpy of atomisation values.
 - (D) Electricity conduction in a single layer of graphite can be considered similar to electricity conduction in metals according to electron sea model.

102. 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 in s-block.

COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

The electronic configuration of three elements, A, B and C are given below. Answer the questions 01 to 04 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$
B	$1s^2$	$2s^2$	$2p^6$
C	$1s^2$	$2s^2$	$2p^6$

Comprehension # 2

$\text{Na}(\text{BH}_4)$ is ionic compound containing BH_4^- tetrahydrido borate ion and in solid state NaBH_4 has sodium chloride structure. Not all tetrahydrido borates are ionic the beryllium, aluminium and transition metal borohydrides become increasingly covalent and volatile. In these type of tertahydrido borate the BH_4^- ion form covalent bond with metal ion. One or more H atoms in BH_4^- act as a bridging and bond to metal forming a 3 center bond with 2 electron shared by 3 atoms. The BH_4^- is usually in that it may form 1, 2 or 3 such 3 center bonds to the metal ion when form covalent bond.

- 107.** Li[AlH₄] is used as a reducing agent in many reactions and it is prepared by excess LiH and AlCl₃. Select incorrect statements about Li[AlH₄].
(A) hybridisation of Al is same as B in Na(BH₄).
(B) Geometry around Al is same as in AlCl₄⁻
(C) AlH₄⁻, BH₄⁻, AlCl₄⁻, are iso structural
(D) AlH₄⁻, BH₄⁻, AlCl₄⁻, are iso electronic

108. Select correct statements about Al(BH₄)₃
(A) All three tetrahydrido borate form two hydrogen bridges
(B) two BH₄⁻ form two hydrogen bridges and one form one hydrogen bridge
(C) one BH₄⁻ form two hydrogen bridges and two form one hydrogen bridge
(D) B form only 2c-2e bond



PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General:

1. The test is of 1 hour duration.
 2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

3. Each part consists of five sections.
 4. Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
 5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
 6. Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
 7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
 8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

- 3. Marking Scheme**

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.

10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be awarded for incorrect answer in this section.

11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

- 1.** Select the correct order of following property
 (A) % s-character : $sp^3 > sp^2 > sp$
 (B) O–N–O bond angle : $NO_3^- > NO_2^+ > NO_2$
 (C) All angles in CH_2F_2 are not identical
 (D) C–F bond length : $CF_4 > CH_3F > CH_2F_2 > CF_3H$

2. F–As–F bond angle in AsF_3Cl_2 can be nearly :
 (A) 90° & 180° only (B) 120° only (C) 90° & 120° only (D) 90° only

3. The correct sequence of polarity of the following molecule :
 1. Benzene 2. Inorganic Benzene 3. PCl_3F_2 4. PCl_2F_3
(P stands for polar and NP stands for non-polar)

1	2	2	4	1	2	2	4
(A) P	NP	NP	P	(B) NP	NP	NP	P
(C) NP	P	NP	P	(D) NP	P	P	NP

Section-2 : (One or More than one options correct Type)

This section contains 5 multipole choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

Section-3 : (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

13. X is the number of maximum atom(s) is/are present in same plane of $\text{B}_3\text{N}_3\text{H}_6$. Find value of X / 2

14. Find the number of molecules which are not having 3C–2e bond from the following :
(a) $\text{Al}_2(\text{CH}_3)_6$ (b) Si_2H_6 (c) B_2H_6 (d) C_2H_6
(e) Si_2Cl_6 (f) Al_2Cl_6 (g) $\text{B}_3\text{N}_3\text{H}_6$

15. Which of the following species having axial bond length greater than equatorial bond length :
 PCl_5 , IF_7 , SF_6 , CCl_4

16. The total number of orbitals involved in the overlapping in XeO_2F_4 ? Give answer after dividing by 4.

17. How many different type of bonds can be formed if any two d orbitals of two different atoms are overlapping with each other ?

18. In which of the following all bond length are not equal ?
(a) PCl_5 (b) SF_4 (c) ClF_3 (d) XeF_2
(e) $[\text{SF}_5]^+$ (f) $[\text{ClF}_4]^+$ (g) $[\text{XeF}_3]^+$ (h) O_3 (i) P_4 (white)



SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21

Hybridisation is the mixing of atomic orbital of comparable energy and the number of hybrid orbitals formed is equal to the number of pure atomic orbitals mixed up and hybrid orbitals are occupied by σ -bond pair and lone pair.

19. Which of the following geometry is most unlikely to form from sp^3d hybridisation of the central atom
(A) Linear (B) Regular Tetrahedral
(C) T-shaped (D) See-Saw

20. The orbital, which does not participate in sp^3d^2 hybridisation.
(A) p_x (B) d_{xy} (C) $d_{x^2-y^2}$ (D) p_z

21. "The hybrid orbitals are at angle of X° to one another" this statement is not valid for which of the following hybridisation. ($X \leq 180^\circ$)
(A) sp^3 (B) sp^2 (C) sp^3d^2 (D) sp

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

- 22.** Match each List-I with List-II and select the correct answer using the code given below the lists.

	List-I		List-II
	(Pair of species)		(Identical Property in pairs of species)
(P)	PCl_3F_2 , PCl_2F_3	(1)	Hybridisation of central atom
(Q)	BF_3 & BCl_3	(2)	Shape of molecule / ion
(R)	CO_2 & CN_2^{-2}	(3)	μ (dipole moment)
(S)	C_6H_6 & $\text{B}_3\text{N}_3\text{H}_6$	(4)	Total number of electrons

Code :

	P	Q	R	S
(A)	1,2	1,2,3	1,2,3,4	1,2,3,4
(B)	1,2,3,4	1,2,3	1,2	1,2,3,4
(C)	1,2,3	1,2	1,2,3,4	1,2,3,4
(D)	1,2,3,4	1,2,3	1,2,3,4	1,2

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

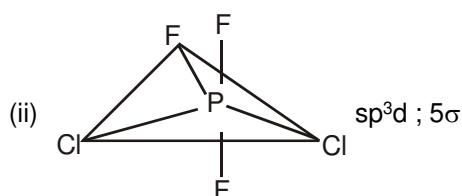
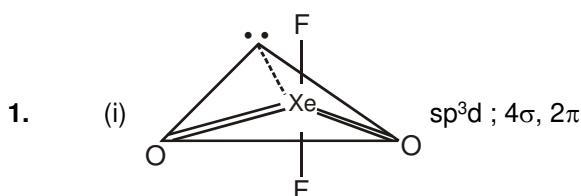
OBJECTIVE RESPONSE SHEET (ORS)

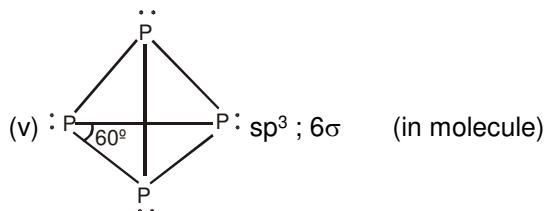
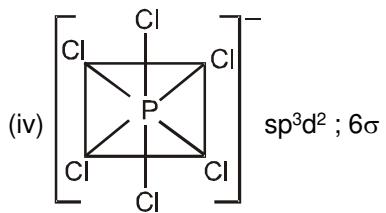
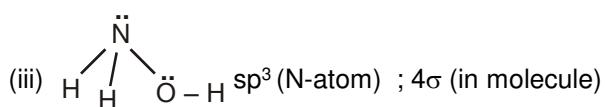
APSP Answers**PART - I**

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (4) | 2. (4) | 3. (4) | 4. (3) | 5. (2) |
| 6. (3) | 7. (4) | 8. (3) | 9. (3) | 10. (2) |
| 11. (1) | 12. (2) | 13. (3) | 14. (1) | 15. (1) |
| 16. (1) | 17. (2) | 18. (2) | 19. (3) | 20. (2) |
| 21. (2) | 22. (4) | 23. (1) | 24. (4) | 25. (4) |
| 26. (2) | 27. (2) | 28. (2) | 29. (3) | 30. (2) |

PART - II

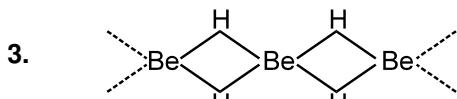
- | | | | | |
|-----------|---------|---------------|---------|-----------|
| 1. (B) | 2. (C) | 3. (A) | 4. (B) | 5. (C) |
| 6. (A) | 7. (C) | 8. (A) | 9. (C) | 10. (B) |
| 11. (D) | 12. (D) | 13. (D) | 14. (A) | 15. (D) |
| 16. (B) | 17. (C) | 18. (A) | 19. (B) | 20. (C) |
| 21. (C) | 22. (A) | 23. (D) | 24. (D) | 25. (D) |
| 26. (A) | 27. (D) | 28. (A) | 29. (C) | 30.* (CD) |
| 31. (C) | 32. (A) | 33. (D) | 34. (B) | 35. (B) |
| 36. (C) | 37. (D) | 38. (A) | 39. (C) | 40. (B) |
| 41. (B) | 42. (D) | 43. (C) | 44. (D) | 45. (B) |
| 46. (C) | 47. (C) | 48. (A) | 49. (D) | 50. (C) |
| 51. (C) | 52. (B) | 53. (B) | 54. (A) | 55. (D) |
| 56. (C) | 57. (A) | 58. (D) | 59. (C) | 60. (C) |
| 61.* (BC) | 62. (C) | 63. (B) | 64. (C) | 65. (B) |
| 66. (B) | 67. (D) | 68. (B) | 69. (D) | 70. (B) |
| 71. (D) | 72. (C) | 73. (A) | 74. (A) | 75. (A) |
| 76. (C) | 77. (D) | 78.* (A or C) | 79. (C) | 80. (B) |
| 81. (D) | 82. (D) | | | |

PART - III

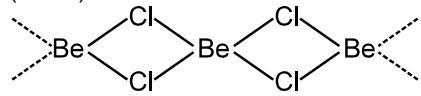


2.

6	4	1	5
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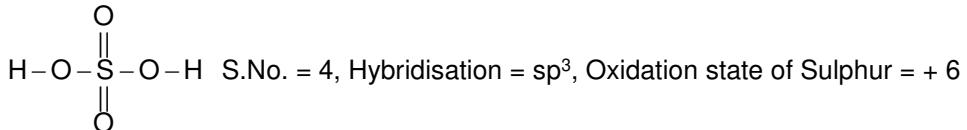


(BeH₂)_n contains 2e–3c bonds whereas

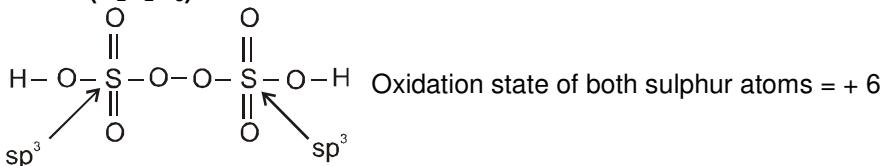


(BeCl₂)_n contain the usual 2e – 2c bonds.

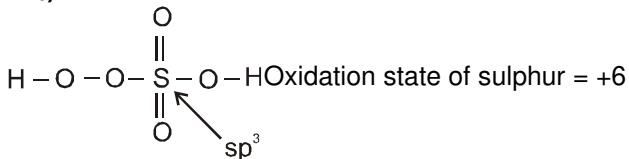
4. Sulphuric acid (H₂SO₄)



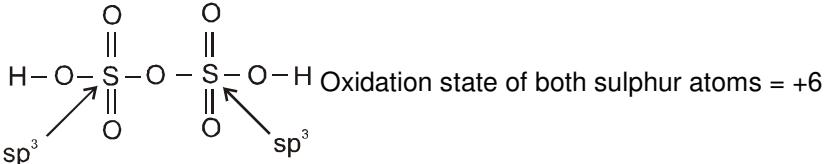
Marshall's acid (H₂S₂O₈)



Caro's acid (H₂SO₅)



Oleum (H₂S₂O₇)

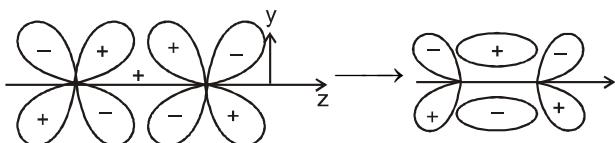


5.

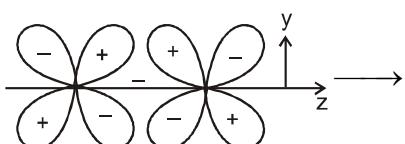
3	1	2	4
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P Q R S

6.



Bonding (3 nodal planes)



Anti bonding (4 nodal planes)

7. (i) $\text{Sc}^{2+} < \text{Ti}^{3+} < \text{V}^{3+} < \text{Cr}^{3+}$ (ii) $\text{Cd}^{2+} < \text{Zn}^{2+} < \text{Hg}^{2+}$ 8. It has highest polarising power due to smallest ionic radius amongst alkali metal, therefore, greater degree of hydration is observed in Li^+ salts.

- | | | | | |
|--|---|---|------------|-------------|
| 9. (D) | 10. (C) | 11. (B) | 12. (C) | 13. (C) |
| 14. (D) | 15. (B) | 16. (C) | 17. (C) | 18. (B) |
| 19. (D) | 20. (A) | 21. (A) | 22. (B) | 23. (A) |
| 24. (C) | 25. (D) | 26. (D) | 27. (D) | 28. (A) |
| 29. (B) | 30. (B) | 31. (C) | 32. (B) | 33. (D) |
| 34. (C) | 35. (C) | 36. (D) | 37. (B) | 38. (A) |
| 39. (C) | 40. (B) | 41. (D) | 42. (D) | 43. (B) |
| 44. (C) | 45. (D) | 46. (B) | 47. (A) | 48. (C) |
| 49. (C) | 50. (B) | 51. (C) | 52. (D) | 53. (D) |
| 54. (B) | 55. (D) | 56. (C) | 57. (C) | 58. (B) |
| 59. (D) | 60. (A) | 61. (C) | 62. (A) | 63. (C) |
| 64. (A) | 65. (C) | 66. (A) | 67. (A) | 68. (B) |
| 69. (C) | 70. (A - p) ; (B - q) ; (C - p) ; (D - s) | 71. (A - r) ; (B - s) ; (C - p, s) ; (D - q, s) | | |
| 72. (A - p, r) ; (B - p, q) ; (C - p, r) ; (D - p, q, s) | | | | |
| 73. 13 (Except, i, iii, iii, x, xiii, xviii) | 74. 6 | 75. 4 | 76. 75 | |
| 77. 25 | 78. 6 | 79. 4 | 80. 20 | 81. (ABCD) |
| 82. (BD) | 83. (BC) | 84. (BD) | 85. (AB) | 86. (AB) |
| 87. (AC) | 88. (AD) | 89. (BC) | 90. (ACD) | 91. (BCD) |
| 92. (BD) | 93. (BCD) | 94. (ABC) | 95. (ABCD) | 96. (ABCD) |
| 97. (ABC) | 98. (D) | 99. (ABC) | 100. (ABD) | 101. (ABCD) |
| 102. (ABD) | 103. (A) | 104. (D) | 105. (D) | 106. (B) |
| 107. (D) | 108. (A) | 109. (B) | 110. (C) | |

PART - IV

- | | | | | |
|-----------|----------|--------------------------|-----------------------|----------|
| 1. (C) | 2. (A) | 3. (B) | 4. (D) | 5. (C) |
| 6. (A) | 7. (C) | 8. (ABD) | 9. (ABC) | 10. (BD) |
| 11. (ABD) | 12. (AC) | 13. 6 | 14. 5 (b, d, e, f, g) | 15. 1 |
| 16. 4 | 17. 3 | 18. 6 (a, b, c, e, f, g) | 19. (B) | 20. (B) |
| 21. (C) | 22. (A) | | | |



APSP Solutions

PART - I

1. Element belongs to d-block in d-block elements ($n - 1$) d and ns electron take part in the bonding.

3. Proper overlapping occurs between p_x and s orbital.

4. $\text{H}_3\text{N}^+ + \text{BF}_3 \longrightarrow \text{H}_3\text{N} \rightarrow \text{BF}_3$
lewis lewis
base acid

5. Bond energy \propto Bond order.

6.
Steric number = 5 ; Hybridisation = sp^3d .

7.
Hybridisation = sp^3 ; Bond angle = 110°

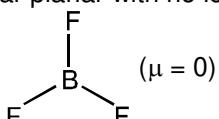
8. Boiling point of covalent molecules is decided by van der Waal force of attraction and vander Waal force of attraction depends on molecular weight.

9.
square planar (All Xe-F bonds are equal)
tetrahedral (All Be-F bonds are equal)
[C=C bond is different from C-H bond]
tetrahedral (All Si-F bonds are equal)

10.
Cl-O-Cl bond angle is more due to large size of Cl and F-O-F bond angle is least due to bent rule.

11. O_2^- has one unpaired electron in π^*2p_y while other do not have unpaired electrons. (explained by MOT)

12. BF_3 has triangular planar with no lone pair.



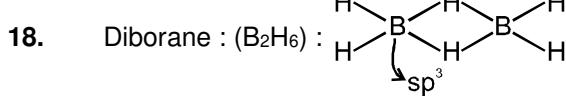
13. Strongest H-bonding is in F-H ----- O as F is most electronegative element hence creating good partial positive charge on H. While O is good donor of electron as compare to F due to use electronegativity.

14. It is fact.

15. Oxygen has unpaired in π^*2p_x and π^*2p_y which explain its paramagnetic behaviour. (Explained by MOT)

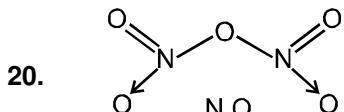
17.
Trigonal bipyramidal

$$\mu = 0$$

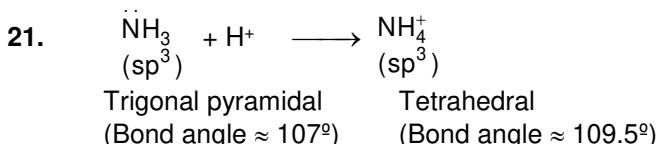


Diamond has sp^3 hybrid carbon and graphite has sp^2 hybrid carbon.

19. NH_4^+ , H_3O^+ and OF_2 all have sp^3 hybridisation and their shapes are tetrahedral, trigonal pyramidal and bent respectively.



It have both covalent as well as coordinate bond.



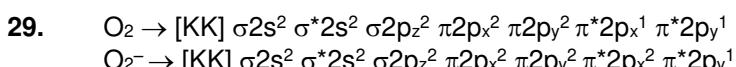
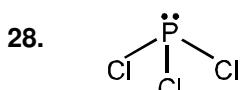
22. Polarisability of anion increase on increasing its size.

23. In CCl_4 , C has more charge therefore Cl is more polarized in CCl_4 .

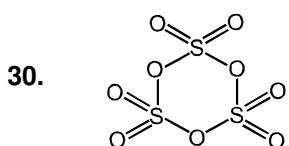
24. For the formation of ionic compound atom should have low ionization energy to form cation while other should have high electron affinity to form anion.

26. Covalent character ionic compound is explained by Fajan rule. Covalent character increase on decreasing the size of cation and increasing charge on cation.

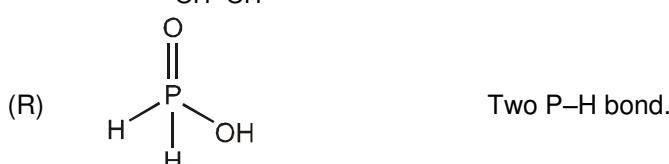
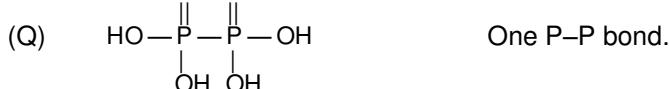
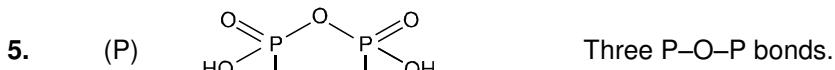
27. More is the electronegativity difference stronger is the bond.

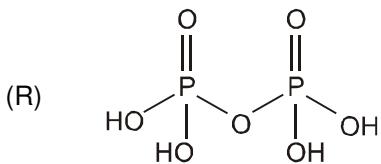


As in O_2 HOMO is $\pi^* 2p_x$ and $\pi^* 2p_y$ and they have one electron each so next electron can be added to these orbitals.



PART - III





Four P-OH bond.

9. In SF_6 , PCl_5 and IF_7 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.

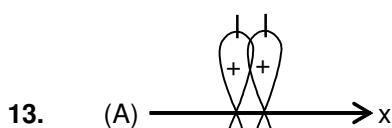
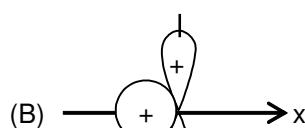
10. Bond energy \propto Bond order

Species	Bond order
CO	3
CO_2	2
CO_3^{2-}	1.33

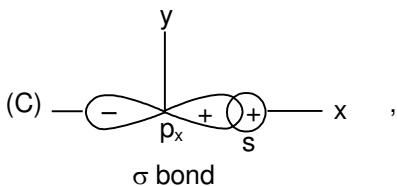
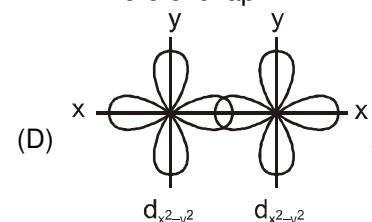
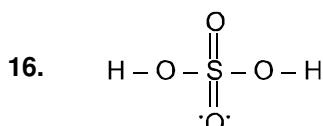
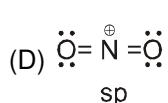
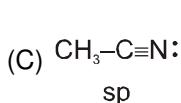
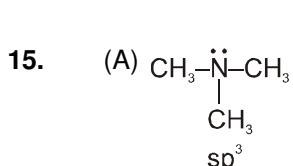
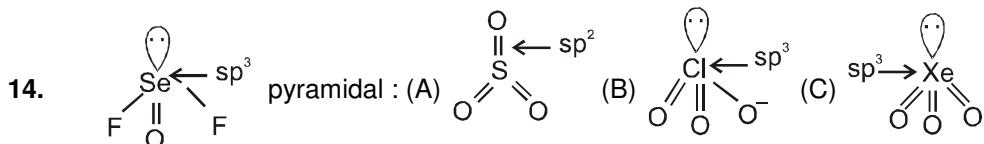
11. Across a period, effective nuclear charge increases. As a result the size of atom, and, therefore, the size of d-orbital decreases leading to progressively stronger $p\pi-d\pi$ bonds.

12. (d) Position of atoms are different.

(e) Has unpaired electrons and this is not possible since the molecule is diamagnetic.

 p_z p_z  p_z

zero overlap

 p_x s  $d_{x^2-y^2}$ $d_{x^2-y^2}$ overlap is not sufficient so, such σ bond do not exist.

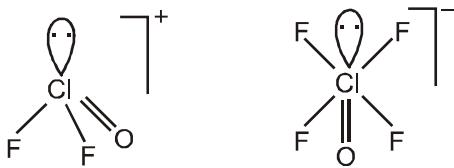
Steric No = 4

hybridization = sp^3

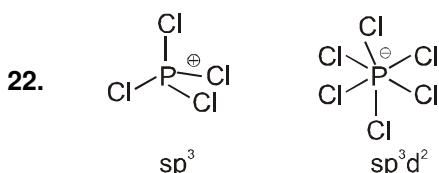
17. (A) both are sp^3d

- (B) both are sp^3d

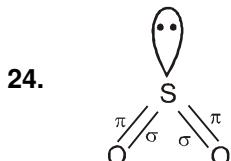
- (C) $[\text{ClF}_2\text{O}]^+$ is sp^3 but $[\text{ClF}_4\text{O}]^-$ is sp^3d^2

(D) both are sp^3d^2

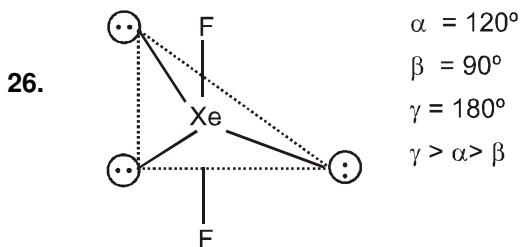
18. The shape of AsF_4^- is see-saw.
19. PH_3 – No Hybridisation
 NH_3 and H_2O bond angle is less than $109^\circ 28'$ due to LP–BP and LP–LP repulsion.
 CH_4 bond angle is $109^\circ 28'$
20. (i) Negative charge is more stable on 'S' than on N (size factor is dominant over EN factor).
(ii) Less formal charge provides more stability.
21. S–S overlap will result into σ bond.



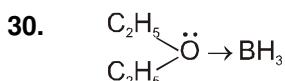
23. I and III are sp^3 hybridised while II and IV are sp^3 hybridised.



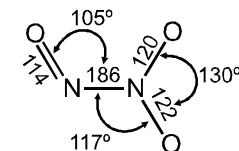
25. P_4 bond angle = 60°
 PH_3 bond angle $\approx 90^\circ$ (Drago's rule)
 H_2O bond angle = 104.5°



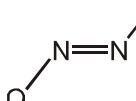
27. (A) Bent rule.
(C) H_2O_2 has more lone pair-lone pair repulsion.



31. (A) N_2O_3 Dinitrogen trioxide

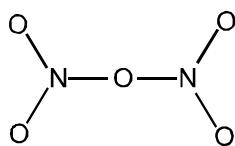


- (B) $N_2O_2^{2-}$ Hyponitrite ion

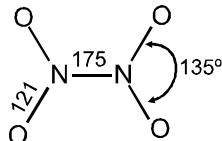


(C) N_2O_5

Dinitrogen pentoxide

(D) N_2O_4

Dinitrogen tetroxide



33. (A) Stability $\text{O}_2^+ > \text{O}_2 > \text{O}_2^-$
Bond order 2.5 2 1.5

(C) In all these molecules all electrons are paired in molecular orbitals.

34. (C) $\text{O}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$
 $\text{O}_2^- : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^2 = \pi^* 2p_y^1)$

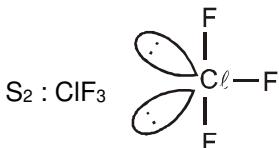
35. (I) $\text{O}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$
Bond order = $1/2(10 - 5) = 2.5$.

(II) NO is derivative of O_2 and isoelectronic with O_2^+ :so $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$
Bond order = $1/2(10 - 5) = 2.5$.(III) $\text{N}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2) (\sigma 2p_z)^1$ 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.

36. Boron trimethyl is a weaker Lewis acid than the boron trihalides or monoborane. The electron donating effect of the methyl groups hinders the complex formation with trimethyl amine. Hence the bond $\text{N} \rightarrow \text{B}$ is weakest in $[(\text{CH}_3)_3\text{N} \rightarrow \text{B}(\text{CH}_3)_3]$. Me_3N as donor (capacity). $\text{BBr}_3 > \text{BCl}_3 > \text{BF}_3 \sim \text{BH}_3 > \text{BMe}_3$.

37. $\text{O} \leftarrow \text{S} = \text{O}$ $\text{H}-\text{O}-\text{N}=\text{O}$ $\text{H}-\text{O}-\text{S}-\text{OH}$ $\text{H}-\text{O}-\text{N}=\text{O}$
- \downarrow
 O
- \downarrow
 O

39. S_1 : as it does not have d-orbitals.



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 π orbitals. As a result, the last two electrons are unpaired in the degenerate (having the same energy) π 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.

40. Bond order of $\text{N}_2 = 3$ bond order of $\text{N}_2^+ = 2.5$; B.O. of $\text{O}_2 = 2$; B.O. of $\text{O}_2^+ = 2.5$

41. M.O for $\text{C}_2 = \sigma_1\text{s}^2 < \sigma_1^*\text{s}^2 < \sigma_2\text{s}^2 < \sigma_2^*\text{s}^2 < \underbrace{\pi_2\text{p}_y^2 = \pi_2\text{p}_z^2}_{\text{HOMO}} < \sigma_2\text{p}_x^2 < \underbrace{\pi_{\text{LUMO}}^2}_{\text{LUMO}}$

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 $\text{C}_2^{2-} \left[\text{C} \equiv \begin{smallmatrix} \pi \\ \text{C} \end{smallmatrix} \right]^{2-}$.

42. (A) $\text{H}_2\text{O}_2 = 1.48 \text{ \AA}$ due to repulsions between non-bonded pairs of electron on O-atoms and $\text{O}_2\text{F}_2 = 1.217 \text{ \AA}$.
(B) In O_2^- very slightly increases due to charge (-ve) on two O atoms.

(C)	Bond Order	Internuclear Distance (pm)	Number of unpaired(s) Electrons
O ₂ ⁺ (dioxygenyl)	2.5	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

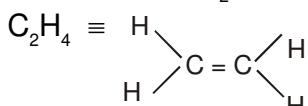
43. OF is derivative of O₂ and isoelectronic with O₂⁻.
 So ($\sigma 1s^2$)² (σ^*1s^2)² ($\sigma 2s^2$)² (σ^*2s^2)² ($\sigma 2p_z^2$)² ($\pi 2p_x^2 = \pi^*2p_y^2$)² ($\pi^*2p_x^2 = \pi^*2p_y^1$)
 The bond order of OF $1/2(10 - 7) = 1.5$.

44. ClO₂ has one unpaired electron.

45. (A) NO B.O = 3 triple bond.

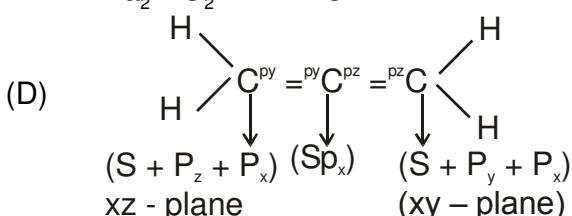
O = N – Cl there is a double bond between N and 'O' atom

(B) CaC₂ \equiv Ca²⁺ + C₂²⁻ (-C \equiv C-)

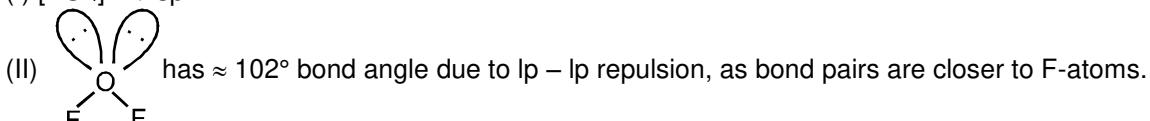


(C) KO₂ \equiv O₂⁻ B.O = 1.5

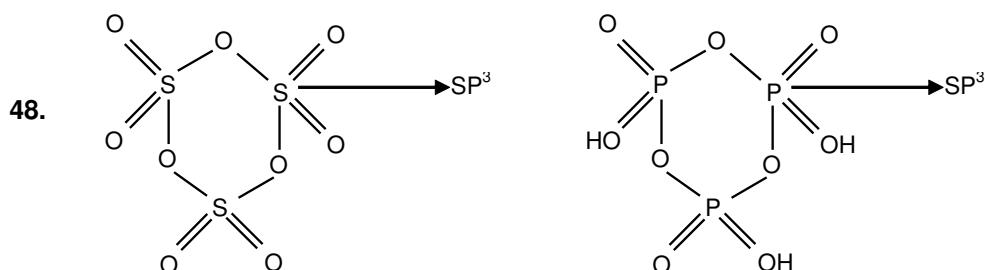
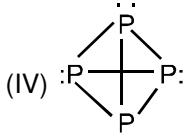
Na₂ \equiv O₂²⁻ B.O = 1



46. (I) [PCl₄]⁺ \rightarrow sp³



(III) All have sp³ hybridisation and one lone pair.



50. Dipole moment of compound if it would have been completely ionic

$$= (4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-8} \text{ cm}) = 12.8 \text{ D}$$

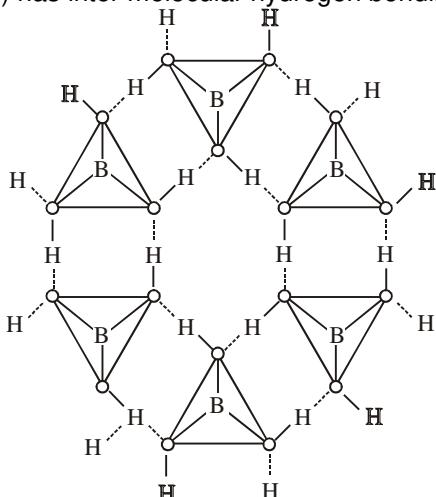
$$\text{so \% ionic character} = \frac{4.0}{12.8} \times 100\% = 31.25\%$$

51. 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^2 hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet.

53. (A) A fact

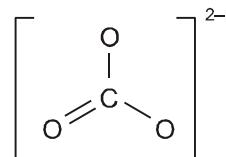
(B) In the solid state and in liquid HF, the HF_2^- ion is held together by hydrogen bonding. In aqueous solutions there is hydrogen bonding but each HF molecule forms hydrogen bonds with the much more prevalent H_2O present, instead of with other HF molecules and H_3O^+ and F^- are much more likely to be formed.

(C) H_3BO_3 (solid) has intermolecular hydrogen bonding.

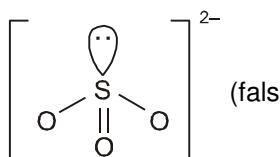


54. (A) intermolecular hydrogen bonded. (true)

- (B) structure of anions are different CO_3^{2-} – trigonal planar (sp^2)



- SO_3^{2-} – trigonal pyramidal (sp^3)



(false)

- (C) $\text{O}=\text{Xe}=\text{O}$ no lone pair of electrons (false)

- (D) True. $\text{D}_2\text{O} = 374.4 \text{ K}$; $\text{H}_2\text{O} = 373.0 \text{ K}$

55. D is less electronegative than H-atom so the results

56. 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).



58. Fluorine is more electronegative but dipole moment is the product of charge and distance between combining atoms (covalently bonded) ; due to more charge separation in CH_3Cl , it has higher dipole moment.

59. (A) As δ^+ charge on central atom increases, the attraction between δ^+ and δ^- increases and thus $\text{Xe}-\text{F}$ bond length decreases. The correct order is $\text{XeF}_2 > \text{XeF}_4 > \text{XeF}_6$
 (B) PH_5 can not undergo sp^3d 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_3Cl is greater than CH_3F due to greater charge separation on carbon and chlorine atoms in CH_3Cl .
 (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.

60. Fact based

61. Fact based

62. NaCl is an ionic compound.

63. The element present in short period will be of 13th group (group no = $10+3=13$) i.e. aluminium and its oxide will be Al_2O_3 which is amphoteric in nature; as react with acids as well as bases forming salts and water.

64. As Pb^{2+} has low polarising power. So PbCl_2 is ionic.

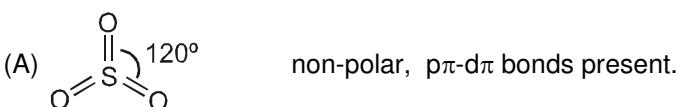
65. Solubility BaCO_3 and MgCO_3 can be explained on the basis of their hydration and lattice energies.

66. AgI is less soluble than AgF due to covalent nature. LiI is more soluble than LiF due to high size difference of ions more ionic nature, more melting point. Higher the charge density, larger will be the hydrated radii.

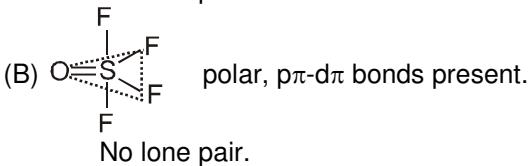
67. Strength of metallic bond \propto number of unpaired electrons.

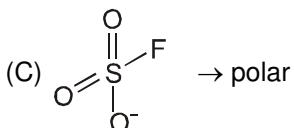
68. (i) Alkali metal, potassium forms K^+ (number of electrons = 18) which is isoelectronic with P^{3-} (number of electrons = 18) $\rightarrow Q$.
 (ii) Transition element, chromium show maximum oxidation state of +6 in $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} and they are coloured $\rightarrow S$.
 (iii) Noble gas, Kr has largest atomic radius because radius is expressed as vander Waal's radius and there is interelectronic repulsions due to completely filled outer most shell. Inert gas has highest first ionisation energy in the respective period because of stable valence shell electron configuration $\rightarrow T$.
 (iv) Element ($Z = 13$), aluminium has intermediate value of electronegativity and therefore its oxide is amphoteric in nature $\rightarrow R$.

70. Steric no. of $\text{I}_3^- = 5$, sp^3d ; Steric no. of $\text{XeO}_3 = 4$, sp^3 ;
 Steric no. of $\text{ClOF}_3 = 4 + 1 = 5$, sp^3d ; Steric no. of $\text{XeF}_5^+ = 5 + 1 = 6$, sp^3d^2

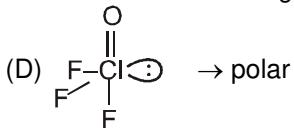


All S–O bonds are identical.
No lone pair.

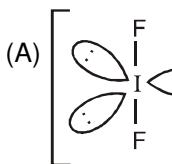


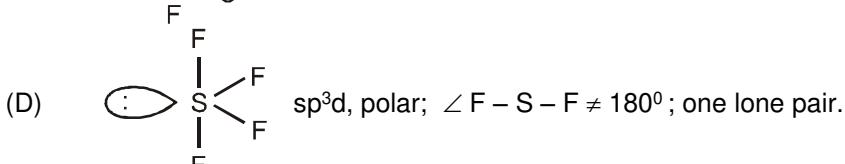
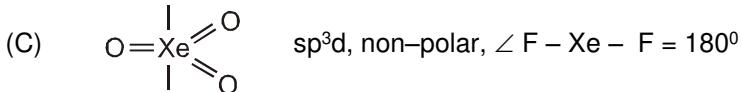
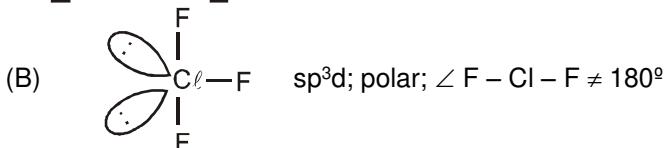


→ p π -d π bonds present.
→ Due to resonance identical
S-O bond length

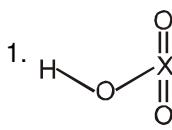
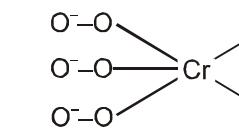
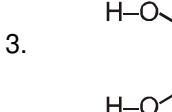


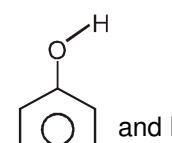
→ p π -d π bonds present.
→ lone pair present.

72. (A)  sp³d; $\angle F - I - F = 180^\circ$; $\mu = 0$



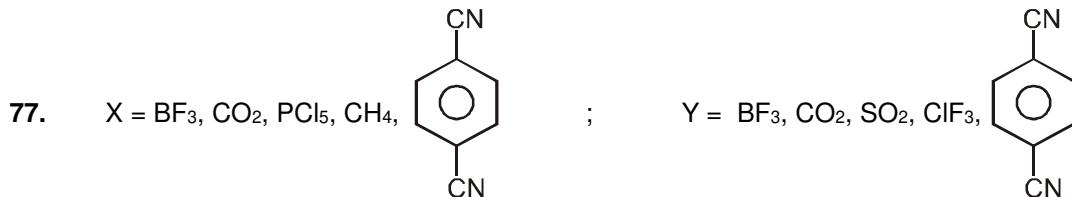
73. H₃PO₄, H₃PO₃, H₃PO₂, HClO₄, HClO₃, HClO₂, H₂SO₃, H₂SO₄, H₂SO₅, H₂S₂O₈, SO₃, SO₂, P₄O₁₀

74. 1.  ⇒ x = 1 2.  ⇒ y = 4
3.  ⇒ z = 1 4. Na₂B₄O₇ ⇒ w = O

75.  and NH₃ will have non-zero dipole moment.

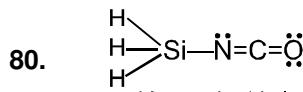
76. $\mu_{\text{cal}} = q \times d = 1.6 \times 10^{-19} \text{ C} \times 150 \times 10^{-12} \text{ m} = 2.4 \times 10^{-29} \text{ Cm}$ $\mu_{\text{obs}} = 1.8 \times 10^{-29} \text{ Cm}$

Percentange ionic character = $\frac{\mu_{\text{cal}}}{\mu_{\text{obs}}} \times 100 = 75\%$



78. (1, 2, 5, 6, 7, 8)

79. (a) PCl_6^- (Coordinate Bond = 1)
 (c) HNO_3 (Coordinate Bond = 1) (b) $\text{NH}_3 \cdot \text{BF}_3$ (Coordinate Bond = 1)
 (D) CO (Coordinate Bond = 1)



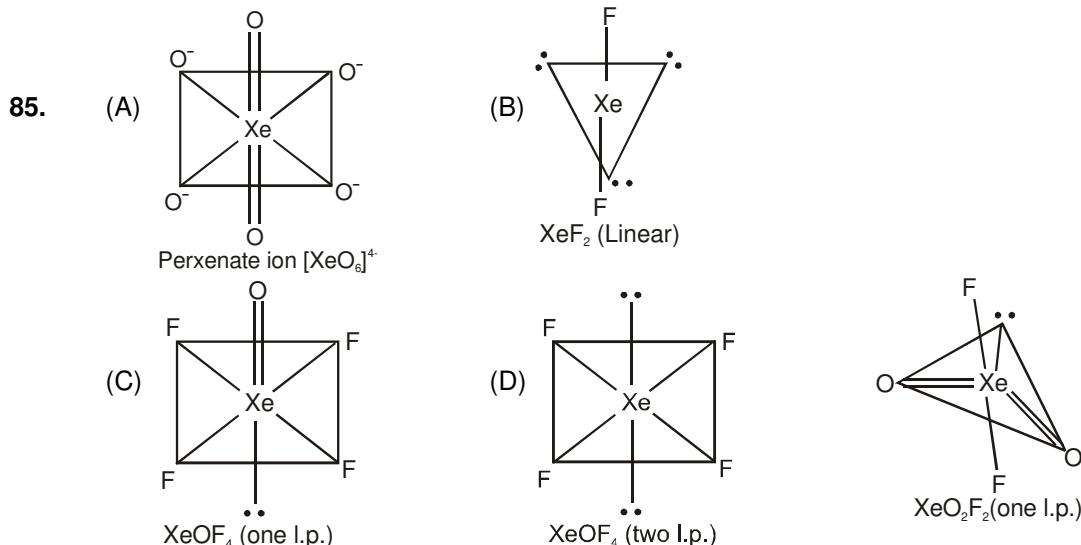
Vacant d-orbitals
 LP of N can be delocalised back bonding ($p\pi - d\pi$). SN of N = 2 sp

81. The species in which the central atom has expanded octet, are called hypervalent compounds.

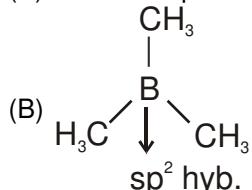
82. (b) If X-axis is internuclear axis, then it will result in π bond.
 (c) It will result in σ bond.
 (d) & (e) It shows zero overlap with no bond formation.

83. In PCl_6^- and BF_4^- , vacant orbital take part in hybridization

84. Bigger atoms, LP and double bond occupy equatorial positions in trigonal bipyramidal structure.

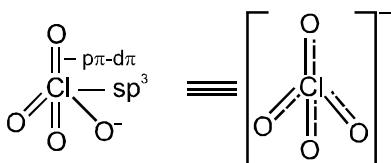


86. (A) Due to the presence of lone pair bond angle decreases.



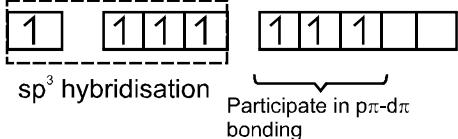
- (C) NH_4Cl is an ionic compound and 'N' is in sp^3 hybridisation.
 (D) S_8 molecule has 16 electron pairs left behind after the bonding.

87.



Valence shell electron configuration of Cl, $3s^2 3p^5$

$3s$ $3p$ $3d$



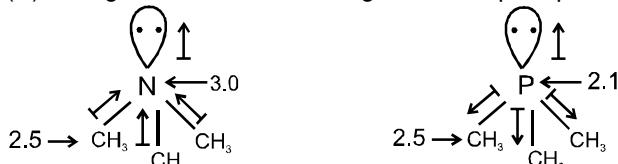
To obtain effective $p\pi-d\pi$ overlap the size of the d orbital must be similar to size of the p orbital. Hence in chlorine, $p\pi-d\pi$ bonding is so strong that no polymerization of oxoanions occurs.

89.

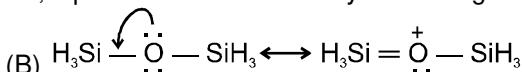
$(CH_3)_2O$: can act as lewis base but $(SiH_3)_2O$ & $(SiH_3)_3N$ can not, as one pairs on O & N are delocalised in to empty orbitals of Si.

90.

(A) Nitrogen is more electronegative than phosphorus.



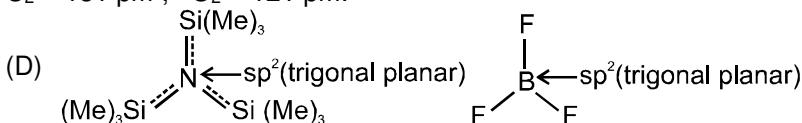
So, dipole moment of trimethylamine is greater than trimethyl phosphine.



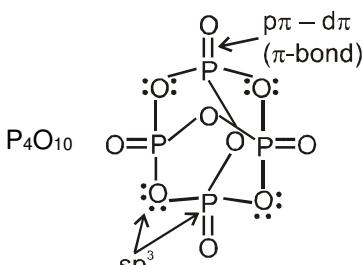
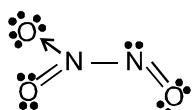
In trisilyl ether the lone pair of electron on oxygen atom is less easily available for donation because of $p\pi-d\pi$ delocalisation due to presence of the vacant d-orbital with Si. This however is not possible with carbon in CH_3-O-CH_3 due to the absence of d-orbital making it more basic.

(C) Bond order of C_2 and O_2 are same i.e., 2. In C_2 molecules both bonds are π -bonds whereas, there is one σ and one π -bond in O_2 molecule

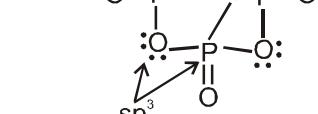
$C_2 = 131$ pm ; $O_2 = 121$ pm.



91.



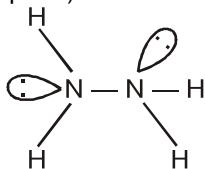
92.



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 sideways with an empty d-orbital on the phosphorus atom. The bond angle POP is 127° and there is no P–P bonds.



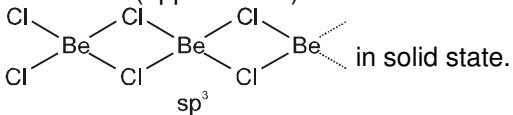
93. (A) Structure is similar to that of ethane. Each N atom is tetrahedrally surrounded by one N, two H and a lone pair. The two halves of the molecules are rotated 95° about N–N bond and occupy a gauche (non-eclipsed) conformation. The bond length is 1.45 Å.



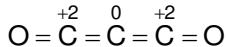
(B) Has partial double bond character due to $\pi\pi$ - $d\pi$ delocalisation.

(C) $OF_2 = 103^\circ$ (approximate) and $OCl_2 = 112^\circ$ (approximate).

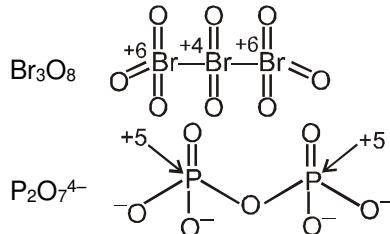
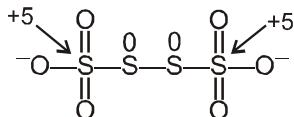
(D) Exist in polymeric structure as



94. C_3O_2



$S_4O_6^{2-}$



96. All the given species contain H-bonded to O, and so are capable of H-bonding.

98. 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.

99. According to Fajan's rule.

100. Group 1 elements have lesser strength of metallic bonding than corresponding group 2 elements due to only one electron per atom participating in metallic bonding in group 1. In group 2 elements, two electrons per metal atom participate in metallic bonding.

101. (A) due to decreasing strength of metallic bond.

(B) Fact

(C) Elements having half-filled stable configurations have lesser strength of metallic bonding.

(D) Electron delocalisation is the main reason for electricity conduction is both.

102. (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.

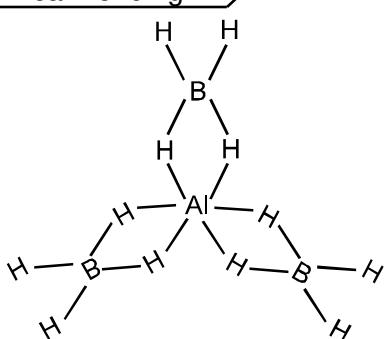
103. $A = Ne$

104. $B_4 = P_4$

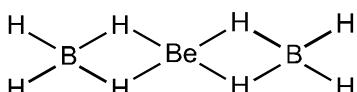
105. $BC_3 = PCl_3$

$BC_5 = PCl_5$

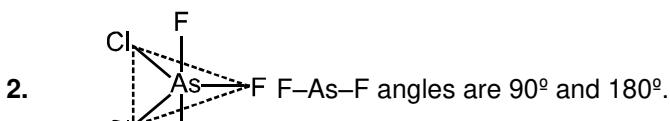
108.



110.

**PART - IV**

1. In CH_2F_2 bond angle are not identical due to bent rule.

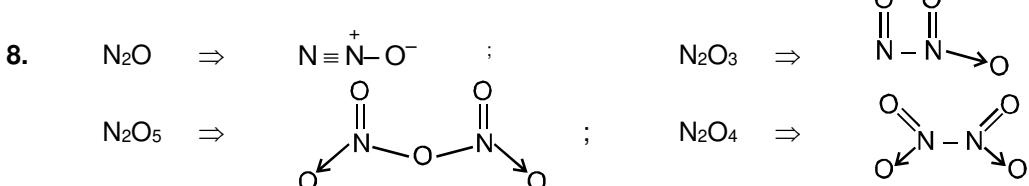
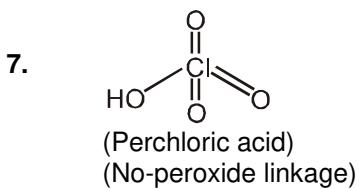


3. Benzene is non polar.
Inorganic benzene is non polar.



4. In BF_3 , BeF_2 , BCl_3 $p\pi-p\pi$ back bonding takes place.
In BF_3 and BeF_2 $2p-2p\pi$ back bond and BCl_3 $2p-3p\pi$ back bond is formed.

5. $\text{PCl}_5(s) \Rightarrow [\text{PCl}_4]^+(109.5^\circ)$, $[\text{PCl}_6]^- (90^\circ)$
 $\text{Cl}_2\text{O}_6(s) \Rightarrow [\text{ClO}_2^+](120^\circ)$, $[\text{ClO}_4^-](109.5^\circ)$
 $\text{N}_2\text{O}_5 \Rightarrow [\text{NO}_2^+](180^\circ)$, $[\text{NO}_3^-](120^\circ)$



9. It is fact.

10. $\text{NH}_3(\text{sp}^3) + \text{H}^+ \rightarrow \text{NH}_4^+(\text{sp}^3) ; \quad \text{NH}_3(\text{sp}^3) \rightarrow \text{NH}_2^-(\text{sp}^3) + \text{H}^+$
 $\text{AlH}_3(\text{sp}^2) + \text{H}^- \rightarrow \text{AlH}_4^-(\text{sp}^3) ; \quad \text{SiF}_4(\text{sp}^3) \rightarrow \text{SiF}_6^{2-}(\text{sp}^3\text{d}^2)$

11. Using MOT, Bond order of $O_2^{2-} = 1$, $O_2^- = 1.5$, $O_2 = 2$, $O_2^+ = 2.5$.

15. PCl_5

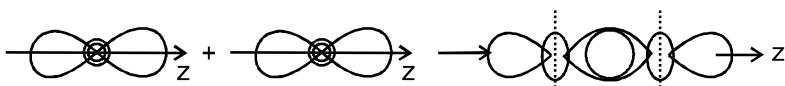
16. Total no. of σ bonds = 6

Total no. of π bonds = 2

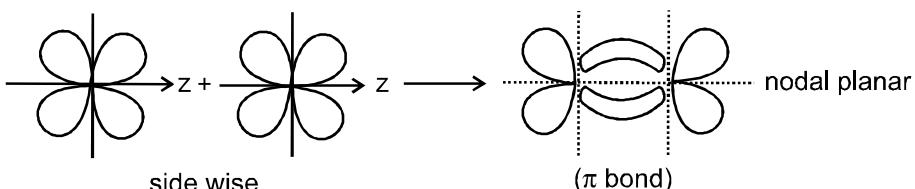
total no. of bonds = $6+2 = 8$

No. of orbitals involved = $2 \times 8 = 16$

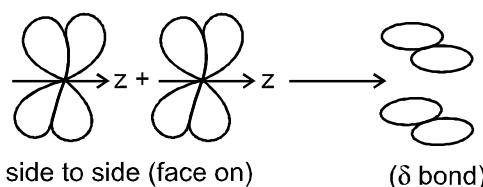
17.



Co-axial



side wise



side to side (face on)

(Source : Schaum series page no. 129)

18. PCl_5 , SF_4 , ClF_3 , $[SF_5]^+$, $[ClF_4]^+$, $[XeF_3]^+$.

