

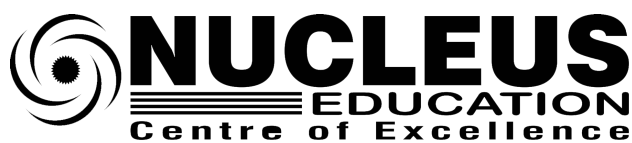
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**NURTURE**

# **IIT CHEMISTRY**

**INORGANIC CHEMISTRY**

**CHEMICAL BONDING**



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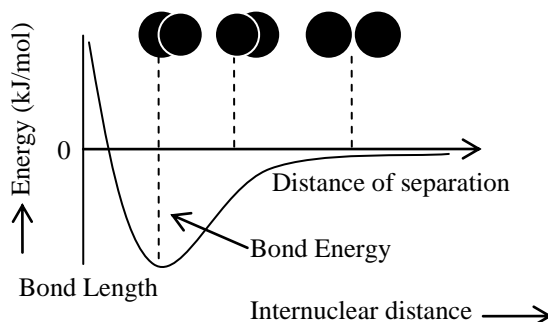
## LECTURE NUMBER - 1

### CHEMICAL BOND

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

#### 1. Tendency to acquire minimum energy:

- When two atoms approach to each other-Nucleus of one atom attracts the electrons of another atom.
- Two nuclei and electrons of both the atoms repel each other.
- If net result is attraction, then the total energy of the system (molecule) decreases. A chemical bond is formed when the net energy of system is least.
- The amount of energy released during bond formation is known as 'Bond Energy'.
- Bond formation is an exothermic process.



Potential Energy diagram

#### 2. Tendency to acquire noble gas configuration (Octet rule):

Atoms combine to complete an octet of electrons in their outer most shell. Hence all atoms have a tendency to acquire octet ( $s^2p^6$ ) configuration or to attain nearest noble gas configuration in their outermost orbit. This can be achieved by combining with other atom or ion.

### EXCEPTIONS TO OCTET RULE

#### 1. Transition metal ions

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

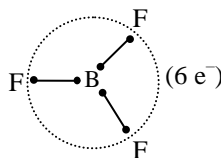
#### 2. Pseudo inert gas configuration [ $s^2p^6d^{10}$ ]

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

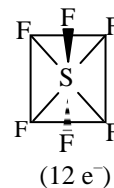
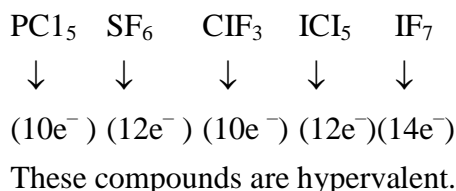
#### 3. Contraction of octet (incomplete octet)

$\text{BeF}_2$	$\text{BF}_3$	$\text{AlCl}_3$	$\text{BCl}_3$
( $4e^-$ )	( $6e^-$ )	( $6e^-$ )	( $6e^-$ )

These compounds are hypovalent.



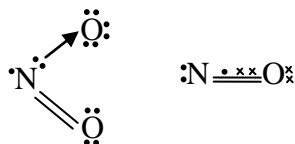
**4. Expansion of Octet (due to empty d-orbitals)**



**5. Odd electron species**

Species which contain odd number of electrons are called Odd electron species.

Ex. NO, NO<sub>2</sub>, ClO<sub>2</sub> etc.



**6. Compounds of Noble gases**

Noble gases which have already completed their octet (or duplet in case of He.) should not form compounds. However, their compounds like XeF<sub>2</sub>, XeF<sub>6</sub> & KrF<sub>2</sub> etc., have been actually prepared.

**Que.** Find the number of chemical specie(s) which does not follow octet rule.

BF<sub>3</sub>, PCl<sub>5</sub>, SF<sub>4</sub>, AlF<sub>3</sub>, CH<sub>4</sub>, SnCl<sub>2</sub>, NO<sub>2</sub>

**Sol.** BF<sub>3</sub>, PCl<sub>5</sub>, SF<sub>4</sub>, SnCl<sub>2</sub>, NO<sub>2</sub>

**Classification of Bonds**

(On the basis of bond energy)

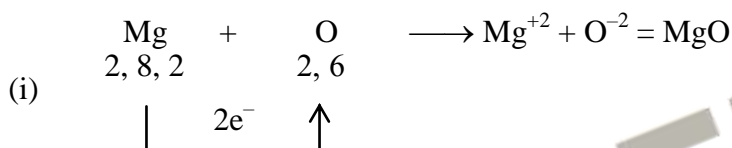
**Types of Bonds**

Force of attraction			
Chemical Bond	Hydrogen Bond	Vander Waal's Bond	Other Interaction
1. Ionic Bond	1. Inter-molecular	1. Dipole – Dipole	1. Ion – Dipole
2. Covalent Bond	Hydrogen Bond	Interaction	Interaction
3. Co-ordinate Bond	2. intra-molecular	2. Dipole – Induced	2. Ion – Induced
4. Metallic Bond	Hydrogen Bond	Dipole Interaction	Dipole Interaction
		3. Instantaneous dipole – Induced dipole Interaction	

**ELECTROVALENT OR IONIC BOND**

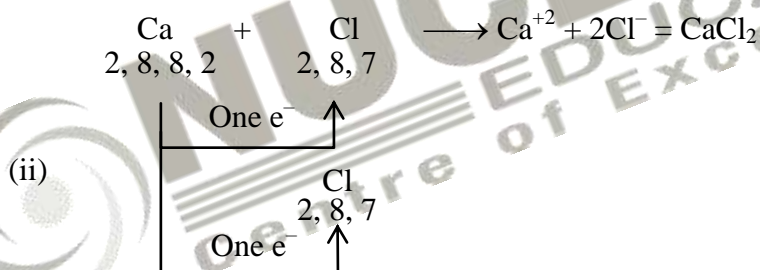
- (a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called as Ionic or electrovalent bond.
- (b) Electropositive atom loses electron
- (c) Electronegative atom gains electron
- (d) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.
- (e) Total number of electrons lost or gained is called electrovalency.

**Ex.**



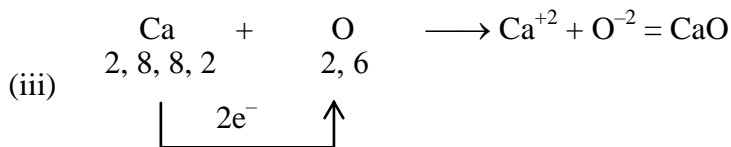
electrovalency of Mg = 2

electrovalency of O = 2



electrovalency of Ca = 2

electrovalency of Cl = 1



electrovalency of Ca = 2

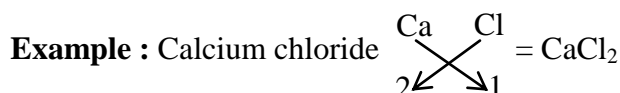
electrovalency of O = 2

- (f) A definite three dimensional structure is formed called crystal lattice.
- (g) The force of attraction is equal in all direction so ionic bond is non-directional.
- (h) Ionic compound do not have molecular formula. It has only empirical formula.

**Ex.** NaCl is empirical formula of sodium chloride

• **Representation of formula of ionic compounds:**

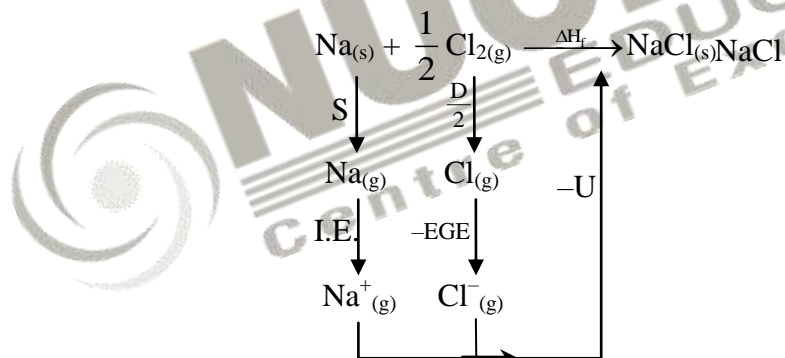
- Write the symbols of the ions side by side in such a way that positive ion is at the left and negative ion is at the right as  $A^+B^-$
- Write their electrovalencies in figure at the top of each symbol as  $A^{+x}B^{-y}$
- Now apply criss-cross rule as  $\begin{matrix} A & B \\ x \swarrow & \searrow y \end{matrix}$ , i.e. formula  $A_yB_x$ .



**FORMATION OF IONIC COMPOUND- BORN HABER CYCLE**

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

Formation of NaCl (s) involves



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

here,  $S$  = heat of sublimation of Na(s)

I.E. = ionisation enthalpy of Na(g)

$D$  = bond dissociation energy of  $Cl_2(g)$

EGE = electron gain enthalpy of  $Cl(g)$

$U$  = lattice energy

$\Delta H_f$  = heat of formation of NaCl(s)

**FACTORS FAVOURING IONIC BONDING**

**(a) Ionisation energy :**

Lesser Ionization energy → Greater tendency to form cation.

Ex.  $\text{Na} > \text{Mg} > \text{Al}$   
 $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$  } Cation formation tendency

**(b) Electron affinity:**

Higher electron affinity → Greater tendency to form anion.

Ex.  $\text{Cl} > \text{F} > \text{Br} > \text{I}$  anion formation tendency

**(c) Lattice energy :**

Greater lattice energy

**(d) Overall lowering of energy:**

Energy must be released during bond formation.

**LECTURE NUMBER - 2**

**COVALENT BOND**

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



$\text{H} - \text{H} ;$   
 $\text{H}_2$  molecule

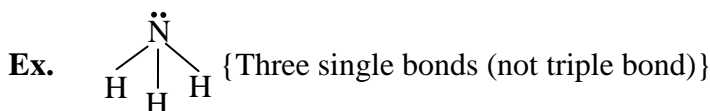


$\ddot{\text{O}} = \ddot{\text{O}} ;$   
 $\text{O}_2$  molecule



$\text{N} \equiv \text{N}$   
 $\text{N}_2$  molecule

- (b) The shared pair of electrons must have opposite spins, and are localised between two atoms concerned.
- (c) On the basis of electrons being shared between two atoms the bonds are of three types -



$\text{H} - \text{H}$  (Single bond),  $\text{O} = \text{O}$  (Double bond),  $\text{N} \equiv \text{N}$  [Triple bond (not three single bond)].

● **Classification of covalent bond:**

1. Classification on the basis of number of covalent bond.

\* Single bond                      \* Double bond                      \* Triple bond

**Note-1:** Maximum number of covalent bond between two atoms is three

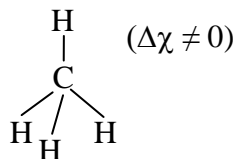
**Note-2:** Maximum number of  $\sigma$  and  $\pi$  bond between two atoms is 1 and 2 respectively.

**Exception :**  $[\text{Cl}_4\text{Re} \equiv \text{ReCl}_4]^{-2}$

2. Classification on the basis of polarity of bond :

- (a) **Polar bond**- Covalent bond in which the electronegativity difference between of combining atoms is non zero.

Eg.  $\text{H} - \text{F}$  ( $\Delta\chi \neq 0$ )



- (b) **Non-polar bond** - Covalent bond in which the electronegativity difference is of combining is zero.

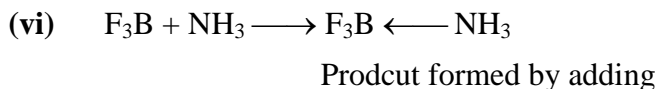
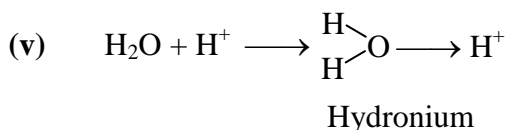
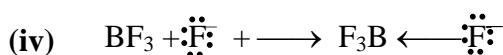
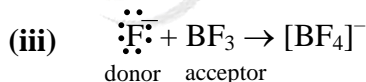
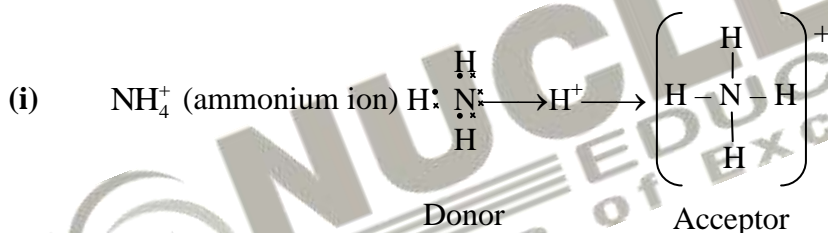
Eg.  $\text{H} - \text{H}$   $\Delta\chi = 0$        $\text{O} = \text{O}$   $\Delta\chi = 0$

3. Classification on the basis of overlapping (Discuss in VBT)

- (a) Sigma ( $\sigma$ ) bond      (b) pi ( $\pi$ ) bond

**COORDINATE BOND (DATIVE BOND)**

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



**Note :**

**Lewis base :** Chemical species which can donate electron pair.

Ex.  $\text{F}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CN}^-$ ,  $\text{HN}_3$ ,  $\text{NO}_2^-$ ,  $\text{N}(\text{CN})_3$ ,  $\text{SO}_4^{2-}$

**Lewis acid:** Chemical species which can accept an electron pair.

Ex.  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{PCl}_3$ ,  $\text{Fe}^{+2}$ ,  $\text{H}^+$ ,  $\text{Me}_3\text{B}$ ,  $\text{AlCl}_3$ ,  $\text{SiF}_4$  etc



• **Other example**

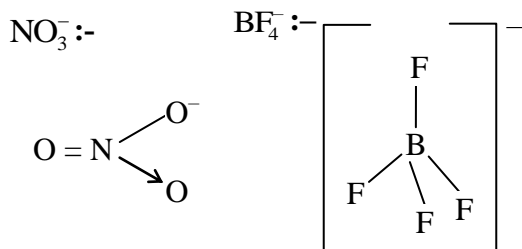


**Que.** The species having co-ordinate bond from the following options is/are-

- (A)  $\text{CO}_3^{2-}$  (B)  $\text{NO}_3^-$  (C)  $\text{NO}_2^-$  (D)  $\text{BF}_4^-$

**Ans.** (B,D)

**Sol.**  $\text{NO}_3^-$  and  $\text{BF}_4^-$  having co-ordinate bond.



☞ **VALENCY**

**Valency:** Combining capacity of an element is called valency.

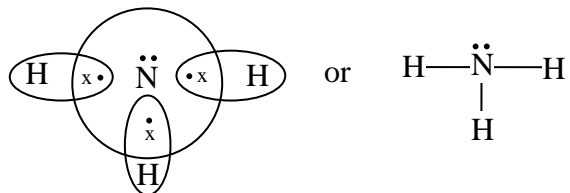
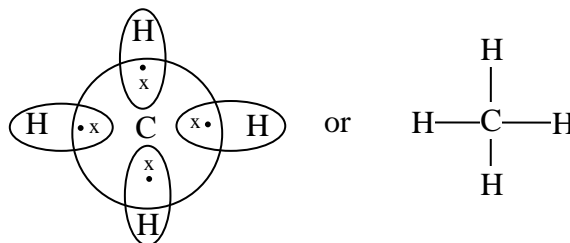
☞ **ELECTROVALENCY**

It is defined as the number of electron gain or loss of an atom during ionic bond formation.

Ex. In NaCl the electrovalency of Na and Cl is 1 and 1 respectively.

☞ **COVALENCY** : Capacity to form covalent bond is known as covalency

It is represented by(–) small line. – means single bond; = means double bond; ≡ means triple bond.



☞ **FIXED COVALENCY**

Due to non-availability of vacant 'd' orbital in N, O, F therefore these elements does not shows variable covalency.





## VARIABLE COVALENCY

- (I) Variable valencies are shown by those elements which have empty orbitals in outermost shell.
- (II) Lone pair electrons gets excited in the subshell of the same shell to form the maximum number of unpaired electrons.
- (III) The energy required for excitation of electrons is called promotion energy.
- (IV) Promotion rule - Excitation of electrons in the same orbit.

### Example:-

(a) Phosphorus → Ground state  $\begin{array}{|c|c|c|c|} \hline \uparrow\downarrow & \uparrow & \uparrow & \uparrow \\ \hline 3s & 3p & & \\ \hline \end{array}$  Covalency=3

Ex.: (PCl<sub>3</sub>)

Phosphorus → Excited state  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & & \\ \hline 3s & 3p & 3d & & & & \\ \hline \end{array}$  Covalency = 5

Ex.: (PCl<sub>5</sub>)

(b) Sulphur → Ground state  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow & & & \\ \hline 3s & 3p & 3d & & & & \\ \hline \end{array}$  Covalency = 2

Ex.: (SF<sub>2</sub>)

Sulphur → Excited state

1<sup>st</sup> excited state  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow & & \\ \hline 3s & 3p & 3d & & & & \\ \hline \end{array}$  Covalency = 4

Ex.: (SF<sub>4</sub>)

2<sup>nd</sup> excited state  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \\ \hline 3s & 3p & 3d & & & & \\ \hline \end{array}$  Covalency = 6

Ex.: (SF<sub>6</sub>)

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

(c) Iodine has three lone pair of electrons

(Ground state)  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & & & \\ \hline 5s & 5p & 5d & & & & \\ \hline \end{array}$

(3<sup>rd</sup> excited state)  $\begin{array}{|c|c|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \\ \hline 5s & 5p & 5d & & & & \\ \hline \end{array}$

Ex.: IF<sub>7</sub>

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

Variable Valencies are 1, 3, 5, 7

**Que.**  $\text{PCl}_5$  is formed but  $\text{NCl}_5$  does not why ?

**Ans.** Due to non-availability of vacant 'd' orbital in N.

**Que.**  $\text{SF}_4$  is formed but  $\text{OF}_4$  does not why?

**Ans.** Same as above

**Que.** Fluorine show only one covalency but other halogen can show variable covalency

**Ans.** same as above

### DO YOURSELF – 1

- Which of the following is an example of super octet molecule ?  
(A)  $\text{ClF}_3$  (B)  $\text{PCl}_5$  (C)  $\text{IF}_7$  (D) All the three
- In which of the following species the bonds are non-directional ?  
(A)  $\text{NCl}_3$  (B)  $\text{RbCl}$  (C)  $\text{BeCl}_2$  (D)  $\text{BCl}_3$
- The maximum covalency is equal to -  
(A) The number of unpaired p-electrons  
(B) The number of paired d-electrons  
(C) The number of unpaired s-and p-electrons  
(D) The actual number of s-and p-electrons in the outermost shell
- What is the number of lone pairs present in  $\text{XeOF}_4$  ?  
(A) 1 (B) 2 (C) 3 (D) 4
- A covalent bond is possible between :  
(A) Only similar atoms (B) Only dissimilar atoms  
(C) Similar and dissimilar atoms (D) Similar molecules

## LECTURE NUMBER – 3



### OXIDATION NUMBER

- It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules ..
- It is calculated on basis of a arbitrary set of rules.
- It is a relative charge in a particular bonded state.



### Rules governing oxidation number:

The following rules are.-helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element

- **Fluorine atom** : Fluorine is most electronegative atom (known). It always has oxidation number equal to, -1 in all its compounds.
- **Oxygen atom** : In general and as well as in its oxides, oxygen atom has oxidation number equal to -2.

**In case of :**

- (i) peroxide (e.g.  $\text{H}_2\text{O}_2, \text{Na}_2\text{O}_2$ ) is -1
- (ii) super oxide (e.g.  $\text{KO}_2$ ) is  $-\frac{1}{2}$
- (iii) ozonide ( $\text{KO}_3$ ) is  $-\frac{1}{3}$
- (iv) oxygen fluoride  $\text{OF}_2$  is +2 & in  $\text{O}_2\text{F}_2$  is +1

- **Hydrogen atom** : In general, H atom has oxidation number equal to + 1. But in metallic hydrides (e.g.  $\text{NaH}, \text{KH}$ ) it is -1.
- **Halogen atom** : In general, all halogen atom ( $\text{Cl}, \text{Br}, \text{I}$ ) has oxidation number equal to -1. But if halogen atom is attached with more electronegative atom then halogen atom will show positive oxidation numbers.

e.g.  $\text{K}\overset{+5}{\text{Cl}}\text{O}_3$      $\text{H}\overset{+5}{\text{Cl}}\text{O}_3$      $\text{H}\overset{+7}{\text{Cl}}\text{O}_4$      $\text{K}\overset{+5}{\text{Br}}\text{O}_3$

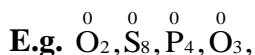
- **Metals :**

- (a) Alkali metal ( $\text{Li}, \text{Na}, \text{K}, \text{Rb}, \dots$ ) always have oxidation number +1.
- (b) Alkaline earth metal ( $\text{Be}, \text{Mg}, \text{Ca}, \dots$ ) always have oxidation number +2.

**Note:** Metal may have positive or zero oxidation number.

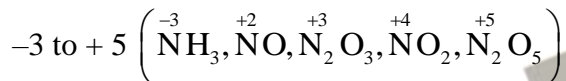
- (c) Aluminium always have +3 oxidation number

- (d) Oxidation number of an element in free state or in allotropic forms is always zero.



- (e) Sum of the charges of elements in a molecule is zero.
- (f) Sum of the charges of all elements in an ions is equal to the charge on the ion.
- (g) If the group no. of an element in periodic table is n then its oxidation number may vary from n to n – 8 (but it is mainly applicable in p-block elements)

E.g. N-atom belongs to group-V in the periodic table therefore as per rule its oxidation number may vary from



• **Calculation of average oxidation number :**

**Solved Examples :**

**Ex.** Calculate oxidation number of underlined element  $\text{Na}_2\underline{\text{S}}_2\text{O}_3$  :

**Sol.** Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

$$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$$

$$x = +2$$

**Ex.**  $\text{Na}_2\underline{\text{S}}_4\text{O}_6$  :

**Sol.** Let oxidation number of S-atom is x

$$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$$

$$x = +2.5$$

- ♦ It's important to note here that  $\text{Na}_2\text{S}_2\text{O}_3$  have two S-atom and there are four S-atom in  $\text{Na}_2\text{S}_4\text{O}_6$  but sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (Oxidation Number) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

**Ex.** Calculate the oxidation state of all the atoms in the following species :

- (i)  $\text{ClO}^-$       (ii)  $\text{NO}_2^-$       (iii)  $\text{NO}_3^-$       (iv)  $\text{CCl}_4$       (v)  $\text{K}_2\text{CrO}_4$       (vi)  $\text{KMnO}_4$

**Sol.** (i) In  $\text{ClO}^-$ , the net charge on the species is  $-1$  and therefore the sum of the oxidation states of Cl and O must be equal to  $-1$ . Oxygen will have an oxidation state of  $-2$  and if the oxidation state of Cl is assumed to be 'x' then  $x - 2$  should be equal to  $-1$ . So x is  $+1$

- (ii)  $\text{NO}_2^-$  :  $2 \times (-2) + x = -1$  (where 'x' is oxidation state of N)

$$\therefore x = +3$$

- (iii)  $\text{NO}_3^-$  :  $x + 3 \times (-2) = -1$  (where 'x' is oxidation state of N)

$$x = +5$$

- (iv) In  $\text{CCl}_4$ , Cl has an oxidation state of  $-1$

$$x + 4 \times (-1) = 0$$

$$\therefore x = +4 \quad (\text{where 'x' is oxidation state of C})$$

- (v)  $\text{K}_2\text{CrO}_4$  : K has O.S. of  $+1$  and O has oxidation state of  $-2$  and let Cr has oxidation state 'x' then,

$$2x + 1 + x + 4 \times (-2) = 0$$

$$\therefore x = +6$$

- (vi)  $\text{KMnO}_4$  :  $+1 + x + 4 \times (-2) = 0$

$$\therefore x = +7 \quad (\text{where x is oxidation state of Mn}).$$

**Ex.2** Calculate the oxidation state in the following:

$$\text{NOF}_3 \quad x + (-2) + 3(-1) = 0$$

$$x = +5$$

$$\text{SF}_4 \quad x + 4(-1) = 0$$

$$x = +4$$

$$\text{H}_2\text{SO}_4 \quad 2(+1) + x + 4(-2) = 0$$

$$x = +6$$

$$\text{HNO}_3 \quad 1 + x + 3(-2) = 0$$

$$x = +5$$

$$\text{XeF}_5^+ \quad x + 5(-1) = +1$$

$$x = +6$$

$$\text{XeF}_5^- \quad x + 5(-1) = -1$$

$$x = +4$$

$$\text{XeO}_6^{4-} \quad x + 6(-2) = -4$$

$$x = +8$$

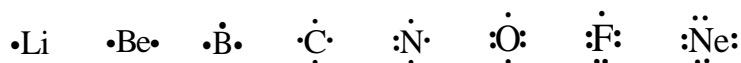
## LECTURE NUMBER - 4

### ☞ LEWIS DOT STRUCTURES OR LEWIS SYMBOLS

Lewis introduced simple notations to represent valence electron in an atom. These notations are called Lewis symbols or Lewis dot structure.

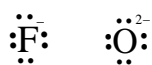
**Lewis symbols for atoms and monoatomic ions :**

Lewis symbol for second period elements are :



Number of dots around the symbol represents the number of valence electrons.

Lewis symbol for some anions are



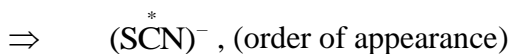
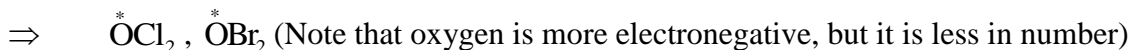
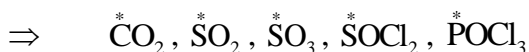
### ☞ How to draw the Lewis electron dot/Bond line structure of inorganic covalent compounds:

1. (i) First of all, identify the central atom in the given species. Central atom in a given molecule/ion is usually that atom which is least electronegative.
- (ii) Hydrogen can't be central atom as its covalency is one.
- (iii) Sometimes the central atom is that atom which is less in number.
- (iv) Sometimes the central atom in the given molecule/ion can't be decided on the basis of electronegativity or number of atoms (less). In such cases, that atom is central atom which appears in central position of given formula of molecule/ion.

To make it more clear, central atoms in the following species are starred (\*).

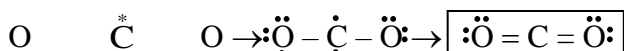


(Note-that electronegativity of H is less than that of central atom).



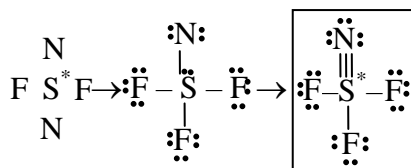
2. Surrounding atoms are the atoms which are directly bonded to central atom.
3. Arrange the surrounding atoms around the central atom and first form single bond between all surrounding atom with central atom.
4. Always make sure that octet of all the surrounding atoms is complete. It is not achieved by forming single bond, then try to make the double bond or triple bond between central atom and surrounding atom, as required to complete the octet of surrounding atoms.

e.g.,  $\text{CO}_2$



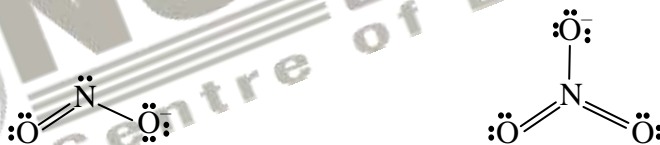


SNF<sub>3</sub>

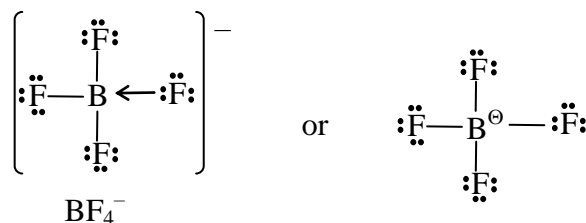
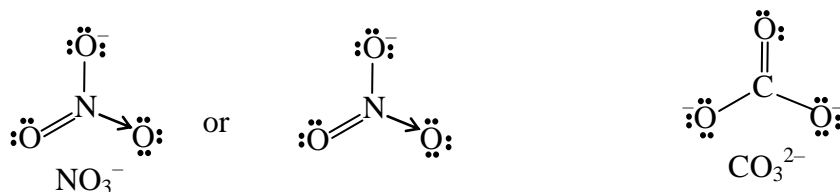


- After the bond formation, represent the lone pair of electrons on central atom as well as on surrounding atoms.
- Make sure that, in the structure you have made, the octet of the all surrounding atoms must be completed.
- If the central atom belongs to second period, it can have < 8 (max.) electrons (i.e. < 4 bonds) but never greater than 8 electrons (i.e. > 4 bonds).
- However, if the central atom belongs to third or lower period it can have > 8 electrons.
- At last verify the covalency of central atom.
- Lewis Structure of ions :**

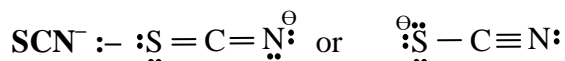
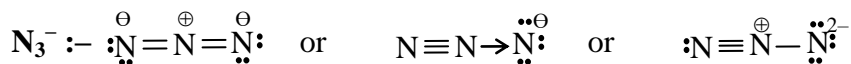
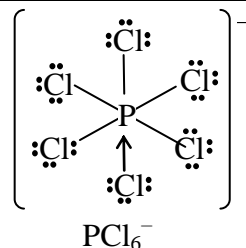
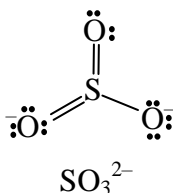
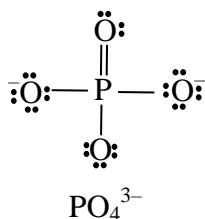
Distribute the negative charge on surrounding atom in such a way that octet of none of the surrounding atom is complete before the bond formation with central atom. If however, the octet of surrounding atom is complete by making it uninegatively charged (particularly in case of halogen which contains seven valence electron), then such surrounding atom will attach itself with central atom through a co-ordinate covalent bond.



But the above structures of NO<sub>3</sub><sup>-</sup> is incorrect as the central nitrogen belongs to second period, it can never form five covalent bond i.e., it can't have more than 8 electrons, so its actual structure is :







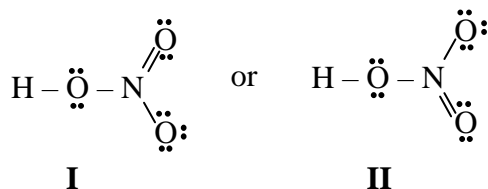
## FORMAL CHARGE

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

The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

Formal charge (F.C.) on an atom in a Lewis structure	=	$\left( \begin{array}{c} \text{Total number of} \\ \text{valence electron} \\ \text{in the free atom} \end{array} \right) - \left( \begin{array}{c} \text{Total number of} \\ \text{non bonding} \\ \text{(lone pair) electrons} \end{array} \right) - 1/2 \left( \begin{array}{c} \text{Total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right)$
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**Ex.** to calculate the formal charges on the various atoms of nitric acid ( $\text{HNO}_3$ ) molecule which has been described by the following Lewis structures:



**The H atom :** It has one valence electron, zero lone pair (or zero nonbonding electrons), and forms one bond (two bonding electrons).

Substituting in Eq. (i), we write  $\text{FC} = (1) - (0) - \frac{1}{2} (2) = 0$ .

**The O atom bonded to H:** It has six valence electrons, two lone pairs (or four nonbonding electrons), and form two bonds (or four bonding electrons).

Hence, we write  $FC = (6) - (4) - \frac{1}{2} (4) = 0.$

**The N atom:** It has five valence electrons, zero lone pair (or zero nonbonding electrons), and forms four bonds (or has eight bonding electrons).

Thus, we write  $FC = (5) - (0) - \frac{1}{2} (8) = +1$

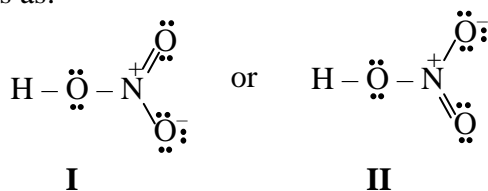
**The end O atom in  $N = O$ :** It has six valence electrons in the free state but in the Lewis structure (I or II), it has two lone pairs (or four nonbonding electrons) and forms two bonds (or has four bonding electrons).

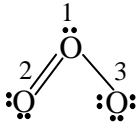
Thus, we can write  $FC = (6) - (4) - \frac{1}{2} (4) = 0$

**The end O atom in  $N - O$ :** It has six valence electrons in the free state but in the Lewis structure (I or II), it has three lone pairs or six nonbonding electrons and forms one bond (or has two bonding electrons).

thus, we write  $FC = (6) - (6) - \frac{1}{2} (2) = -1$

We can now write the Lewis structures (I and II) for nitric acid molecule including the formal charges as:-

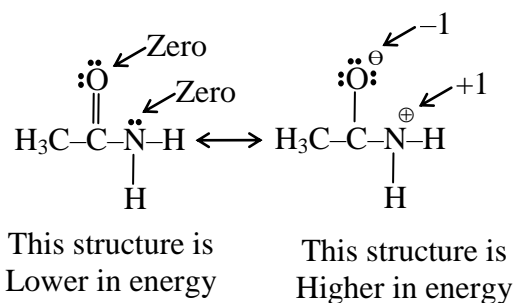


Molecule	Structure	Formal charge
$\text{O}_3$		$\begin{aligned} \text{O}(1) &= 6 - 2 - \frac{1}{2} (6) = +1 \\ \text{O}(2) &= 6 - 4 - \frac{1}{2} (4) = 0 \\ \text{O}(3) &= 6 - 6 - \frac{1}{2} (2) = -1 \end{aligned}$
		$S = 6 - 2 - \frac{1}{2} \times 6 = +1$

SO <sub>2</sub>	$\begin{array}{c} \ddot{\text{S}} \\ \diagup \quad \diagdown \\ (2)\ddot{\text{O}} \quad \ddot{\text{O}}:(1) \end{array}$	$\text{O}(1) = 6 - 6 - \frac{1}{2} \times 2 = -1$ $\text{O}(2) = 6 - 4 - \frac{1}{2} \times 4 = 0$
CO	$\ddot{\text{C}} \equiv \ddot{\text{O}}$	$\text{C} = 4 - 2 - \frac{1}{2} \times 6 = -1$ $\text{O} = 6 - 2 - \frac{1}{2} \times 6 = +1$
CN <sup>⊖</sup>	$\bar{\text{C}} \equiv \ddot{\text{N}}$	$\text{C} = 4 - 2 - \frac{1}{2} \times 6 = -1$ $\text{N} = 5 - 2 - \frac{1}{2} \times 6 = 0$
NH <sub>4</sub> <sup>+</sup>	$\left[ \begin{array}{c} \text{H}^1 \\   \\ {}^2\text{H} - \text{N} - {}^4\text{H} \\   \\ \text{H}^3 \end{array} \right]^+$	$\text{N} = 5 - 2 - \frac{1}{2} (8) = +1$ $\text{On each H} = 1 - 0 - \frac{1}{2} (2) = 0$
NO <sub>2</sub> <sup>⊖</sup>	$\begin{array}{c} \text{I} \quad \quad \text{II} \\ \ddot{\text{O}} = \ddot{\text{N}} - \ddot{\text{O}}^- \end{array}$	$\text{N} = 5 - 2 - \frac{1}{2} (6) = 0$ $\text{O(I)} = 6 - 4 - \frac{1}{2} (4) = 0$ $\text{O(II)} = 6 - 6 - \frac{1}{2} (2) = -1$

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.

**For example:**



Formal charges are useful for helping decide which of the several possible Lewis structures is best.

1. A Lewis structure with small formal charges are preferable to large formal charges.
2. Lewis structure with negative formal charges on the more electronegative atom are preferable than Lewis structures with negative formal charges on the less electronegative atom.
3. Lewis structures with unlike charges close together are more likely than Lewis structure with opposite charges widely separated.
4. Lewis structures with like charges on adjacent atoms are very unlikely.

## LECTURE NUMBER – 5

**Hypovalent compound :** The covalent compound in which central atom having less than 8 valence electron.

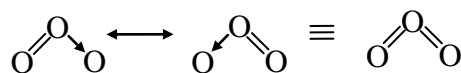
Ex.  $\text{BF}_3$ ,  $\text{BeCl}_2$  etc.

**Hypervalent compound :** The covalent compound in which central atom having greater than 8 valence electron.

Ex.  $\text{PCl}_5$ ,  $\text{IF}_7$ ,  $\text{SF}_6$  etc.

### RESONANCE

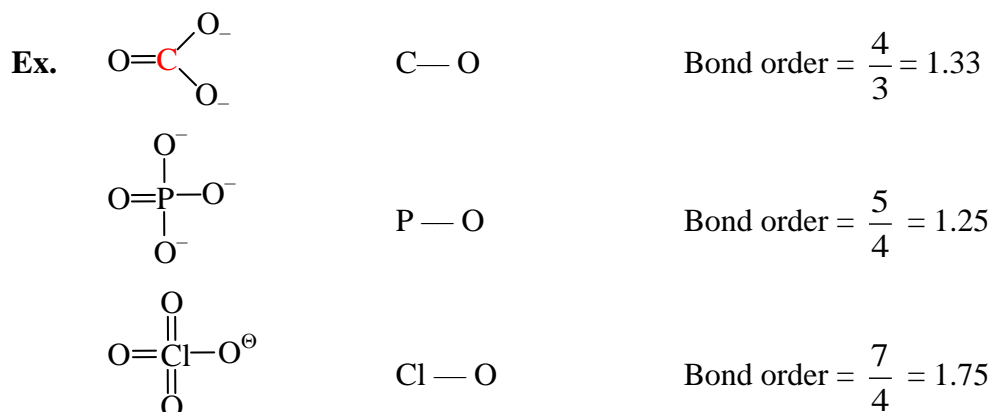
- (a) The concept of resonance was introduced by Heisenberg (1920), and later developed by Pauling and Ingold, to explain the properties of certain molecules.
- (b) It has been found that the observed properties of certain compounds cannot be satisfactorily explained by writing a single lewis structure.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



Resonance hybrid

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

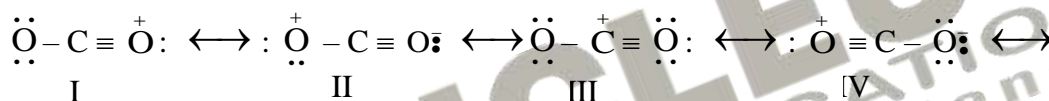
$$\text{Bond order} = \frac{\text{Total number of bonds in a molecule}}{\text{Resonating Structures}}$$



**Q.1** Which of the following ions has resonating structures ?

- (1)  $\text{SO}_4^{2-}$  (2)  $\text{PO}_4^{3-}$  (3)  $\text{SO}_3^{2-}$  (4) All of these

**Q.2** Which of the following resonating structure is correct for  $\text{CO}_2$  ?



- (1) I (2) II (3) III (4) IV

**Q.3** How many resonating structures can be drawn for  $\text{NO}_2$  ?

- (1) Six (2) Four (3) Five (4) Two

**Q.4** Which of the following is true for nitrate anion ?

- (1) Formal charge on N is zero (2) Bond order of NO bond is  $\frac{4}{3}$   
 (3) Average formal charge on oxygen is  $-\frac{1}{3}$  (4) There are 2  $\pi$ -bonds in the ion

**Q.5** Discuss resonance and formal charge in  $\text{N}_3^-$  and  $\text{N}_2\text{O}$ ?

**Q.6** Give the average formal charge and average bond order of X—O bond in the following oxy compounds?

- (a)  $\text{SO}_4^{2-}$  (b)  $\text{SO}_3^{2-}$  (c)  $\text{NO}_2^-$  (d)  $\text{ClO}_2^-$  (e)  $\text{ClO}_3^-$  (f)  $\text{ClO}_4^-$   
 (g)  $\text{HCO}_3^-$  (h)  $\text{CO}_3^-$  (i)  $\text{HSO}_3^-$  (j)  $\text{PO}_4^{3-}$

## LECTURE NUMBER - 6 & 7

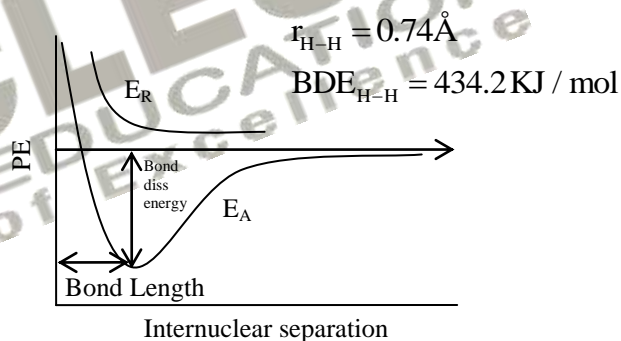
### ☛ VALENCE BOND THEORY

**Valence bond theory** was introduced by Heitler and London ( 1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals and the hybridization of atomic orbitals.

**Formation of H<sub>2</sub> molecule :** When two 'H'-atoms approaches towards each other for the formation of H<sub>2</sub> molecule. The following interactions takes place.

- (i) e-e repulsion
- (ii) e-p attraction
- (iii) p-p repulsion

Experimentally, it has been found that the magnitude of attractive forces is more than the repulsive forces. As a result, when two atoms approach each other then potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy.



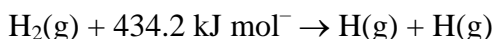
The potential energy curve for the formation of H<sub>2</sub> molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H<sub>2</sub>.

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.

**Bond Length :** Internuclear distance at minimum potential energy is called bond length.

**Bond Dissociation Energy :** The amount of energy released when one mole of same type of bonds are formed is called B.D.E.

434.2 kJ/mol of energy is required to dissociate one mole of H<sub>2</sub> molecule.





## ☞ ORBITAL OVERLAP CONCEPT

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

### Directional Properties of Bonds :

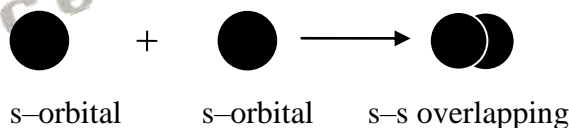
The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals.

### Types of Overlapping and Nature of Covalent Bonds

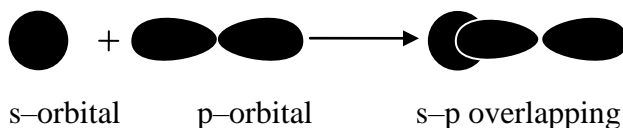
The covalent bond may be classified into following types depending upon the types of overlapping :-

(i) sigma ( $\sigma$ ) bond      (ii) pi ( $\pi$ ) bond      (iii) delta ( $\delta$ ) bond

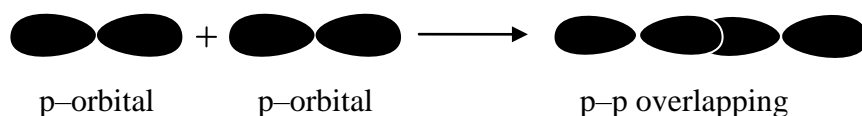
- (i) **Sigma ( $\sigma$ ) bond :** This type of covalent bond is formed by the end to-end (head on or axial) overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combinations of atomic orbitals.
- s-s overlapping : In this case, there is overlap 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-orbital of one atom and half filled p-orbital of another atom.



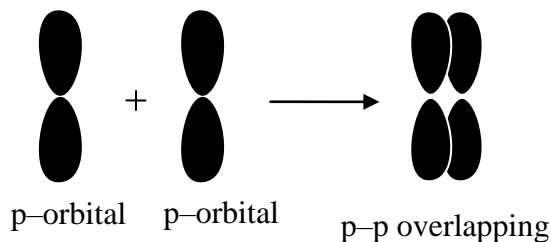
- p-p overlapping : This type of overlap takes place between half filled similar p-orbitals of the two approaching atoms.



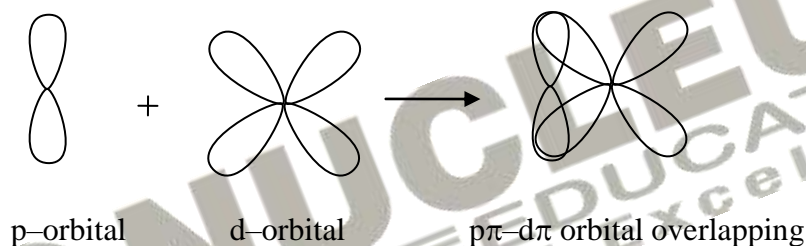


- (ii)  **$\pi(\pi)$  bond** : In the formation of  $\pi$  bond the atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below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

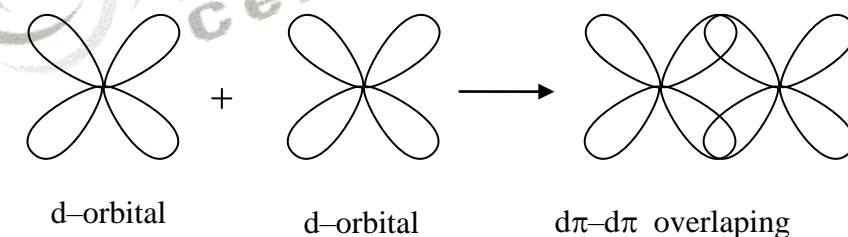
(a)  **$p_\pi - p_\pi$**



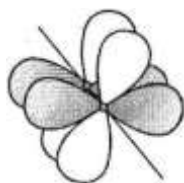
(b)  **$p_\pi - d_\pi$**



(c)  **$d_\pi - d_\pi$**



- (iii)  **$\delta$  bond** : are the covalent bonds where four lobes of d-orbital of one atom overlap with four lobes of the similar d-orbital of other atom. Except  $d_{z^2}$  all d orbitals form  $\delta$  bond.



**Q.1** In which molecule s - p overlapping occurs ?

- (a) CH<sub>4</sub>                      (2) NH<sub>3</sub>                      (3) H<sub>2</sub>O                      (4) All are wrong

**Sol.** (4) Because s - p overlapping occurs only in diatomic molecules.

**Q.2** Predict the nature of bond

Orbitals	Internuclear axis	Bond
s + s	any axis	$\sigma$
s + p <sub>x</sub>	x-axis	$\sigma$
s + p <sub>y</sub>	y-axis	$\sigma$
s + p <sub>z</sub>	z-axis	$\times$
p <sub>x</sub> + p <sub>x</sub>	x-axis	$\sigma$
p <sub>y</sub> + p <sub>y</sub>	y-axis	$\sigma$
p <sub>z</sub> + p <sub>z</sub>	z-axis	$\sigma$
p <sub>x</sub> - p <sub>x</sub>	y or z-axis	$\pi$
p <sub>y</sub> + p <sub>y</sub>	x or z axis	$\pi$
p <sub>z</sub> + p <sub>z</sub>	x or y axis	$\pi$
d <sub>xy</sub> + p <sub>x</sub>	y-axis	$\pi$
d <sub>xy</sub> + p <sub>y</sub>	x-axis	$\pi$
d <sub>xy</sub> + p <sub>z</sub>	any axis	$\times$
d <sub>xy</sub> + p <sub>x</sub>	x-axis	$\times$
d <sub>xy</sub> + p <sub>y</sub>	z-axis	$\times$
d <sub>yz</sub> + p <sub>y</sub>	z-axis	$\pi$
d <sub>yz</sub> + p <sub>z</sub>	y-axis	$\pi$
d <sub>xz</sub> + p <sub>x</sub>	z-axis	$\pi$
d <sub>xz</sub> + p <sub>z</sub>	x-axis	$\pi$

### 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)

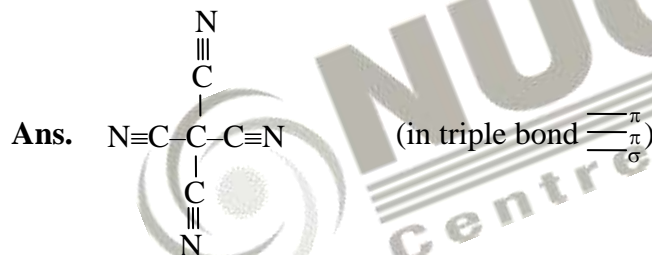
☞ **Advantages of VBT :**

- ❖ It explain various bond characteristics e.g., bond length, bond strength.
- ❖ It explains the quantitative relationship between the extent of overlapping and bond dissociation energy.
- ❖ This theory accounts for shape and nature of bonding of the molecule whose covalency is not according to the number of half-filled orbitals present in the ground state.
- ❖ This theory redefined the stability of molecules e.g.  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$  etc which are exception to octet rule.

☞ **Disadvantages of VBT :**

- ❖ According to this theory three bond angle in  $\text{CH}_4$  should be  $90^\circ$ , as these are formed by p-p overlapping, but actually it has six  $109^\circ 28'$  angles. In  $\text{NH}_3$  &  $\text{H}_2\text{O}$ , angle should be  $90^\circ$ . This is in disagreement with the actual bond angles of  $107^\circ$  &  $104.5^\circ$  in  $\text{NH}_3$  &  $\text{H}_2\text{O}$  molecules respectively.
- ❖ In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  etc. Pauling introduced the concept of hybridisation.

**Ex.1** What are the total number of  $\sigma$  &  $\pi$  bonds in tetracyanomethane.



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

**Comparison between Sigma and  $\pi$  bond**

	$\sigma$ bond		$\pi$ bond
1	Formed by axial overlapping	1	Formed by side by side overlapping
2	Involves s-s, s-p, p-p (axial) & hybrid orbitals	2	Involve p-p, p-d & d-d orbital
3	Extent of overlapping is stronger	3	Extent of overlapping is less so weaker
4	Free rotation around $\sigma$ bond is possible	4	Free rotation around $\pi$ bond is not possible
5	Hybridized or unhybridized orbital forms $\sigma$ bond	5	Hybridized orbital never forms $\pi$ bond
6	Independent existence of $\sigma$ -bond.	6	No independent existence.

**Practice Set**

**Q.1** Give correct order of bond strength for  $\sigma$  bond.

1s-1s, 2p-2p, 2s-2s, 3s-3p, 2s-3s, 3s-3s, 3p-3p, 1s-2s, 1s-2p, 2s-2p, 2s-3p

**Sol.** 1s-1s > 1s-2p > 1s-2s > 2p-2p > 2s-2p > 2s-2s > 2s-3p > 2s-3s > 3p-3p > 3s-3p > 3s-3s

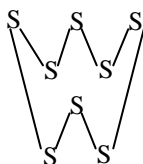
**Hint:** If internuclear distance is incomparable than B.S.  $\propto$  Bond distance

If internuclear distance is comparable than B.S.  $\propto$  Extent of overlapping (directional of nature)

**Q.2** O<sub>2</sub> exists but S<sub>2</sub> does not exist at room temperature? Why ?

**Sol.** For S<sub>2</sub>, 3p $\pi$ -3p $\pi$  bond is less effective.

Hence S<sub>8</sub> is formed



**Q.3** Compare bond strength.

HF, HCl, HBr, HI

**Sol.** HF > HCl > HBr > HI

1s-2p 1s-3p 1s-4p 1s-5p

**Q.4** According to the valence bond theory, when a covalent bond is formed between two reacting atoms, the potential energy of the system becomes-

(1) negative (2) positive (3) minimum (4) maximum

**Q.5** The strongest covalent bond is formed by the overlap of-

(1) *s* and *p* orbitals (2) *s* and *s* orbitals  
(3) *p* and *d* orbitals (4) *p* and *p* collateral orbitals

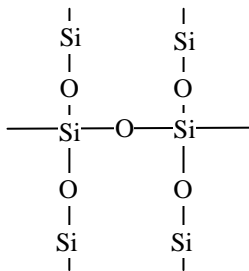
**Q.6** Explain

(i) N<sub>2</sub> exist but P<sub>2</sub> does not

(ii) CO<sub>2</sub> is gas but SiO<sub>2</sub> is covalent solid.

**Sol.** (i) For P<sub>2</sub>, 3p $\pi$ -3p $\pi$  bonding is not effective.

(ii) In SiO<sub>2</sub>, Si does not have tendency to form  $\pi$ -bond so as the size increases the  $\pi$  bond formation tendency decreases. Due to large size of Si. Hence it forms 3D network structure.



**Q.7** If x is the internuclear axis then which overlapping results  $\pi$  bond

- (1)  $d_{xy}-d_{xy}$                       (2)  $p_x-p_y$                       (3)  $s-p_x$                       (4)  $p_x-p_x$

**Ans.** (1)

**Sol.**  $p_x - p_y \rightarrow$  zero overlapping

$s - p_x \rightarrow \sigma$  bond

$p_x - p_x \rightarrow \sigma$  bond

$d_{xy} - d_{xy} \rightarrow \pi$  bond

### DO YOUR SELF – 2

**Q.1** A sigma bond is formed by the overlapping of :

- (A) s-s orbital alone  
(B) s and p orbitals alone  
(C) s-s, s-p or p-p orbitals along internuclear axis  
(D) p-p orbital along the sides

**Q.2** Which of the following compound is formed in the second excitation state of sulphur atom?

- (A)  $SF_4$                       (B)  $SF_6$                       (C)  $SF_2$                       (D) None

**Q.3** The strength of bonds by  $2s - 2s$ ,  $2p - 2p$  and  $2p - 2s$  overlapping has the order:

- (A)  $2s - 2s > 2p - 2p > 2s - 2p$                       (B)  $2s - 2s > 2p - 2s > 2p - 2p$   
(C)  $2p - 2p > 2s - 2p > 2s - 2s$                       (D)  $2p - 2p > 2s - 2s > 2p - 2s$

**Q.4** Fluorine molecule is formed by:

- (A) the axial p-p orbital overlap                      (B) the sideways p-p orbital overlap  
(C) the s-s orbital overlap                      (D) the s-p orbital overlap

**LECTURE NO. – 8 & 9**

**☞ HYBRIDISATION THEORY**

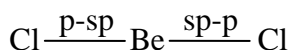
- (a) It is introduced by Pauling and Slater, to explain equivalent nature of covalent bonds in a molecule. Consider an example of  $\text{BeCl}_2$

If it is formed without hybridisation then –



both the Be-Cl bonds should have different parameters and p-p bond strength > s-p bond strength. But experimentally bond parameters of both the Be-Cl bonds are same. This can be explained by the concept of hybridisation.

- (b) Hybridisation : Phenomenon of intermixing of atomic orbitals of same or nearly same energy and thus producing hybrid orbitals of same energy and same shape is called as hybridisation. Now after considering s-p hybridisation in  $\text{BeCl}_2$



bond strength of both the bonds will be equal.

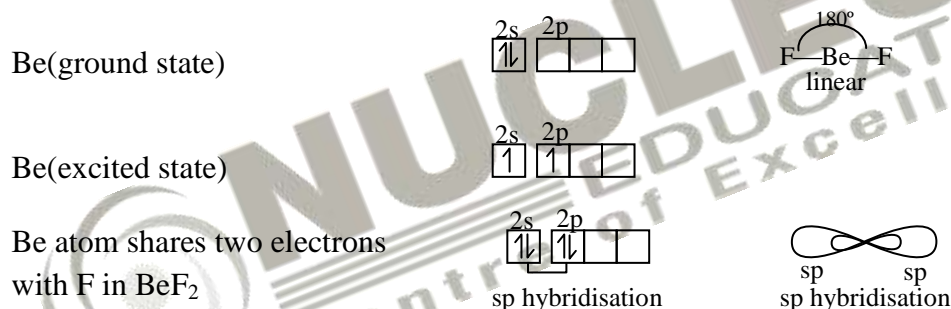
- **Salient features of hybridisation:** The main features of hybridisation are as under:
  1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
  2. The hybridised orbitals are always equivalent in energy and shape.
  3. The hybrid orbitals are more effective 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. Therefore, the type of hybridisation indicates the geometry of the molecules.
- **Important conditions for hybridization**
  - (i) The orbitals present in the valence shell of the atom are hybridised .
  - (ii) The orbitals undergoing hybridisation should have almost equal energy.
  - (iii) Promotion of electron is not essential condition prior to hybridisation.
  - (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation .



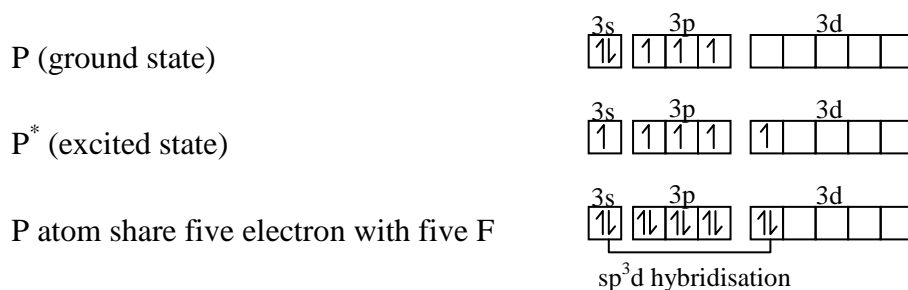
☞ **Types of hybridization**

Hybrid Orbital	Hybridisation	Atomic orbital involved	Shape	Bond Angle
2	sp	$sp_x / sp_y / sp_z$	Linear	$180^\circ$
3	$sp^2$	$sp_x p_y / sp_y p_z / sp_x p_z$	Trigonal planar	$120^\circ$
4	$sp^3$	$sp_x p_y p_z$	Tetrahedral	$109^\circ 28'$
5	$sp^3 d$	$sp_x p_y p_z d_{z^2}$	Trigonal bipyramidal	$120^\circ, 90^\circ, 180^\circ$
6	$sp^3 d^2$	$sp_x p_y p_z d_{x^2-y^2} d_{z^2}$	Octahedral	$90^\circ$
7	$sp^3 d^3$	$sp_x p_y p_z d_{x^2-y^2} d_{z^2} d_{xy}$	Pentagonal bipyramidal	$72^\circ, 90^\circ, 180^\circ$

**Ex.1** Hybridisation in  $BeCl_2$



**Ex.2** For example,  $PF_5$  showing  $sp^3 d$  hybridization



☞ **Determination of hybridisation state –**

To predict hybridisation following formula may be used :

● **Method-1 :**

No. of hybrid orbital =  $\frac{1}{2}$  [Total number of valence  $e^-$  in the central atom + total number of monovalent atoms - charge on cation + charge on anion]



• **Method-2 :**

Steric Number (S.N.) = Number of  $\sigma$ -bond around that atom + Number of lone pair on that atom.

Molecule	Method-1	Method-2	Hybridisation
$\text{NH}_4^+$	$\frac{1}{2} [5 + 4 - 1] = 4$	S.N. = 4 + 0 = 4	$\text{sp}^3$ hybridisation
$\text{SF}_4$	$\frac{1}{2} [6 + 4] = 5$	S.N. = 4 + 1 = 5	$\text{sp}^3\text{d}$ hybridisation
$\text{SO}_4^{2-}$	$\frac{1}{2} [6 + 2] = 4$	S.N. = 4 + 0 = 4	$\text{sp}^3$ hybridisation

• **Method : 3**

In proper Lewis structure count the number of lone pairs and number of  $\sigma$  bonds with which that atom is directly connected to other atoms. The sum of lone pair and  $\sigma$  bonds gives the number of hybrid orbitals of that atom.

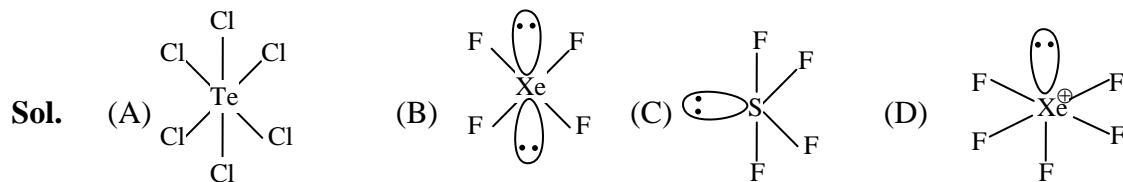
1. Find hybridisation of following species :-

(i)	$\text{CH}_2\text{Cl}_2$	$\longrightarrow \sigma \text{ bonds} = 4$ L.P. = 0	$\text{sp}^3$
(ii)	$\text{PF}_5$	$\longrightarrow \sigma \text{ bonds} = 5$ L.P. = 0	$\text{sp}^3\text{d}$
(iii)	$\text{ICl}_2^+$	$\longrightarrow \sigma \text{ bonds} = 2$ L.P. = 3	$\text{sp}^3\text{d}$
(iv)	$\text{BrF}_5$	$\longrightarrow \sigma \text{ bonds} = 5$ L.P. = 1	$\text{sp}^3\text{d}^2$
(v)	$\text{XeOF}_4$	$\longrightarrow \sigma \text{ bonds} = 5$ L.P. = 1	$\text{sp}^3\text{d}^2$
(vi)	$\text{SO}_3$	$\longrightarrow \sigma \text{ bonds} = 3$ L.P. = 0	$\text{sp}^2$
(vii)	$\text{I}_3^-$	$\longrightarrow \sigma \text{ bonds} = 2$ L.P. = 3	$\text{sp}^3\text{d}$

2. Which of the following molecule (s) is/are having  $\text{sp}^3\text{d}^2$  hybridisation for their central atom.

- (A)  $\text{TeCl}_6$                       (B)  $\text{XeF}_4$                       (C)  $\text{SF}_4$                       (D)  $\text{XeF}_5^+$

**Ans. (A,B,D)**



4. Which of the following orbital is not used in  $sp^3d$  hybridisation to get square pyramidal geometry -

- (A)  $d_{x^2-y^2}$  (B)  $d_{z^2}$  (C)  $p_z$  (D)  $p_x$

Ans. (B)

Sol.  $sp^3d$  (TBP geometry) is made up of  $(s + p_x + p_y + p_z + d_{x^2-y^2})$

5. Which of the following d orbital does not participate in  $sp^3d^3$  hybridisation.

- (A)  $d_{x^2-y^2}$  (2)  $d_{z^2}$  (3)  $d_{xy}$  (4)  $d_{yz}$

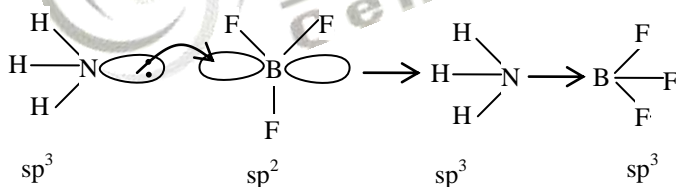
Ans. (4)

Sol. Atomic orbital involved in  $sp^3d^3$

$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}, d_{xy}$

6. Find the change in hybridisation when  $NH_3$  reacts with  $BF_3$ .

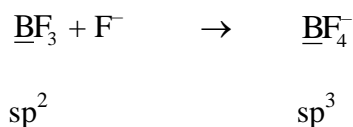
Sol. Adduct formation



7. In which of the following process the hybridisation of underlined atom gets changed.

- (A)  $\underline{N}H_3 + H^+ \longrightarrow NH_4^+$  (B)  $\underline{B}F_3 + F^- \longrightarrow BF_4^-$   
(C)  $\underline{B}_2H_6 + R_3N \longrightarrow 2BH_3R_3N$  (D)  $H_2\underline{O} + H^+ \longrightarrow H_3O^+$

Ans (B)



Hybridisation of following species in specified state :		
Species	Cationic part	Anionic part
$\text{PCl}_5(\text{s})$	$\text{PCl}_4^+(\text{sp}^3)$	$\text{PCl}_6^-(\text{sp}^3\text{d}^2)$
$\text{PBr}_5(\text{s})$	$\text{PBr}_4^+(\text{sp}^3)$	$\text{Br}^-$
$\text{XeF}_6(\text{s})$	$\text{XeF}_5^+(\text{sp}^3\text{d}^2)$	$\text{F}^-$
$\text{N}_2\text{O}_5(\text{s})$	$\text{NO}_2^+(\text{sp})$	$\text{NO}_3^-(\text{sp}^2)$
$\text{I}_2\text{Cl}_6(\text{liquid})$	$\text{ICl}_2^+(\text{sp}^3)$	$\text{ICl}_4^-(\text{sp}^3\text{d}^2)$
$\text{Cl}_2\text{O}_6(\text{s})$	$\text{ClO}_2^+(\text{sp}^2)$	$\text{ClO}_4^-(\text{sp}^3)$
$\text{I}_2(\text{liquid})$	$\text{I}_3^+(\text{sp}^3)$	$\text{I}_3^-(\text{sp}^3\text{d})$

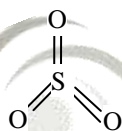
**Q.8** What is the hybridisation of the anionic part of  $\text{PCl}_5$  solid  
 (A)  $\text{sp}^3$  (B)  $\text{sp}^3\text{d}$  (C)  $\text{sp}^3\text{d}^2$  (D) none of these

**Ans.** (C)

**Sol.:**  $\text{PCl}_5(\text{s}) \longrightarrow \text{PCl}_4^+ + \text{PCl}_6^-$

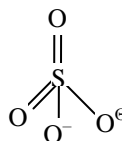
**Sol.** **DETERMINATION OF  $\pi$ -BOND :**

**Ex.** (i)



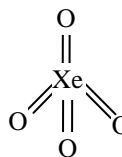
Hybridisation =  $\text{sp}^2$   
 $2(\text{p}_\pi - \text{d}_\pi), 1(\text{p}_\pi - \text{p}_\pi)$

(ii)



$\text{SO}_4^{2-}$  Hybridisation =  $\text{sp}^3$   
 $2(\text{p}_\pi - 3\text{d}_\pi)$

(iii)



$\text{XeO}_4$  Hybridisation =  $\text{sp}^3$   
 $4(\text{p}_\pi - \text{d}_\pi)$

**Q.1** Select the incorrect statements :

- (A)  $S_2O_3^{2-}$  ion has  $3d_{\pi}-2p_{\pi}$  bonding  
(B)  $ClO_3^-$  ion has three  $3d_{\pi}-2p_{\pi}$  bonding  
(C)  $PO_4^{3-}$  ion has no lone pair  
(D)  $CO_3^{2-}$  ion has higher (C–O) bond length than that of  $HCOO^-$  ion

**Ans. (B,C)**

In  $ClO_3^-$  two  $3d_{\pi} - 2p_{\pi}$  bonds are present.

$PO_4^{3-}$  has 11 lone pair

**Q.2** From the following options most effective  $\pi$ -bond is -

- (A)  $3p_{\pi}-2p_{\pi}$  (B)  $2p_{\pi}-3d_{\pi}$  (C)  $3d_{\pi}-3d_{\pi}$  (D)  $3p_{\pi}-3p_{\pi}$

**Ans. (B)**

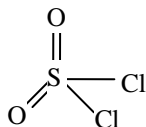
overlapping area increases  $\pi$ -bond formation increases.

**Q.3** How many  $p_{\pi}-d_{\pi}$  bonds are present in the compound  $SO_2Cl_2$  -

- (1) 0 (2) 1 (3) 2 (4) 3

**Ans. (3)**

**Sol.**



$sp^3$  hybridisation  $2p_{\pi}-3d_{\pi}$  bonds


















## LECTURE NUMBER - 10



### VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

- (a) Molecules having covalent bond have definite geometry as covalent bonding has directional characteristics. A simple theory was given for the molecular shape of the covalent molecules by Gillespie and Nyholm in 1957.
- (b) This theory predicts the shape of the molecule by considering the most stable configuration of the bond angles in the molecule. This theory states
- Electron pairs in the valence shell of the central atom of a molecule, whether bonding or lone pairs are regarded as occupying localized orbitals. These orbitals arrange themselves to minimize the mutual electronic repulsions.
  - The magnitude of the different types of electronic repulsions follows the order given below:  
**lone pair-lone pair > lone pair - bond pair > bond pair - bond pair**
  - The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible.

☞ **SHAPES OF MOLECULES BASE ON VSEPR THEORY**

Total no. of hybrid orbital	No. of b.p. (bond pairs)	No. of unshared pair i.e. $I_p$	General formula	Type of hybridisation	Stereo chemical formula/str.	Shape	Exam.
2	2	0	$AB_2$	$sp$		Linear	$BeCl_2$
3	3	0	$AB_3$	$sp^2$		Trigonal planar	$BF_3$
3	2	1	$AB_2$	$sp^2$		V or Bent or angular	$SO_2$
4	4	0	$AB_4$	$sp^3$		Tetrahedron	$CH_4$
4	3	1	$AB_3$	$sp^3$		Trigonal pyramidal	$NH_3$ $CH_3^-$
4	2	2	$AB_2$	$sp^3$		V or Bent or angular	$H_2O$ $SF_2$
4	1	3	$AB$	$sp^3$		linear	$ClO^-$
5	5	0	$AB_5$	$sp^3d$		Trigonal bipyramidal	$PCl_5$
5	4	1	$AB_4$	$sp^3d$		Seesaw	$SF_4$
5	3	2	$AB_3$	$sp^3d$		T-shaped	$ClF_3$
5	2	3	$AB_2$	$sp^3d$		Linear	$IF_2^-$
6	6	0	$AB_6$	$sp^3d^2$		Octahedral	$SF_6$ $IF_6^+$
6	5	1	$AB_5$	$sp^3d^2$		Square pyramidal	$XeF_5^+$
6	4	2	$AB_4$	$sp^3d^2$		Square planar	$XeF_4$
7	7	0	$AB_7$	$sp^3d^3$		Pentagonal bipyramidal	$IF_7$
7	6	1	$AB_6$	$sp^3d^3$		Distorted octahedral	$XeF_6$ $IF_6^-$
7	5	2	$AB_5$	$sp^3d^3$		Pentagonal planar	$XeF_5^-$

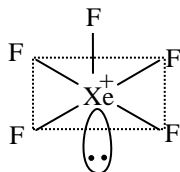
Practice Set

**Q.1** Which of the following species / molecule is not planar

- (A)  $\text{XeF}_5^-$  (B)  $\text{XeF}_5^+$  (C)  $\text{XeF}_4$  (D)  $\text{NO}_2\text{Cl}$

**Ans. (B)**

$\text{XeF}_5^+ \Rightarrow$  It is square pyramidal which is non planar.



**Q.2** The 'BENT' molecular geometry can be obtained from which of the following electron geometry

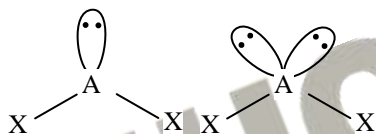
- (A)  $\text{sp}^3\text{d}$  (B)  $\text{sp}^3$  (C)  $\text{sp}^3\text{d}^2$  (D)  $\text{sp}^2$

**Ans. (B,D)**

$\text{sp}^2$  and  $\text{sp}^3$  having bent molecular geometry i.e.

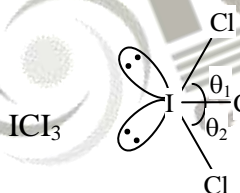
$\text{sp}^2$ :-

$\text{sp}^3$ :-



**Q.3** Find the number of exact  $90^\circ$  angles in  $\text{ICl}_3$

**Ans. (0)**



Both are less than  $90^\circ$  angles to L.P. – B.P. repulsion.

**Q.4** Choose the correct option in which all compounds are having same electron geometry of their central atom :-

- (I)  $\text{XeO}_2\text{F}_2$  (II)  $\text{BrF}_3$  (III)  $\text{SiF}_2\text{Cl}_2$  (IV)  $\text{XeO}_3\text{F}_2$   
(A) I and II only (B) II and III only (C) I, II and III only (D) I, II and IV only

**Ans. (D)**

Molecule	$e^-$ geometry
$\text{XeO}_2\text{F}_2$	$\longrightarrow$ Trigonal bipyramidal
$\text{BrF}_3$	$\longrightarrow$ Trigonal bipyramidal
$\text{SiF}_2\text{Cl}_2$	$\longrightarrow$ Tetrahedral
$\text{XeO}_3\text{F}_2$	$\longrightarrow$ Trigonal bipyramidal

**Q.5** In trigonal bipyramidal electronic geometry we get the following repulsion at  $90^\circ$ ,

l.p. - l.p. = 0,

l.p. - b.p. = 4,

b.p. - b.p. = 2,

which type of molecule is satisfying the above conditions.

(A)  $AB_5$

(B)  $AB_4L$

(C)  $AB_3L_2$

(D)  $AB_2L_3$

(A = central atom, B = bond atom, L = lone pair)

**Ans.** (C)

**Q.6** Which of the following is isoelectronic and isostructural with  $H_3O^+$

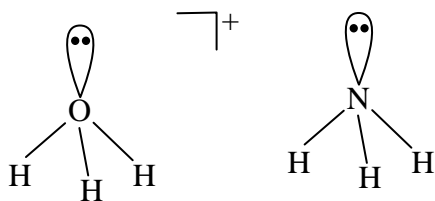
(A)  $H_2F$

(B)  $BH_4^-$

(C)  $NH_3$

(D) All of these

**Ans.** (C)



Both species have same structure and same number of electrons i.e. 10

**Q.7** Which of the following has/have  $sp^3d$  hybridisation and linear structure

(A)  $ClF_3$

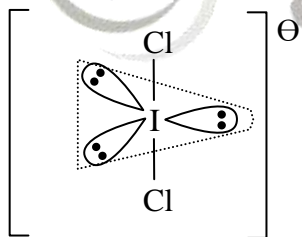
(B)  $ICl_2^-$

(C)  $XeF_2$

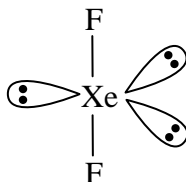
(D)  $XeF_4$

**Ans.** (B, C)

(B)



(C)



**Q.8** Which of the following molecules(s)/ion(s) is/are NOT non-linear -

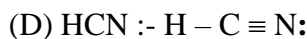
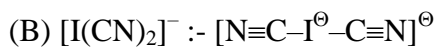
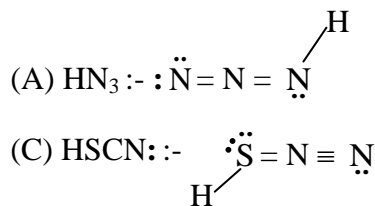
(A)  $HN_3$

(B)  $[I(CN)_2]^-$

(C)  $HSCN$

(D)  $HCN$

**Ans.** (B, D)



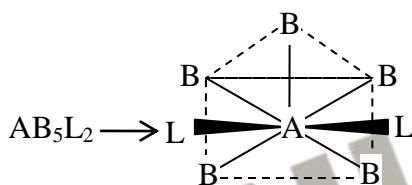
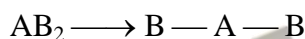
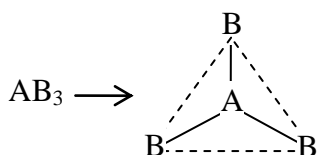
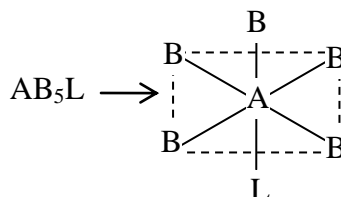
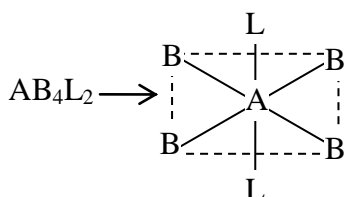


**Q.9** In which of the following 4 'B' atoms are in same plane ?

- (A)  $AB_4$  (B)  $AB_4L$  (C)  $AB_4L_2$  (D)  $AB_5$   
(E)  $AB_5L$  (F)  $AB_5L_2$  (G)  $AB_3$  (H)  $AB_2$

**Sol.**  $AB_4 \rightarrow$  Tetrahedral  
 $AB_4L \rightarrow$  See saw structure  
 $AB_5 \rightarrow$  Trigonal bipyramidal

} '4' B atoms are not in same plane



**Q.10** Which of the following specie has maximum number of lone pair -

- (A)  $SiF_6^{2-}$  (B)  $XeF_6$  (C)  $PCl_6^-$  (D)  $SF_6$

**Ans. (B)**

ion/molecule

total number of lone pair

$SiF_6^{2-}$  18

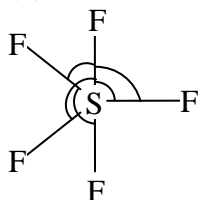
$XeF_6$  19

$PCl_6^-$  18

$SF_6$  18

**Q.11** Find the maximum number of identical angles in  $[SF_5]^+$  which are all less than  $180^\circ$ .

**Ans. (6)**



**Q.12** Shape of  $NH_3$  is very similar to -

- (A)  $CH_4$  (B)  $CH_3^-$  (C)  $BH_3$  (D)  $CH_3^+$

**Ans. (B)** Both have the same state of hybridization  $sp^3$  with one lone pair of  $e^-$  each.

**Q.13** Find the number of molecule which are planar.



**Ans.** (4)

$\text{XeF}_4$  - square planar

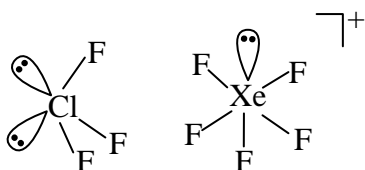
$\text{H}_2\text{O}$  - V-shaped

$\text{XeF}_3^+$  - T-shaped

$\text{BrF}_3$  - T-shaped

**Q.14** Find the ratio of lone pairs on the central atom of  $\text{ClF}_3$  and  $\text{XeF}_5^+$

**Ans.** (2)



ratio of lone pairs on the central atom = 2

**Q.15** Find the number of angles which are less than  $90^\circ$  in perfect pentagonal bipyromidal geometry.

**Ans.** (5)

PBP contain five  $90^\circ$  angles which are present at equatorial position.

**Q.16** Which of the following has pyramidal shape-

(A)  $\text{XeO}_3$  (B)  $\text{XeF}_4$  (C)  $\text{XeF}_2$  (D)  $\text{XeF}_6$

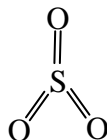
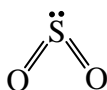
**Ans.** (A) Due to presence of lone pair of electron.

**Q. 17** Find number of planer species out of



**Ans.** (3)

**Sol.** Planar species are



**Q.18** Which of the following molecule have see-saw shape

(1)  $\text{CH}_4$

(2)  $\text{SF}_4$

(3)  $\text{XeF}_4$

(4)  $\text{CCl}_4$

**Ans.** (2)

**Sol.** (1)  $\text{CH}_4$  – Tetrahedral

(2)  $\text{SF}_4$  – See saw

(3)  $\text{XeF}_4$  – Square planar

(4)  $\text{CCl}_4$  – Tetrahedral

**Q.19** Which of the following molecule is linear and central atom is  $sp^3d$  hybridised -

- (1)  $XeF_2$                       (2)  $CO_2$                       (3)  $SO_2$                       (4)  $HCN$

**Ans.** (1)

**Sol.**  $XeF_2$   $sp^3d$  linear  
 $CO_2$   $sp$  linear  
 $SF_4$   $sp^3d$  See saw  
 $NH_3$   $sp^3$  Pyramidal

**Q.20** Which of the following is expected to be planar where B is univalent bonded atom & E is lone pair on central atom -

- (1)  $AB_4E$                       (2)  $AB_5E$                       (3)  $AB_3E$                       (4)  $AB_2E$

**Ans.** (4)

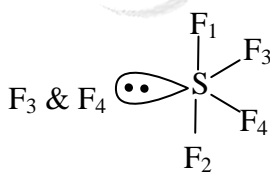
**Sol.**  $AB_5E$  Square pyramidal  
 $AB_4E$  See saw  
 $AB_3E$  Pyramidal  
 $AB_2E$  V-shape

**Q.21** Find the maximum number of identical bond angle in  $SF_4$  is-

- (1) 2                      (2) 3                      (3) 4                      (4) 6

**Ans.** (3)

**Sol.** Total four bond angles are identical, two formed by  $F_1$ , with  $F_3$  &  $F_4$  and two are formed by  $F_2$  with

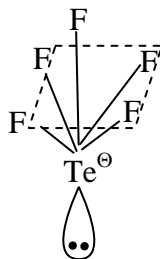


**Q.22** In Which of the following there is no bonds at right angle -

- (1)  $ICl_4^-$                       (2)  $PCl_6^-$                       (3)  $PCl_5$                       (4)  $TeF_5^-$

**Ans.** (4)

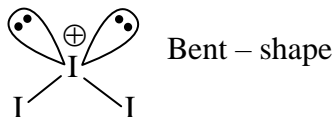
**Sol.**  $TeF_5^-$  is square pyramidal in which all bond angles are less than  $90^\circ$ .



**Q.23** Which of the following molecule/ion is non-linear

- (A) HCN                      (B)  $I_3^-$                       (C)  $I_3^+$                       (D)  $CO_2$

**Ans.** (C)



### DO YOUR SELF – 3

**Q.1** The pair of species with similar shape is

- (A)  $PCl_3$ ,  $NH_3$                       (B)  $CF_4$ ,  $SF_4$                       (C)  $PbCl_2$ ,  $CO_2$                       (D)  $PF_5$ ,  $IF_5$

**Q.2** The shape of sulphate ion is –

- (A) hexagonal                      (B) square planar  
(C) trigonal bipyramidal                      (D) tetrahedral

**Q.3** What is not true for  $SiH_4$  molecule –

- (A) Tetrahedral hybridisation                      (B)  $109^\circ$  angle  
(C)  $4\sigma$  bond                      (D) 4-lone pair of electrons

**Q.4** The structure of  $Br_3^-$  involves hybridisation of the type –

- (A)  $sp^3d$                       (B)  $sp^3d^2$                       (C)  $sp^3d$                       (D)  $d^2sp^3$

**Q.5** The structure of  $ICl_2^-$  is –

- (A) Trigonal planar                      (B) Octahedral                      (C) Square planar                      (D) Linear

**LECTURE NO. -11**

**BOND PARAMETERS**

(I) Bond Angle      (II) Bond Length (Bond distance)      (III) Bond Energy

**(I) Bond angle:**

Angle between two adjacent bond in any species is called the Bond angle. The following factors affect bond angle.

**(a) State of Hybridization :**

With the change in state of hybridization relative percentage of s-character changes and with increasing percentage of s-character, the bond angle increase.

State of hybridization %	s-character	Bond angle
sp	50	180°
sp <sup>2</sup>	33.33	120°
sp <sup>3</sup>	25	109° 28'

If state of hybridization of central atom is same and all the surrounding atoms are identical and identically attached as well, the bond angle remains the same (as predicted by its hybridization state) no matter what the central atom and what surrounding atoms are.

For example, bond angles in CF<sub>4</sub>, CCl<sub>4</sub>, CBr<sub>4</sub> is same i.e. 109° 28'

**(b) Presence of lone pair :**

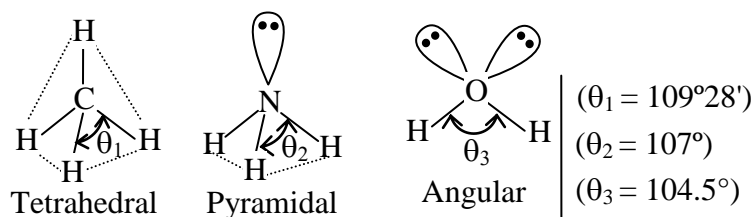
Since the lone pair occupies more space around central atom, so the space available for bond pairs is less and hence bond angle decreases.

The extent of repulsive interaction follows the order

lone pair - lone pair > lone pair – bond pair > bond pair – bond pair

**Example :**

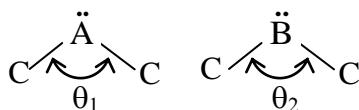
The bond angle of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O.



As there is no lone pair of electron on carbon in CH<sub>4</sub> molecule, so all the  $\text{H}\hat{\text{C}}\text{H}$  bond angles are equal ( $=109^\circ 28'$ ) but due to presence of one lone pair on N in NH<sub>3</sub> and two lone pair on O in H<sub>2</sub>O, the lone pairs occupy more space around central atom, thus bond angle in CH<sub>4</sub> is maximum and in H<sub>2</sub>O it is minimum. Hence,  $\theta_1 > \theta_2 > \theta_3$

(c) **Electronegativity of central atom :**

Let us consider the molecule  $\ddot{A}C_2$  and  $\ddot{B}C_2$  in which electronegativity of  $A > B$



State of hybridisation of A and B =  $sp^2$

Due to greater electronegativity of A than B, the bond pair of electron in  $AC_2$  is more closer to A than B in  $BC_2$ . Due to decrease in distance between bond pairs in  $AC_2$ , bp-bp repulsion is more than that in  $BC_2$ .

So the bond angle order is  $\theta_1 > \theta_2$

(d) **Electronegativity of surrounding atom :**

Let us consider two molecules  $\ddot{A}B_2$  and  $\ddot{A}C_2$  in both A is  $sp^2$  hybridised and electronegativity of  $B > C$ . Due to greater electronegativity of B than that of C, the shared electron the pair is attracted towards B, so the repulsion between bp-bp in  $AB_2$  is less than that in  $AC_2$ . Hence  $\theta_1 < \theta_2$ .



(e) **Size of surrounding atom:**

Let us consider the two molecules  $OCl_2$  and  $OBr_2$  where O-atom is  $sp^3$  hybrid and Br atom is larger than Cl-atom, so Br will occupy more space around central atom than Cl-atom, hence bond angle in  $OBr_2$  is more than that in  $OCl_2$ .

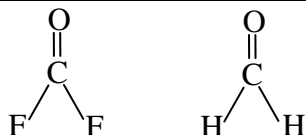
Moreover, it has been experimentally found that the bond angle in  $OBr_2$  is  $112^\circ$  and in  $OCl_2$  it is  $111^\circ$ , the bond angle is more than even the normal tetrahedral angle ( $109^\circ 28'$ ). This may be due to steric repulsion of two Cl-atom in  $OCl_2$  and two Br-atoms in  $OBr_2$  and some effect of back bonding.

(f) **Multiple bond orbital repel other orbitals more strongly than single bond orbitals.**

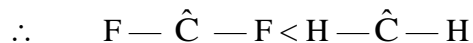
The multiple bond orbital possess extra electron density and naturally exert stronger repulsion on neighboring electron pair than a single bond does. Thus a double bond containing four electrons exerts a greater repulsive effect on other sigma bonds present in the molecule and result in a smaller bond angle.



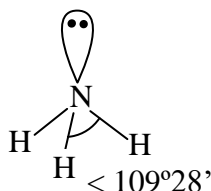
Ex.



Fluorine is more electronegative than hydrogen.



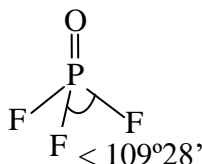
Ex.



lp-bp > bp-bp (repulsion)

shape – pyramidal

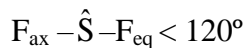
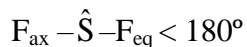
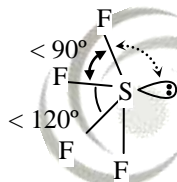
Ex.



D.B-S.B > S.B-S.B

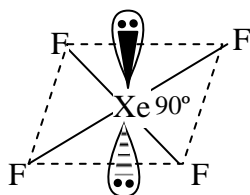
shape – pyramidal

Ex.



lp-bp > bp-bp (repulsion)

Ex.

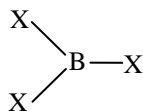


Both lone pair cancel out their effect

shape = square planar

**Ex.** Compare the bond angle in the following

- (a)  $\text{BF}_3, \text{BCl}_3, \text{BBr}_3, \text{BI}_3$  ( $\text{X}-\hat{\text{B}}-\text{X}$ )

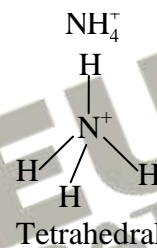
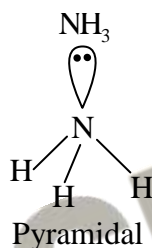
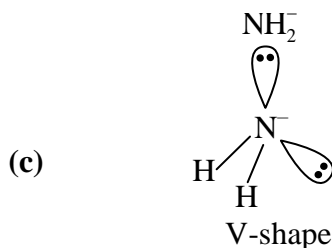


having perfect geometry therefore there is no effect of electronegativity of surrounding atom.

- (b)  $\text{NH}_3, \text{NF}_3$  ( $\text{X}-\hat{\text{N}}-\text{X}$ )

solution: Fluorine is more electronegative than hydrogen therefore electron cloud is more shifted towards surrounding atom in  $\text{NF}_3$  than  $\text{NH}_3$ .

$\therefore \text{NF}_3 < \text{NH}_3$  ( $\text{X}-\hat{\text{N}}-\text{X}$ )

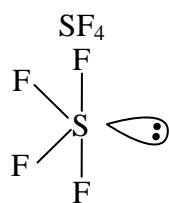


In all the above species N is  $\text{sp}^3$  hybridized and all the attach surrounding atoms are identical in all species.

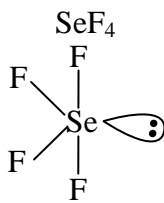
$\therefore$  greater the number of lone pair  $\text{NH}_2^- < \text{NH}_3 < \text{NH}_4^+$  ( $\text{H}-\hat{\text{A}}-\text{H}$ )

( $\text{F}-\hat{\text{A}}-\text{F}$ )

- (d) In both cases central atom is  $\text{sp}^3\text{d}$  hybridized and surrounding atoms are same therefore greater the electro negativity of central atom greater will be the bond angle.

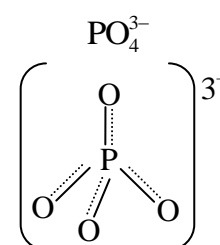
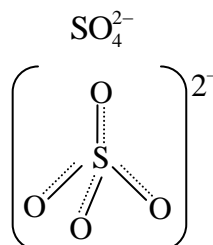


$\text{SF}_4 > \text{SeF}_4$



( $\text{F}-\hat{\text{A}}-\text{F}$ )

(e)



Due to equivalent resonance both having perfect geometry therefore all the bond angle is same.

**Ex.** Ether  $\text{R}-\text{O}-\text{R}$  and water  $\text{H}-\text{O}-\text{H}$  have same hybridization of oxygen. What angle would you expect for them –

**Ans.** In  $\text{H}_2\text{O}$  bond angle is less than  $109^\circ 28'$  due to lone pair and bond pair repulsion. But in ether, due to strong mutual repulsion between two alkyl groups bond angle becomes greater than  $109^\circ 28'$

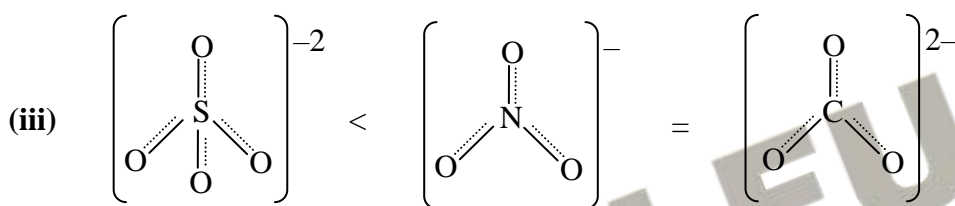
**Ex.** Compare the bond angle in following:

- (i)  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_3$                       (ii)  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{SiCl}_4$   
 (iii)  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$               (iv)  $\text{COF}_2$ ,  $\text{COCl}_2$ ,  $\text{COBr}_2$ ,  $\text{COI}_2$   
 (v)  $\text{OF}_2$ ,  $\text{Cl}_2\text{O}$ ,  $\text{Br}_2\text{O}$

**Ans.** (i)  $\text{CO}_2$     $\text{SO}_2$     $\text{SO}_3$   
           $sp$     $sp^2$     $sp^2$   
 $\text{CO}_2 > \text{SO}_3 > \text{SO}_2$

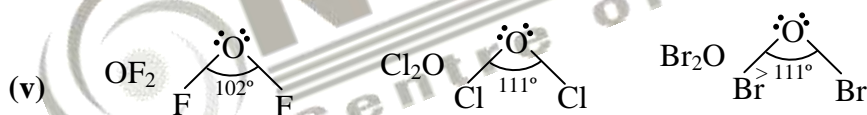
In  $\text{SO}_2$  molecule, due to presence of lone pair, bond angle decreases.

(ii)  $\text{SiH}_4 = \text{SiF}_4 = \text{SiCl}_4$



(iv)  $\text{COF}_2 < \text{COCl}_2 < \text{COBr}_2 < \text{COI}_2$

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



Bond pairs of electrons are more closer to the fluorine atoms (because of high electronegativity of fluorine). So the  $lp - lp$  repulsion is more than  $bp - bp$ .

Thus the  $\text{F}-\text{O}-\text{F}$  bond angle decreases to  $102^\circ$  from  $109.5^\circ$ .

In  $\text{Cl}_2\text{O}$ , the bond angle  $\text{Cl}-\text{O}-\text{Cl}$  increases to  $\approx 111^\circ$  due to  $bp - bp$  repulsion and repulsion between larger Cl atoms.

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

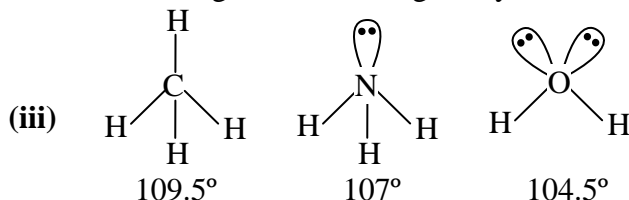
**Q.1** Compare bond angle.

- (i)  $\text{CH}_4$ ,  $\text{BF}_3$ ,  $\text{BeCl}_2$                       (ii)  $\text{NCl}_3$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$   
 (iii)  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$                       (iv)  $\text{OF}_2$ ,  $\text{OCl}_2$ ,  $\text{OBr}_2$ ,  $\text{OI}_2$

Sol. (i)  $\text{CH}_4 < \text{BF}_3 < \text{BeCl}_2$   
 $\text{sp}^3 \quad \text{sp}^2 \quad \text{sp}$

(ii)  $\text{NCl}_3 > \text{PCl}_3 > \text{AsCl}_3 > \text{SbCl}_3$

Bond angle  $\propto$  Electronegativity of central atom.



Number of lone pair increase bond angle decreases.

(iv)  $\text{OF}_2 < \text{OCl}_2 < \text{OBr}_2 < \text{OI}_2$

Size of surrounding atom  $\propto$  Bond angle.

Q.2 Which of the following bond angle order is incorrect -

(A)  $\text{BF}_3 = \text{BCl}_3$       (B)  $\text{CH}_4 = \text{CCl}_4$       (C)  $\text{NH}_3 = \text{NF}_3$       (D)  $\text{CO}_3^{2-} = \text{NO}_3^-$

Ans. (C)

Bond angle  $\text{NH}_3 > \text{NF}_3$

Q.3 Which of the following is incorrect order of X – P – X bond angle. (X = halogen atom)

(A)  $\text{PBr}_3 > \text{PCl}_3 > \text{PF}_3$       (B)  $\text{OPBr}_3 > \text{OPCl}_3 > \text{OPF}_3$   
(C)  $\text{PBr}_4^+ > \text{PCl}_4^+ > \text{PF}_4^+$       (D)  $\text{PCl}_4^+ > \text{PCl}_3$

Ans. (C)

$\text{PBr}_4^+$ ,  $\text{PCl}_4^+$ ,  $\text{PF}_4^+$  are perfect tetrahedral therefore all the bond angle are equal.

Q.4 Which of the following bond angle order is correct

(A)  $\text{PH}_3 > \text{PH}_4^+$       (B)  $\text{NH}_4^+ > \text{PH}_4^+$       (C)  $\text{H}_2\text{O} > \text{H}_3\text{O}^+$       (D)  $\text{OF}_2 < \text{H}_2\text{O}$

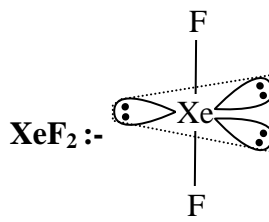
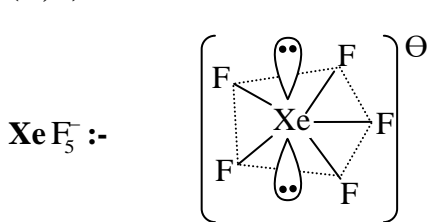
Ans. (D)

As electronegativity of surrounding atom decreases, bond angle increases so bond angle of  $\text{H}_2\text{O} > \text{OF}_2$ .

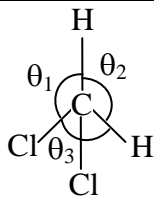
Q.5 In which of the following molecule(s) presence of l.p. does not affect the idealized bond angle according to hybridisation :-

(A)  $\text{XeF}_5^-$       (B)  $\text{XeF}_2$       (C)  $\text{XeF}_5^+$       (D)  $\text{SF}_4$

Ans. (A,B)



Q.6



For the above figure.

- (A)  $\theta_1 = \theta_2 = \theta_3$       (B)  $\theta_3 > \theta_1 > \theta_2$       (C)  $\theta_3 < \theta_2 < \theta_1$       (D) None of these

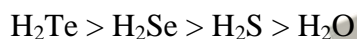
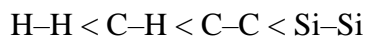
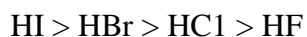
**Sol.** Due to large size of Cl atoms, repulsion increase, hence bond angle increase. Correct option is (B).

## LECTURE NUMBER – 12

(II) **Bond Length :-** The average distance between the nucleus of two atoms is known as bond length.

### Factors affecting bond length

- (a) Size of atoms: As size of atom increases bond length increases

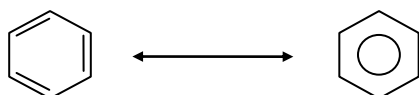


- (b) Effect of bond order or number of bonds: As number of bonds or bond order increases bond length decreases.



- (c) Effect of Resonance (due to resonance bond length is affected)

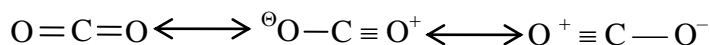
eg. In Benzene :



We know that C—C bond length is 154 pm and C=C bond length is 134 pm but in benzene the C—C bond length is between single & double bond due to resonance which is equal to 139 pm.

eg. Bond length of C—O in  $\text{CO}_2$  is 115 pm due to resonance.

Resonance occurs in  $\text{CO}_2$  as follows-



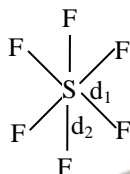
- (d) **Effect of Electronegativity difference :**

Generally as electronegativity difference of bonded atom increases bond length decreases.

- (f) **Effect of Hybridisation :** In hybrid orbitals bond length decreases as the s-character increases.

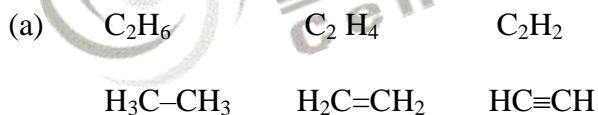
Example :-	Compound	Hybridisation	Bond length
<div style="display: flex; align-items: center;"> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">s-character increases</div> <div style="margin-left: 10px;"> </div> </div>	$\text{>C-C<}$	$\text{sp}^3\text{--sp}^3$	1.54 Å
	$\text{>C-C=}$	$\text{sp}^3\text{--sp}^2$	1.51 Å
	$\text{>C-C}\equiv$	$\text{sp}^3\text{--sp}$	1.47 Å
	$\text{=C-C=}$	$\text{sp}^2\text{--sp}^2$	1.48 Å
	$\text{=C-C}\equiv$	$\text{sp}^2\text{--sp}$	1.43 Å
	$\text{}\equiv\text{C-C}\equiv$	$\text{sp--sp}$	1.38 Å

**Ex.**  $\text{SF}_6$



All hybrid orbital of 'S' having equal length

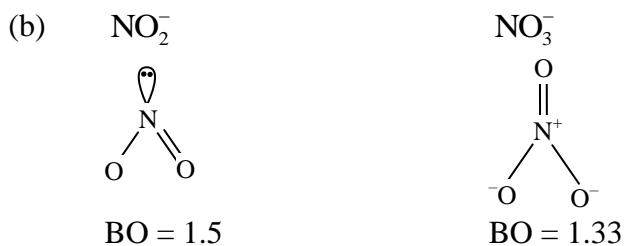
**Ex.** Compare the bond length in the following as given,



BO : 1      BO : 2      BO : 3

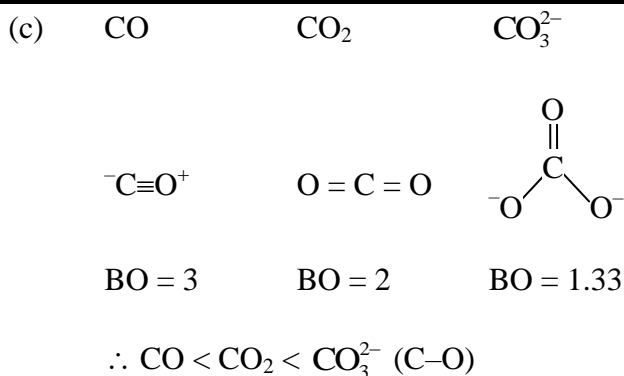
$\therefore \text{C}_2\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2$  (C-C)

Note:      BO  $\uparrow$       BL  $\downarrow$



$\therefore \text{NO}_2^- < \text{NO}_3^-$  (B.L.)





**Ex.** Find the maximum number of equal angle in CH<sub>4</sub> and NH<sub>3</sub>

**Ans.** 6 and 3

**Ex.** Find the maximum number of 90° angle in SF<sub>4</sub>, SF<sub>6</sub>, PCl<sub>5</sub> and IF<sub>5</sub>

**Ans.** 0, 12, 6, 0 respectively

**Q.2** If number of identical bond length in CH<sub>4</sub> is 'x' and number of identical bond angles in CH<sub>4</sub> is

'y'. Find value of  $\frac{y-x}{y+x}$ .

**Sol.**  $\frac{y-x}{y+x} = \frac{6-4}{6+4} = 0.2$

**(III) Bond Energy (BE) :-** Bond energy may be defined as-

- (a) Bond formation energy:- Energy released, when one mole of same type of bonds are formed, is known as bond formation energy or bond energy.
- (b) Bond dissociation energy:- Energy required to dissociate one mole of same types of bond is known as bond dissociation energy.

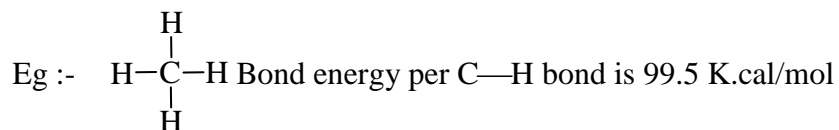
**Case-I** In diatomic molecule:

Bond energy = bond dissociation energy

Eg :- N<sub>2</sub> > O<sub>2</sub> > H<sub>2</sub> > F<sub>2</sub>

**Case-II** For polyatomic molecule

Bond energy = Bond dissociation energy (D)



Theoretical values of bond dissociation energy (D) of individual C—H bonds  $\text{CH}_4$  are given below-

$$D(\text{CH}_3-\text{H}) = 102 \text{ K.Cal/mol}$$

$$D(\text{CH}_2-\text{H}) = 105 \text{ K.Cal/mol}$$

$$D(\text{CH}-\text{H}) = 108 \text{ K.Cal/mol}$$

$$D(\text{C}-\text{H}) = 83 \text{ K.Cal/mol}$$

Hence bond energy E per C—H bond in methane =  $\frac{398}{4} = 99.5 \text{ K.Cal/mol}$ .

Bond dissociation energy (D) is related to the state of hybridisation.

**Que.** Compare the bond energy in the following

(a)  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$

**Ans.**  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$  Bond energy order (Experimental facts)

**Que.** Compare the bond energy in the following :

(a) C—C, Si—Si      (b) N—N, P—P      (c) O—O, S—S

**Ans.** (a) C — C      (b) P — P      (c) S — S

## LECTURE NUMBER –13

### ☛ DIPOLE MOMENT : (IONIC NATURE IN COVALENT BOND)

Due to difference in electronegativity a covalent bond acquires a partial polar character. The two charged ends of the polar bond behave as electric dipoles and degree of polarity is expressed in term of dipole moment.

Dipole moment is defined as the product of the magnitude of charge on any one of the atoms and the distance between them

$$\mu = q \times d$$

$q$  = charge on any one of the atom which is in the order of  $10^{-10}$  esu or  $10^{-19}$  coulomb and

$d$  = distance between charged atoms is in the order of  $10^{-8}$  cm.

**$10^{-18}$  esu cm = 1 debye (unit of dipole moment)**

In S.I. system

$$1 \text{ esu} = \frac{1.6 \times 10^{-19}}{4.8 \times 10^{-10}} = 3.33 \times 10^{-10} \text{ C}$$

$$1 \text{ cm} = 10^{-2} \text{ m}$$

$$1 \text{ D} = 10^{-18} \times 3.33 \times 10^{-10} \times 10^{-2} \text{ cm}$$

$$1 \text{ D} = 3.33 \times 10^{-30} \text{ cm}$$

Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment.

The polarity of molecule on the whole is the vector sum of the individual dipole moment.

Dipole moment can be determined experimentally and its value can give an idea of the polar character of a molecule. It is a vector quantity, as it has a direction as well as magnitude. The direction of dipole is towards negative centre. It is represented by an arrow pointing from positive centre towards the negative centre ( $\longrightarrow$ )

The resultant dipole moment depends upon magnitude of bond moments and the angles between the bonds and given by parallelogram law as:

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

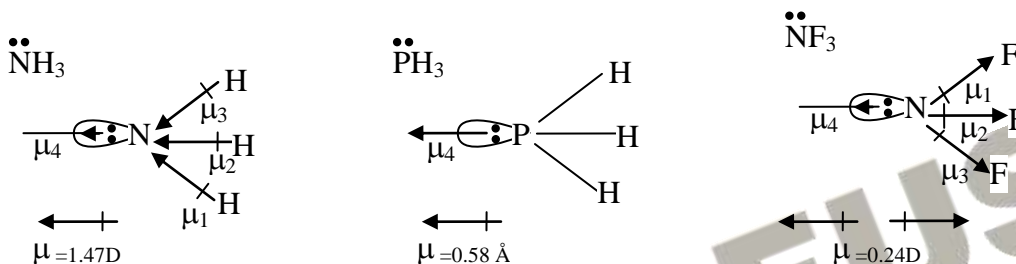
In a bond H–X, the hydrogen atom is the positive end of dipole where X is an atom more electronegative than H.

In a bond C–X, the carbon atom is the positive end of the dipole where X is an atom other than carbon. However, in the C–H bonds of hydrocarbons, the value and directions of the dipole are not constant and depends upon the state of hybridization of the carbon.

● **Characteristics of Dipole Moment :**

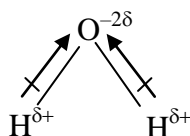
1. For diatomic molecule  $\mu = e \times d$
2. In polyatomic molecule with angle 0, resultant dipole moment is the vector summation of the vector moments.
3. **Polyatomic molecules:** A poly atomic molecules is made up of more than two atoms joined by polar covalent bonds and their dipole moment will be the vector sum of dipole moment of different bonds which depends on spatial orientation of bond.

**For example:**



4. Dipole moment is a vector quantity. Therefore individual dipole moments should be added vectorially to get net dipole moment.
5. Symmetrical molecule without lone pair of electrons has  $\mu = 0$ . e.g.  $\text{CO}_2$ ,  $\text{BeF}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ , etc.

(XI) Dipole moment of  $\text{H}_2\text{O}$  is 1.85 D which is resultant  $\mu$  of two O–H bonds.



**Application of dipole moment :**

**(A) To determine polarity and geometry of molecule -**

If  $\mu = 0$  compound is non polar and symmetrical

eg.  $\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_4$ .  $\text{BeF}_2$  etc.

If  $\mu \neq 0$  compound will be polar and unsymmetrical.

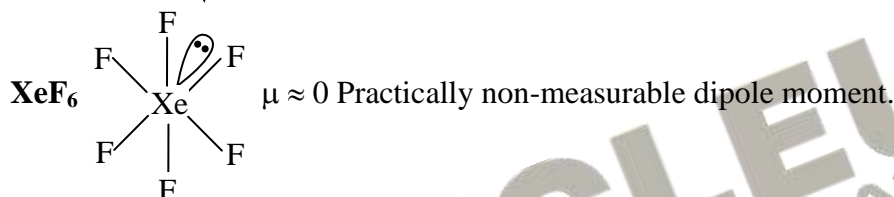
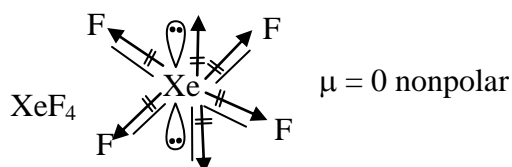
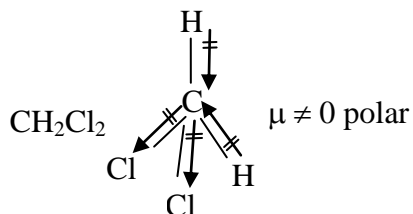
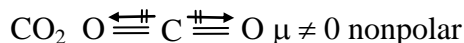
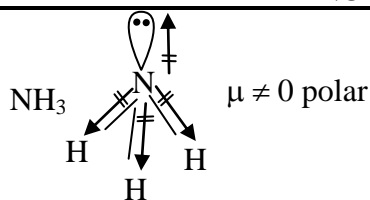
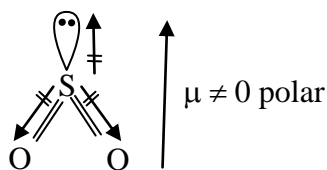
$\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2\text{O}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  etc.

**Ex 1.** Which of the following bond is most polar -

- (A) O – H                      (B) P – H                      (C) C – F                      (D) S – Cl

**Sol.** (C) Due to maximum electronegativity difference.

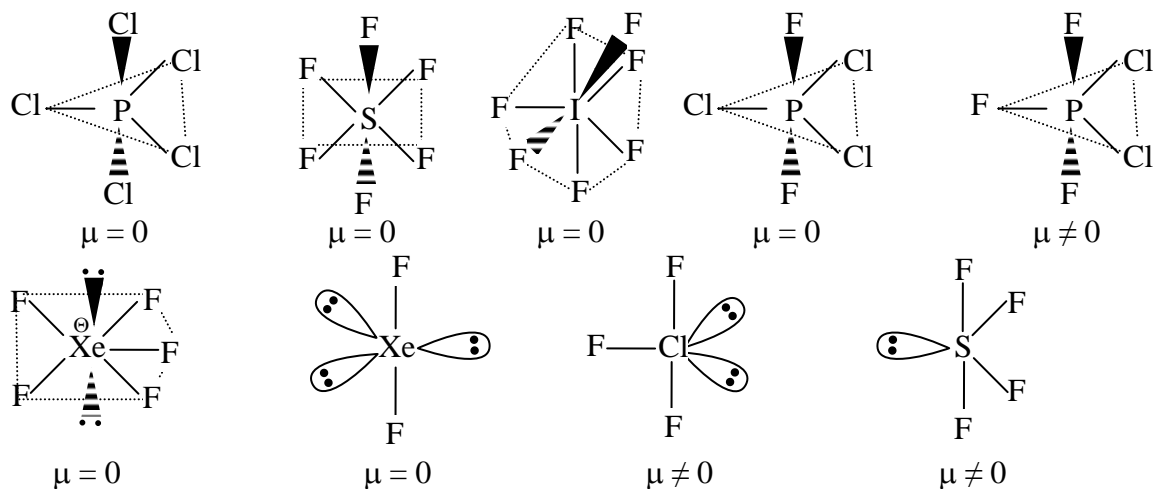
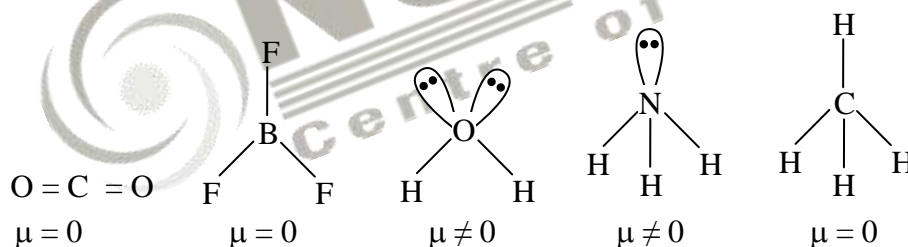
Ex 2.



**Q.3** Which of the following have zero dipole moment ?

$\text{CO}_2$ ,  $\text{BF}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{PCl}_5$ ,  $\text{SF}_6$ ,  $\text{IF}_7$ ,  $\text{PCl}_3\text{F}_2$ ,  $\text{PCl}_2\text{F}_3$ ,  $\text{XeF}_5^-$ ,  $\text{XeF}_2$ ,  $\text{ClF}_3$ ,  $\text{SF}_4$ .

**Sol.**



**Some important orders of dipole moments -**

- |   |  |
|---|--|
| (i) $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{NF}_3$                                | (vi) $\text{H}_2\text{O} > \text{H}_2\text{S}$     |
| (ii) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$  | (vii) $\text{BF}_3 < \text{NF}_3 < \text{NH}_3$    |
| (iii) $\text{HF} > \text{H}_2\text{O} > \text{SO}_2 > \text{NH}_3$ $\text{PH}_3 < \text{PCl}_3$ | (viii) $\text{H}_2\text{O} < \text{H}_2\text{O}_2$ |
| (iv) $\text{NO}_2^- > \text{NO}_2 > \text{NO}_2^+$  |  |
| (v) $\text{CH}_3\text{Cl} > \text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$              |  |
- (B) To calculate % ionic character**

$$\% \text{ ionic character} = \frac{\text{Experimental value of } \mu}{\text{Theoretical value of } \mu} \times 100$$

- Ex 1.** Bond length of HCl is  $1.275 \text{ \AA}$  (Charge =  $4.8 \times 10^{-10} \text{ e.s.u.}$ ) if  $\mu = 1.02 \text{ D}$ , then HCl is-  
 (A) 100% ionic (B) 83% covalent (C) 50% covalent (D) 40% ionic

**Sol.** (B) % ionic character

$$= \frac{\text{observed } \mu}{\text{theoretical } \mu} \times 100 = \frac{102}{1.275 \times 4.8} \times 100 = 17\% \text{ ionic} = 83\% \text{ covalent}$$

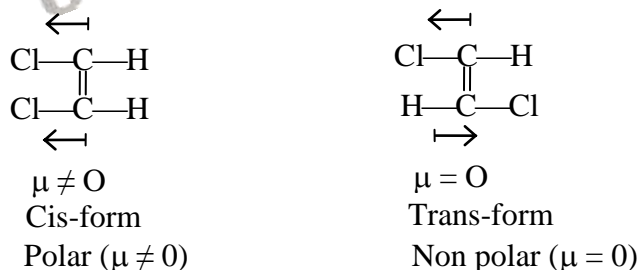
- Ex 2.** For HCl molecule observed dipole moment is  $1.03 \text{ D}$  and bond length is  $1.275 \text{ \AA}$ . Calculate % ionic character.

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

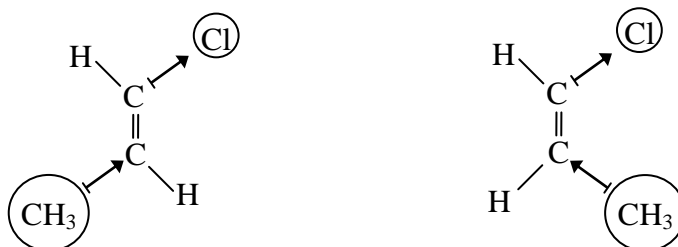
$$\% \text{ ionic character} = \frac{1.03 \times 100}{1.275 \times 4.8} \approx 17\%$$

**(C) To distinguish cis form or trans form :-**

**Ex.** Dipole moment of cis isomers is normally higher than trans isomers.



**Ex.** If two groups have opposite inductive effect then trans-isomer will have greater dipole moment.  
 e.g. -

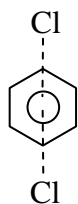




(D) To locate position of substituents in aromatic compounds.

$$(\text{Dipole Moment}) \mu \propto \frac{1}{\text{Bond angle}}$$

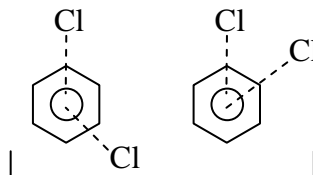
(I) If same substituents are present in the symmetrical position of benzene ring,  $\mu$  of compounds will be zero.



$$\mu = 0$$

Angle  $180^\circ$

p-dichloro benzene



$$\mu = 0$$

Angle  $120^\circ$

m-dichloro benzene

Angle  $60^\circ$

o-dichloro benzene

(II) As angle between substituents decreases value of  $\mu$  increases.

**Q.1** Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contain polar covalent bonds but  $\text{CO}_2$  is nonpolar while  $\text{H}_2\text{O}$  is polar because-

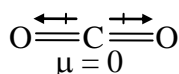
- (1) H atom is smaller than C atom
- (2)  $\text{CO}_2$  is a linear molecule while  $\text{H}_2\text{O}$  is an angular molecule
- (3) O – H bond is more polar than C – H bond
- (4)  $\text{CO}_2$  contains multiple bonds while  $\text{H}_2\text{O}$  has only single bonds

**Ans.** (2)

**Sol.:**

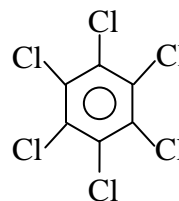
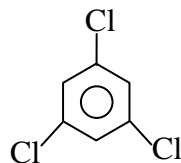
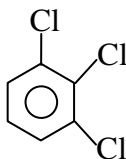
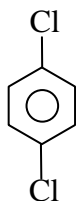
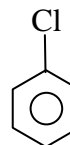


(Angular geometry)



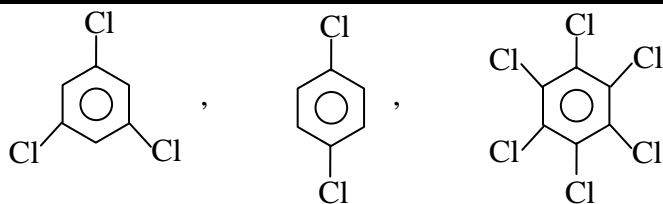
(Linear geometry)

**Q.2** Find the number of molecule having dipole moment less than the dipole moment of



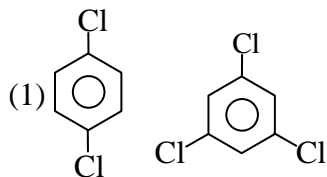
**Ans.** (3)

Sol.



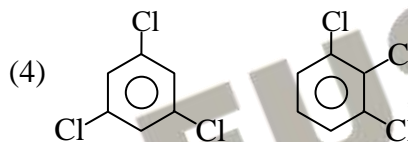
Have zero dipole moment

**Q.3** In which pair, first compound has more dipole moment than second compound



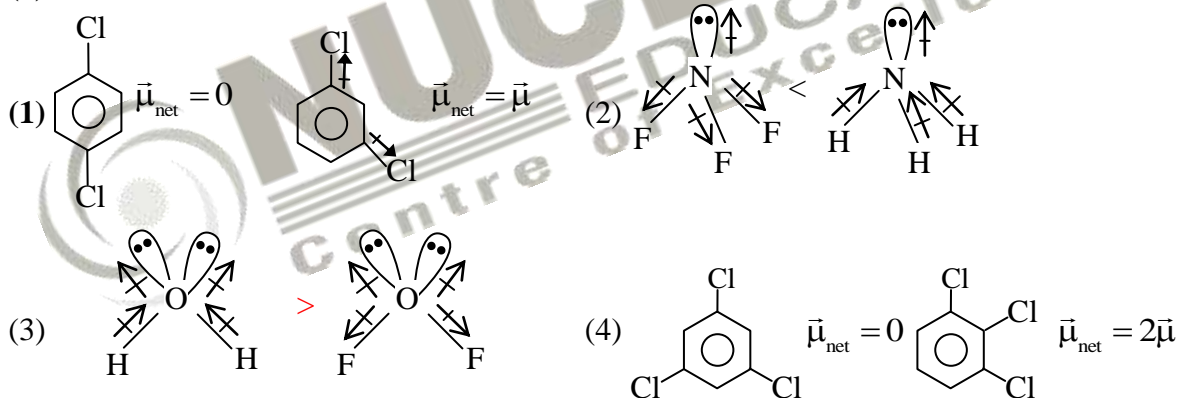
(2)  $\text{NF}_3$ ,  $\text{NH}_3$

(3)  $\text{H}_2\text{O}$ ,  $\text{OF}_2$

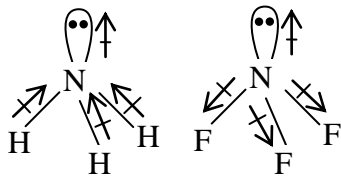


Ans. (3)

Sol.

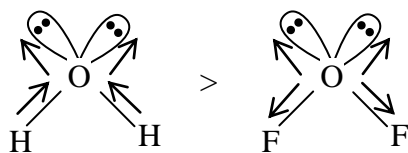


**Q.4** Explain  $\mu$  of  $\text{NH}_3$  and  $\text{NF}_3$



In case of  $\text{NF}_3$ , dipole moment of lone pair reduces the overall dipole moment whereas in  $\text{NH}_3$ , dipole moment of lone pair adds to the dipole moment of molecule.

**Q.5** Explain  $\mu$  of  $\text{H}_2\text{O}$  and  $\text{OF}_2$



In  $\text{OF}_2$ , lone pair moment oppose the moment due to O-F bond hence dipole moment decreases.

**Q.6** Compare dipole moment in  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ .

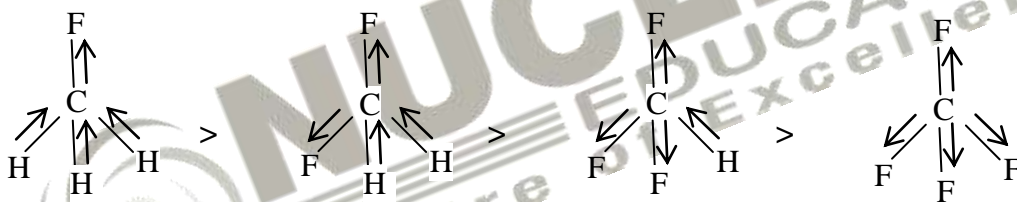
**Sol.** Expected order  $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

Actual order  $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

In case of Cl, due to sudden increase in size, dipole moment increases. Here distance factor becomes more dominating than charge. ( $\mu = q \times d$ )

**Q.7** Compare dipole moment in  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CHF}_3$  &  $\text{CF}_4$

**Sol.**  $\text{CH}_3\text{F} > \text{CH}_2\text{F}_2 > \text{CHF}_3 > \text{CF}_4$



As number of F increases, it opposes dipole moment due to other bonds.

**Q.8** Compare dipole moment of

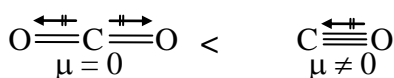
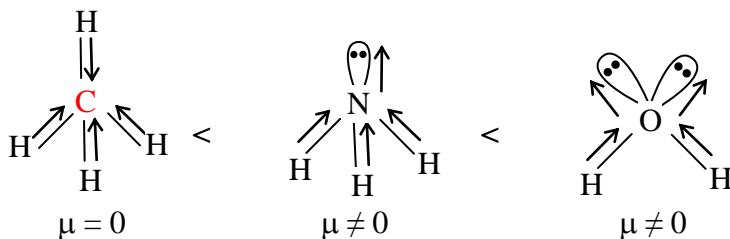
(i)  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$

(ii)  $\text{NH}_3$  and  $\text{NF}_3$

(iii)  $\text{H}_2\text{O}$  and  $\text{OF}_2$

(iv)  $\text{CO}$  &  $\text{CO}_2$

**Sol.**



(Linear geometry)

**Q.9** Dipole moment of HBr is 7.95D & intermolecular distance is  $1.94 \times 10^{-10}$  m. Find % ionic character.

**Sol.** % Ionic character =  $\frac{7.95 \times 3.33 \times 10^{-30}}{1.60 \times 10^{-19} \times 1.94 \times 10^{-10}} \times 100 = 85.2\%$

**Q.10** Calculate the  $\mu$  of HCl ? If bond distance is  $1.34 \text{ \AA}$ , charge =  $4.8 \times 10^{-10}$  esu and calculate % ionic character if experimental value of  $\mu = 1.08 \text{ D}$  ?

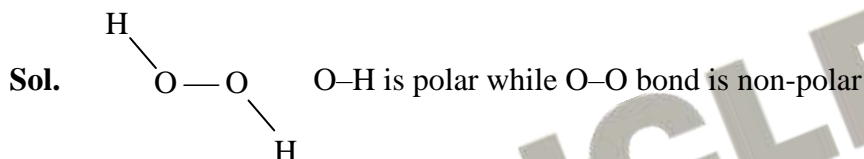
**Sol.**  $\mu = q \times d = 4.8 \times 10^{-10} \times 1.34 \times 10^{-8}$   
 $\mu = 6.4 \times 10^{-18} \text{ esu cm.}$

% ionic character =  $\frac{1.08}{6.4 \times 10^{-18}} = 16.79\%$

**Q.11** Which of the following contains polar and nonpolar bonds?

- (1)  $\text{H}_2\text{O}_2$                       (2)  $\text{CH}_4$                       (3)  $\text{HCN}$                       (4)  $\text{NH}_4\text{Cl}$

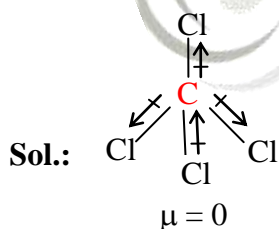
**Ans.** (1)



**Q.12** Carbon tetrachloride has no net dipole moment because of-

- (1) Similar electron affinities of C and Cl      (2) its regular tetrahedral geometry  
(3) its planar geometry                      (4) similar sizes of C and Cl atoms

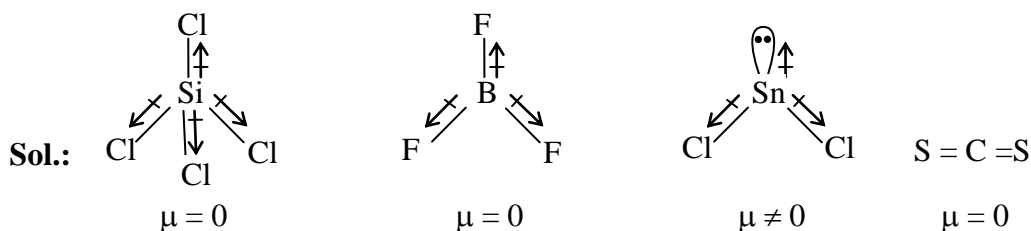
**Ans.** (2)



**Q.13** Which of the following molecules is nonpolar?

- (i)  $\text{SiCl}_4$                       (ii)  $\text{BF}_3$                       (iii)  $\text{SnCl}_2$                       (iv)  $\text{CS}_2$   
(1) (i), (ii), (iii)                      (2) (i), (ii), (iii), (iv)                      (3) (i), (ii), (iv)                      (4) (ii), (iii), (iv)

**Ans.** (3)



**Q.14** Which of the following has the highest dipole moment ?

- (1) *o*-Dichlorobenzene (2) *m*-Dichlorobenzene  
(3) *p*-Dichlorobenzene (4) All have equal values

**Ans.** (1)

**Sol.:** *o*-dichlorobenzene have minimum bond angle.

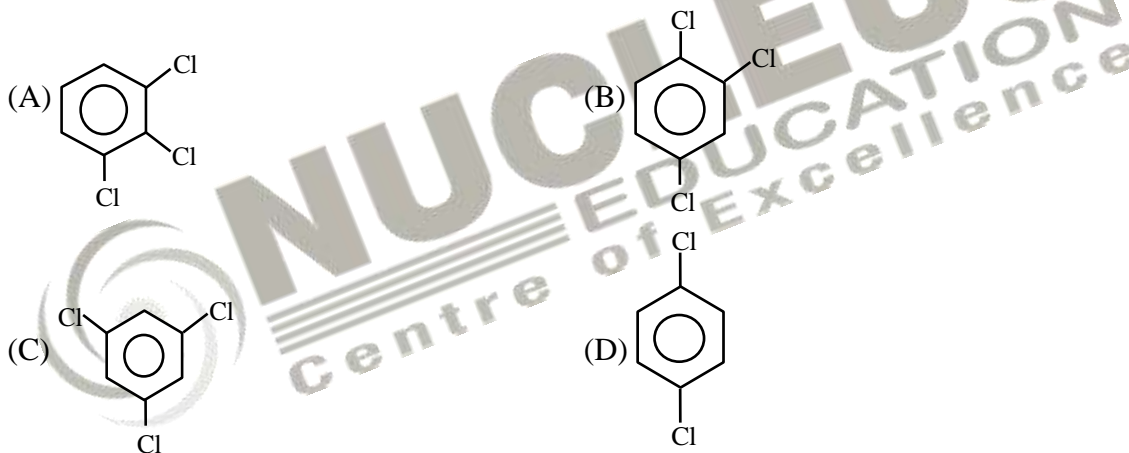
Hence have maximum dipole moment  $\mu \propto \frac{1}{BA}$

### DO YOUR SELF – 4

**Q.1** Which of the following molecules are polar ?

- (A) ClO<sub>2</sub> (B) SO<sub>2</sub> (C) NO<sub>2</sub> (D) All of the given

**Q.2** Which of the following species have maximum dipole moment ?



**Q.3** The species that will have the maximum dipole moment is –

- (A) CH<sub>3</sub>Cl (B) CH<sub>2</sub>Cl<sub>2</sub>  
(C) CHCl<sub>3</sub> (D) CH<sub>3</sub>F

**Q.4** The dipole moments of the given molecules are such that -

- (A) BF<sub>3</sub> > NF<sub>3</sub> > NH<sub>3</sub> (B) NF<sub>3</sub> > BF<sub>3</sub> > NH<sub>3</sub>  
(C) NH<sub>3</sub> > NF<sub>3</sub> > BF<sub>3</sub> (D) NH<sub>3</sub> > BF<sub>3</sub> > NF<sub>3</sub>

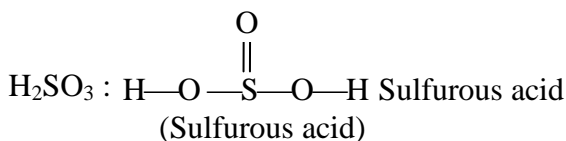
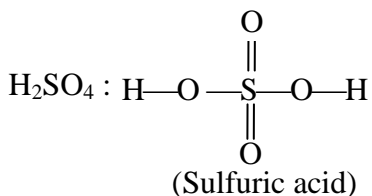
**Q.5** Of the following molecules, the one, which has permanent dipole moment, is -

- (A) SiF<sub>4</sub> (B) BF<sub>3</sub> (C) PF<sub>3</sub> (D) PF<sub>5</sub>

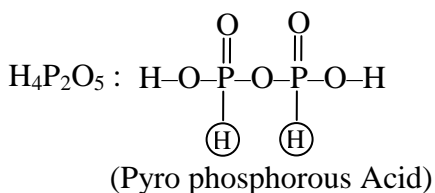
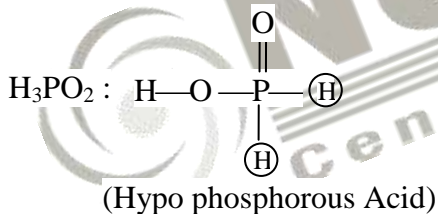
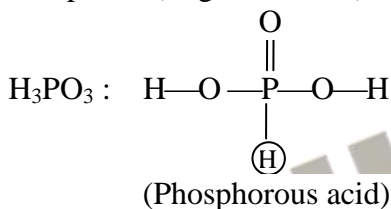
LECTURE NUMBER – 14 & 15

**INORGANIC OXY-ACIDS**

Those compounds which contain X–O–H bond are called oxy-acids. Where X is usually a non-metal. But sometimes X may also be a metal.

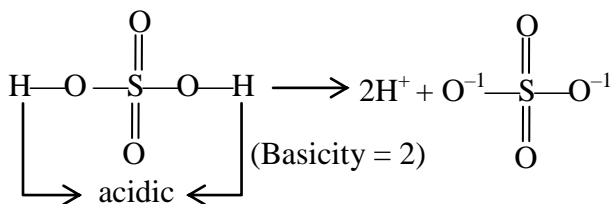


In oxy acids, all the hydrogens are attached with oxygen. Although there are a very few exceptions (as given below), in which all hydrogens are not attached with oxygen.



In these three oxyacids circled hydrogens are not attached with oxygen.

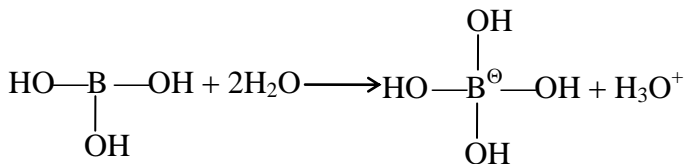
In oxyacids, those hydrogens which are attached with oxygen are acidic in nature, i.e., they ionize in solution.





Number of hydrogens attached with oxygen is known as basicity of the acid. One notable exception is  $\text{H}_3\text{BO}_3$  in which all the three hydrogens are attached with oxygen yet, they do not ionise in solution.

In fact,  $\text{H}_3\text{BO}_3$  when dissolved in water, it behaves as a monobasic acid.



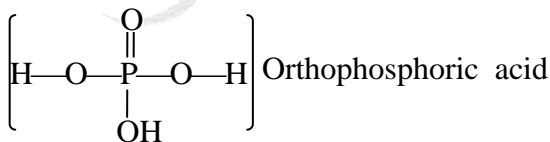
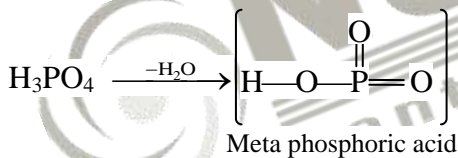
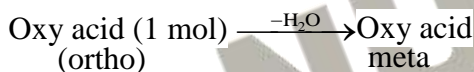
Some acids have suffix-ic acid and some has-ous acid. Usually, when the central atom in oxy acid is in highest oxidation state the name of the acid ends with -ic acid and when the central atom is in lower oxidation state, it's name ends with-ous acid.

Oxyacids can be classified as

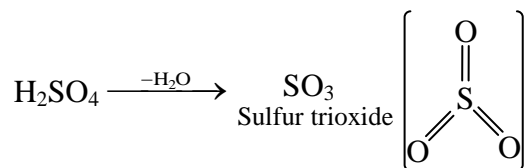


### ORTHO ACIDS AND META ACIDS

When one mole of  $\text{H}_2\text{O}$  is removed from one mole of an oxy acid, the resulting compound, if an oxy acid (i.e. it contains at least one X-OH bond) then the oxy acid from which  $\text{H}_2\text{O}$  is removed is named as ortho acid and the product oxyacid is known as **meta acid**.



An ortho acid must contain at least three hydrogens.

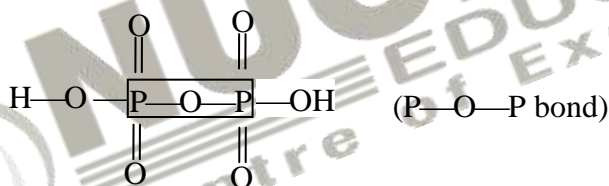
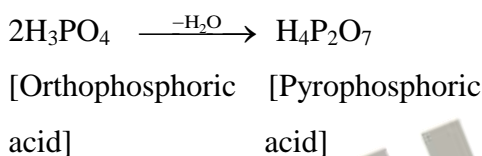
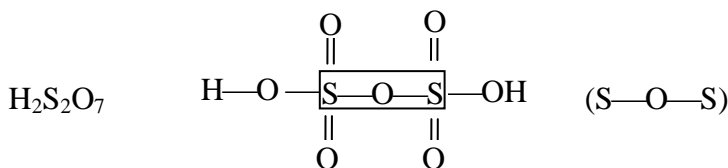
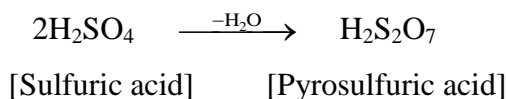
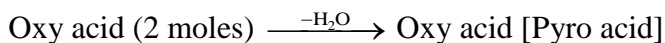


As  $\text{SO}_3$  does not contain any hydrogen, So  $\text{SO}_3$  is not an oxy acid rather it is anhydride of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) so,  $\text{H}_2\text{SO}_4$  can't be prefixed with ortho, and its name does not contain any prefix and it is named as sulfuric acid.

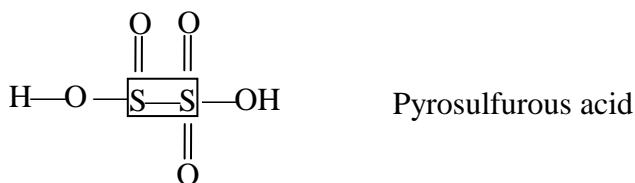
**PREFIX USED FOR OXY ACID**

• **PYRO ACIDS :**

When one mole of water is removed from two moles of an oxyacid, the resultant oxy acid is known as pyro acid, pyro acids contain X—O—X bonds. (X is central atom)

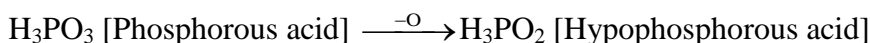


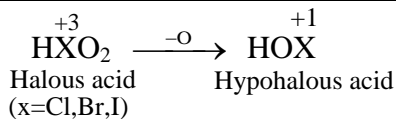
Exception :  $\text{H}_2\text{S}_2\text{O}_5$  [Pyrosulfurous acid] does not contain S—O—S linkage.



• **HYPHO ACID :**

Hypo prefix is added to those oxy acids which is obtained when one oxygen atom is removed from-ous form of parent oxy acid.

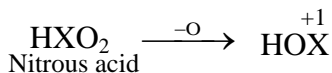




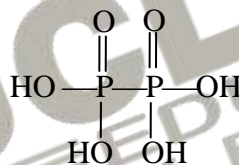
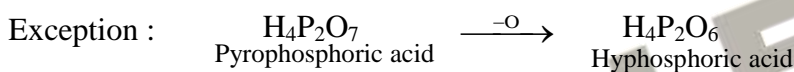
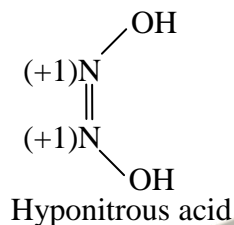
HOCl – Hypochlorous acid

HOBr – Hypobromous acid

HOI – Hypoiodous acid



HNO exist in dimeric form i.e. as  $(\text{HNO})_2 = \text{H}_2\text{N}_2\text{O}_2$

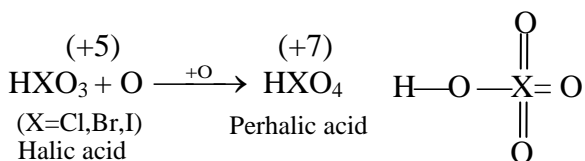


$\text{H}_2\text{S}_2\text{O}_6$  : Hyposulphuric

$\text{H}_2\text{SO}_2$  : Hyposulphurous acid/Sulphoxalic acid

### ● Per Acid and Peroxy Acid :

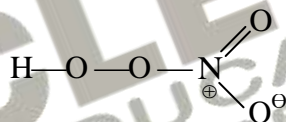
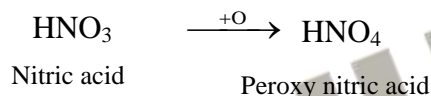
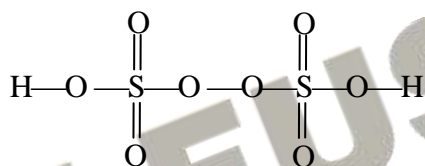
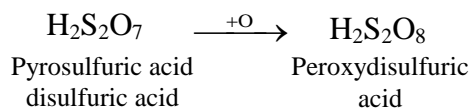
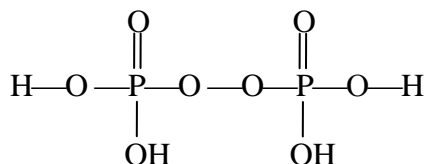
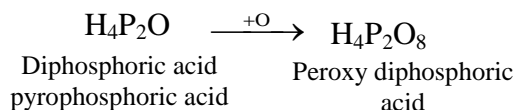
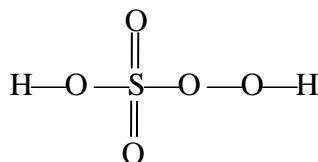
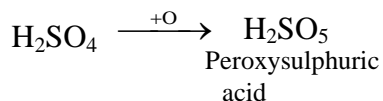
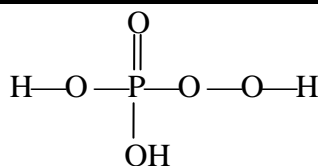
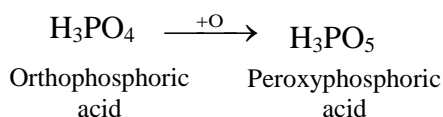
When one oxygen is added to –ic form of acid and if the oxidation number of central atom in resulting oxy acid is more than the –ic form of acid, then it is per acid.



**Ex.:**  $\text{HClO}_4$  perchloric acid

$\text{HBrO}_4$  - Perbromic acid.

Peroxy prefix is added to those oxy acids which are obtained when one oxygen is added to -ic form of acid and the oxidation number of central atom remains the same. Peroxy acids contain peroxy linkage ( $-\text{O}-\text{O}-$ )

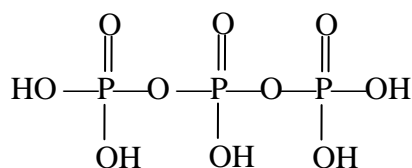


**Note :** Peroxynitric acid does not contain N-O-H bond, yet it is considered to be oxy acid.

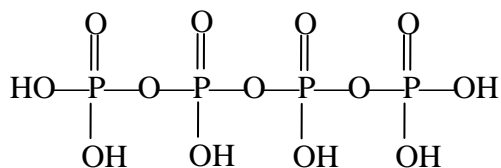
• **Polyphosphoric acids :**

Oxy acids having general formula  $\text{H}_{(n+2)} \text{P}_n\text{O}_{(3n+1)}$  are known as polyphosphoric acids. These contain (n-1) P-O-P bonds.

$\text{H}_5\text{P}_3\text{O}_{10}$  – Tripolyphosphoric acid

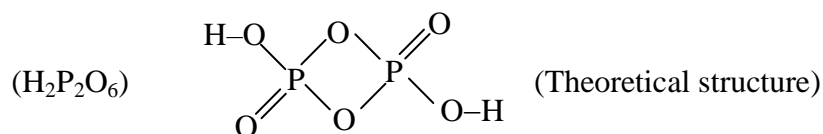


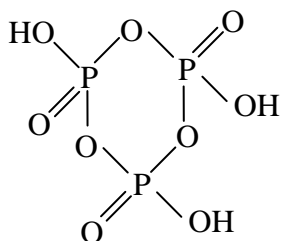
$\text{H}_6\text{P}_4\text{O}_{13}$  – Tetrapolyphosphoric acid



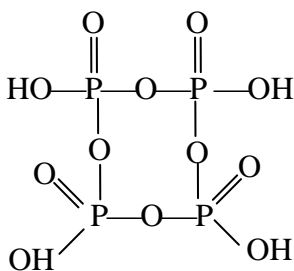
• **Cyclic metaphosphoric acids :**

$(\text{HPO}_3)_2$  – Dimetaphosphoric acid



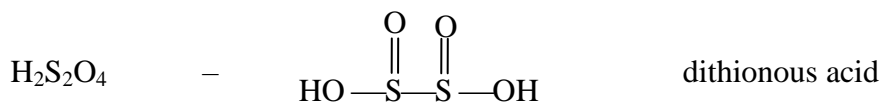


Trimetaphosphoric acid

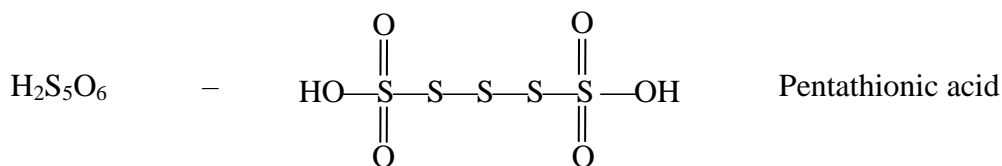
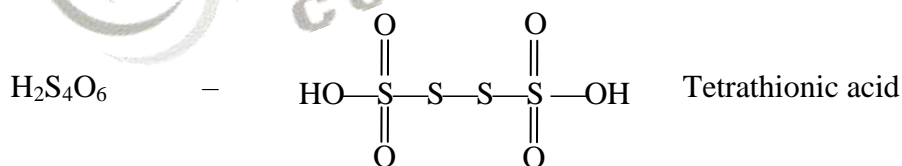
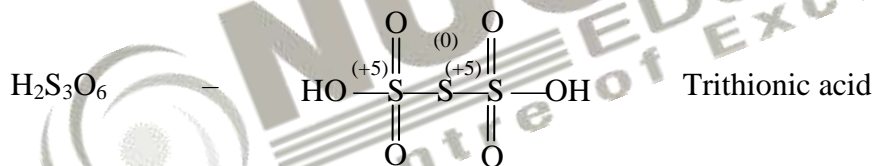
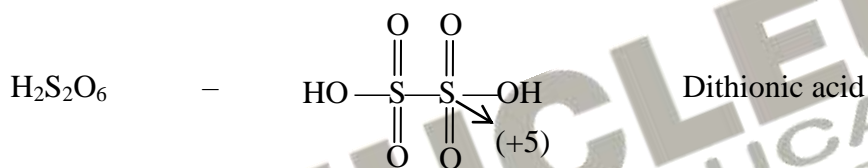


Tetrametaphosphoric acid

- **Thio acids** : Oxy acids of sulfur containing S—S bond are known as thio acids.

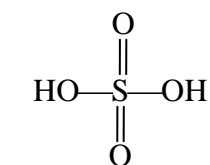


- **Thionic acids** : Oxy acids of sulfur containing S—S bond and having general formula  $\text{H}_2\text{S}_{(n+2)}\text{O}_6$  are known as thio acids.

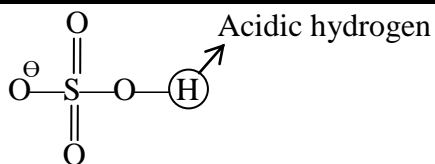


- **Naming of salts of oxy anion :**

- (1) The name of salt ends with - ate if the name of the oxy acid ends with - ic acid.
- (2) If the name of the oxy acid ends with ous acid then the name of the salt ends with 'ite'.
- (3) If all the ionisable hydrogens are not removed from the acid to form salt, then the hydrogen word is added to the name of the salt containing acidic hydrogens.



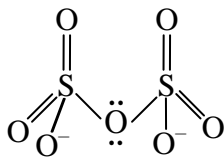
Sulphuric acid



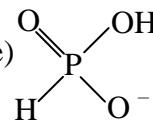
Hydrogen sulphate

Acidic hydrogen

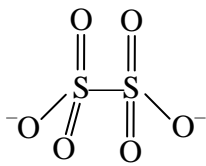
Ex.  $\text{S}_2\text{O}_7^{2-}$  (Pyrosulphate)



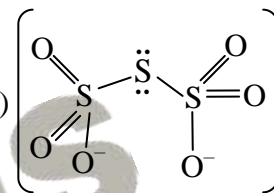
Ex.  $\text{H}_2\text{PO}_3^-$  (Hydrogen phosphite)



Ex.  $\text{S}_2\text{O}_6^{2-}$  (dithionate ion)



Ex.  $\text{S}_3\text{O}_6^{2-}$  (trithionate ion)



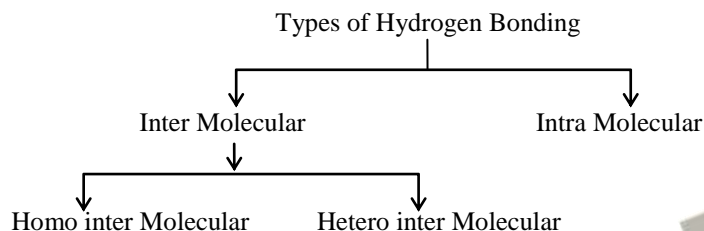
• **Other example**

$\text{S}_2\text{O}_3^{2-}, \text{S}_2\text{O}_5^{2-}, \text{S}_4\text{O}_6^{2-}, \text{NO}_3^-, \text{H}_2\text{PO}_3^-, \text{IO}_6^{5-}, \text{IO}_5^{3-}, \text{ClO}_4^-, \text{ClO}_2^-$  etc.

**LECTURE NUMBER – 16 & 17**

**☞ Hydrogen Bond - Special case of dipole -dipole interaction :**

A hydrogen atom normally forms a single bond. In some compounds, however, the hydrogen atom may be located between two atoms acting as a bridge between them. Hydrogen atom is now involved in the two bonds, one is a normal covalent bond and the other is a hydrogen bond. A hydrogen bond is always formed between two small size, high electronegative atoms such as fluorine, oxygen and nitrogen.



● **Intermolecular Hydrogen Bonding - Molecular Association**

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

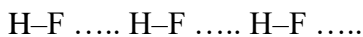
These are two types.

**(a) Homo-intermolecular :-** H-bond between molecules of same compounds.

**Examples:**

**(i) Hydrogen fluoride:**

HF is a polar molecule, with the fluorine atom acquiring a slight negative charge and the hydrogen atom acquiring an equal positive charge. The electrostatic attraction between the oppositely charged ends results in hydrogen bonding as shown below.



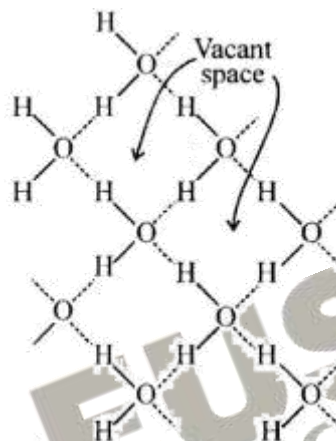
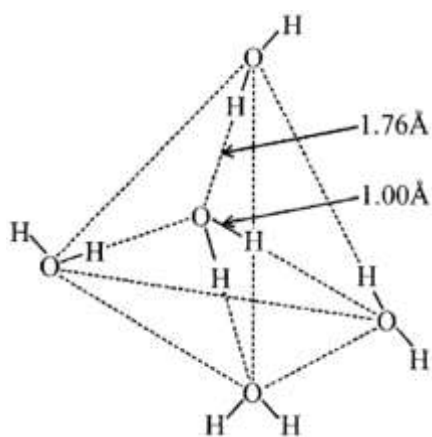
Many H-F units are held together, as  $(\text{HF})_n$  by hydrogen bonding. The covalent H-F bond is much shorter than the HF hydrogen bond; so hydrogen bond is much weaker than a covalent bond. Fluorine, with the highest electronegativity forms the strongest hydrogen bond. The nature of bond is considerably electrostatic.

**(ii) Water :**

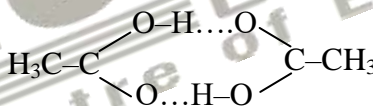
The high boiling point of water compared to that of hydrogen sulphide is due to molecular association through hydrogen bonding.



The crystal structure of ice shows a tetrahedral arrangement of water molecules. Each oxygen atom is surrounded tetrahedrally by 4 others. Hydrogen bond link pairs of oxygen atoms together as shown in Fig. The arrangement of water molecules in ice is a very open structure and this explains the low density of ice. When ice melts, the structure breaks down and the molecules pack more closely together so that water has a higher density; this packing goes to a maximum upto a temperature of 4°C.



(iii) **Carboxylic acids** : Some carboxylic acids exist as dimers e.g., the dimer of acetic acid represented as



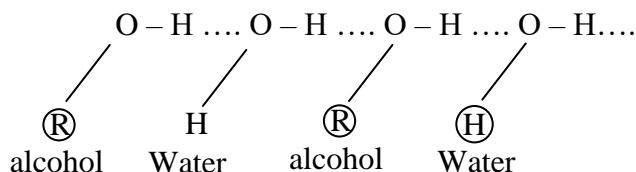
In aqueous solution molecules of carboxylic acid link up with water molecules through hydrogen bonding rather than forming dimers.

(b) **Hetero intermolecular:** H-bond between molecules of different compounds.

**Example:**

(i) **Alcohols and water :**

Lower alcohols and phenols are associated due to intermolecular hydrogen bonding. Methanol, ethanol and phenol have relatively much higher boiling points than methane or chloromethane, ethane or chloroethane, benzene or chlorobenzene respectively.

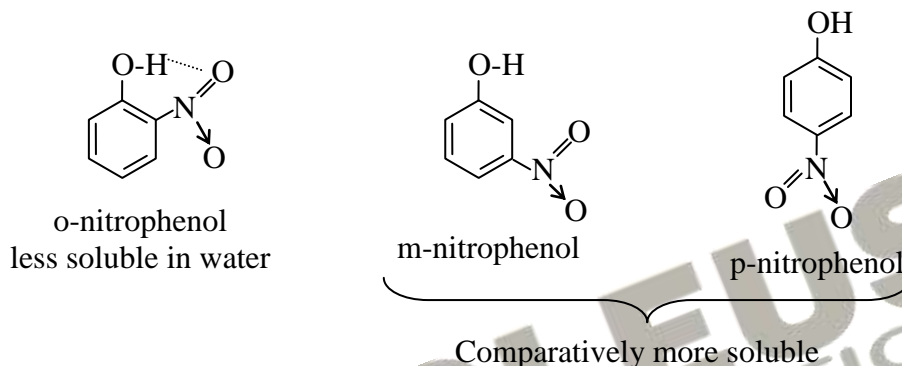


● **Intramolecular Hydrogen Bonding - Chelation**

Sometimes hydrogen bonding may take place within a molecule; this is known as intramolecular (or internal) hydrogen bonding. It may lead to the linkage of two groups to form a ring; such an effect is known as chelation,

**Examples :**

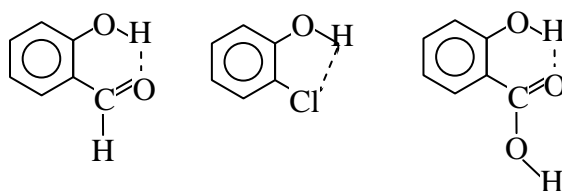
(i) **Nitrophenols**



Because of the proximity of  $-OH$  and  $-NO_2$  groups in o-nitrophenol there is intramolecular hydrogen bonding which prevents intermolecular hydrogen bonding between two or more molecules. Since molecular association cannot take place, the boiling point of o-nitrophenol is lower than that of the other two. Because of the distance between  $-OH$  and  $-NO_2$  groups in m- and p-nitrophenols there is no possibility of intramolecular hydrogen bonding. Intermolecular hydrogen bonding may take place to a certain extent which cause some degree of molecular association; this is responsible for the higher boiling points of the two nitrophenols.

Further the formation of intramolecular hydrogen bonding in o-nitrophenol prevents it from entering into intermolecular hydrogen bonding with water and this explains its reduced solubility.

- (ii) Other molecules in which intramolecular hydrogen bonding is present are o-hydroxybenzaldehyde, o-chlorophenol and o-hydroxybenzoic acid.



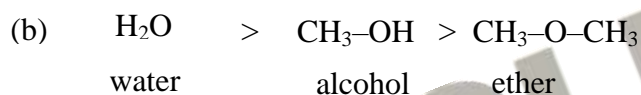
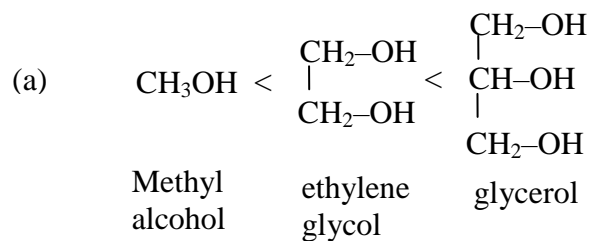
● **Effect of H-Bonding on Physical Properties**

(i) **Solubility**

Due to **intermolecular** H-bonding solubility increases for example alcohol and glucose are soluble in water. Due to **intramolecular** H-bonding solubility decreases for example o-hydroxybenzaldehyde is less soluble in water as compare to p-hydroxybenzaldehyde

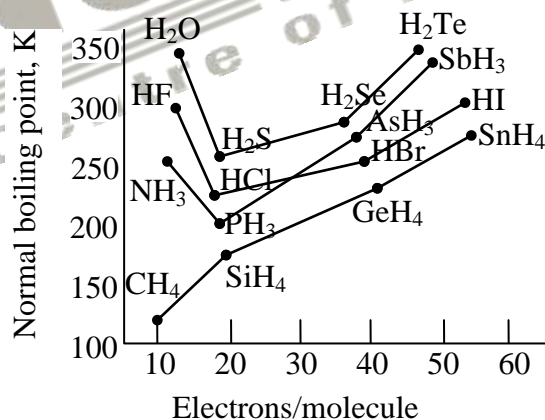
(ii) **Viscosity**

It is the measure of resistance to flow. Due to intermolecular H-bonding association takes place so viscosity increases for example:

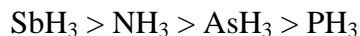
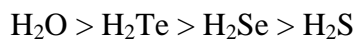
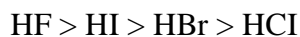


(iii) **Melting and boiling Point :**

Due to intermolecular H-bonding melting point and boiling point of compound increases for example :



Order of boiling points of VA, VIA, VIIA hydrides is as follows

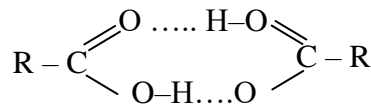


**Intramolecular** H-bonding gives rise to ring formation, So the force of attraction among these molecules are vander waal force, so M.P. and B.P are low.

(iv) **Molecular weight**

Due to intermolecular H bonding molecular weight increases.

**For example:** Molecular wt. of  $\text{CH}_3\text{COOH}$  is double of its molecular formula in benzene, due to dimer formation by H-bonding



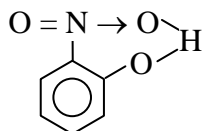
(v) **Physical State :**

H-bonding affects physical state (solid, liquid, gas) of compound. For example  $\text{H}_2\text{O}$  is liquid whereas  $\text{H}_2\text{S}$  is gas at room temperature.

**Ex 1.** Which one of the following does not have intermolecular H-bonding -

- (A)  $\text{H}_2\text{O}$  (B) o-Nitrophenol (C) HF (D)  $\text{CH}_3\text{OH}$

**Sol.** O-Nitrophenol has intramolecular H bonding as shown below



Hence Ans. is (2)

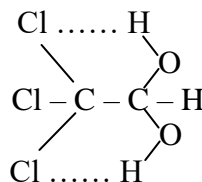
**Ex 2.** Arrange in increasing order of boiling

- (i) HF, HCl, HBr, HI (ii)  $\text{H}_2\text{O}$ , HF,  $\text{NH}_3$   
(iii)  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , HCl (iv)  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$

- Sol.** (i)  $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$  (ii)  $\text{NH}_3 < \text{HF} < \text{H}_2\text{O}$   
(iii)  $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$  (iv)  $\text{CH}_3\text{OCH}_3 < \text{CH}_3\text{OH} < \text{H}_2\text{O}$

**Ex 3.** Why chloral hydrate is a stable molecule ?

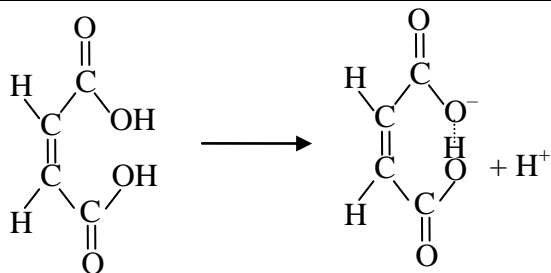
**Sol.** Chloral hydrate is a stable due to H-bonding (intramolecular)



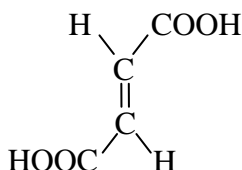
Chloral hydrate

**Ex 4.** Why maleic acid (cis) is stronger acid than fumaric acid(trans) ?

**Sol.** Maleic acid (cis) is stronger acid than fumaric acid (trans) because conjugate base of maleic acid is stable due to intramolecular H-bonding.



Stable conjugate base of maleic acid



Fumaric acid (No-intramolecular H-bonding)

**Que.** Which structure of HF is correct ?

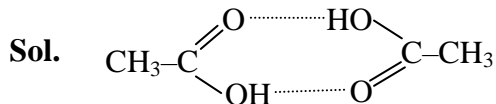


**Sol.** F has 3 lone pair hence linear structure around F is not possible. Hence correct option is (i).

**Que.** Heat of vapourisation of water is higher than HF. However strength of H-Bond in HF is higher than water.

**Sol.** H<sub>2</sub>O is surrounded by 4 other H<sub>2</sub>O molecules whereas HF is surrounded by only 2 molecules. Due to this, extent of hydrogen bonding in H<sub>2</sub>O is more, hence Heat of vapourisation of water is higher.

**Que.** Experimental molecular weight of acetic acid is just double than theoretical molecular weight. Why ?



Observed molecular weight = 120

Due to intermolecular, H-Bonding

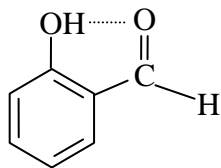
**Q.** KHF<sub>2</sub> exists but KHBr<sub>2</sub> & KHI<sub>2</sub> does not. Why ?

**Sol.**  $\text{KHF}_2 \rightarrow \text{K}^+ + \text{HF}_2^-$  [ $\text{F}^- \cdots \text{H}-\text{F}$ ] H-bonding  
 $\text{KHBr}_2 \rightarrow \text{K}^+ + \text{HBr}_2^-$  [not stable]  
 $\text{KHI}_2 \rightarrow \text{K}^+ + \text{HI}_2^-$  [not stable]

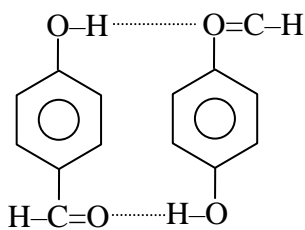
} No hydrogen bonding

**Que.** o-hydroxybenzaldehyde is liquid while p-hydroxybenzaldehyde is solid at room temperature ?  
Why ?

**Sol.**



Intramolecular  
H-bonding



Intermolecular  
H-bonding

### DO YOUR SELF – 5

**Q.1** Which one among the following does not have the hydrogen bond ?

- (A) Phenol                      (B)  $\text{NH}_3(\ell)$                       (C)  $\text{H}_2\text{O}(\ell)$                       (D)  $\text{HCl}(\ell)$

**Q.2** Among the following the strongest hydrogen bond is

- (A)  $\text{O}-\text{H} \cdots \text{S}$                       (B)  $\text{S}-\text{H} \cdots \text{O}$                       (C)  $\text{F}-\text{H} \cdots \text{F}$                       (D)  $\text{O}-\text{H} \cdots \text{O}$

**Q.3** Which of the following compounds is most volatile ?

- (A)  $\text{HF}$                       (B)  $\text{HCl}$                       (C)  $\text{HBr}$                       (D)  $\text{HI}$

**Q.4** The hydrogen bond is strongest in:

- (A)  $\text{O}-\text{H} \cdots \text{S}$                       (B)  $\text{S}-\text{H} \cdots \text{O}$                       (C)  $\text{F}-\text{H} \cdots \text{F}$                       (D)  $\text{O}-\text{H} \cdots \text{O}$

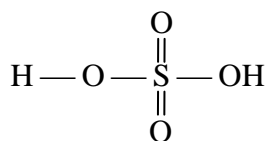
**Q.5** Weakest hydrogen bond is:

- (A)  $\text{O}-\text{H} \cdots \text{N}$                       (B)  $\text{S}-\text{H} \cdots \text{S}$                       (C)  $\text{F}-\text{H} \cdots \text{F}$                       (D)  $\text{N}-\text{H} \cdots \text{N}$

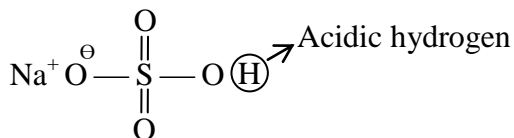


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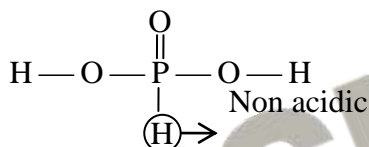
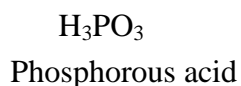
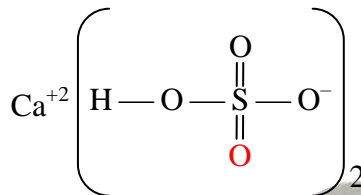
- Naming and structure of salts of oxy acids :



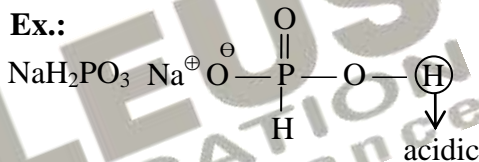
Sulphuric acid



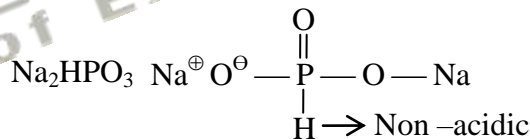
Sodium hydrogen sulphate



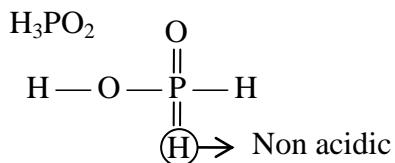
Ex.:



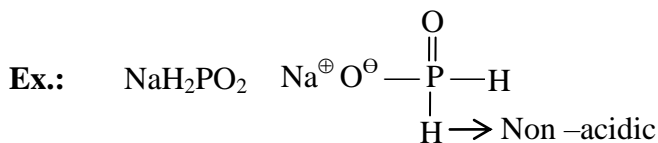
Sodium hydrogen phosphite



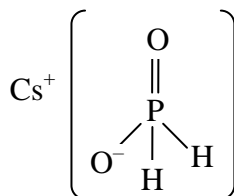
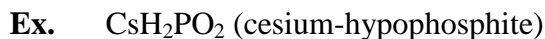
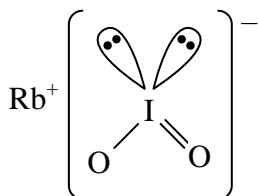
Sodium phosphite



Hypophosphorous acid  
(monobasic)

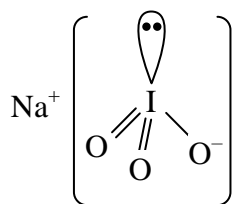


Sodium hypophosphite but not sodium  
Dihydrogen phosphate as H is not acidic

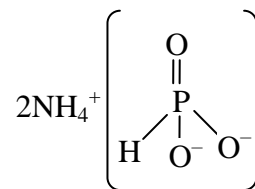




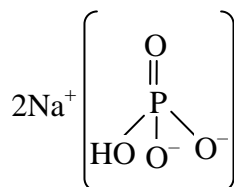
**Ex.**  $\text{NaIO}_3$  (sodium iodate)



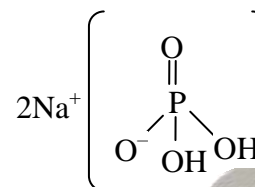
**Ex.** Ammonium phosphite  $(\text{NH}_4)_2\text{HPO}_3$



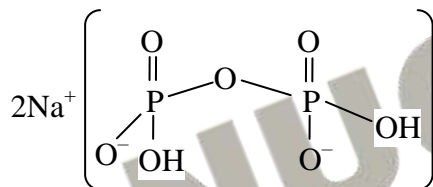
**Ex.** Sodium Hydrogen phosphate



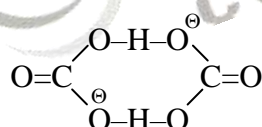
**Ex.**  $\text{NaH}_2\text{PO}_4$  (Sodium dihydrogen phosphate)



**Ex.**  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  {Sodium dihydrogen pyrophosphate}

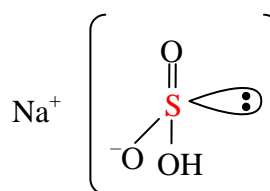


**Ex.** Potassium bi carbonate  $(\text{KHCO}_3)$

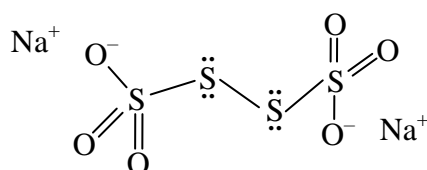


Compact H bonding

**Ex.**  $\text{NaHSO}_3$  (Sodium bisulphite)



**Ex.**  $\text{Na}_2\text{S}_4\text{O}_6$  (sodium tetrathionate)



• Some Other example -

$\text{H}_2\text{SO}_4$	$\text{Na}_2\text{SO}_4$ – Sodium sulphate
Sulphuric acid	$\text{K}_2\text{SO}_4$ – Potassium sulphate
	$\text{BaSO}_4$ – Barium sulphate
	$\text{FeSO}_4$ – Ferrous sulphate
	$\text{Al}_2(\text{SO}_4)_3$ – Aluminium sulphate
$\text{H}_3\text{PO}_4$	$\text{Na}_3\text{PO}_4$ – Sodium orthophosphate
Orthophosphoric acid	$\text{K}_3\text{PO}_4$ – Potassium orthophosphate
	$\text{Ca}_3(\text{PO}_4)_2$ – Calcium Orthophosphate
	$\text{AlPO}_4$ – Aluminium orthophosphate
$\text{HPO}_3$	$\text{NaPO}_3$ – Sodium metaphosphate
Meta phosphoric acid	$\text{KPO}_3$ – Potassium metaphosphate
	$\text{Ca}(\text{PO}_3)_2$ – Calcium metaphosphate
	$\text{Al}(\text{PO}_3)_3$ – Aluminium metaphosphate
$\text{HClO}_3$	$\text{KClO}_3$ – Potassium chlorate
Chloric acid	$\text{NaClO}_3$ – Sodium chlorate
	$\text{Ca}(\text{ClO}_3)_2$ – Calcium chlorate
$\text{HClO}_4$	$\text{NaClO}_4$ – Sodium perchlorate
Perchloric acid	$\text{KClO}_4$ – Potassium perchlorate
	$\text{NH}_4\text{ClO}_4$ – Ammonium perchlorate
	$\text{Ca}(\text{ClO}_4)_2$ – Calcium perchlorate
$\text{H}_3\text{PO}_4$	$\text{KH}_2\text{PO}_4$ potassium dihydrogen orthophosphate
Orthophosphoric acid	$\text{Ca}(\text{H}_2\text{PO}_4)_2$ calcium dihydrogen orthophosphate
$(\text{HPO}_3)_6 = \text{H}_6\text{P}_6\text{O}_{18}$	$\text{Na}_6\text{P}_6\text{O}_{18}$

Hexametaphosphoric acid	Sodium hexametaphosphate
$\text{HBiO}_3$	$\text{NaBiO}_3$ . Sodium metabismuthate
Metabismuthic acid	$\text{KBiO}_3$ . Potassium metabismuthate
$\text{HBO}_2$	$\text{NaBO}_2$ sodium metaborate
Metaboric acid	
$\text{H}_2\text{SO}_5$	$\text{Na}_2\text{SO}_5$ . Sodium peroxy sulphate
Peroxy sulphuric acid	
$\text{H}_4\text{P}_2\text{O}_7$	$\text{Na}_4\text{P}_2\text{O}_7$ – Sodium pyrophosphate
Pyrophosphoric acid	
$\text{HClO}_2$	$\text{NaClO}_2$ sodium chlorite
Chlorous acid	$\text{KClO}_2$ potassium chlorite
	$\text{Ca}(\text{ClO}_2)_2$ calcium chlorite
$\text{H}_3\text{PO}_3$	$\text{Na}_2\text{HPO}_3$ potassium phosphite
(dibasic acid)	$\text{Ca}(\text{HPO}_3)_2$ calcium phosphite
$\text{H}_2\text{SO}_3$	$\text{Na}_2\text{SO}_3$ sodium sulphite
Sulphurous acid	$\text{K}_2\text{SO}_3$ potassium sulphite
$\text{HNO}_2$	$\text{NaNO}_2$ sodium nitrite
Nitrous acid	$\text{KNO}_2$ potassium nitrite
$\text{HOCl}$	$\text{NaOCl}$ sodium hypochlorite
Hypochlorous acid	$\text{KBrO}$ potassium hypobromite
	$\text{NaOI}$ sodium hypoiodite
$\text{H}_3\text{PO}_2$	$\text{NaH}_2\text{PO}_2$ sodium hypophosphite
Hypophosphorous acid	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ Barium hypophosphite
(monobasic acid)	

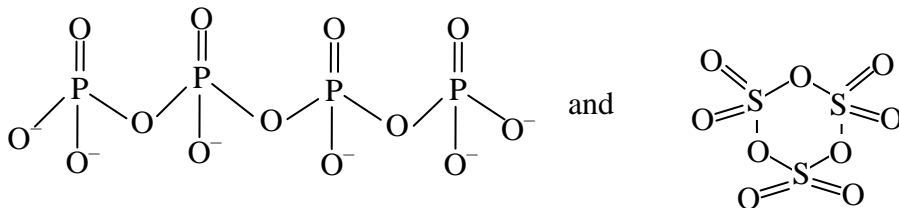
**Q.1** Which of the following species has the same number of X–O–X linkage as present in  $S_3O_9$

(i.e.  $\gamma$ - $SO_3$ )



**Ans.** (C)

X–O–X linkages in  $S_3O_9$  is 3 and in  $P_4O_{13}^{6-}$  also it is 3.



**Q.2** Find the number of ions in which  $\frac{\sigma}{\pi}$  ratio is 4 from the following.



**Ans.** 6

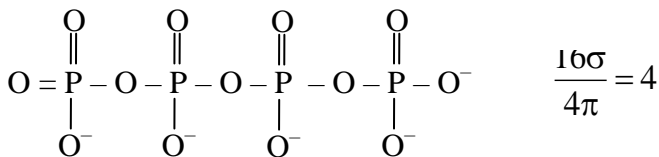
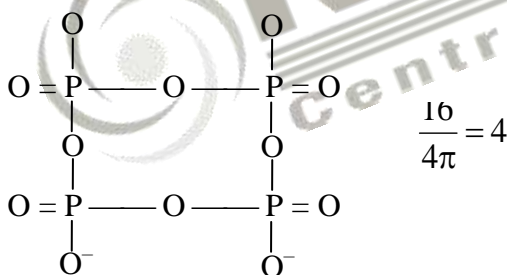
In following anion

$$\text{no. of } \sigma \text{ bond} \Rightarrow n \times 4$$

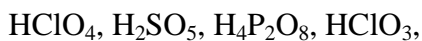
$$\text{no. of } \pi \text{ bond} \Rightarrow n$$

Where n is no. of central atom. Hence the ratio of  $\sigma$  and  $\pi$  bond is 4 for each ion.

$P_4O_{12}^{4-}$  :-



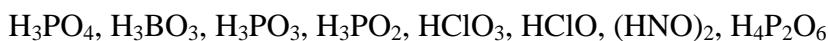
**Q.3** Find the number of molecules which are per acid as well as peroxy acid.



**Ans.** 2

$H_2SO_5$  and  $H_4P_2O_8$  having per oxy linkage.

**Q.4** Find the number of acid(s) which are having hypo prefix in it's name from the following.



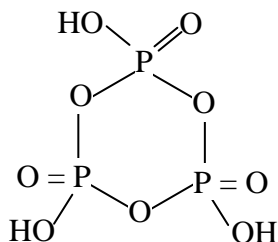
**Ans.** (4)

- $\text{H}_3\text{PO}_2 \rightarrow$  Hypo phosphorous acid  
 $\text{HClO} \rightarrow$  Hypo chlorous acid  
 $(\text{HNO})_2 \rightarrow$  Hypo nitrous acid  
 $\text{H}_4\text{P}_2\text{O}_6 \rightarrow$  Hypo phosphoric acid

**Q.5** Which of the following statement is correct for  $\text{H}_3\text{P}_3\text{O}_9$

- (1) trimetaphosphoric acid                      (2) tribasic acid  
 (3) has cyclic structure                      (4) All are correct

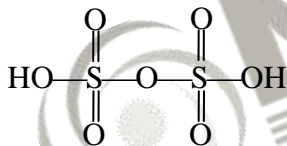
**Ans.** (4)



**Q.6** Which of the following having S-O-S linkage -

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

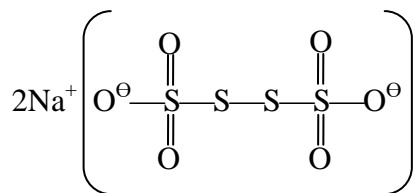
**Ans.** (B)



**Q.7** The number of S-S linkages in sodium tetrathionate

- (A) 1                      (B) 2                      (C) 3                      (D) 4

**Ans.** (C)

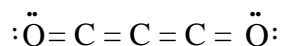


**LECTURE NUMBER - 19**

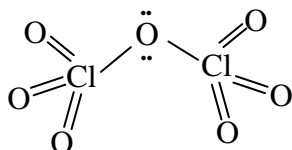
- Structures of few important compounds

**Oxides**

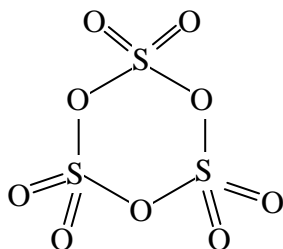
**Ex.**  $C_3O_2$  (Carbon suboxide)



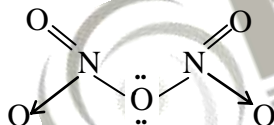
**Ex.**  $Cl_2O_7$  (Dichlorine heptoxide)



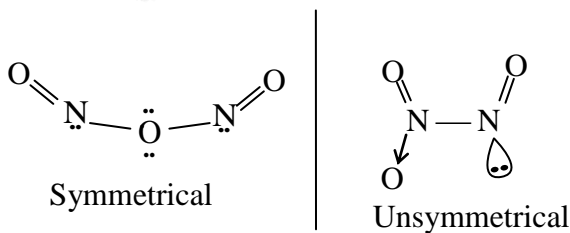
**Ex.**  $S_3O_9$  (cyclic trimer of  $SO_3$ )



**Ex.**  $N_2O_5$  (Dinitrogen pentoxide)



**Ex.**  $N_2O_3$  (Dinitrogen trioxide)

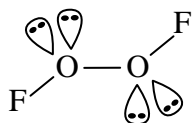


- Other example :

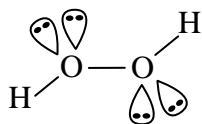
$N_2O$ ,  $C_{12}O_9$ ,  $SO_2$ ,  $SO_3$ ,  $N_2O_4$ ,  $N_2O_5$  etc.

• **Open book like structure:**

Ex.  $O_2F_2$  (Dioxygen di fluoride)

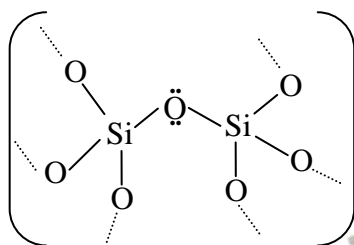


$H_2O_2$  (Hydrogen peroxide)



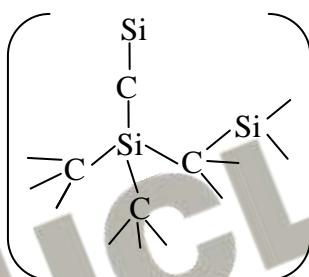
• **3D Structures**

Ex.  $SiO_2$  (Silicon dioxide)

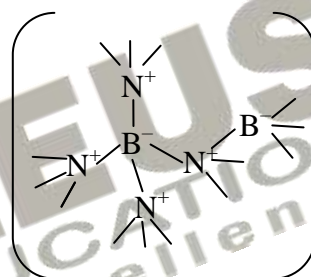


(Inorganic graphite)

Carborandum

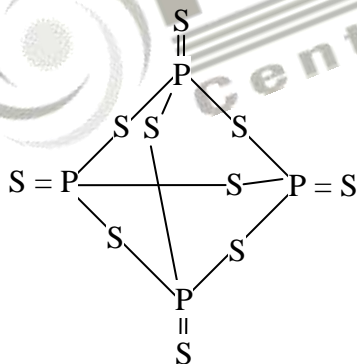


3-D Borazone



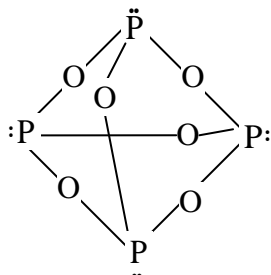
• **Cyclic structure**

Ex.  $P_4S_{10}$  (Phosphorous pentasulphide)



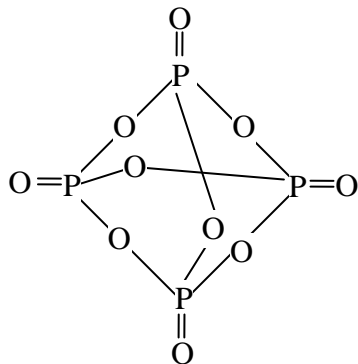
Ex.  $P_4O_6$  (Phosphorous trioxide)

Chemical formula  $\rightarrow P_2O_3$  or  $P_4O_6$

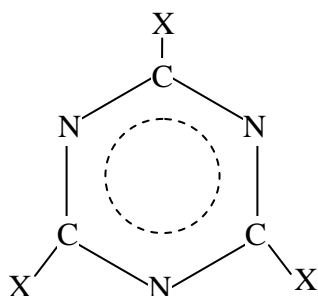




Ex.  $P_4O_{10}$  (Phosphorous pentoxide)



Ex.



$X = -N_3^-, -NH_2, Cl^-$

$C_3N_3Cl_3$  Cyanuric trichloride

$C_3N_3(NH_2)_3$  Cyanuric triamide

$C_3N_3(N_3)_3$  Cyanuric triazide

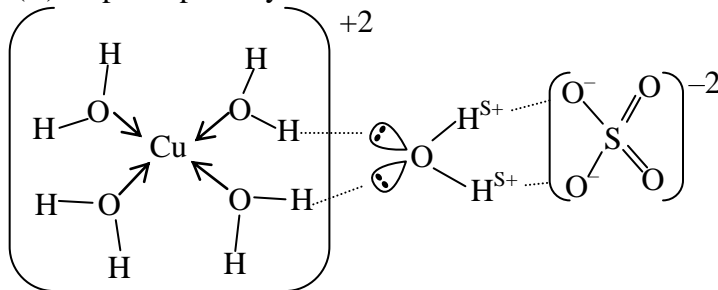
**Other example**

$(BO_2^{2-})_3, B_3N_3H_6, C_6H_6$

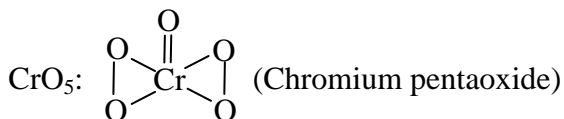
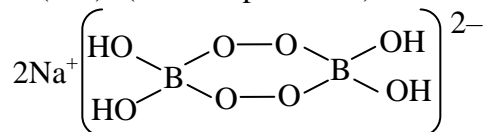
• **Special Structures**

Ex.  $CuSO_4 \cdot 5H_2O$

Copper (II) sulphate pentahydrate

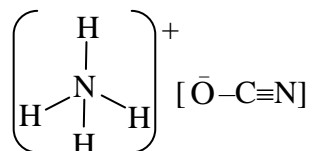


$Na_2B_2O_4(OH)_4$  (Sodium perborate)



• Other examples:

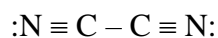
Ex.  $\text{NH}_4\text{OCN}$  (Ammonium cyanate)



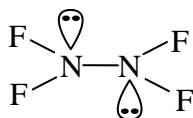
Ex.  $\text{CaC}_2$  (Calcium carbide)



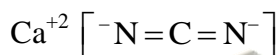
Ex.  $(\text{CN})_2$  cyanogen



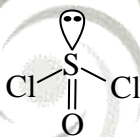
Ex.  $\text{N}_2\text{F}_4$   $\left\{ \begin{array}{l} \text{Tetra fluoro hydrazine} \\ \text{or} \\ \text{Dinitrogen tetrafluoride} \end{array} \right\}$



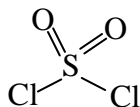
Ex.  $\text{CaCN}_2$  (Calcium cyanamide)



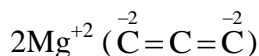
Ex.  $\text{SOCl}_2$  (Thionyl chloride)



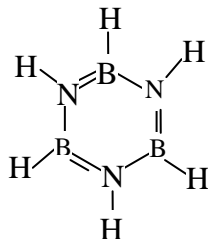
Ex. Sulphuryl chloride ( $\text{SO}_2\text{Cl}_2$ )



$\text{Mg}_2\text{C}_3$



Ex. Inorganic benzene ( $\text{B}_3\text{N}_3\text{H}_6$ )



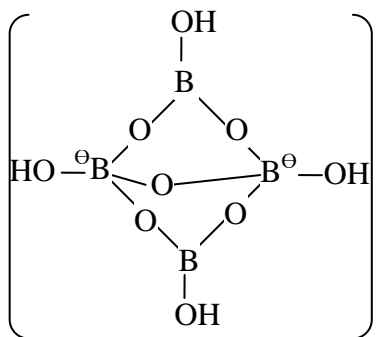
• Other examples



**Q.1** Find the number of B — O — B linkage in the following :-  $[B_4O_5(OH)_4]^{2-}$

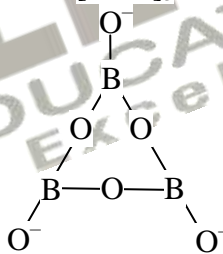
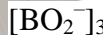
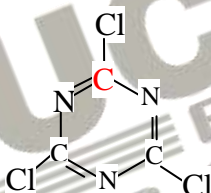
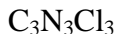
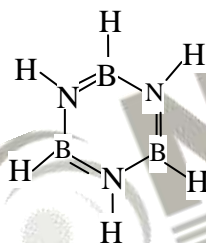
**Ans.** (005)

**Sol.**



**Q.2** Find the number of planar molecules/ions which are cyclic -  
 $B_3N_3H_6$ ,  $C_3N_3Cl_3$ ,  $(BO_2^-)_3$ ,  $S_2O_8^{2-}$

**Ans.** (3)



**Q.3** Find the maximum number of atoms present in one plane in  $C(CN)_4$  :-

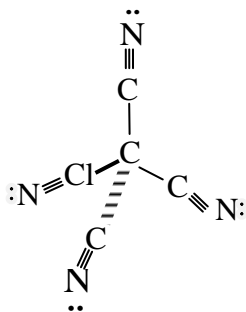
(A) 3

(B) 5

(C) 7

(D) 9

**Ans.** (B)



Maximum 5-atom in one plane

**Q.4** The number of plane containing maximum number of atoms in  $C(CN)_4$  :-

(A) 8

(B) 10

(C) 4

(D) 6

**Ans.** (D)

**Q.5** Find the number of molecules in which  $\frac{\sigma}{\pi}$  ratio is four

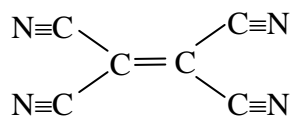


**Ans.** 3

Molecules	$\sigma/\pi$ ratio
$\text{C}_3\text{N}_3\text{Cl}_3$	3
$\text{B}_3\text{N}_3\text{H}_6$	4
$\text{P}_2\text{O}_7^{4-}$	4
$\text{S}_2\text{O}_7^{2-}$	2
$\text{HP}_2\text{O}_6^{3-}$	4

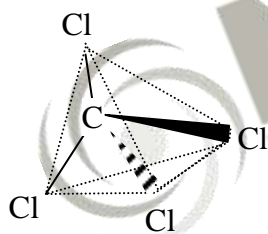
**Q.6** Find the number of atoms are lying in the same plane of  $\text{C}_2(\text{CN})_4$

**Ans.** (10)

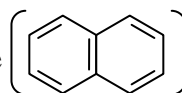


**Q.7** Find the maximum number of plane having maximum same type of atom in  $\text{CCl}_4$ .

**Ans.** (4)

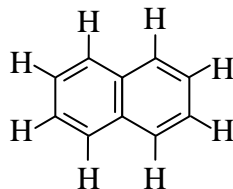


**Q.8** Find the total number of sigma bond(s) in naphthalene



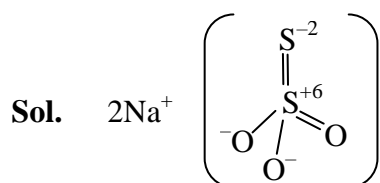
**Ans.** (19)

Total number of  $\sigma$ -bond = 19



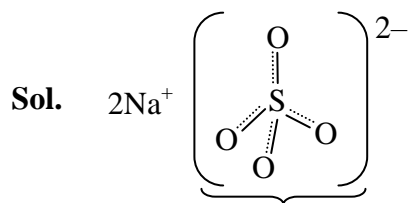
**Q.9** Find the average oxidation number of S atoms in sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ )

**Ans.** (2)



**Q.10** Find the number of identical  $\widehat{\text{OSO}}$  angles in  $\text{Na}_2\text{SO}_4$  molecule.

**Ans.** (6)



Due to equivalent  
Resonance All the  
bond angle are equal

**Q.11** The shape of  $\text{IO}(\text{OH})_5$  is supposed to nearly with respect to I-atom.

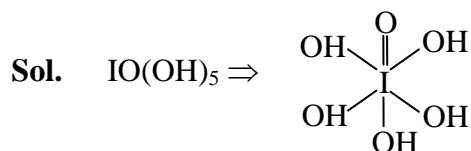
(A) Trigonal bipyramidal

(B) Square pyramidal

(C) Octahedral

(D) See-saw

**Ans** (C)



**Q.12** Number of atoms that are in same plane in Benzene is

(A) 6

(B) 12

(C) 5

(D) 10

**Ans.** (B)

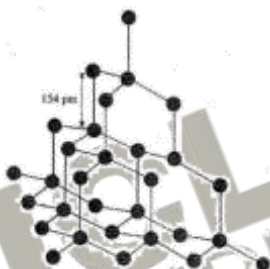
## LECTURE NUMBER – 20

### ALLOTROPE OF CARBON FAMILY

☞ Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E. Smalley and R.F. Curl. For this discovery they were awarded the Nobel Prize in 1996.

- **Diamond** (*kinetically most stable allotrope of carbon, meta stable phase of carbon*)

It has a crystalline lattice. In diamond each carbon atom undergoes  $sp^3$  hybridisation and linked to four other carbon atoms by using hybridized orbitals in tetrahedral fashion. The C—C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms.



*The structure of diamond*

In this structure, directional covalent bonds are present throughout the lattice. It is very difficult to break extended covalent bonding and, therefore, diamond is a very hard substance. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

- **Problem**

Diamond is covalent, yet it has high melting point. Why ?

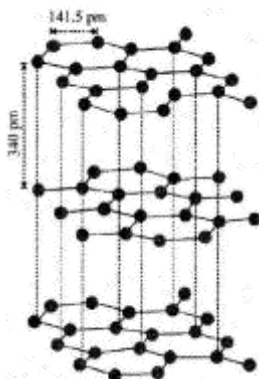
#### **Solution**

Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

- **Graphite** (*Thermodynamically most stable allotrope of carbon*)

Graphite has layered structure. Layers are held by vander Waals 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 makes three sigma bonds with three neighbouring carbon atoms. Fourth

electron forms a  $\pi$  bond. The electrons are delocalised over the whole sheet. Thus, graphite is lustrous.



*The structure of graphite*

Electrons are mobile and therefore, graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

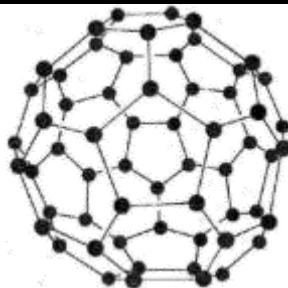
#### • Fullerenes

Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised small molecules consists of mainly  $C_{60}$  with smaller quantity of  $C_{70}$  and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.  $C_{60}$  molecule has a shape like soccer ball and called **Buckminsterfullerene**.

It contains twenty, six-membered rings and twelve, five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalized in molecular orbitals, which in turn give aromatic character to molecule. However, because of non-planar nature of fullerenes, their aromatic character gets diminished and reactivity increases.

This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.





[The structure of  $C_{60}$  Buckminsterfullerene : note that molecule has the shape of a soccer ball (football)]

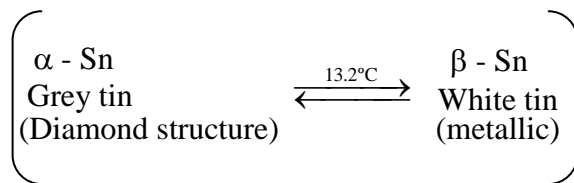
It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore,  $\Delta H_f$  of graphite is taken as zero.  $\Delta H_f$  values of diamond and fullerene,  $C_{60}$  are 1.90 and 38.1  $\text{kJ mol}^{-1}$ , respectively.

Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

#### • Uses of Carbon

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalis. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

Si, Ge and Sn have a diamond type of structure, though Sn exists as a metallic form. Pb exists only in the metallic form. Ge is unusual because the liquid expands when it forms the solid. This property is unique to Ga, Ge and Bi.



## ☞ ALLOTROPES OF OXYGEN FAMILY

Oxygen occurs as two non-metallic forms, dioxygen  $O_2$  and ozone  $O_3$ . Dioxygen  $O_2$  is stable as a diatomic molecule.  $O_3$  molecule is diamagnetic while  $O_2$  is paramagnetic.

Six allotropes of selenium are known.

Tellurium has only one crystalline form, which is silvery white and semimetallic.

This is similar to grey Se, but has stronger metallic interaction.

- **Sulphur Allotropic forms :**

Sulphur forms numerous allotropes of which the yellow rhombic ( $\alpha$ -sulphur) and monoclinic ( $\beta$ -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

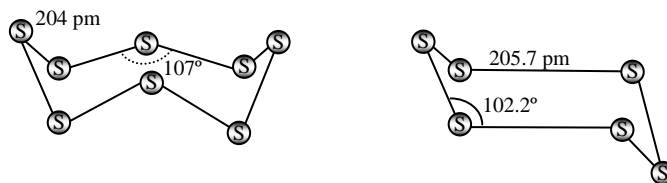
- **Rhombic sulphur ( $\alpha$ -sulphur)** (*Most stable sulphur allotrope at room temperature*)

This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in  $CS_2$ . It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in  $CS_2$ .

- **Monoclinic sulphur ( $\beta$ -sulphur)**

Its m.p. is 393 K and specific gravity 1.98. It is soluble in  $CS_2$  while water insoluble. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of  $\beta$ -sulphur are formed. It is stable above 369 K and transforms into  $\alpha$ -sulphur below it. Conversely,  $\alpha$ -sulphur is stable below 369 K and transforms into  $\beta$ -sulphur above this. At 369 K, both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have  $S_8$  molecules. These  $S_8$  molecules are packed to give different crystal structures. The  $S_8$  ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in the figure.



The structures of (a)  $S_8$  ring in Rhombic sulphur and (b)  $S_6$  form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last two decades. In cyclo- $S_6$ , the ring adopts the chair form and the molecular dimensions are as shown in figure. At elevated temperatures ( $\sim 1000$  K),  $S_2$  is the dominant species and is paramagnetic just like  $O_2$ .

**Note:** Engel's sulphur ( $\epsilon$ -sulphur) is unstable and contains  $S_6$  rings arranged in the chair conformation. It is made by pouring  $Na_2S_2O_3$  solution into concentrated HCl and extracting the S with toluene. Plastic sulphur-( $\chi$ ) is obtained by pouring liquid sulphur into water.

**Example**

Which form of sulphur shows paramagnetic behavior ?

**Solution**

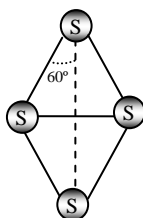
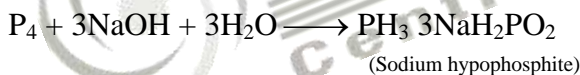
In vapour state sulphur partly exists as  $S_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$  orbitals like  $O_2$  and, hence, exhibits paramagnetism.

• **Allotropes of nitrogen Family :**

Solid As, Sb and Bi each exist in several allotropic forms. Arsenic vapour contains tetrahedral  $As_4$  molecules. A reactive yellow form of the solid resembles white phosphorus and is thought to contain tetrahedral  $As_4$  units. Sb also has a yellow form. All three elements have much less reactive metallic or  $\alpha$ -forms.

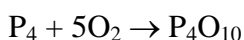
**PHOSPHORUS ALLOTROPIC FORMS**

- Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus is a translucent, white, waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving  $PH_3$ .



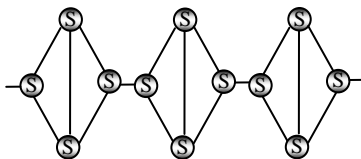
White Phosphorus

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the  $P_4$  molecule where the angles are only  $60^\circ$ . It readily catches fire in air to give dense white fumes of  $P_4O_{10}$ .



It consists of discrete tetrahedral  $P_4$  molecule as shown in Fig.

- **Red phosphorus** is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses iron grey lustre. It is odourless, nonpoisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. It is polymeric, consisting of chains of  $P_4$  tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

- **Black phosphorus** has two forms  $\alpha$ -black phosphorus and  $\beta$ -black phosphorus  $\alpha$ -black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. it can be sublimed in air and has opaque monoclinic or rhombic crystals it does not oxidize in air.  $\beta$ -Black phosphorus is prepared by heating white phosphorus at 473K under high pressure. It does not burn in air upto 673 K.



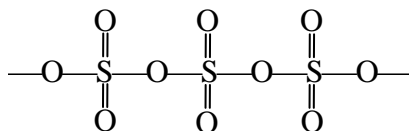
**Thermodynamic stability order :** Black phosphorus > Red phosphorus > White phosphorus

**Reactivity order :** Black phosphorus < Red phosphorus < White phosphorus

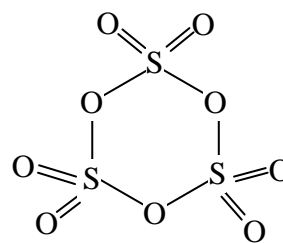
### ALLOTROPIC FORM OF $SO_3$

- $SO_3$  have three allotropic forms  $\alpha$ - $SO_3$ ,  $\beta$ - $SO_3$ , and  $\gamma$ - $SO_3$

$\alpha$ - $SO_3$   
Cross linked solid



Polymeric chain structure  
 $\beta$ - $SO_3$



$\gamma$ - $SO_3$   
( $S_3O_9$ )  
Cyclic trimer

**QUESTION OF HYDROGEN BONDING**

- Q.1** Explain the structure of Boric acid in solid state.
- Q.2** Boiling point of o-Nitrophenol is less than meta and para nitrophenol. Why ?
- Q.3** Maleic acid is more acidic than fumaric acid. Why ?
- Q.4** H - F is only liquid among halogen acid. Why ?
- Q.5** Ammonia is more easily liquefied than HCl, explain.
- Q.6** Why ice floats on water ?
- Q.7** Water shows maximum density at 4°C. Why ?
- Q.8** HI is the strongest halogen acid, whereas H-F is the weakest. Why ?
- Q.9** Wood pieces are used to hold ice-cream. Why ?
- Q.10**  $\text{KHF}_2$  is possible but not  $\text{KBr}_2$  or  $\text{KI}_2$ . Why?
- Q.11** O - Nitrophenol is less soluble in  $\text{H}_2\text{O}$  than p - Nitrophenol. Why?
- Q.12** o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.
- Q.13** Glycerol is more viscous than ethanol. Explain.
- Q.14**  $\text{CH}_4$  and  $\text{H}_2\text{O}$  have nearly same molecular weight. Yet  $\text{CH}_4$  has a boiling point 112 K and water 373 K. Explain.
- Q.15** The experimental molecular weight of acetic acid is just double than theoretical molecular weight of acetic acid. Why?
- Q.16** Although chlorine has same electronegativity as nitrogen but the former does not form effective H-bonding. Explain.
- Q.17** Molar entropy change of vapourization of acetic acid is less than that of water. Explain.
- Q.18** Heat of vapourization of water is higher than HF, however strength of H-bond in HF is higher than water. Explain

## EXERCISE # 1

### INTRODUCTION

- The molecule which contain same number of  $\sigma$  and  $\pi$  bonds is  
(A)  $(\text{CN})_2$  (B)  $\text{C}_2\text{H}_2$  (C)  $\text{HNO}_2$  (D)  $\text{HCN}$
- Correct energy order of hybrid orbital is:  
(A)  $sp < sp^2 < sp^3$  (B)  $sp < sp^3 < sp^2$  (C)  $sp^3 < sp^2 < sp$  (D)  $sp^2 < sp^3 < sp$

### LEWIS DOT STRUCTURES

- Which of the following is hypovalent species?  
(A)  $\text{ICl}$  (B)  $\text{SO}_2$  (C)  $\text{NO}_2^+$  (D)  $\text{NH}_2^+$
- Which one of the following element do not have tendency to form hyper valent compound ?  
(A) P (B) N (C) S (D) Se
- Which of the following set of species are hypovalent?  
(A)  $\text{NH}_3, \text{CO}_2$  (B)  $\text{SO}_2, \text{CO}_2$  (C)  $\text{BeH}_2, \text{BF}_3$  (D)  $\text{BeCl}_2, \text{PCl}_3$
- Which of the following pair of species are isostructural but not isoelectronic ?  
(A)  $\text{N}_2\text{O}$  and  $\text{SO}_2$  (B)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^{-1}$  (C)  $\text{NF}_3$  and  $\text{NH}_3$  (D)  $\text{O}_3$  and  $\text{NO}_2^{\oplus}$
- Which of the following xenon compound has the same number of lone pairs as in  $\text{I}_3^-$  :-  
(A)  $\text{XeO}_4$  (B)  $\text{XeF}_4$  (C)  $\text{XeF}_2$  (D)  $\text{XeO}_3$
- Which of the following molecules is adequately represented by a single Lewis structure?  
(A)  $\text{O}_3$  (B)  $\text{NOC1}$  (C)  $\text{SO}_2$  (D)  $\text{N}_2\text{O}$

### TYPES OF BOND

- The molecule which contain both polar and non-polar covalent bond present in its structure?  
(A)  $\text{H}_2\text{F}_2$  (B)  $\text{O}_2\text{F}_2$  (C)  $\text{O}_3$  (D) All of these
- Which one of the following species have coordinate bond present in its Lewis structure  
(A)  $\text{SO}_2$  (B)  $\text{O}_3$  (C)  $\text{NO}_2$  (D) All of them



11.  $[\text{Re}_2\text{Cl}_8]^{-2}$  molecule has  
(A) only  $\sigma$  bond (B) only  $\pi$  bond (C) quadruple bond (D) None of these
12. Which of the following statement is correct regarding covalent bond ?  
(A) Filled orbitals of two or more atoms overlap with one another.  
(B) Unoccupied orbitals of two or more atoms overlap with one another  
(C) Electrons are simultaneously attracted between more than one nucleus.  
(D) Electrons are transferred from one atom to another atom.

### VBT

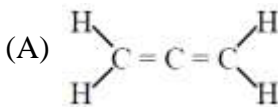
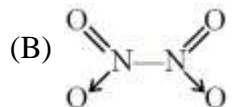
13. If x is internuclear axis,  $\delta$  bond can be formed by :  
(A)  $d_{x^2-y^2} + d_{x^2-y^2}$  (B)  $d_{xy} + d_{yz}$   
(C)  $d_{yz} + d_{yz}$  (D)  $d_{xz} + d_{xy}$
14. Which of the following leads to non-bonding on z-axis  
(A)  $p_x + p_x$  (B)  $p_y + p_y$  (C)  $d_{xy} + d_{xy}$  (D)  $d_{xy} + d_{yz}$
15. Which of the following statement is false ?  
(A)  $\delta$ -bond is a result of 4-lobe interaction between two p-orbitals.  
(B)  $\delta$ -bond is weaker than  $\pi$ -bond  
(C)  $\delta$ -bond &  $\sigma$ -bond have unequal bond strength  
(D) Representative elements do not have tendency to form  $\delta$ -bond.
16. Choose the incorrect order of bond strength :-  
(A)  $3p_\pi - 3p_\pi < 2p_\pi - 3d_\pi$  (B)  $3p_\pi - 3p_\pi < 3d_\pi - 3d_\pi$   
(C)  $3p_\pi - 3d_\pi < 2p_\pi - 3d_\pi$  (D)  $3p_\pi - 3d_\pi < 3p_\pi - 3p_\pi$
17. Which of the following specie does not contain  $p_\pi - d_\pi$  bond(s) ?  
(A)  $\text{SO}_2\text{Cl}_2$  (B)  $\text{N}_2\text{O}$  (C)  $\text{H}_2\text{PO}_3^\ominus$  (D)  $\text{SO}_3^{2-}$
18. Correct order of bond strength is:  
(A)  $1s - 1s > 1s - 2s > 2s - 2p$  (B)  $1s - 1s < 1s - 2s < 2s - 2p$   
(C)  $1s - 2s > 2s - 2p > 1s - 1s$  (D) None of the above



19. If x is internuclear axis,  $\delta$  bond can be formed by :
- (A)  $d_{x^2-y^2} + d_{x^2-y^2}$  (B)  $d_{xy} + d_{yz}$   
(C)  $d_{yz} + d_{yz}$  (D)  $d_{xz} + d_{xy}$
20. Choose the **CORRECT** statement about the structure of  $\text{SO}_2$ .
- (A) Two  $2p_\pi - 3d_\pi$  bond (B) Two  $2p_\pi - 3d_\pi$  bond  
(C) One  $2p_\pi - 3d_\pi$  & one  $2p_\pi - 3p_\pi$  bond (D) It is hypovalent
21. The species having no  $P_\pi - P_\pi$  bond but has bond order equal to that of  $\text{O}_2$ .
- (A)  $\text{ClO}_3^-$  (B)  $\text{PO}_4^{3-}$  (C)  $\text{SO}_4^{2-}$  (D)  $\text{XeO}_3$
22. Which of the following orbital cannot form  $\sigma$  bond with  $d_{xy}$  orbital.
- (A) s (B)  $p_x$  (C)  $d_{x^2-y^2}$  (D) All of these
23. Which of the following statement is correct ?
- (A) s-orbital always forms  $\sigma$  bond with p orbital  
(B) s-orbital is more directional than  $\pi$ -orbital  
(C) p-orbital always form  $\pi$ -bond  
(D) a covalent bond is directional in nature.
24. Which of the following overlapping is correct regarding  $\sigma$ -bond formation ?
- (A)  $2p_x + 2p_x$ , when y-axis is inter nuclear axis  
(B)  $1s + 2p_x$ , when x-axis is inter nuclear axis  
(C)  $2p_y + 2p_y$ , when z-axis is inter nuclear axis  
(D)  $2p_y + 2p_z$ , when x-axis is inter nuclear axis
25. Which of the following shows maximum covalency ?
- (A) F (B) I (C) S (D) O
26. Which of the following overlapping is not present in  $\text{XeO}_3$  molecule ?
- (A)  $sp^3 + p_x$  (B)  $sp^3 + p_y$  (C)  $d_{xz} + p_x$  (D)  $sp^3 + s$
27. According to VBT, which of the following overlapping results  $\pi$ -type covalent bond in  $\text{O}_2$  molecule formation, when Z-axis is internuclear axis?
- (I)  $2s - 2s$  (II)  $2p_x - 2p_x$  (III)  $1s - 1s$  (IV)  $2p_y - 2p_y$  (V)  $2p_z - 2p_z$   
(A) I, III (B) III, IV (C) II, IV (D) IV, V

28. Which of the following would result in the formation of strongest  $\pi$ -bond if the molecular axis is x-axis?  
(A)  $2p_x + 2p_x$  (B)  $2p_y + 2p_y$  (C)  $2p_y + 3d_{xy}$  (D)  $2p_z + 4p_z$
29. In which of the following species  $p_\pi-d_\pi$  bond is present but  $p_\pi-p_\pi$  bond is absent?  
(A)  $\text{SiH}_4$  (B)  $\text{CS}_2$  (C)  $\text{SO}_2$  (D)  $\text{SO}_2\text{Cl}_2$

### HYBRIDISATION

30. The set of planar chemical species in which d-orbital participate in hybridisation.  
(A)  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  (B)  $\text{XeF}_5^\ominus$ ,  $\text{IF}_4^\ominus$ ,  $\text{XeF}_4$   
(C)  $\text{XeF}_5^\ominus$ ,  $\text{XeF}_6$ ,  $\text{XeF}_4$  (D)  $\text{IF}_7$ ,  $\text{ClF}_3$ ,  $\text{SF}_4$
31. Hybridisation of N in  $\text{NO}_2$  is ?  
(A)  $sp^3$  (B)  $sp$  (C)  $sp^2$  (D) N atom is unhybridised
32. Which one is only V-shaped molecule or ion-  
(A)  $\text{I}_3^-$  (B)  $\text{N}_3^-$  (C)  $\text{S}_3$  (D)  $\text{C}_3^{4-}$
33. In which of the following molecules hybridisation of central atom is  $sp^3d^2$ .  
(A)  $\text{XeF}_6$  (B)  $\text{S}_2\text{F}_{10}$  (C)  $\text{SF}_4$  (D)  $\text{PEt}_3$
34. Which of the following molecule involve  $d_{z^2}$  orbital in its hybridisation  
(A)  $\text{XeF}_4$  (B)  $\text{XeOF}_4$  (C)  $\text{XeO}_2\text{F}_2$  (D) All of these
35. Hybridisation of  $\text{ClFO}_3$ ,  $\text{SF}_4$  &  $\text{SOF}_4$  respectively will be  
(A)  $sp^3$ ,  $sp^3d$   $sp^3d$  (B)  $sp^3$ ,  $sp^3$   $sp^3$   
(C)  $sp^3$ ,  $sp^3d^2$   $sp^3d^2$  (D) All  $sp^3d$
36. Electron geometry of the molecule  $\text{XeF}_2$  &  $\text{ICl}_2^-$  are respectively ?  
(A) square bipyramidal, tetrahedral (B) linear & linear  
(C) Trigonal bipyramidal & tetrahedral (D) Both Trigonal bipyramidal
37. Which of the following molecule have all atoms  $sp^2$  Hybridised ?  
(A)  (B)   
(C) Benzene (D) None of these

38. Which of the following statement is **CORRECT**?
- (A) Lattice energy is always highest for compound with highest ionic character  
(B) Hydrated radius is inversely proportional to hydration energy  
(C) Dissolution of salt in water depends upon lattice energy and hydration energy  
(D) None of these
39. Correct statement about a molecule of type  $AB_3L$  where A = central atom, L = lone pair, B = bond pair.
- (A) It is pyramidal in shape (B)  $NH_3$  is one of the example of this case  
(C) It has tetrahedral electron geometry (D) All are correct.
40.  $\Phi$  bond is present in
- (A)  $Mn_2(CO)_{10}$  (B)  $U_2$  (C)  $O_2$  (D) None of these
41. Which of the following compound is planar ?
- (A)  $PH_4^+$  (B)  $XeF_4$  (C)  $XeOF_4$  (D)  $SF_6$
42. Hybridisation of cationic part of  $Cl_2O_6(s)$  is -
- (A)  $sp^2$  (B)  $sp^3$  (C)  $sp^3d$  (D)  $sp^3d^2$
43. Which compound given below has  $sp^3$ ,  $sp^2$  and  $sp$  orbitals in the ratio of 6 : 3 : 2 ?
- (A)  $CH_3 - CH = CH - CH_2 - C \equiv C - CH_3$  (B)  $CH_3 - CH = CH - CH_2 - C \equiv CH$   
(C)  $CH_3 - CH_2 - C \equiv C - CH = CH_2$  (D)  $CH_3 - CH = CH - C \equiv CH$
44. The molecule/ion in which bond angle is less than  $107^\circ$ .
- (A)  $NF_4^+$  (B)  $CCl_4$  (C)  $ClO_4^-$  (D) None of these
45. Select pair of compounds in which both have different hybridisation but have same molecular geometry.
- (A)  $BF_3$ ,  $BrF_3$  (B)  $ICl_2^-$ ,  $BeCl_2$  (C)  $BCl_3$ ,  $PCl_3$  (D)  $PCl_3$ ,  $NCl_3$
46. Choose the correct option for following statements :
- (I)  $sp^3$  hybrid orbitals are at  $90^\circ$  to one another  
(II)  $sp^3d^2$  adjacent hybrid orbitals are at  $90^\circ$  to one another  
(III)  $sp^2$  hybrid orbitals are at  $120^\circ$  to one another  
(IV) Bond order of N–O bond in  $NO_3^-$  is 1.33
- (A) T F T F (B) T T F F (C) F T T T (D) F T F T

47. Which of the following species has  $sp^3d^3$  hybridisation ?  
(A)  $XeF_5^-$  (B)  $SO_3$  (C)  $SO_2$  (D)  $XeF_2$
48. If x is the no. of hybrid orbital containing 33.3% s-character and y is the number of hybrid orbital's containing 50% s-character then, find the value of  $x \div y$  for allene.  
(A) 2 (B) 3 (C) 6 (D) 3.5
49. All fluorine atoms are in same plane in:  
(A)  $CHF_3$  (B)  $ClF_3$  (C)  $XeOF_4$  (D) All of these
50. Select hybridisation which have non planar geometry when all are bond pair, but planar when there are 2 lone pairs on central atom:  
(A)  $sp^3$  (B)  $sp^3d$  (C)  $sp^3d^2$  (D) All of these
51. Select correct statement for  $BrF_5$ .  
(A) All fluorine atoms are in same plane  
(B) Four fluorine atoms and Br atom is in same plane  
(C) Four fluorine atoms are in same plane  
(D) It has all F – Br – F bond angles at  $90^\circ$
52. In which of following cases, the central atom is not perfectly  $sp^3$  hybridised?  
(A)  $BF_4^-$  (B)  $SiF_4$  (C)  $CHF_3$  (D)  $CCl_4$
53. Which of the following compound has the smallest bond angle (X – A – X) in each series respectively :  
(A)  $OSF_2$   $OSCl_2$   $OSBr_2$   
(B)  $SbCl_3$   $SbBr_3$   $SbI_3$   
(C)  $PI_3$   $AsI_3$   $SbI_3$   
(A)  $OSF_2$ ,  $SbCl_3$  and  $PI_3$  (B)  $OSBr_2$ ,  $SbI_3$  and  $PI_3$   
(C)  $OSF_2$ ,  $SbI_3$  and  $PI_3$  (D)  $OSF_2$ ,  $SbCl_3$  and  $SbI_3$
54. Molecule which does not contain any F – X – F bond angle which is less than  $90^\circ$ :  
(X = central atom)  
(A)  $IF_7$  (B)  $BrF_3$  (C)  $PF_5$  (D)  $SF_4$

55. What is the geometry of the  $\text{IBr}_2^-$  ion ?  
 (A) Linear  
 (B) Bent shape with bond angle of about  $90^\circ$   
 (C) Bent shape with bond angle of about  $109^\circ$   
 (D) Bent shape with bond angle of about  $120^\circ$
56. What is the shape of the  $\text{ClF}_3$  molecule ?  
 (A) Trigonal planar (B) Trigonal pyramidal  
 (C) T-shaped (D) Tetrahedral
57. The  $\text{H}-\text{O}-\text{H}$  bond angles in  $\text{H}_3\text{O}^+$  are approximately  $107^\circ$ . The orbitals used by oxygen in these bonds are best described as :  
 (A) p-orbitals (B) sp-hybrid orbitals  
 (C)  $\text{sp}^2$ -hybrid orbital (D)  $\text{sp}^3$ -hybrid orbital
58. The shape of  $\text{XeF}_3^+$  is :  
 (A) Trigonal planar (B) Pyramidal (C) Bent T-shape (D) See-saw
59. Which of the following shape are not possible for possible value of 'n' in  $\text{XeF}_n$  molecule?  
 (A) Linear (B) Square planar  
 (C) Trigonal planar (D) Capped octahedral
60. Which of the following is the correct set with respect to molecule, hybridization and shape?  
 (A)  $\text{BeCl}_2$ ,  $\text{sp}^2$ , linear (B)  $\text{BeCl}_2$ ,  $\text{sp}^2$  triangular planar  
 (C)  $\text{BCl}_3$ ,  $\text{sp}^2$ , triangular planar (D)  $\text{BCl}_3$ ,  $\text{sp}^3$ , tetrahedral
61. The pair of species with similar shape is :  
 (A)  $\text{PCl}_3$ ,  $\text{NH}_3$  (B)  $\text{CF}_4$ ,  $\text{SF}_4$  (C)  $\text{PbCl}_2$ ,  $\text{CO}_2$  (D)  $\text{PF}_5$ ,  $\text{IF}_5$
62. The hybridization of the central atom in  $\text{ICl}_2^+$  is :  
 (A)  $\text{dsp}^2$  (B) sp (C)  $\text{sp}^2$  (D)  $\text{sp}^3$
63. The state of hybridization of the central atom is not the same as in the others :  
 (A) B in  $\text{BF}_3$  (B) O in  $\text{H}_3\text{O}^+$  (C) N in  $\text{NH}_3$  (D) P in  $\text{PCl}_3$

64. Which is the following pairs of species have identical shapes ?  
 (A)  $\text{NO}_2^+$  and  $\text{NO}_2^-$  (B)  $\text{PCl}_5$  and  $\text{BrF}_5$   
 (C)  $\text{ClO}_3^-$  and  $\text{SO}_3^{2-}$  (D)  $\text{TeCl}_4$  and  $\text{XeO}_4$
65. The shapes of  $\text{XeF}_4$ ,  $\text{XeF}_5^-$  and  $\text{SnCl}_2$  are :  
 (A) Octahedral, trigonal bipyramidal and bent  
 (B) Square pyramidal, pentagonal planar and linear  
 (C) Square planar, pentagonal planar and angular  
 (D) See-saw, T-shaped and linear
66. Which is not correctly matched ?  
 (A)  $\text{XeO}_3$  — Trigonal bipyramidal (B)  $\text{ClF}_3$  — bent T-shape  
 (C)  $\text{XeOF}_4$  — Square pyramidal (D)  $\text{XeF}_2$  — Linear shape
67. The geometry of ammonia molecule can be best described as :  
 (A) Nitrogen at one vertex of a regular tetrahedron, the other three vertices being occupied by three hydrogens  
 (B) Nitrogen at the centre of the tetrahedron, three of the vertices being occupied by three hydrogens  
 (C) Nitrogen at the centre of an equilateral triangle, three corners being occupied by three hydrogens  
 (D) Nitrogen at the junction of a T, three open ends being occupied by three hydrogens

### BOND LENGTH / BOND ORDER

68. Which of the following bond length is shortest ?  
 (A) H-F (B) H-O (C) H-N (D) H-Cl
69. CORRECT order of bond length is :-  
 (A)  $\text{Si-O} < \text{P-O} < \text{S-O} < \text{Cl-O}$  (B)  $\text{Cl-O} < \text{S-O} < \text{Si-O} < \text{P-O}$   
 (C)  $\text{Cl-O} < \text{S-O} < \text{P-O} < \text{Si-O}$  (D)  $\text{S-O} < \text{P-O} < \text{Cl-O} < \text{Si-O}$
70. The average charge on each O atom and average bond order of I-O bond in  $\text{IO}_6^{5-}$  is :  
 (A) -1 and 1.67 (B)  $-5/6$  and 1.67 (C)  $-5/6$  and 1.33 (D)  $-5/6$  and 1.167
71. The correct order of C-N bond length ?  
 P :  $\text{CH}_3\text{CN}$  Q :  $\text{HNCO}$  R :  $\text{CH}_3\text{CONH}_2$   
 (A)  $\text{P} > \text{Q} > \text{R}$  (B)  $\text{P} = \text{Q} = \text{R}$  (C)  $\text{R} > \text{Q} > \text{P}$  (D)  $\text{R} > \text{P} > \text{Q}$



**BOND ENERGY**

72. Which of the following has maximum oxidising character.  
(A)  $F_2$  (B)  $Cl_2$  (C)  $Br_2$  (D)  $I_2$
73. Which of the following having second highest bond dissociation energy (out of given molecules).  
(A)  $F_2$  (B)  $Cl_2$  (C)  $Br_2$  (D)  $I_2$

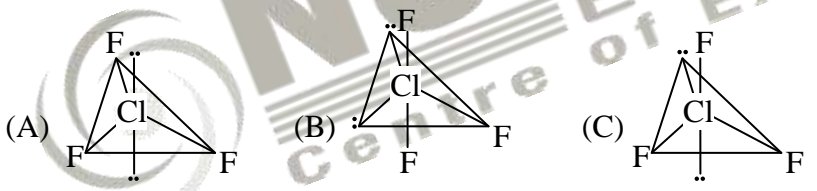
**BOND ANGLE**

74. Which is the correct order of the bond angle ?  
(A)  $NH_3 < NF_3$  (B)  $H_2O > Cl_2O$  (C)  $PH_3 < SbH_3$  (D)  $H_2Te < H_2S$
75. Which of the following order is/are **CORRECT** :-  
(A)  $CO_3^{2-} < CO_2$  (C–O bond length) (B)  $NO_3^- < NO_2^+$  (N–O bond length)  
(C)  $O_2 < O_3$  (O–O bond length) (D)  $C_6H_6 < C_2H_4$  (C–C bond length)
76. **CORRECT** order of bond angle is ?  
(A)  $BCl_3 > BF_3$  (B)  $CCl_4 > BF_3$  (C)  $BF_3 > BF_4^-$  (D)  $H_2O = O(CH_3)_2$
77. Which of the following has smallest bond angle X–A–X is present ? (X is halogen & A is central atom)  
(A)  $COCl_2$  (B)  $COF_2$  (C)  $POCl_3$  (D)  $POF_3$
78. Maximum bond angle will be present in which of the following molecule?  
(A)  $CH_4$  (B)  $CF_4$   
(C)  $Cl_4$  (D) All have same bond angle
79. Which one of the following has maximum bond angle ?  
(A)  $CH_4$  (B)  $CF_4$   
(C)  $CCl_4$  (D) All have same bond angle
80. Number of C-atoms in next homologue of first member of ester family is :  
(A) 5 (B) 4 (C) 3 (D) 2



81. The bond angles of  $\text{NH}_3$ ,  $\text{NH}_4^+$  and  $\text{NH}_2^-$  are in the order  
 (A)  $\text{NH}_2^- > \text{NH}_3 > \text{NH}_4^+$  (B)  $\text{NH}_4^+ > \text{NH}_3 > \text{NH}_2^-$   
 (C)  $\text{NH}_3 > \text{NH}_2^- > \text{NH}_4^+$  (D)  $\text{NH}_3 > \text{NH}_4^+ > \text{NH}_2^-$
82. In which of the following pair of species, all bond angles are equal  
 (A)  $\text{CO}_3^{2-}$ ,  $\text{COCl}_2$  (B)  $\text{PO}_4^{3-}$ ,  $\text{POCl}_3$   
 (C)  $\text{BF}_4^-$ ,  $\text{BH}_4^-$  (D)  $\text{CH}_3\text{F}$ ,  $\text{CH}_4$
83. The correct order of bond angle is  
 (A)  $\text{H}_2\text{O} > \text{OF}_2 > \text{SF}_2$  (B)  $\text{H}_2\text{O} > \text{SF}_2 > \text{OF}_2$   
 (C)  $\text{H}_2\text{O} < \text{OF}_2 > \text{SF}_2$  (D)  $\text{H}_2\text{O} > \text{OF}_2 < \text{SF}_2$

### VSEPR THEORY

84. The shape of  $[\text{ClF}_4]^-$  and  $[\text{ClF}_2]^-$  ions is respectively  
 (A) See-saw and linear (B) See-saw and bent  
 (C) Tetrahedral and linear (D) Square planar and linear.
85. More correct structure of  $\text{ClF}_3$  is :  
 (D) All of the above
86. Which of the following molecules/species has the minimum number of lone pairs?  
 (A)  $\text{ICl}_3$  (B)  $\text{BF}_4^-$  (C)  $\text{SnCl}_2$  (D)  $\text{XeF}_4$
87. The number of  $\widehat{\text{FIF}}$  adjacent angles ( $90^\circ + 72^\circ$ ) in  $\text{IF}_7$  molecule is  
 (A) 10 (B) 15 (C) 20 (D) 14
88. The number of  $\text{F-I-F}$  angles less than  $90^\circ$  and equal to  $90^\circ$  are respectively in  $\text{IF}_7$   
 (A) 5 and 5 (B) 10 and 5 (C) 5 and 10 (D) 10 and 15
89. The number of  $\text{I-F}$  bonds having the longer and shorter lengths are respectively in  $\text{IF}_7$   
 (A) 5 and 2 (B) 2 and 5 (C) 5 and 5 (D) 2 and 2

90. Find the pair of species having the same shape but different hybridization of the central atom.  
(A)  $\text{SO}_3$ ,  $\text{CO}_3^{2-}$  (B)  $\text{NO}_2^-$ ,  $\text{ClO}_2^-$  (C)  $\text{BeCl}_2$ ,  $\text{HCN}$  (D)  $\text{XeF}_2$ ,  $\text{SnCl}_2$
91. The pair of species with similar shape is?  
(A)  $\text{XeF}_4$  &  $\text{SF}_4$  (B)  $\text{PF}_5$  &  $\text{IF}_5$   
(C)  $\text{XeO}_2\text{F}_2$  &  $\text{SeF}_4$  (D) All pairs are iso-structural
92. Which of the following molecule have all the bond angle equal is?  
(A)  $\text{PF}_5$  (B)  $\text{SF}_4$  (C)  $\text{NH}_3$  (D) None of these
93. Which of the following is isostructural with  $\text{XeOF}_4$ ?  
(A)  $\text{BrF}_5$  (B)  $\text{PCl}_3\text{F}_2$  (C)  $\text{SeF}_4$  (D)  $\text{XeO}_2\text{F}_2$
94. Which of the following is planar?  
(A)  $\text{XeO}_3$  (B)  $\text{BrF}_5$  (C)  $\text{ClF}_3$  (D) All are planar
95. The number of species given below having angles equal to  $90^\circ$  are ?  
 $\text{BrF}_3$ ,  $\text{IF}_5$ ,  $\text{SeF}_6$ ,  $\text{ICl}_4^-$ ,  $\text{PCl}_5$   
(A) 3 (B) 4 (C) 5 (D) 2
96. Which of the following molecule contain maximum number of atoms in one plane ?  
(A)  $\text{CCl}_4$  (B)  $\text{PF}_5$  (C)  $\text{XeF}_5^-$  (D)  $\text{SF}_6$
97. Which of the following specie is non-planar ?  
(A)  $\text{ClF}_3$  (B)  $\text{H}_3\text{O}^+$  (C)  $\text{NO}_2^-$  (D)  $\text{ClO}_2^-$
98. Molecular shape of  $\text{XeF}_3^+$ ,  $\text{SF}_3^+$  and  $\text{CF}_3^+$  are :  
(A) the same with 2, 1 and 0 lone pairs of electrons, respectively  
(B) different with 2, 1 and 0 lone pairs of electrons, respectively  
(C) different with 0, 1 and 2 lone pairs of electrons, respectively  
(D) the same with 2, 0 and 1 lone pairs of electrons, respectively
99. Which of the following statements is incorrect ?  
(A) In  $\text{H}_2\text{O}$ , the bond angle is less than  $\text{OF}_2$   
(B) In  $\text{ClF}_3$ , the axial Cl-F bond length is larger than equatorial Cl-F bond length.  
(C) In  $\text{SF}_4$ , F-S-F equatorial bond angle is not equal to  $120^\circ$  due to lone pair-bond pair repulsions.  
(D) In  $\text{ICl}_4^-$ , bond angles is  $90^\circ$

- 100.** According to VSEPR theory, in which species do all the atoms lie in the same plane ?  
 1.  $\text{CH}_3^+$                       2.  $\text{CH}_3^-$   
 (A) 1 only                      (B) 2 only                      (C) both 1 and 2                      (D) neither 1 nor 2
- 101.** In  $\text{SNF}_3$ , the  $\angle \text{FSF}$  should be :  
 (A) less than  $120^\circ$  and more than  $109^\circ 28'$                       (B) less than  $109^\circ 28'$   
 (C) less than  $180^\circ$  and more than  $120^\circ$                       (D) Exactly equal to  $109^\circ 28'$
- 102.** Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false :  
 (I) The order of repulsion between different pair of electrons is  $l_p - l_p > l_p - b_p > b_p - b_p$   
 (II) In general, as the number of lone pair of electrons on central atom increases, value of bond angle from normal bond angle also increases  
 (III) The number of lone pair on O in  $\text{H}_2\text{O}$  is 2 while on N in  $\text{NH}_3$  is 1  
 (IV) The structures of xenon fluorides and xenon oxyfluorides could not be explained on the basis of VSEPR theory  
 (A) T T T F                      (B) T F T F                      (C) T F T T                      (D) T F F F
- 103.** The  $\text{H}-\text{C}-\text{H}$  bond angle in  $\text{CH}_4$  is  $109.5^\circ$ , due to lone pair repulsion, the  $\text{H}-\text{O}-\text{H}$  angle in  $\text{H}_2\text{O}$  will :  
 (A) remain the same                      (B) increase                      (C) decrease                      (D) become  $180^\circ$
- 104.** The compound  $\text{MX}_4$  is tetrahedral. The number of  $\angle \text{XMX}$  angles in the compound is :  
 (A) three                      (B) four                      (C) five                      (D) six

### SOLID OR LIQUID STATE HYBRIDISATION

- 105.** The number of non-axial set of 'd' orbital participate in the hybridisation of the anionic part of  $\text{PCl}_5$   
 (A) 1                      (B) 2                      (C) 3                      (D) 0
- 106.** The  $(\text{Cl}-\text{P}-\text{Cl})$  adjacent angle difference in cationic part and anionic part in  $\text{PCl}_5(\text{s})$  is :  
 (A) 60                      (B) 90                      (C) 19.5                      (D) 10.5
- 107.** Hybridisation of cationic part of  $\text{Cl}_2\text{O}_6(\text{s})$  is -  
 (A)  $\text{sp}^2$                       (B)  $\text{sp}^3$                       (C)  $\text{sp}^3\text{d}$                       (D)  $\text{sp}^3\text{d}^2$

**STRUCTURES**

- 108.** Ratio of  $\sigma/\pi$  present in the  $\text{XeO}_3$  will be  
(A) 1 : 4 (B) 1 : 2 (C) 1 : 1 (D) 2 : 1
- 109.** Oxidation state of Cr in  $\text{CrO}_5$  is -  
(A) +10 (B) +8 (C) +6 (D) +5
- 110.** Which of the following compound has peroxy linkage present in its structure ?  
(A)  $\text{K}_3\text{CrO}_8$  (B)  $\text{Cl}_2\text{O}_6$  (C)  $\text{N}_2\text{O}_5$  (D)  $\text{H}_2\text{S}_2\text{O}_7$
- 111.** Which of the following species have maximum  $p\pi-p\pi$  bonds ?  
(A)  $\text{P}_4\text{S}_{10}$  (B)  $\text{HCO}_3^-$  (C)  $\text{S}_3\text{O}_9$  (D)  $\text{P}_4\text{O}_{10}$
- 112.** Find the correct statement about  $\text{P}_4\text{O}_8$  :  
(A) molecule does not exist  
(B) five P–O–P linkage  
(C) four P=O bonds present in it's structure  
(D) Six P–O–P linkage
- 113.** In the structure of  $\text{H}_2\text{CSF}_4$ , which of the following statement is incorrect ?  
(A) Two C – H bonds are in the same plane of axial S – F bonds.  
(B) Two C – H bonds are in the same plane of equatorial S – F bonds.  
(C) Total Six atoms are in the same plane.  
(D) Equatorial S – F bonds are Perpendicular to nodal plane of  $\pi$  bond.

**RESONANCE**

- 114.** Total number of resonating structure possible of the molecule  $\text{ClO}_4^-$  is -  
(A) 2 (B) 3 (C) 4 (D) 5
- 115.** The formal charges on the three atoms in  $\text{O}_3$  molecule are :  
(A) 0,0,0 (B) 0,0,-1 (C) 0,0, +1 (D) 0, +1, -1
- 116.** Minimum number of resonating structure possible in : -  
(A)  $\text{O}_3$  (B)  $\text{NO}_2^-$  (C)  $\text{N}_3^-$  (D)  $\text{COCl}_2$

117. The compound having shortest S–O bond length ?

- (A)  $\text{SO}_3\text{F}^-$  (B)  $\text{SO}_4^{-2}$  (C)  $\text{SOF}_4$  (D)  $\text{SOCl}_2$

**OXY ACID**

118. Which of the following acid have highest number of P–H bonds :-

- (A)  $\text{H}_4\text{P}_2\text{O}_8$  (B)  $\text{H}_4\text{P}_2\text{O}_7$  (C)  $\text{H}_4\text{P}_2\text{O}_5$  (D)  $\text{H}_3\text{PO}_3$

119. Oxidation state of S in  $\text{H}_2\text{S}_2\text{O}_8$  is ?

- (A) +5, +5 (B) +6, +5 (C) +5, +6 (D) +6, +6

120. Which of the following oxy acid have sulphur atoms with different oxidation states?

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

121. Which of the following compound has different value of basicity from the others ?

- (A)  $\text{H}_3\text{PO}_3$  (B)  $\text{H}_4\text{P}_2\text{O}_5$  (C)  $\text{H}_3\text{BO}_3$  (D)  $\text{H}_2\text{SO}_5$

122. Which of the following acid have highest number of P–H bonds :-

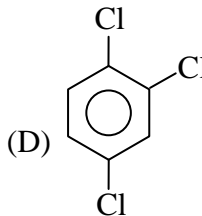
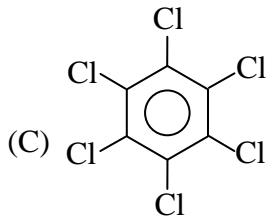
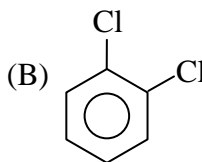
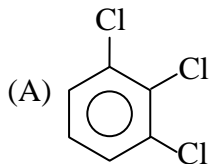
- (A)  $\text{H}_4\text{P}_2\text{O}_8$  (B)  $\text{H}_4\text{P}_2\text{O}_7$  (C)  $\text{H}_4\text{P}_2\text{O}_5$  (D)  $\text{H}_3\text{PO}_3$

123. Find the value of  $\frac{a-b}{c}$  if; a is the total number of  $\text{sp}^3$  hybridised atoms, b is total  $\text{p}_\pi\text{--p}_\pi$  bonds and c is the total  $\text{sp}^2$  hybridised atoms in the structure of  $\text{H}_4\text{P}_4\text{O}_{12}$ .

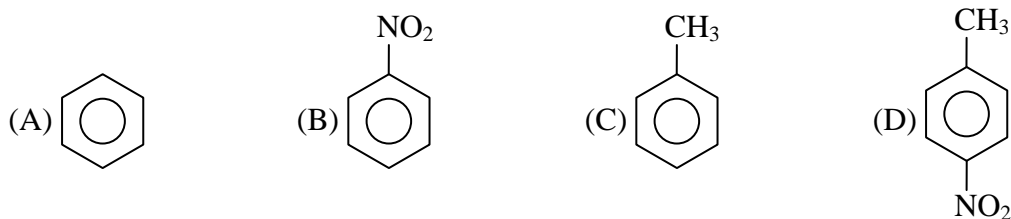
- (A) 2 (B) 1 (C) 3 (D) 4

**DIPOLE MOMENT**

124. Which of the following have maximum dipole moment?



125. Which of the following is most polar in nature ?



126. Which of the following molecule has permanent dipole moment:

- (A)  $\text{SO}_3$  (B)  $\text{SO}_2$  (C)  $\text{CO}_2$  (D)  $\text{BF}_3$

127. The correct sequence of polarity of the following molecule :

- I.  $\text{XeF}_4$  II.  $\text{XeF}_2$  III.  $\text{XeF}_5^-$  IV.  $\text{XeO}_3$

(P stands for polar and NP stands for non-polar)

- |     | I  | II | III | IV |
|-----|----|----|-----|----|
| (A) | P  | NP | NP  | P  |
| (B) | NP | NP | NP  | P  |
| (C) | NP | P  | NP  | P  |
| (D) | NP | P  | P   | NP |

128. Which of the following is most polar in nature?

- (A)  $\text{CH}_2\text{Cl}_2$  (B)  $\text{CHCl}_3$  (C)  $\text{CH}_3\text{Cl}$  (D)  $\text{CH}_3\text{F}$

129. Total number of polar species among the following will be ?

$(\text{OH})_2$ ,  $(\text{SCN})_2$ ,  $\text{C}_2\text{F}_3$ ,  $\text{C}_3\text{O}_2$ ,  $\text{SeF}_4$

- (A) 2 (B) 4 (C) 5 (D) 3

130. Arrange the following in increasing order of their polarity.

(I) Ortho/chloro/Toluene (II) Meta/chloro/Toluene (III) Para/chloro/Toluene

- (A)  $\text{III} > \text{II} > \text{I}$  (B)  $\text{II} < \text{I} > \text{III}$  (C)  $\text{III} > \text{I} > \text{II}$  (D)  $\text{I} < \text{II} < \text{III}$

131. Which of the following molecule / species is polar.

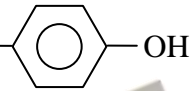
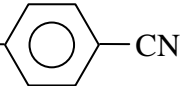
- (A)  $\text{O}_3$  (B)  $\text{NO}_2^+$   
(C) paradichlorobenzene (D) None of these

132. Which of the following molecule is non polar?

- (A)  $\text{NF}_3$  (B)  $\text{ClF}_3$  (C)  $\text{XeO}_3$  (D)  $\text{SO}_3$



**HYDROGEN BONDING**

- 133.** Which of the following have intramolecular H-bonding ?  
 (A) Chloral (B) Orthochlorophenol  
 (C) Paranitrophenol (D)  $C_6H_6$
- 134.** What is the order of boiling point of the following compounds ?  
 $HF, NH_3, H_2O, CH_4$   
 (A)  $CH_4 > NH_3 > H_2O > CH_4$  (B)  $HF > H_2O > NH_3 > CH_4$   
 (C)  $H_2O > HF > NH_3 > CH_4$  (D)  $H_2O > NH_3 > HF > CH_4$
- 135.** Which of the following have weakest intermolecular forces ?  
 (A)  $CH_3COOH$  (B)   
 (C)  (D)  $H_2O_2$
- 136.** Select the **INCORRECT** statement ?  
 (A) Cationic part of  $NH_4F$  can form hydrogen bond with water  
 (B) Hydrogen bonding is not present in ethene ( $H_2C = CH_2$ )  
 (C) Anionic part of  $NaHCO_3$  have inter molecular hydrogen bonding  
 (D) Vapour pressure decreases due to intramolecular H-bonding.
- 137.** The strength of H-bonding order is  
 (A)  $H_2O > H_2O_2 > HF$  (B)  $H_2O_2 > H_2O > HF$   
 (C)  $HF > H_2O > H_2O_2$  (D)  $HF = H_2O = H_2O_2$
- 138.** Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.  
 (i) HF boils at a higher temperature than HCl  
 (ii) HBr boils at lower temperature than HI  
 (iii)  $K_{a1}$  of maleic acid is higher than that of fumaric acid  
 (iv)  $K_{a2}$  of maleic acid is higher than that of fumaric acid  
 (A) TFTT (B) TTTF (C) TFTF (D) TTTT
- 139.** Strongest hydrogen bond present in :  
 (A)  $O - H \cdots S$  (B)  $S - H \cdots O$  (C)  $F - H \cdots F$  (D)  $F - H \cdots O$



140. Which of the following will prefer intramolecular hydrogen bonding :  
 (A)  $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$  (B) Orthodichlorobenzene  
 (C) Sulphuric acid (D) Both (A) & (B)
141. Which of the following is correct order for extent of Hydrogen Bonding  
 (A)  $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF} > \text{NH}_3$  (B)  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3 > \text{H}_2\text{O}_2$   
 (C)  $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{NH}_3 > \text{HF}$  (D)  $\text{H}_2\text{O}_2 > \text{NH}_3 > \text{H}_2\text{O} > \text{HF}$

**MISCELLANEOUS**

142. Which is correct about  $\text{D}_2\text{O}$   
 (A) Its boiling point is higher than that of  $\text{H}_2\text{O}$  ( $\ell$ )  
 (B)  $\text{O} - \text{D} - - - \text{O}$  bond is stronger than  $\text{O} - \text{H} - - - \text{O}$  bond.  
 (C)  $\text{D}_2\text{O}(\text{s})$  sinks in  $\text{H}_2\text{O}$  ( $\ell$ ).  
 (D) all the above are correct.
143. Which of the following do not exist?  
 (A)  $\text{KHF}_2$  (B)  $\text{CsHCl}_2$  (C)  $\text{KHCl}_2$  (D)  $\text{KF}$
144. Which of the following species is an example of odd electron molecule?  
 (A)  $\text{NO}_2$  (B)  $\text{N}_2\text{O}$  (C)  $\text{ClO}_3$  (D) Both (A) and (C)

**EXERCISE # 2**

**LEWIS DOT STRUCTURES**

- Lewis theory fails to explain which of the following structure(s) ?  
(A)  $\text{SF}_6$  (B)  $\text{XeF}_2$  (C)  $\text{XeF}_4$  (D)  $\text{BeCl}_2$
- In which of the following molecule/ion the central atom have + 1 formal charge ?  
(A)  $\text{O}_3$  (B)  $\text{N}_3^-$  (C)  $\text{NO}_3^-$  (D)  $\text{CO}_3^{-2}$
- In which of the following molecule all the atoms are present in ground state ?  
(A)  $\text{PH}_3$  (B)  $\text{CO}$  (C)  $\text{SF}_4$  (D)  $\text{HOF}$
- In which of the following molecule number of lone pairs & number of covalent bonds are equal ?  
(A)  $\text{SO}_3$  (B)  $\text{SO}_2$  (C)  $\text{CO}_2$  (D)  $\text{H}_2\text{Se}$
- Which of the following statement is incorrect regarding molecule  $\text{NOCl}$ ?  
(A) It has covalent as well as ionic bond present in its structure.  
(B) It has  $\text{Cl}$  atom present as a central atom.  
(C) It has one lone pair.  
(D) It has linear structure.
- Lewis theory fails to explain which of the following structure(s) ?  
(A)  $\text{SF}_6$  (B)  $\text{XeF}_2$  (C)  $\text{XeF}_4$  (D)  $\text{BeCl}_2$

**TYPES OF BOND**

- Type of bonds present in  $\text{PH}_4\text{I}$  is/are:  
(A) Ionic (B) Covalent (C) Co-ordinate (D) H-bond
- Which of the following set of elements have tendency to combine with each other by sharing of valence electron.  
(A)  $\text{Mg}$  &  $\text{O}$  (B)  $\text{B}$  &  $\text{F}$  (C)  $\text{Na}$  &  $\text{H}$  (D)  $\text{P}$  &  $\text{F}$
- Coordinate bond is present in the following molecule(s) :  
(A)  $\text{NO}_2$  (B)  $\text{N}_2\text{O}_4$  (C)  $\text{PCl}_4^+$  (D)  $\text{CO}_3^{-2}$
- Which of the following set contains covalent as well as ionic species ?  
(A)  $\text{NO}$ ,  $\text{CO}$ ,  $\text{OF}_2$  (B)  $\text{NH}_3$ ,  $\text{BF}_3$ ,  $\text{AlF}_3$  (C)  $\text{CO}_2$ ,  $\text{CsCl}$ ,  $\text{NO}_2$  (D)  $\text{SO}_3$ ,  $\text{BCl}_3$ ,  $\text{CaO}$

**VBT**

11. Which of the following statement is correct?  
 (A) Extent of overlapping :  $3p - 4s < 3s - 3s$   
 (B) s-orbital can never form  $\pi$ -bond  
 (C) p-orbital can form  $\sigma$  and  $\pi$  as well as  $\delta$  bond.  
 (D) non axial d-orbitals ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) have more directional nature than the axial d-orbitals ( $d_{z^2}$  &  $d_{x^2-y^2}$ )
12. Select the correct statement(s) :  
 (A)  $\sigma$  bond is stronger than  $\delta$  bond  
 (B)  $\pi$  bond is the result of collateral overlapping between two half filled atomic orbitals.  
 (C) s-orbital & py-orbital can be never form bond on z-axis.  
 (D)  $p_y$  &  $p_y$  on z-axis form  $\delta$  bond
13. Choose the correct order(s) of strength of overlapping of orbitals :  
 (A)  $2p - 2p > 2p - 3p > 3p - 3p$  (B)  $3d - 3d > 3p - 3d > 3p - 3p$   
 (C)  $2s - 3s > 3p - 3p > 3s - 3p$  (D)  $2s - 2s > 2s - 2p > 2p - 2p$
14. Which of the following molecules have  $P_\pi - d_\pi$  bond in their structure ?  
 (A)  $\text{SOF}_4$  (B)  $\text{SO}_2\text{F}_2$  (C)  $\text{CO}_3^{-2}$  (D) CO

**HYBRIDISATION**

15. Which of the following specie(s) contains all bond angles equal?  
 (A)  $\text{PCl}_4^+$  (B)  $\text{AsF}_5$  (C)  $\text{CH}_2\text{F}_2$  (D)  $\text{XeF}_4$
16. Which of the following combination of bond pair (b.p.) & lone pair (l.p.) gives same shape?  
 (i) 3b.p. + 1 l.p. (ii) 2 b.p. + 2 l.p. (iii) 3 b.p. + 2 l.p.  
 (iv) 2.b.p. + 3 l.p. (v) 2 b.p. + 1 l.p. (vi) 2 b.p. + 0 l.p.  
 (A) (ii) & (v) (B) (vi) & (iv) (C) (iii) & (iv) (D) (i) & (iii)
17. Which of the following molecules has/have linear structure  
 (A)  $\text{BeCl}_2$  (B)  $\text{XeF}_2$  (C)  $\text{XeO}_4$  (D)  $\text{SF}_4$
18. Which of the following molecules have H Bonding  
 (A)  $\text{H}_2\text{O}$  (B)  $\text{NH}_3$  (C) HF (D)  $\text{CH}_4$

19. Which of the following molecules is/are  $sp^3d$  hybridised  
(A)  $PCl_5$  (B)  $PCl_6^-$  (C)  $XeO_2F_2$  (D)  $IF_7$
20. Which of the following molecules has/have  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals in hybridisation  
(A)  $SF_6$  (B)  $XeF_4$  (C)  $SF_2$  (D)  $NO_2^+$
21. Which of the following molecules has/have capped octahedral geometry  
(A)  $XeF_6$  (B)  $IF_6^-$  (C)  $XeOF_5^-$  (D)  $XeF_2$
22. In which of following, vacant orbital take part in hybridisation :  
(A)  $BF_3$  (B)  $PCl_6^-$  (C)  $BF_4^-$  (D)  $\ddot{N}H_3$
23. Which of the following is correct match for  $AB_xL_y$  (where B = Bond pair & L = lone pair).  
(A)  $x = 3, y = 2$  planar & polar (B)  $x = 3, y = 1$  polar & non planar  
(C)  $x = 2, y = 3$  non planar & non polar (D)  $x = 4, y = 1$ , non planar & polar

### BONED LENGTH / BOND ORDER

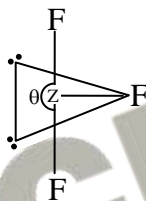
24. Select the **INCORRECT** Order ?  
(A)  $SO_3 < SO_3^{-2} < SO_4^{-2}$  (S – O bond order)  
(B)  $CO > CO_2 > CO_3^{-2}$  (C – O bond order)  
(C)  $CN^- < NCN^{-2} < RCNH_2$  (C – N bond order)  
(D)  $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$  (Cl – O bond order)

**BOND ENERGY**

25. The correct order of bond dissociation energy will be ?
- (A)  $\text{H-H} > \text{Cl-Cl} > \text{Br-Br}$  (B)  $\text{Si-Si} > \text{P-P} > \text{Cl-Cl}$   
(C)  $\text{C-C} > \text{N-N} > \text{O-O}$  (D)  $\text{F-F} > \text{Cl-Cl} > \text{Br-Br}$

**VSEPR THEORY**

26. There are three elements X, Y and Z which belong to the p-block of periodic table they all form trifluorides with  $\text{F}_2$ , such that ' $\text{XF}_3$ ' is lewis acid but ' $\text{YF}_3$ ' is weak Lewis base (dipole moment = 0.23D). These two compounds react with each other in presence of  $\text{F}_2$  to produce  $\text{YF}_4^+ \text{XF}_4^-$ . The compound  $\text{ZF}_3$  is a T-shape interhalogen molecule. Which of the following is/are correct statements with reference to above information ?



- (A) All the Z-F bond lengths are equal in  $\text{ZF}_3$  molecules  
(B) In the structure the angle  $\theta \neq 180^\circ$   
(C) The Y and X both are  $\text{sp}^3$  hybridised in  $\text{YF}_4^+ \text{XF}_4^-$   
(D) The elements X, Y, Z can be B, N and Cl respectively
27. In which of the following species all bond lengths are not identical ?  
(A)  $\text{ClF}_6^+$  (B)  $\text{SeF}_4$  (C)  $\text{SO}_4^{2-}$  (D)  $\text{IF}_3$
28. Which of the following molecule(s) is/are planar  
(A)  $\text{BF}_3$  (B)  $\text{H}_2\text{O}$  (C)  $\text{ICl}_2^-$  (D)  $\text{ClF}_3$

**STRUCTURES**

29. Which of the following statements is/are true for  $\text{P}_4\text{O}_6$  molecule -
- (A) It contains six P-O bonds and three P-P-bonds  
(B) It contains six P-O-P linkage and 16 lone pairs  
(C) It has all atoms  $\text{sp}^3$ -hybridised  
(D) It has planar structure

30. Select the **CORRECT** statement about  $C_3N_3(N_3)_3$  (cyanuric triazide) :
- (A) Total number of  $sp^2$  hybridized atom in the molecule is 12  
 (B) Total number of  $\sigma$  bond present in molecule is 15  
 (C) Total number of  $\pi$  bond present in molecule is 9  
 (D) Total number of lone pair present in molecule is 12
31. Find the correct statement about croconate ion  $C_5O_5^{-2}$
- (A) It is cyclic compound  
 (B) It is in particular aromatic and symmetric as the double bond and the negative charge become delocalized over the five CO units  
 (C)  $C_5O_5^{-2}$  has four  $\pi$  bonds  
 (D)  $C_5O_5^{-2}$  has three  $\pi$  bonds in rings.

**OXY ACID**

32. Select the **INCORRECT** statement(s) about the structure of  $H_2S_2O_3$ .
- (A) Two  $2p\pi - 3d\pi$  bonds present in the structure.  
 (B) Hybridization of each 'S' atom is  $sp^3$   
 (C) Oxidation states of 'S' are + 6 & -2  
 (D) Total number of lone pair present in molecule is 8.
33. Which of the following oxy acid have per-oxy linkage :-
- (A)  $H_2S_2O_8$                       (B)  $H_3PO_5$                       (C)  $HNO_3$                       (D)  $H_2S_2O_3$

**DIPOLE MOMENT**

34. Which of the following statement (s) is/are true about lone pair moments ?
- (A)  $sp > sp^2 > sp^3$  : Order of lone pair moment  
 (B) The unshared pairs residing in pure s or p orbitals do not contribute to the resultant molecular polarity  
 (C) The unshared pair residing in hybrid orbitals contributes to the resultant molecular polarity  
 (D) The lone pair moments acts in the opposite directions in which it is projected.
35. Correct Statement among following ?
- (A) Dipole moment order  $BF_3 = CCl_4 = PCl_5 = SF_6$   
 (B) dipole moment of  $CHCl_3 > CHF_3$   
 (C)  $\mu_{\text{experimental}}$  is less than  $\mu_{\text{theoretical}}$  for CO molecule  
 (D) If a  $AX_4$  type molecule has  $\mu = 0$  then it can have either tetrahedral or octahedral electron geometry (A = central atom, X = side atom)

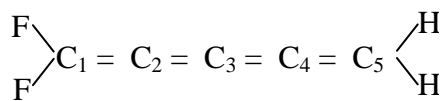


**HYDROGEN BONDING**

36. Choose the **INCORRECT** order(s) of boiling point .  
 (A)  $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$  (B)  $\text{H}_2\text{O} > \text{TeH}_2 > \text{SeH}_2 > \text{SH}_2$   
 (C)  $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$  (D)  $\text{CH}_4 > \text{SnH}_4 > \text{GeH}_4 > \text{SiH}_4$
37. Which of the following statement(s) is/are not correct ?  
 (A) Density of water increases from  $0^\circ\text{C}$  to  $4^\circ\text{C}$  then further increases on increasing the temperature  
 (B) Solid boric acid has 2-D sheet like structure due to intermolecular hydrogen bonding  
 (C) Urea has high boiling point due to intramolecular hydrogen bonding.  
 (D)  $\text{HCl}_2^-$  ion exists with  $\text{Cs}^+$ .
38. Hydrogen bonding is responsible for ?  
 (A) Lower volatility of HF than that of HCl.  
 (B) More viscosity of glycerol than glycol.  
 (C) Stability of chloral hydrate  
 (D) High boiling point of  $\text{SbH}_3$  than that of  $\text{NH}_3$
39. Which of the following contain H-Bonding ?  
 (A)  $\text{K}_2\text{HPO}_4$  (B)  $\text{K}_2\text{HPO}_3$   
 (C) Chloral hydrate (D) O-nitro phenol

**MISCELLANEOUS**

40. Choose the **CORRECT** statement about given molecule : -



If  $\begin{array}{c} \text{F} \\ \diagdown \\ \text{C}_1 \\ \diagup \\ \text{F} \end{array}$  lies in xz plane then

- (A) Nodal plane of  $\pi$ -bond between  $\text{C}_1 - \text{C}_2$  lies in xz plane.  
 (B) Nodal plane of  $\pi$ -bond between  $\text{C}_3 - \text{C}_4$  lies in xz plane.  
 (C)  $\begin{array}{c} \text{H} \\ \diagup \\ \text{C}_5 \\ \diagdown \\ \text{H} \end{array}$  part lies in yz plane  
 (D) Maximum number of atom in plane is 7



**EXERCISE # 3**

**INTEGER**

1. Find total number of orbitals in which electron density is observed along any of the axis (x, y or z).

$p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$

2. Total number of molecules which follow octet rule among the given molecules are:  
 $AlBr_3, BeCl_2, MgF_2, SF_4, NO_2, NO, CO, LiF, SO_2Cl_2, XeF_2, PH_3,$

3. The number of set of orbitals given below forming  $\pi$ -bonds are ?

**Orbitals**

**Inter Nuclear Axis**

(1) $p_x + p_y$	—	x
(2) $p_z + p_z$	—	y
(3) $d_{xy} + d_{xy}$	—	z
(4) $d_{yz} + d_{yz}$	—	z
(5) $d_{yz} + p_z$	—	z
(6) $d_{xz} + p_z$	—	x
(7) $d_{x^2-y^2} + p_y$	—	x

4. Number of orbitals which can form  $\pi$  bond with  $p_x$  orbital on y -axis :

$d_{z^2}, d_{xy}, p_x, p_z, s, d_{x^2-y^2}, d_{xz}$

5. Atomicity of O,S,P and He are p, q, r & s respectively : Calculate the value of  $p + q + r + s$  ?  
[Write your answer as sum of digits till you get the single digit answer]

6. How many sets of given orbitals can form  $\pi$  bond ?

(z - axis is internuclear axis)

$p_x + p_y, p_y + p_y, p_z + p_x, p_z + p_z, d_{x^2-y^2} + d_{z^2}, p_z + d_{xy}, p_z + d_{xz}, p_z + d_{yz}, d_{xz} + d_{yz}, d_{yz} + d_{yz}, d_{xy} + d_{xy}, d_{xy} + d_{x^2-y^2}.$

7. Find the number of molecules having  $sp^3d$  hybridisation

$I_3^-, SF_4, BeCl_2, XeF_4,$

8. Find out the number of species which have at least one atom is  $sp^3d$  hybridised among the following :-  
 $O_3$  ,  $O_2F_2$  ,  $I_3^-$  ,  $I(CN)_2^-$  ,  $PF_3Cl_2$  ,  $XeF_6$  ,  $IOF_5$  ,  $XeF_5^+$
9. The number of planes of symmetry in  $SbF_5$  is -
10. Find the number of  $p\pi-d\pi$  bonds present in  $P_4S_{10}$
11. Total number of angle(s) in  $SeCl_4$  which are less than  $90^\circ$
12. Number of molecules having all bond angles equal are ?  
 $CH_2F_2$ ,  $BHF_2$ ,  $NF_3$ ,  $XeF_5^-$
13. Total number of identical bond angle in  $CF_2Cl_2$  is -
14. How many of the following are planar molecules/ions  
 $XeO_2F_2$  ,  $IF_5$  ,  $XeO_4$  ,  $BrF_3$  ,  $I(CN)_2^-$
15. Total number of molecules which contain any  $F-\hat{X}-F$  bond angle which is less than  $90^\circ$  ?  
 (X = Central atom)  
 $IF_7$  ,  $BrF_3$  ,  $PF_5$  ,  $SF_4$  ,  $XeOF_4$  ,  $SF_6$
16. How many planes are present in  $PCl_3F_2$  molecule which contains maximum number of atoms ?
17. Number of non-polar molecule among the following is x and number of planar molecule is y.  
 calculate the value of  $x + y$ .  
 $BF_3$  ,  $CO_2$  ,  $SO_2$  ,  $PCl_5$  ,  $ClF_3$  ,  $NH_3$  ,  $CH_4$
18. Number of atomic orbitals involve in hybridisation of anion part of  $Cl_2O_6(s)$  is -
19. In tetrathionic acid number of  $p\pi-p\pi$  bonds is :
20. In the structure of  $P_4S_{10}$  molecule, total number of  $sp^3$  Hybridised atoms = x, total number of  $p\pi-d\pi$  bonds = y, total number of bridging sulphur = z, calculate the value of  $x + y + z$ .

21. Total number of species among the following in which X–O–X linkage is present [X=P, S]  
 $\text{H}_2\text{S}_2\text{O}_6$ ,  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_7$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{S}_4\text{O}_6^{2-}$ ,  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{P}_4\text{O}_6$
22. The number of water molecules(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is –
23. Observe the following statements about the structure of molecule  $\text{F}_3\text{SSF}$   
 (a) Total number of lone, pairs present in molecule is x  
 (b) Number of S –S bond present is y  
 Calculate the value of 'x + y' ?  
**[Write your answer as sum of digits till you get the single digit answer]**
24. The sum of oxidation states of all P atoms in the following compound of phosphorus is-  
 $\text{P}_4$ ,  $\text{PH}_3$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{P}_2\text{O}_5$
25. How many of the following contains peroxy linkage in their structures :  
 $\text{S}_2\text{O}_6^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{SO}_5^{2-}$ ,  $\text{CrO}_3$
26. Find the number of lone pair in  $\text{N}_3\text{S}_3\text{Cl}_3$ .  
**Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.**
27. Find the correct statements about  $[\text{N}(\text{PCl}_2)_3]$  (phosphazene).  
 (i) Resonance structure can be drawn analogous to those for benzene indicating aromaticity in the rings.  
 (ii) The  $d_{xz}$  orbital of the phosphorous atom overlaps with the  $p_z$  orbitals of nitrogen atoms adjacent to it (if x is inter nuclear axis).  
 (iii)  $\text{PCl}_2$  monomer is analogous to  $\text{RCN}$ .  
 (iv)  $\sigma/\pi$  ratio is 3 in  $[\text{N}(\text{PCl}_2)_3]$ .
28. In tetrathionic acid number of  $p_\pi - p_\pi$  bonds is :
29. In  $(\text{HF})_4$  the number of H bonds is .....
30. Total number of molecules which can have intermolecular hydrogen bonding ?  
 $\text{CH}_3\text{Cl}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{SiH}_4$ , metafluorophenol, orthochlorophenol.
31. Find the number of H bond form by one boric acid in solid state
32. Find the number of hexagonal rings in  $\text{C}_{60}$  fullerene.  
**Fill your answer as sum of digits till you get the single digit answer.**
33. Number of following species which are planar & polar ?  
 $\text{XeF}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{ClF}_3$ ,  $\text{SO}_2$ ,  $\text{XeO}_3$
34. Find the number of chemical species(s) which are planar and nonpolar in the following :-  
 $\text{NO}_2^-$ ,  $\text{O}_2\text{F}_2$ ,  $\text{XeF}_5^+$ ,  $\text{HCN}$ ,  $\text{XeF}_5^-$ ,  $\text{B}_3\text{N}_3\text{H}_6$

## EXERCISE # 4

### Paragraph for question no. 1 to 2

According to Lewis Longmuir concept atoms combine to complete their respective octet.

- The species following the octet rule is  
(A)  $ICl_3$  (B)  $SbCl_3$  (C)  $BeCl_2$  (D)  $AlCl_3$
- From the species given below which one is hypervalent ?  
(A)  $AlF_3$  (B)  $SF_4$  (C)  $OCl_2$  (D)  $NF_3$

### Paragraph for question nos. 3 to 4

The formation of  $BH_3$ ,  $CH_4$  &  $NH_3$  like compounds cannot be explained by V.B.T. For example the all equal bond lengths of  $CH_4$  molecule & also the bond angles ( $109^\circ 28'$ ) cannot be explained. Hence a new phenomenon is introduced to explain the above observation, which is known as hybridisation. Hybridisation can be defined as the mixing of pure atomic orbitals of comparable energy.

- Select the correct statement ?  
(A) Hybridisation takes place in all covalent as well as ionic compounds.  
(B) Intermixing of different shells takes place in hybridisation  
(C) Hybrid orbitals are more directional than the pure atomic orbitals.  
(D) If % p character increases in hybrid orbital, it becomes bulkier & shorter.
- Which of the following orbital may involve in hybridisation in  $PCl_5$  ?  
(A)  $d_{xz}$  (B)  $d_{yz}$  (C)  $d_{z^2}$  (D)  $d_{x^2-y^2}$

### Paragraph for question no. 5 to 6

Valence Bond Theory explains the formation of covalent bond such as two filled atomic orbitals having  $e^-$  with opposite spin combine axially or collaterally to form  $\sigma$  and  $\pi$  bond respectively.

- Which of the following orbital cannot form  $\sigma$  bond with  $d_{xy}$  orbital .  
(A) s (B)  $p_x$  (C)  $d_{x^2-y^2}$  (D) All of these
- Which of the following statement is correct ?  
(A) s -orbital always forms  $\sigma$  bond with p orbital  
(B) s-orbital is more directional than p-orbital  
(C) p-orbital always form  $\pi$ -bond  
(D) a covalent bond is directional in nature.

**Paragraph for question no. 7 to 9**

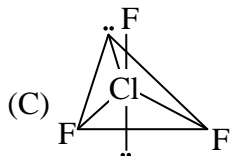
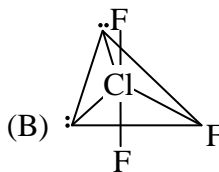
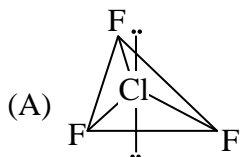
$\text{IF}_7$  is a molecule in which I atom is in the maximum oxidation state, and the hybridization for I atom is  $\text{sp}^3\text{d}^3$ .

7. The number of  $\widehat{\text{FIF}}$  adjacent angles ( $90^\circ + 72^\circ$ ) in  $\text{IF}_7$  molecule is  
(A) 10 (B) 15 (C) 20 (D) 14
8. The number of  $\widehat{\text{FIF}}$  angles less than  $90^\circ$  and equal to  $90^\circ$  are respectively  
(A) 5 and 5 (B) 10 and 5 (C) 5 and 10 (D) 10 and 15
9. The number of I – F bonds having the longest and shortest lengths are respectively  
(A) 5 and 2 (B) 2 and 5 (C) 5 and 5 (D) 2 and 2

**Paragraph for question no. 10 to 11**

hybridisation helps to determine the shape of a molecule but shape of a molecule is mainly define by VSEPR theory According to this theory  $\text{l.p} - \text{l.p} > \text{l.p} - \text{b.p} > \text{b.p} - \text{b.p}$

10. In which of the following pairs hybridisation of the central atom is not same?  
(A)  $\text{ClF}_3$ ,  $\text{ClF}_3\text{O}$ , (B)  $\text{ClF}_3\text{O}$ ,  $\text{ClF}_3\text{O}_2$   
(C)  $[\text{ClF}_2\text{O}]^+$   $[\text{ClF}_4\text{O}]^-$  (D)  $[\text{ClF}_4\text{O}]^-$   $[\text{XeOF}_4]$
11. More correct structure of  $\text{ClF}_3$  is :



(D) All of the above

**Paragraph for question no. 12 to 13**

Valence shell electron pair repulsion theory (VSEPR) can be used to predict the approximate shape of a molecule. Electrons in bonds and in lone pairs can be thought of as “charge cloud” that repel one another and stay as far apart possible, thus causing molecules to assume specific shapes.

The repulsive interactions of electron pairs decrease in the order :

Lone pair-lone pair > Lone pair - bond pair > Bond pair-bond pair.

These repulsions result in deviations from idealized shapes and alteration in bond angles in molecules.

12. Molecular shape of  $\text{XeF}_3^+$ ,  $\text{SF}_3^+$  and  $\text{CF}_3^+$  are :
- (A) the same with 2, 1 and 0 lone pairs of electrons, respectively  
 (B) different with 2, 1 and 0 lone pairs of electrons, respectively  
 (C) different with 0, 1 and 2 lone pairs of electrons, respectively  
 (D) the same with 2, 0 and 1 lone pairs of electrons, respectively
13. Which of the following statements is **incorrect** ?
- (A) In  $\text{H}_2\text{O}$ , the bond angle is less than  $\text{OF}_2$   
 (B) In  $\text{ClF}_3$ , the axial Cl-F bond length is larger than equatorial Cl-F bond length.  
 (C) In  $\text{SF}_4$ , F-S-F equatorial bond angle is not equal to  $120^\circ$  due to lone pair-bond pair repulsions.  
 (D) In  $\text{ICl}_4^-$ , bond angles is  $90^\circ$

**Paragraph for Question 14 to 15**

According to the VSEPR theory of molecular geometry in chemistry, which is based on the general principle of maximizing the distances between points, a square antiprism is the favored geometry when eight pairs of electrons surround a central atom. Square antiprism, in which the eight atoms occupy the eight vertices of the antiprism, and the eight triangle edges of the antiprism correspond to single covalent bonds.

14. Which of the following molecules have square anti prismatic structure
- (A)  $\text{XeF}_8^{-2}$                       (B)  $\text{PaF}_8^{-3}$                       (C)  $\text{S}_8$                       (D)  $\text{XeF}_6$
15. In molecule nitrosonium octa fluoro xenate (VI) central atom Xe has
- (A)  $\text{fsp}^3\text{d}$                       (B)  $\text{d}^4\text{sp}^3$                       (C)  $\text{sp}^3\text{d}^3$                       (D) no hybridisation



**Paragraph for question no. 16 to 17**

Various oxy acids of non metals are found in nature. Some derivatives of oxy acids can also be derived from the parent oxy acid.

Derivatives of oxy acid can be derived by removing  $\text{H}_2\text{O}$  molecule from the parent oxy acids such as :

2 moles of oxy acid —  $\text{H}_2\text{O}$  = pyro acid.

1 mole of oxy acid —  $\text{H}_2\text{O}$  = meta acid.

**16.** Parent oxy acid of  $\text{H}_4\text{P}_2\text{O}_5$  acid is ?

- (A) phosphorous acid (B) ortho phosphoric acid  
(C) pyro phosphorous acid (D) hypophosphorous acid

**17.** Which of the following is not a hypo acid ?

- (A)  $\text{H}_2\text{N}_2\text{O}_2$  (B)  $\text{HOCl}$  (C)  $\text{H}_2\text{S}_2\text{O}_7$  (D)  $\text{H}_4\text{P}_2\text{O}_6$

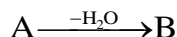
**Paragraph for Question 18 to 19**

Various derivatives of oxy acids can be derived from the parent oxy acids for example pyro acids and meta acids can be derived from various parent oxy acid by removing a water molecule, from two moles of oxy acid (for pyro acid) and from one mole of oxy acid (for meta acid) respectively.

**18.** For which of the following oxy acid meta acid is not possible :

- (A)  $\text{H}_2\text{S}_2\text{O}_8$  (B)  $\text{H}_2\text{S}_2\text{O}_6$  (C)  $\text{H}_3\text{PO}_4$  (D)  $\text{H}_2\text{SO}_3$

**19.** For A is any parent acid observe the following reaction :



Which of the following statement is **INCORRECT** ?

- (A) If A is  $\text{H}_3\text{PO}_4$  then there are four P—O—P linkage present in the cyclic trimer of B.  
(B) If A is  $\text{H}_2\text{SO}_4$  then there are 6 shorter S—O bond lengths are present in cyclic trimer of B.  
(C) If A is  $\text{HNO}_3$  then meta form of A does not exist.  
(D) If A is  $\text{HNO}_2$  then on removing one mole of water from A will give a mixed anhydride.



**Paragraph for Question 20 to 21**

Polar covalent molecules exhibit dipole moment. Dipole moment is equal to the product of charge separation  $q$  and the bond length  $d$  for the bond. Unit of dipole moment is debye. One debye is equal to  $10^{-18}$  esu cm.

Dipole moments is a vector quantity. It has both magnitude and direction. Hence, dipole moment of a molecule depends upon the relative orientation of the bond dipoles, but not on the polarity of bonds alone. A symmetrical structure shows zero dipole moment. Thus, dipole moment helps to predict the geometry of a molecule. Dipole moment values can be used to distinguish between *cis*- and *trans*-isomers, *ortho*-, *meta*- and *para*-forms of a substance, etc.

20. Arrange the following in increasing order of their polarity.

- (I) Ortho chloro Toluene      (II) Meta chloro Toluene      (III) Para chloro Toluene  
(A) III > II > I      (B) II < I > III      (C) III > I > II      (D) I < II < III

21. Correct Statement among following ?

- (A) Dipole moment order  $\text{BF}_3 = \text{CCl}_4 = \text{PCl}_5 = \text{SF}_6$   
(B) dipole moment of  $\text{CHCl}_3 > \text{CHF}_3$   
(C)  $\mu_{\text{experimental}}$  is less than  $\mu_{\text{theoretical}}$  for CO molecule  
(D) If a  $\text{AX}_4$  type molecule has  $\mu = 0$  then it can have either tetrahedral or octahedral electron geometry (A = central atom, X = side atom)

**Paragraph for Question 22 to 24**

The attractive force that binds hydrogen atom of one molecule with electronegative atom of the other molecule of the same or different substance is known as hydrogen bond.

22. Which of the following chemical species having inter molecular hydrogen bonding.

- (A) Ortho boric acid      (B) Ortho nitrophenol  
(C) Ortho hydroxybenzaldehyde      (D) Ortho chlorophenol

23. Which of the following boiling point order is **INCORRECT**.

- (A)  $\text{H}_3\text{BO}_3 > \text{B(OMe)}_3$       (B)  $\text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{OCH}_3$   
(C)  $\text{HF} > \text{HCl}$       (D)  $\text{NH}_3 > \text{SbH}_3$

24. Which of the following molecule will form Hydrogen-bond with water ?

- (A) Chloral hydrate      (B)  $\text{C}_6\text{H}_5\text{OH}$       (C)  $\text{NH}_3$       (D)  $\text{C}_2\text{H}_5\text{OH}$

**Paragraph for question no. 25 to 26**

A hydrogen bond is an electrostatic attraction between two polar groups that occurs when a hydrogen atom covalently bound to a highly electronegative atom.

25. Correct order of boiling point is -  
 (A)  $\text{H}_2\text{O} > \text{NH}_3 > \text{HF}$  (B)  $\text{HF} > \text{NH}_3 > \text{H}_2\text{O}$   
 (C)  $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$  (D)  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$
26. In which of the following compound H-bond is not present ?  
 (A)  $\text{KH}_2\text{PO}_3$  (B)  $\text{K}_2\text{HPO}_3$  (C)  $\text{KH}_2\text{PO}_4$  (D)  $\text{K}_2\text{HPO}_4$

**Paragraph for question no. 27 to 28**

In an oxy acid the acidic hydrogen is connected to the oxygen atom covalently. And generally the oxygen is covalently bonded to a non-metal. And in Hydra acid Hydrogen is covalently bonded to a more electronegative atom (**Eg.:** halogen) except oxygen.

27. Which of the following has higher boiling point  
 (A) HF (B) HI (C) HCl (D) HBr
28. Which of the following compound(s) doesn't have hydrogen bond  
 (A)  $\text{K}_3\text{PO}_4$  (B)  $\text{K}_2\text{HPO}_4$  (C)  $\text{KH}_2\text{PO}_4$  (D)  $\text{H}_3\text{PO}_4$

**Paragraph for question no. 29 to 30**

Hydrogen bonding originates from the dipole-dipole interaction between H-atom and any of the other atom like F, O, N and in some cases with Cl atom. There are two types of H-bonding like intermolecular and intramolecular H-bonding.

29. Which of the following molecule consist of intramolecular H-bonding.  
 (A) HF (B) Ice (C) Boric acid (D) Chloral hydrate
30. Which of following statement is incorrect  
 (A) Boiling point of  $\text{H}_2\text{O}_2$  is greater than that of  $\text{H}_2\text{O}$   
 (B) Ortho-nitrophenol has less boiling point than para-nitrophenol.  
 (C) In ice each 'O' atom is tetrahedrally bonded by four H-atoms which are all equidistant.
- (D)  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array}$  (Ethylene glycol) is less viscous than  $\begin{array}{c} \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \\ | \\ \text{CH}_2\text{-OH} \end{array}$  (Glycerol)
31. Which of the following is correct order for extent of Hydrogen Bonding  
 (A)  $\text{NH}_3 > \text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF}$  (B)  $\text{H}_2\text{O} > \text{HF} > \text{NH}_3 > \text{H}_2\text{O}_2$   
 (C)  $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF}$  (D)  $\text{H}_2\text{O}_2 > \text{NH}_3 > \text{H}_2\text{O} > \text{HF}$

**EXERCISE # 5**

**MATRIX MATCH**

**1. Column-I**

- (A)  $\text{N}_3^-$   
(B)  $\text{NO}_3^-$   
(C)  $\text{I}_3^-$   
(D) CO

**Column-II**

(Sum of lone pair + Bond pair +  $\pi$  bond)

- (P) 11  
(Q) 10  
(R) 7  
(S) 13

**2. Column-I**

- (A)  $\text{XeO}_3$   
(B)  $\text{XeO}_2\text{F}_4$   
(C)  $\text{XeO}_2\text{F}_2$

**Column-II**

- (P) Pyramidal geometry  
(Q) Non-planar molecule  
(R)  $d_{z^2}$  orbital is involved in hybridization of central atom

**3. Column-I**

- (A)  $\text{NH}_2^-$   
(B)  $\text{XeOF}_2$   
(C)  $\text{ICl}_4^-$   
(D)  $[\text{SbF}_5]^{2-}$

**Column-II**

- (P) Square pyramidal  
(Q) V-shaped  
(R) T-shaped  
(S) Square planar

**4. Match the compounds with their properties.**

**Column-I**

- (A)  $\text{BCl}_3$   
(B)  $\text{SiF}_4$   
(C) SiC

**Column-II**

- (P) All atoms are central atom.  
(Q) It has only  $\sigma$ -bond.  
(R) It is non-planar.

**5. List-I**

(Oxy Acid)

- (P)  $\text{H}_3\text{BO}_3$   
(Q)  $\text{H}_3\text{PO}_3$   
(R)  $\text{H}_4\text{SiO}_4$   
(S)  $\text{H}_3\text{PO}_4$

**List-II**

(Basicity)

- (1) Tetrabasic  
(2) Tribasic  
(3) Dibasic  
(4) Monobasic

**Code:**

	P	Q	R	S
(A)	1	2	3	4
(C)	4	3	1	2

	P	Q	R	S
(B)	4	3	2	1
(D)	1	2	4	3

6. **List-I**  
(P) HF  
(Q)  $\text{H}_3\text{BO}_3$   
(R)  $\text{H}_3\text{PO}_4$   
(S) chloral hydrate
- List-II**  
(1) 2-D sheet like structure  
(2) inter molecular H-bonding  
(3) Zig-zag chain like  
(4) 5 membered chelate ring found in structure

**Code:**

	P	Q	R	S
(A)	1	2	3	4
(C)	4	3	2	1

	P	Q	R	S
(B)	3	1	2	4
(D)	1	3	2	4

7. Match the following list :-

**List-I (Molecules)**

- (P)  $\text{SF}_4$   
(Q)  $\text{H}_2\text{O}$   
(R)  $\text{SF}_6$   
(S)  $\text{CO}_2$

**Code:**

	P	Q	R	S
(A)	1	2	3	4
(C)	2	3	4	1

**List-II (Molecular properties)**

- (1) Planar and polar  
(2) Non-planar and polar  
(3) Planar and non-polar  
(4) Non-planar and non-polar

	P	Q	R	S
(B)	2	1	4	3
(D)	3	2	1	4

8. **Column-I**  
(A)  $\text{H}_2\text{S}_2\text{O}_6$   
(B)  $\text{H}_2\text{S}_2\text{O}_3$   
  
(C)  $\text{B}_3\text{N}_3\text{H}_6$   
(D) Trimeta phosphoric acid

**Column-II**

- (P) Basicity = 3  
(Q) X-X single bond is present  
(where x is a central atom)  
(R) Aromatic nature present in its structure  
(S) Weakest  $\text{p}\pi\text{-d}\pi$  bond present in structure  
among the given molecules

9. **Column-I**  
(Pair of species)  
(A)  $\text{PCl}_3\text{F}_2$ ,  $\text{PCl}_2\text{F}_3$   
(B)  $\text{BF}_3$  and  $\text{BCl}_3$   
(C)  $\text{CO}_2$  and  $\text{NO}_2^+$   
(D)  $\text{C}_6\text{H}_6$  and  $\text{B}_3\text{N}_3\text{H}_6$

**Column-II**

- (Identical property in pairs of species)  
(P) Hybridisation of central atom  
(Q) Shape of molecule / ion  
(R)  $\mu_{\text{net}}$  (dipole moment)  
(S) Total number of electrons  
(T) All bond length are equal within molecule

**EXERCISE – 6 # JEE–MAIN**

- Which of the following statements is true ? [AIEEE-2002]
  - HF is less polar than HBr
  - Water does not contain any ions
  - Chemical bond formation takes place when forces of attraction overcome the forces of repulsion
  - In covalent bond, transfer of electrons takes place
- Which one of the following pairs of molecules will have permanent dipole moments for both members [AIEEE-2003]
  - NO<sub>2</sub> and CO<sub>2</sub>
  - NO<sub>2</sub> and O<sub>3</sub>
  - SiF<sub>4</sub> and CO<sub>2</sub>
  - SiF<sub>4</sub> and NO<sub>2</sub>
- The pair of species having identical shapes for molecules of both species is [AIEEE-2003]
  - XeF<sub>2</sub>, CO<sub>2</sub>
  - BF<sub>3</sub>, PCl<sub>3</sub>
  - PF<sub>5</sub>, IF<sub>5</sub>
  - CF<sub>4</sub>, SF<sub>4</sub>
- The correct order of bond angles (smallest first) in H<sub>2</sub>S, NH<sub>3</sub>, BF<sub>3</sub> and SiH<sub>4</sub> is : [AIEEE-2004]
  - H<sub>2</sub>S < NH<sub>3</sub> < SiH<sub>4</sub> < BF<sub>3</sub>
  - NH<sub>3</sub> < H<sub>2</sub>S < SiH<sub>4</sub> < BF<sub>3</sub>
  - H<sub>2</sub>S < SiH<sub>4</sub> < NH<sub>3</sub> < BF<sub>3</sub>
  - H<sub>2</sub>S < NH<sub>3</sub> < BF<sub>3</sub> < SiH<sub>4</sub>
- Lattice energy of an ionic compound depends upon [AIEEE-2005]
  - charge on the ion only
  - size of the ion only
  - packing of the ion only
  - charge and size of the ion
- Of the following sets which one does not contain isoelectronic species ? [AIEEE-2005]
  - PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>
  - CN<sup>-</sup>, N<sub>2</sub>, C<sub>2</sub><sup>2-</sup>
  - SO<sub>3</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>
  - BO<sub>3</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>
- In which of the following molecules/ions are all the bonds **not** equal? [AIEEE-2006]
  - XeF<sub>4</sub>
  - BF<sub>4</sub><sup>-</sup>
  - SF<sub>4</sub>
  - SiF<sub>4</sub>
- Which of the following hydrogen bonds is the strongest [AIEEE-2007]
  - F–H.....F
  - O–H.....O
  - O–H.....F
  - O–H.....N
- The hybridisation of orbitals of N atom in NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>+</sup> and NH<sub>4</sub><sup>+</sup> are respectively:-

[AIEEE-2011]

- (1)  $sp, sp^3, sp^2$       (2)  $sp^2, sp^3, sp$       (3)  $sp, sp^2, sp^3$       (4)  $sp^2, sp, sp^3$

10. The structure of  $IF_7$  is :- [AIEEE-2011]

- (1) octahedral      (2) pentagonal bipyramid  
(3) square pyramid      (4) trigonal bipyramid

11. Which of the following has maximum number of lone pairs associated with Xe [AIEEE-2011]

- (1)  $XeO_3$       (2)  $XeF_4$       (3)  $XeF_6$       (4)  $XeF_2$

12. The molecule having smallest bond angle is :- [AIEEE-2012]

- (1)  $PCl_3$       (2)  $NCl_3$       (3)  $AsCl_3$       (4)  $SbCl_3$

13. In which of the following pairs the two species are not isostructural ? [AIEEE-2012]

- (1)  $AlF_6^{3-}$  and  $SF_6$       (2)  $CO_3^{2-}$  and  $NO_3^-$       (3)  $PCl_4^+$  and  $SiCl_4^+$       (4)  $PF_5$  and  $BrF_5$

14. The number of S-S bonds in  $SO_3$ ,  $S_2O_3^{2-}$ ,  $S_2O_6^{2-}$  and  $S_2O_8^{2-}$  respectively are :-

[JEE-MAINS-2012]

- (1) 1, 0, 1, 0      (2) 0, 1, 1, 0      (3) 1, 0, 0, 1      (4) 0, 1, 0, 1      (On line)

15. Among the following species which two have trigonal bipyramidal shape ?

[JEE-MAINS-2012]

- (I)  $Nl_3$       (II)  $I_3^-$       (III)  $SO_3^{2-}$       (IV)  $NO_3^-$       (On line)  
(1) II and III      (2) III and IV      (3) I and IV      (4) I and III

16. Which of the following has the square planar structure :- [JEE-MAINS-2012]

- (1)  $NH_4^+$       (2)  $CCl_4$       (3)  $XeF_4$       (4)  $BF_4^-$       (On line)

17. The compound of Xenon with zero dipole moment is :- [JEE-MAINS-2012]

- (1)  $XeO_3$       (2)  $XeO_2$       (3)  $XeF_4$       (4)  $XeOF_4$       (On line)

18. Among the following the molecule with the lowest dipole moment is :- [JEE-MAINS-2012]

- (1)  $CHCl_3$       (2)  $CH_2Cl_2$       (3)  $CCl_4$       (4)  $CH_3Cl$       (On line)



19. The formation of molecular complex  $\text{BF}_3 - \text{NH}_3$  results in a change in hybridisation of boron :—  
[JEE-MAINS-2012]  
(1) from  $\text{sp}^3$  to  $\text{sp}^3\text{d}$  (2) from  $\text{sp}^2$  to  $\text{dsp}^2$  (On line)  
(3) from  $\text{sp}^3$  to  $\text{sp}^2$  (4) from  $\text{sp}^2$  to  $\text{sp}^3$
20. Trigonal bipyramidal geometry is shown by: [JEE-MAINS-2013]  
(1)  $\text{XeO}_3\text{F}_2$  (2)  $\text{XeOF}_2$  (3)  $\text{XeO}_3$  (4)  $\text{FXeOSO}_2\text{F}$  (On line)
21. Which one of the following molecules is polar? [JEE-MAINS-2013]  
(1)  $\text{CF}_4$  (2)  $\text{SbF}_5$  (3)  $\text{IF}_5$  (4)  $\text{XeF}_4$  (On line)
22. Oxidation state of sulphur in anions  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$  increases in the orders :  
[JEE-MAINS-2013]  
(1)  $\text{S}_2\text{O}_6^{2-} < \text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-}$  (2)  $\text{SO}_3^{2-} < \text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-}$  (On line)  
(3)  $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-}$  (4)  $\text{S}_2\text{O}_4^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_3^{2-}$
23.  $\text{XeO}_4$  molecule is tetrahedral having : [JEE-MAINS-2013]  
(1) Two pp-dp bonds (2) Four pp-dp bonds (On line)  
(3) One pp-dp bond (4) Three pp-dp bonds
24. Bond distance in HF is  $9.17 \times 10^{-11}$  m. Dipole moment of HF is  $6.104 \times 10^{-30}$  Cm. The percent ionic character in HF will be : (electron charge =  $1.60 \times 10^{-19}$  C) [JEE-MAINS-2013]  
(1) 61.0% (2) 38.0% (3) 35.5% (4) 41.5% (On line)
25. The shape of  $\text{IF}_6^-$  is : [JEE-MAINS-2013]  
(1) distorted octahedron (2) Pyramidal (On line)  
(3) Octahedral (4) Square antiprism
26. Which has trigonal bipyramidal shape ? [JEE-MAINS-2013]  
(1)  $\text{XeOF}_4$  (2)  $\text{XeO}_3$  (3)  $\text{XeO}_3\text{F}_2$  (4)  $\text{XeOF}_2$  (On line)
27. The catenation tendency of C, Si and Ge is in the order  $\text{Ge} < \text{Si} < \text{C}$ . The bond energies (in  $\text{kJ mol}^{-1}$ ) of C—C, Si—Si and Ge—Ge bonds are respectively :  
[JEE-MAINS-2013 (On line)]  
(1) 348, 260, 297 (2) 348, 297, 260 (3) 297, 348, 260 (4) 260, 297, 348



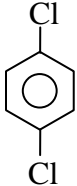
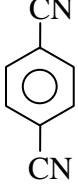
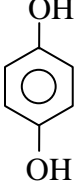
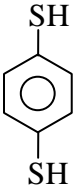
28. In which of the following sets, all the given species are isostructural ?

[JEE-MAINS-2013 (On line)]

- (1)  $\text{BF}_3$ ,  $\text{NF}_3$ ,  $\text{PF}_3$ ,  $\text{AlF}_3$  (2)  $\text{PCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ ,  $\text{SbCl}_3$   
(3)  $\text{BF}_4^-$ ,  $\text{CCl}_4$ ,  $\text{NH}_4^+$ ,  $\text{PCl}_4^+$  (4)  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{ClO}_2$ ,  $\text{SiO}_2$

29. For which of the following molecule significant  $\mu \neq 0$

[JEE-M-2014]

- (1)  (2)  (3)  (4)   
(1) Only (3) (2) (3) and (4) (3) Only (1) (4) (1) and (2)

30. Among the following oxoacids, the correct decreasing order of acid strength is :-

[JEE-M-2014]

- (1)  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl}$   
(2)  $\text{HClO}_2 > \text{HClO}_4 > \text{HClO}_3 > \text{HOCl}$   
(3)  $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$   
(4)  $\text{HClO}_4 > \text{HOCl} > \text{HClO}_2 > \text{HClO}_3$

31. The number and type of bonds in  $\text{C}_2^{2-}$  ion in  $\text{CaC}_2$  are:

[AIEEE-2005, AIEEE-2011, JEE-MAINS-2014 (On line)]

- (1) Two  $\sigma$  bonds and one  $\pi$  - bond  
(2) Two  $\sigma$  bonds and two  $\pi$  - bonds  
(3) One  $\sigma$  bond and two  $\pi$  - bonds  
(4) One  $\sigma$  bond and one  $\pi$  - bond

32. For the compounds

[JEE-MAINS-2014]

$\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{F}$ ,

(On line)

the correct order of increasing C-halogen bond length is :

- (1)  $\text{CH}_3\text{F} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl} < \text{CH}_3\text{I}$   
(2)  $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$   
(3)  $\text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{I}$   
(4)  $\text{CH}_3\text{F} < \text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{Cl}$

33. Shapes of certain interhalogen compounds are stated below. Which one of them is not correctly stated? [JEE-MAINS-2014]  
 (1)  $\text{IF}_7$  : Pentagonal bipyramid (2)  $\text{BrF}_5$  : Trigonal bipyramid (On line)  
 (3)  $\text{ICl}_3$  : Planar dimeric (4)  $\text{BrF}_3$  : Planar T-shaped
34. Which of the following molecules has two sigma( $\sigma$ ) and two pi( $\pi$ ) bonds :- [JEE-MAINS-2014]  
 (1) HCN (2)  $\text{C}_2\text{H}_2\text{Cl}_2$  (3)  $\text{N}_2\text{F}_2$  (4)  $\text{C}_2\text{H}_4$  (On line)
35. The species in which the N atom is in a state of sp hybridization is [JEE-MAINS(offline)-2016]  
 (1)  $\text{NO}_2$  (2)  $\text{NO}_2^+$  (3)  $\text{NO}_2^-$  (4)  $\text{NO}_3^-$
36. The pair in which phosphorous atoms have a formal oxidation state of + 3 is :- [JEE-MAINS(offline)-2016]  
 (1) Pyrophosphorous and pyrophosphoric acids  
 (2) Orthophosphorous and pyrophosphorous acids  
 (3) Pyrophosphorous and hypophosphoric acids  
 (4) Orthophosphorous and hypophosphoric acids
37. The group of molecules having identical shape is : [JEE-MAINS(online)-2016]  
 (1)  $\text{SF}_4$ ,  $\text{XeF}_4$ ,  $\text{CCl}_4$  (2)  $\text{ClF}_3$ ,  $\text{XeOF}_2$ ,  $\text{XeF}_3^+$   
 (3)  $\text{PCl}_5$ ,  $\text{IF}_5$ ,  $\text{XeO}_2\text{F}_2$  (4)  $\text{BF}_3$ ,  $\text{PCl}_3$ ,  $\text{XeO}_3$
38. **Assertion** : Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. [JEE-MAINS(online)-2016]  
**Reason** : Hybridization of carbon in diamond and graphite are  $\text{sp}^3$  and  $\text{sp}^2$ , respectively.  
 (1) Assertion is incorrect statement, but the reason is correct.  
 (2) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.  
 (3) Both assertion and reason are incorrect.  
 (4) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
39. Aqueous solution of which salt will not contain ions with the electronic configuration  $1s^2 2s^2 2p^6 3s^2 3p^6$  ? [JEE-MAINS(online)-2016]  
 (1) NaCl (2)  $\text{CaI}_2$  (3) KBr (4) NaF

40. In the following reactions, ZnO is respectively acting as a/an: [JEE-MAINS(offline)-2017]  
 (a)  $\text{ZnO} + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{ZnO}_2$  (b)  $\text{ZnO} + \text{CO}_2 \rightarrow \text{ZnCO}_3$   
 (1) base and base (2) acid and acid (3) acid and base (4) base and acid
41.  $\text{sp}^3\text{d}^2$  hybridization is not displayed by : [JEE-MAINS(online)-2017]  
 (1)  $\text{SF}_6$  (2)  $\text{BrF}_5$  (3)  $\text{PF}_5$  (4)  $[\text{CrF}_6]^{3-}$
42. The number of S = O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are :  
 (1) (2 and 4) and (2 and 4) (2) (4 and 2) and (4 and 2)  
 (3) (4 and 2) and (2 and 4) (4) (2 and 2) and (2 and 2)
43. The group having triangular planar structure is : [JEE-MAINS(online)-2017]  
 (1)  $\text{BF}_3$ ,  $\text{NF}_3$ ,  $\text{CO}_3^{2-}$  (2)  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_3$   
 (3)  $\text{NH}_3$ ,  $\text{SO}_3$ ,  $\text{CO}_3^{2-}$  (4)  $\text{NCl}_3$ ,  $\text{BCl}_3$ ,  $\text{SO}_3$
44. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) respectively are : [JEE-MAINS(online)-2017]  
 (1) five and four (2) four and five (3) five and five (4) four and four
45. The correct sequence of decreasing number of  $\pi$ -bonds in the structure of  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_7$  is : [JEE-MAINS(online)-2017]  
 (1)  $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4$  (2)  $\text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$   
 (3)  $\text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7 > \text{H}_2\text{SO}_3$  (4)  $\text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 > \text{H}_2\text{S}_2\text{O}_7$
46. The decreasing order of bond angles in  $\text{BF}_3$ ,  $\text{NH}_3$ ,  $\text{PF}_3$  and  $\text{I}_3^-$  is :- [JEE-MAINS-2018]  
 (1)  $\text{I}_3^- > \text{BF}_3 > \text{NH}_3 > \text{PF}_3$  (2)  $\text{BF}_3 > \text{NH}_3 > \text{PF}_3 > \text{I}_3^-$   
 (3)  $\text{I}_3^- > \text{NH}_3 > \text{PF}_3 > \text{BF}_3$  (4)  $\text{BF}_3 > \text{I}_3^- > \text{PF}_3 > \text{NH}_3$
47.  $\text{H} - \overset{\text{(I)}}{\text{N}} - \text{---} - \overset{\text{(II)}}{\text{N}} - \text{---} - \text{N}$   
 In hydrogen azide (above) the bond orders of bonds (I) and (II) are :- [JEE-MAINS-2018]  

	(I)	(II)		(I)	(II)
(1)	> 2	< 2	(2)	< 2	< 2
(3)	< 2	> 2	(4)	> 2	> 2
48. Identify the pair in which the geometry of the species is T-shape and square-pyramidal, respectively :- [JEE-MAINS-2018]  
 (1)  $\text{IO}_3^-$  and  $\text{IO}_2\text{F}_2^-$  (2)  $\text{XeOF}_2$  and  $\text{XeOF}_4$  (3)  $\text{ICl}_2^-$  and  $\text{ICl}_5$  (4)  $\text{ClF}_3$  and  $\text{IO}_4^-$
49. The type of hybridisation and number of lone pair(s) of electrons of Xe in  $\text{XeOF}_4$  respectively, are: [JEE-MAINS-2019]  
 (1)  $\text{sp}^3\text{d}$  and 2 (2)  $\text{sp}^3\text{d}^2$  and 2 (3)  $\text{sp}^3\text{d}$  and 1 (4)  $\text{sp}^3\text{d}^2$  and 1

**EXERCISE – 7 # JEE–ADVANCED**

**Integer Type**

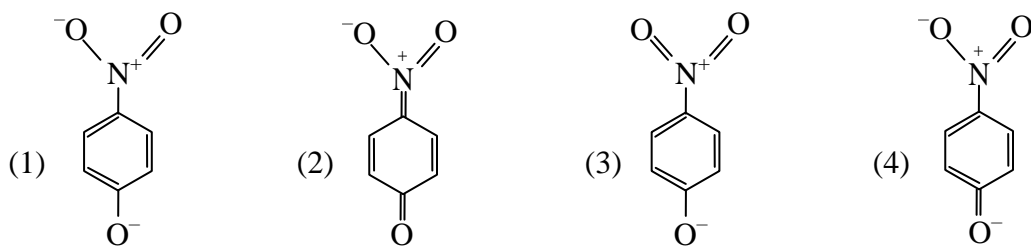
- The number of water molecule(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is [JEE 2009]
- Based on VSEPR theory, the number of 90 degree F–Br–F angles in  $\text{BrF}_5$  is [JEE 2010]
- The difference in the oxidation numbers of the two types of sulphur atoms in  $\text{Na}_2\text{S}_4\text{O}_6$  is. [JEE 2011]
- The total number of lone-pairs of electrons in melamine is [JEE Adv. 2013]

**One or more than one correct**

- The linear structure is assumed by : [IIT—1991]  
(A)  $\text{SnCl}_4$  (B)  $\text{NCO}^-$  (C)  $\text{CS}_2$  (D)  $\text{NO}_2^+$
- Which of the following has zero dipole moment? [IIT—1993]  
(A)  $\text{ClF}$  (B)  $\text{PCl}_3$  (C)  $\text{SiF}_4$  (D)  $\text{CFCl}_3$
- Among the following molecules, which one is planar? [IIT—1994]  
(A)  $\text{BCl}_3$  (B)  $\text{SO}_2\text{Cl}_2$  (C)  $\text{NH}_3$  (D)  $\text{NF}_3$
- Which of the following species is / are non-linear? [IIT—1995]  
(A)  $\text{H}_2\text{S}$  (B)  $\text{NH}_3$  (C)  $\text{CO}_2$  (D)  $\text{SO}_2$
- Which contains both polar and non-polar bonds? [IIT—1997]  
(A)  $\text{CH}_4$  (B)  $\text{HCN}$  (C)  $\text{H}_2\text{O}_2$  (D)  $\text{NH}_4\text{Cl}$
- Which of the following compounds has  $\text{sp}^2$  hybridisation? [IIT—1997]  
(A)  $\text{CO}_2$  (B)  $\text{SO}_2$  (C)  $\text{N}_2\text{O}$  (D)  $\text{CO}$
- Which one of the following molecules is planar? [IIT—1996]  
(A)  $\text{NF}_3$  (B)  $\text{NCl}_3$  (C)  $\text{BF}_3$  (D)  $\text{PH}_3$
- The number and type of bonds between two carbon atoms in  $\text{CaC}_2$  are: [IIT—1996]  
(A)  $1\sigma$  and  $1\pi$  (B)  $1\sigma$  and  $2\pi$  (C)  $1\sigma$  and  $1.5\pi$  (D)  $1\sigma$

13. Among the species  $\text{NF}_3$ ,  $\text{NO}_3^-$ ,  $\text{BF}_3$ ,  $\text{H}_3\text{O}^+$  and  $\text{HN}_3$ , identify the isostructural species :  
[IIT—1996]
- (A)  $(\text{NF}_3, \text{NO}_3^-)$  and  $(\text{BF}_3, \text{H}_3\text{O}^+)$  (B)  $(\text{NF}_3, \text{HN}_3)$  and  $(\text{NO}_3^-, \text{BF}_3)$   
(C)  $(\text{NF}_3, \text{H}_3\text{O}^+)$  and  $(\text{NO}_3^-, \text{BF}_3)$  (D)  $(\text{NF}_3, \text{H}_3\text{O}^+)$  and  $(\text{HN}_3, \text{BF}_3)$
14. Among the following the one that is polar and has the central atom with  $\text{sp}^2$  hybridisation is :  
[IIT—1997]
- (A)  $\text{H}_2\text{CO}_3$  (B)  $\text{SiF}_4$  (C)  $\text{BF}_3$  (D)  $\text{HClO}_2$
15. The geometry & the type of hybrid orbitals present about the central atom in  $\text{BF}_3$  is :  
[JEE98]
- (A) linear,  $\text{sp}$  (B) trigonal planar,  $\text{sp}^2$   
(C) tetrahedral  $\text{sp}^3$  (D) pyramidal,  $\text{sp}^3$
16. Which one of the following statement (s) is (are) correct? [JEE1998]
- (A) The electronic configuration of Cr is  $[\text{Ar}] 3d^5 4s^1$ . (Atomic No. of Cr = 24)  
(B) The magnetic quantum number may have a negative value  
(C) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic No. of Ag = 47)  
(D) The oxidation state of nitrogen in  $\text{HN}_3$  is  $-3$ .
17. Element X is strongly electronegative and element Y is strongly electropositive. Both are univalent. The compound formed would be : [JEE1998]
- (A)  $\text{X}^+ \text{Y}^-$  (B)  $\text{Y}^+ \text{X}^-$  (C)  $\text{X}^- \text{Y}^+$  (D)  $\text{Y}^- \text{X}^+$
18. The correct order of increasing C - O bond length of,  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$  is :- [JEE '99]
- (A)  $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$  (B)  $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$   
(C)  $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$  (D)  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$
19. The geometry of  $\text{H}_2\text{S}$  and its dipole moment are [JEE '99]
- (A) angular & non zero (B) angular & zero  
(C) linear & non zero (D) linear & zero
20. In compounds type  $\text{ECl}_3$ , where E = B, P, As or Bi, the angles  $\text{Cl-E-Cl}$  for different E are in the order [JEE '99]
- (A)  $\text{B} > \text{P} = \text{As} = \text{Bi}$  (B)  $\text{B} > \text{P} > \text{As} > \text{Bi}$   
(C)  $\text{B} < \text{P} = \text{As} = \text{Bi}$  (D)  $\text{B} < \text{P} < \text{As} < \text{Bi}$

21. The most likely representation of resonance structure of p-nitrophenoxide is :



22. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is [JEE 2000]

- (A)  $\text{H}_2\text{O}$  because of hydrogen bonding  
(B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
(C)  $\text{H}_2\text{S}$  because of hydrogen bonding  
(D)  $\text{H}_2\text{Se}$  because of lower molecular weight

23. The hybridization of atomic orbitals of nitrogen in  $\text{NO}_2^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are [JEE 2000]

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

24. The correct order of hybridization of the central atom in the following species  $\text{NH}_3$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is [JEE 2001]

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

25. Specify hybridization of N and B atoms in a 1 : 1 complex of  $\text{BF}_3$  and  $\text{NH}_3$  [JEE 2002]

- (A) N : tetrahedral,  $\text{sp}^3$ ; B : tetrahedral,  $\text{sp}^3$   
(B) N : pyramidal,  $\text{sp}^3$ ; B : pyramidal,  $\text{sp}^3$   
(C) N : pyramidal,  $\text{sp}^3$ ; B : planar,  $\text{sp}^2$   
(D) N : pyramidal,  $\text{sp}^3$ ; B : tetrahedral,  $\text{sp}^3$

26. The nodal plane in the  $\pi$ -bond of ethene is located in [JEE 2002]

- (A) the molecular plane  
(B) a plane parallel to the molecular plane  
(C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon  $\sigma$  bond at right angle  
(D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.

27. Which of the following are isoelectronic and isostructural ?  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{ClO}_3^-$ ,  $\text{SO}_3$

[JEE 2003]

- (A)  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  (B)  $\text{SO}_3$ ,  $\text{NO}_3^-$  (C)  $\text{ClO}_3^-$ ,  $\text{CO}_3^{2-}$  (D)  $\text{CO}_3^{2-}$ ,  $\text{SO}_3$



28. Which species has the maximum number of lone pair of electrons on the central atom ? [JEE 2005]  
(A)  $\text{ClO}_3^-$  (B)  $\text{XeF}_4$  (C)  $\text{SF}_4$  (D)  $\text{I}_3^-$
29. The percentage of p-character in the orbitals forming P–P bonds in  $\text{P}_4$  is [JEE 2007]  
(A) 25 (B) 33 (C) 50 (D) 75
30. The structure of  $\text{XeO}_3$  is [JEE 2007]  
(A) linear (B) planar (C) pyramidal (D) T-shaped
31. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid. because  
**Statement-2** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [JEE 2007]  
(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.
32. **Statement-1** : In water, orthoboric acid behaves as a weak monobasic acid. because  
**Statement-2** : In water, orthoboric acid acts as a proton donor. [JEE 2007]  
(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.
33. The nitrogen oxide(s) that contain(s) N–N bond(s) is/are [JEE 2009]  
(A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (C)  $\text{N}_2\text{O}_4$  (D)  $\text{N}_2\text{O}_5$
34. The species having pyramidal shape is/are : [JEE 2010]  
(A)  $\text{SO}_3$  (B)  $\text{BrF}_3$  (C)  $\text{SiO}_3^{2-}$  (D)  $\text{OSF}_2$



35. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen-  
(A)  $\text{HNO}_3$ , NO,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$  (B)  $\text{HNO}_3$ , NO,  $\text{N}_2$ ,  $\text{NH}_4\text{Cl}$  [JEE 2012]  
(C)  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ , NO,  $\text{N}_2$  (D) NO,  $\text{HNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$
36. The shape of  $\text{XeO}_2\text{F}_2$  molecule is : [JEE 2012]  
(A) Trigonal bipyramidal (B) Square planar  
(C) tetrahedral (D) see-saw
37. The compound(s) with TWO lone pairs of electrons on the central atom is(are) [JEE 2016]  
(A)  $\text{BrF}_5$  (B)  $\text{ClF}_3$  (C)  $\text{XeF}_4$  (D)  $\text{SF}_4$
38. The crystalline form of borax has [JEE 2016]  
(A) Tetranuclear  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  unit  
(B) All boron atoms in the same plane  
(C) Equal number of  $\text{sp}^2$  and  $\text{sp}^3$  hybridized boron atoms  
(D) One terminal hydroxide per boron atom
39. The sum of the number of lone pairs of electrons on each central atom in the following species is  $[\text{TeBr}_6]^{2-}$ ,  $[\text{BrF}_2]^+$ ,  $\text{SNF}_3$ , and  $[\text{XeF}_3]^-$  [JEE 2017]  
(A) Atomic numbers: 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54)
40. The order of the oxidation state of the phosphorus atom in  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$ , and  $\text{H}_4\text{P}_2\text{O}_6$  is:- [JEE 2017]  
(A)  $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6$  (B)  $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_4$   
(C)  $\text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6$  (D)  $\text{H}_3\text{PO}_4 > \text{H}_4\text{P}_2\text{O}_6 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_2$
41. The option (s) with only amphoteric oxides is(are) : [JEE 2017]  
(A)  $\text{Cr}_2\text{O}_3$ , BeO, SnO,  $\text{SnO}_2$  (B) ZnO,  $\text{Al}_2\text{O}_3$ , PbO,  $\text{PbO}_2$   
(C) NO,  $\text{B}_2\text{O}_3$ , PbO, SnO (D)  $\text{Cr}_2\text{O}_3$ , CrO, SnO, PbO
42. The total number of compounds having at least one bridging oxo group among the molecules given below is \_\_\_\_\_.  
 $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{P}_4\text{O}_6$ ,  $\text{P}_4\text{O}_7$ ,  $\text{H}_4\text{P}_2\text{O}_5$ ,  $\text{H}_5\text{P}_3\text{O}_{10}$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_5$  [JEE 2018]
43. Each of the following options contains a set of four molecules. Identify the option(s) where all four molecules possess permanent dipole moment at room temperature. [JEE 2019]  
(1)  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{POCl}_3$ ,  $\text{CH}_3\text{Cl}$  (2)  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{BCl}_3$ ,  $\text{CHCl}_3$   
(3)  $\text{SO}_2$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{H}_2\text{Se}$ ,  $\text{BrF}_5$  (4)  $\text{BF}_3$ ,  $\text{O}_3$ ,  $\text{SF}_6$ ,  $\text{XeF}_6$

## ANSWER KEY

### DO YOURSELF – 1

Question	1	2	3	4	5
Answer	D	B	D	A	C

### DO YOURSELF – 2

Question	2	3	4	5			
Answer	C	B	C	A			

### DO YOURSELF – 3

Question	1	2	3	4	5		
Answer	A	D	D	A	D		

### DO YOURSELF – 4

Question	1	2	3	4	5
Answer	D	A	A	C	C

### DO YOURSELF – 5

Question	1	2	3	4	5
Answer	D	C	B	C	B

**EXERCISE # 1**

1.	D	2.	A	3.	D	4.	B	5.	C	6.	C	7.	C
8.	B	9.	B	10.	D	11.	C	12.	C	13.	C	14.	D
15.	A	16.	D	17.	B	18.	A	19.	C	20.	C	21.	D
22.	D	23.	D	24.	B	25.	B	26.	D	27.	C	28.	B
29.	D	30.	B	31.	C	32.	C	33.	B	34.	D	35.	D
36.	D	37.	D	38.	C	39.	D	40.	B	41.	B	42.	A
43.	A	44.	D	45.	B	46.	C	47.	A	48.	B	49.	D
50.	D	51.	C	52.	C	53.	D	54.	C	55.	A	56.	C
57.	D	58.	C	59.	C	60.	C	61.	A	62.	D	63.	A
64.	C	65.	C	66.	A	67.	B	68.	A	69.	C	70.	D
71.	C	72.	A	73.	C	74.	D	75.	C	76.	C	77.	D
78.	D	79.	D	80.	C	81.	B	82.	C	83.	A	84.	D
85.	B	86.	C	87.	B	88.	C	89.	A	90.	B	91.	C
92.	C	93.	A	94.	C	95.	A	96.	C	97.	B	98.	B
99.	A	100.	A	101.	B	102.	B	103.	C	104.	D	105.	D
106.	C	107.	A	108.	C	109.	C	110.	A	111.	B	112.	D
113.	B	114.	C	115.	D	116.	D	117.	C	118.	C	119.	D
120.	D	121.	C	122.	C	123.	C	124.	A	125.	D	126.	B
127.	B	128.	C	129.	B	130.	D	131.	A	132.	D	133.	B
134.	C	135.	C	136.	D	137.	C	138.	B	139.	C	140.	D
141.	C	142.	D	143.	C	144.	D						

**EXERCISE # 2**

1.	A,B,C,D	2.	A,B,C	3.	A,B,D	4.	A,C,D
5.	A,B,C,D	6.	A,B,C,D	7.	A,B,C	8.	B,D
9.	A,B,C	10.	B,C,D	11.	A,B	12.	A,B,C
13.	A,B,C	14.	A,B	15.	A,D	16.	A,B
17.	A,B	18.	A,B,C	19.	A,C	20.	A,B
21.	A,B,C	22.	B,C	23.	A,B,D	24.	A,C,D
25.	A,C	26.	B,C,D	27.	B,D	28.	A,B,C,D
29.	B,C	30.	A,B,C,D	31.	A,B,C	32.	A,B
33.	A,B	34.	A,B,C	35.	A,B,C,D	36.	A,D
37.	A,C	38.	A,B,C	39.	A,C,D	40.	A,B,C

**EXERCISE # 3**

1.	5	2.	4	3.	3	4.	2	5.	15	6.	2	7.	2
8.	3	9.	4	10.	4	11.	4	12.	2	13.	4	14.	2
15.	4	16.	4	17.	8	18.	4	19.	0	20.	20	21.	3
22.	4	23.	16	24.	8	25.	2	26.	15	27.	3	28.	0
29.	3	30.	4	31.	6	32.	2	33.	3	34.	2		

**EXERCISE # 4**

1.	B	2.	B	3.	C	4.	C	5.	D	6.	D	7.	B
8.	C	9.	A	10.	C	11.	B	12.	B	13.	A	14.	A,B,C
15.	B	16.	A	17.	C	18.	A,B,D	19.	A,D	20.	D	21.	A,B,C,D
22.	A	23.	D	24.	B,C,D	25.	D	26.	B	27.	A	28.	A
29.	D	30.	C	31.	C								

**EXERCISE # 5**

- (A)  $\rightarrow$  (Q) ; (B)  $\rightarrow$  (S) ; (C)  $\rightarrow$  (P) ; (D)  $\rightarrow$  (R)
- (A) – (PQ) ; (B) – (QR) ; (C) – (QR)
- (A)  $\rightarrow$  (Q) ; (B)  $\rightarrow$  (R) ; (C)  $\rightarrow$  (S) ; (D)  $\rightarrow$  (P)
- (A)  $\rightarrow$  (Q) ; (B)  $\rightarrow$  (Q,R) ; (C)  $\rightarrow$  (P,Q,R)
- C
- B
- B
- (A)  $\rightarrow$  (Q) ; (B)  $\rightarrow$  (S) ; (C)  $\rightarrow$  (R) ; (D)  $\rightarrow$  (P)
- [(A) P,Q ; (B) P,Q,R,T ; (C) P,Q,R,S,T ; (D) P,Q,R,S]

**EXERCISE - 6 # JEE-MAIN**

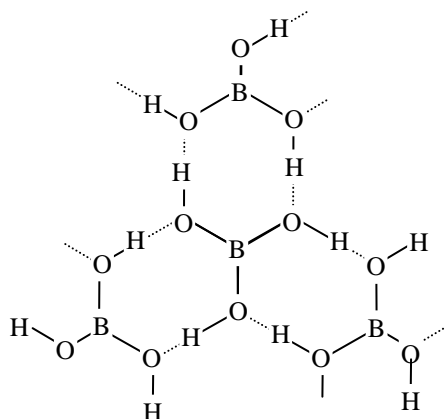
Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	2	1	1	4	3	3	1	4	2
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	4	4	4	2	BONUS	3	3	3	4	1
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	2	4	1	3	2	3	2	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	3	2	2	1	2	2	2	4	4	3
Que.	41	42	43	44	45	46	47	48	49	
Ans.	3	2	2	2	2	1	3	2	4	

**EXERCISE - 7 # JEE-ADVANCED**

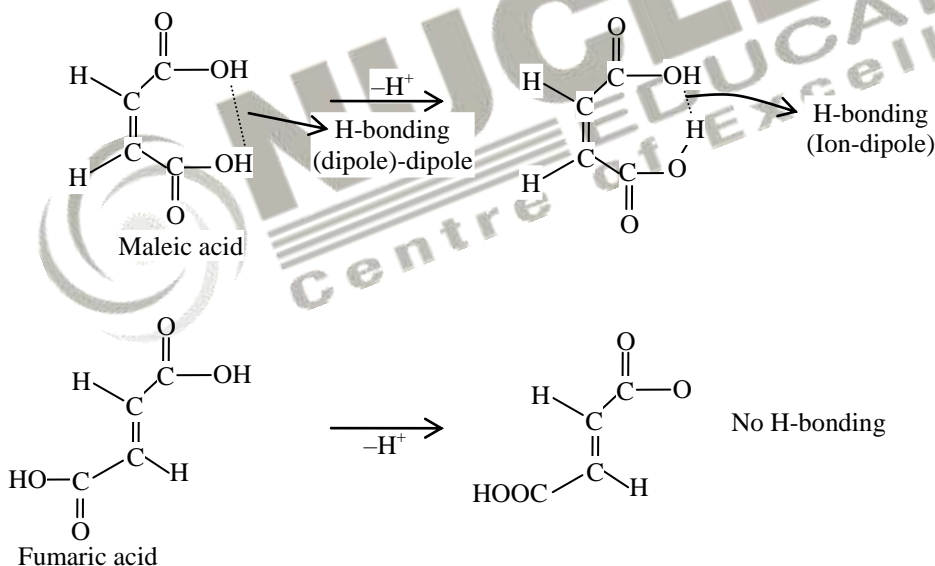
Que.	1	2	3	4	5	6	7	8	9	10
Ans.	4	0	5	6	B,C,D	C	A	A,B,D	C	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	B	C	A	B	A,B,C	B	D	A	B
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	A	A	B	B	A	A	A	D	D	C
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	C	A,B,C or A,C	D	B	D	B,C	A,C,D	6	D
Que.	41	42	43							
Ans.	AB	5,6	1,3							

ANSWER OF HYDROGEN BONDING

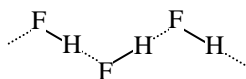
1.



2. Inter molecular H-Bonding in case of para nitro phenol is strong enough to increase boiling point which is not favoured in o-nitro phenol.
3. Maleic acid anion gets stabilize due to intra molecular H-bonding which is not possible in anion of Fumaric acid. So  $H^+$  releasing tendency is more in case of maleic acid.



4. Due to strong H-Bonding in H-F

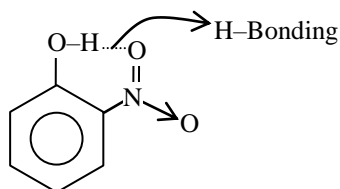


5. Due to H-Bonding in  $NH_3$ .
6. Density of ice is higher than that of water due to cage like structure of ice volume of ice increases and density decreases.

7. On heating ice in temperature range 0–4°C H-bonds of ice break down, which decreases volume, hence density of H<sub>2</sub>O increases. On heating ice after 4°C thermal vibrations of H<sub>2</sub>O molecules increases which increases effective volume of ice, so density of ice again decreases.
8. H-I bond is weak as compare to H-F so it can be dissociated easily and can give H<sup>+</sup> easily.
9. The organic matter in wood participate in H-bonding with water molecules in ice-cream.
10.  $K^+[F-H \cdots F]$  But KHBr<sub>2</sub> & KHI<sub>2</sub> can't form H-Bond.

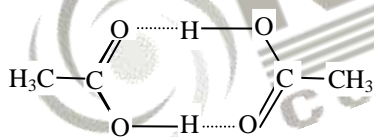
↓  
H-bonding

11. In o-Nitrophenol intra molecular H-bond is present which it's solubility in water.



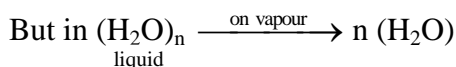
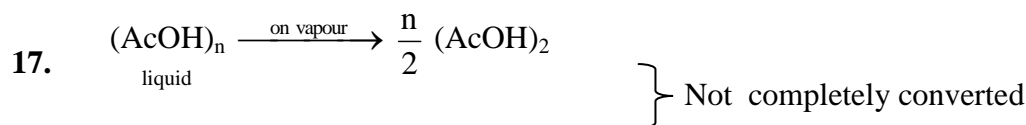
Ortho Nitro-phenol

12. In o-hydroxy benzaldehyde intramolecular H-bond is present which is less stronger than intermolecular H-bond in p-hydroxy benzaldehyde.
13. Extent of H-bonding in glycerol is more as compare to ethanol so it is more viscous.
14. Due to H-bonding in H<sub>2</sub>O
15. Due to H-bonding in acetic acid it forms dimer so overall molecular weight is just double of original



Dimer of CH<sub>3</sub>COOH

16. Due to bigger size of 'Cl' atom it's interaction is not enough to evolve the amount of energy which lies in the range of H-bond.



Here all H<sub>2</sub>O molecule gets vaporised. So change is more

18. As extent of H-bond is more in H<sub>2</sub>O as compare to HF, heat of vaporisation of water is higher than HF.



