

# **Chemical Bonding**

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# Syllabus

# **Chemical Bonding**

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

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# **CHEMICAL BONDING**

#### CHEMICAL BOND :

- (I) A force that acts between two or more atoms to hold them together as a stable molecule.
- (II) It is union of two or more atoms involving redistribution of e<sup>-</sup> among them.
- (III) This process accompanied by decrease in energy.
- (IV) Decrease in energy  $\propto$  Strength of the bond.
- (V) Therefore molecules are more stable than atoms.

#### CAUSE OF CHEMICAL COMBINATION

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

- (I) When two atoms approaches to each other. Nucleus of one atom attracts the electron of another atom.
- (II) Two nuclei and electron of both the atoms repells each other.
- (III) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.

#### (IV) So Attraction $\infty$ 1/energy $\infty$ Stability.

(V) Bond formation is an exothermic process

#### 2. Tendency to acquire noble gas configuration :

- (I) Atom combines to acquire noble gas configuration.
- (II) Only outermost electron i.e. ns, np and (n-1)d electrons participate in bond formation.
- (III) Inert gas elements do not participate, as they have stable electronic configuration and hence minimum energy. (Stable configuration 1s<sup>2</sup> or ns<sup>2</sup>np<sup>6</sup>)

#### **CLASSIFICATION OF BONDS :**



#### ELECTROVALENT OR IONIC BOND :

- (I) 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 **lonic or electrovalent bond.**
- (II) Electro +ve atom loses electron (group IA to IIIA)
- (III) Electro -ve atom gains electron (group VA to VIIA)
- (IV) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond. Electronegativity difference  $\infty$  nature of ionic bond.

Example IA and VIIA group elements form maximum ionic compound.



(V) More the distance between two elements in periodic table more will be ionic character of bond.



#### Representation of formula of compounds :

- (a) 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-
- (b) Write their electrovalencies in figure at the top of each symbol as  $A^{x}B^{y}$
- (c) Now apply criss cross rule as  $A = B^{X}$ , i.e formula AyBx.

Examples :

Calcium chloride 
$$\begin{array}{c} 2 \\ Ca \\ Ca \\ Cl \end{array} = CaCl_2$$

#### **CONDITIONS FOR FORMING IONIC BONDS :**



Energy changes are involved in the following steps -

 $A + IE = A^{+} + e^{-}$  and  $B + e^{-} = B^{-} + EA$ 

This concludes that for lower value of IE and higher value of EA there is more ease of formation of the cation & anion respectively and consequently more chances of electrovalent bond formation.

#### **DETERMINATION OF LATTICE ENERGY:**

#### Born-Haber Cycle (Indirect Method) :

It inter relates the various energy terms involved during formation of an ionic compound.

It a thermochemical cycle based on the Hess's law of constant heat summation.

Hess's Law is the net enthalpy change of a chemical reaction or of any process always remain same whether the reaction takes place in one step or many steps as given in following flow chart.

$$M(s) + \frac{1}{2} X_2(g) \longrightarrow M^+ X^-(s), \qquad \Delta H$$

 $\Delta H_{f}$  = heat of formation of M<sup>+</sup>X<sup>-</sup>  $IE_1 = ionisation energy of M$  $\Delta H_{eg}$  = electron gain enthalpy of X  $\Delta H_{L,E}$  = Lattice energy of M<sup>+</sup> X<sup>-</sup>. So according to Hess's law.  $\Delta H_{f} = \Delta H_{(sub)} + IE_{1} + \Delta H_{(diss)} + \Delta H_{ea} + \Delta H_{L.E.}$ 





#### **HYDRATION:**

All the simple salts dissolve in water, producing ions, and consequently the solution conduct electricity. Since Li<sup>+</sup> is very small, it is heavily hydrated. This makes radius of hydrated Li<sup>+</sup> ion large and hence it moves only slowly. In contrast, Cs<sup>+</sup> is the least hydrated because of its bigger size and thus the radius of the Cs<sup>+</sup> ion is smaller then the radius of hydrated Li<sup>+</sup>, and hence hydrated Cs<sup>+</sup> moves faster, and conducts electricity more readily.



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lon Ionic radius (Å)		Ionic mobility at infinite dilution	Approx. radius of hydrated ion (Å)
Li+	0.76	33.5	3.40
Na+	1.02	43.5	2.76
K+	1.38	64.5	2.32
Rb+	1.52	67.0	2.28
Cs+	1.67	68.0	2.28

Some water molecules touch the metal ion and bond to it, forming a complex. These water molecules constitute the primary shell of water. Thus Li<sup>+</sup> is tetrahedrally surrounded by four water molecules forming coordinate covalent bond between metal ion and four water molecules using a lone pair of electrons on each oxygen atom.



#### **PROPERTIES OF IONIC COMPOUNDS :**

(a) Physical state : Ionic compounds are hard, crystalline and brittle due to strong force of attraction.

**(b) Isomorphism :** Simple ionic compounds do not show isomerism but isomorphism is their important characteristic. Crystals of different ionic compounds having similar crystal structures are known to be isomorphs to each other and the phenomenon is known as isomorphism.

e.g., FeSO<sub>4</sub>.7H<sub>2</sub>O | MgSO<sub>4</sub>.7H<sub>2</sub>O

#### Conditions for isomorphism :

(i) The two compounds must have the same formula type e.g., MgSO<sub>4</sub> & ZnSO<sub>4</sub>; BaSO<sub>4</sub> & KMnO<sub>4</sub> are isomorphous because they have same formula type. All alums are isomorphous because they have same general formula :

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

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



(b)  $NaNO_3 \& NaClO_3$  they have same formula type yet they are not isomorphous because  $NO_3^-$  is trigonal planar but  $ClO_3^-$  pyramidal.



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



#### (c) Boiling point and melting point -

lonic compounds have high boiling point and melting point due to strong electrostatics force of attraction among oppositely charged ions.

#### (d) Conductivity -

It depends on ionic mobility. In solid state - No free ions - Bad conductor of electricity. In fused state or aqueous solution Due to free ions - Good conductor of eletricity. conductivity order : Solid state > Fused state < Aqueous solution

#### (e) Solubility -

- Highly soluble in water (Polar solvents). Example : NaCl in water
- (I) The Na<sup>+</sup> ions get associates with- vely charged 'O' of water
- (II) And CI<sup>-</sup> ions associates with +vely charged 'H' of water.



Oxygen atom of  $H_2O$  give its electron to Na<sup>+</sup>



H atom of  $H_2O$  gain electron from  $CI^{-}$ 

(III) Thus charge on Na<sup>+</sup> and Cl<sup>-</sup> decreases and electrostatics force of attraction also decreases which leads to free ion.

(IV) The energy released due to interaction between solvent and solute is called solvation energy.If water is used as solvent it is called hydration energy.

(V) For an ionic compound to be soluble in water - Hydration energy > Lattice energy

Lattice energy  $\propto \frac{1}{\text{Solubility}}$ Hydration energy  $\propto$  Solubility.

Hydration energy (H)  $\propto \frac{1}{r^+} + \frac{1}{r^-} \{r^+ \& r^- \text{ are radius of cation and anion}\}$ 

(VI) Hydration energy mainly depends on the cation radius because the value  $\frac{1}{r^{-}}$  is negligible in

comparison to  $\frac{1}{r^+}$ .

(VII) Down the group both the lattice energy & hydration energy decreases, if decreases in lattice is greater than hydration energy, solubility increases down the group and vice versa.

#### **POLARISATION :**

#### (Fajan's Rule) (Covalent nature in ionic bond) :

#### **Polarisation Power :**

The ability of cation to polarise a nearby anion is called Polarisation power of cation.

$$\bigcirc \qquad (\overline{A}) \qquad \longrightarrow \qquad \bigcirc (\overline{A})$$

#### Polarizability :

- (I) ability of anion to get polarised by the cation.
- (II) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
- (III) Polarisation  $\propto$  Covalent character
- (IV) Magnitude of polarisation depends upon a no. of factors, suggested by Fajan and are known as Fajan's rule.



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#### Fajan's rule : (Factors Affecting Polarisation) :

(a) Size of cation : - Polarisation of the anion increases as the size of cation decreases.

 $\begin{array}{c|c} Polarisation \propto \frac{1}{size \ of \ cation} \\ In \ a \ group \ - \\ BeCl_2 \\ MgCl_2 \\ CaCl_2 \\ SrCl_2 \\ BaCl_2 \\ BaCl_2 \end{array} + \begin{array}{c} Size \ of \ cation \ increases \\ - \ Covalent \ character \ decreases \\ - \ Ionic \ character \ increases \\ BaCl_2 \end{array}$ 

 Greatest polarising power of Be<sup>2+</sup>, shows its maximum covalent character In a period –

Na⁺, Mg⁺², Al⁺³, Si⁺⁴

- Size of cation decreases

- Covalent charater increases

(b) Size of anion : - If the size of the anion increases for a given cation, the covalent character increases/Nature Polarisation  $\propto$  size of anion.

CaF<sub>2</sub> CaCl<sub>2</sub> - Size of anion increases CaBr<sub>2</sub> - Covalent character increases Cal<sub>2</sub> - Ionic character decreases

- (c) Charge on cation and anion : -
- Polarisation  $\infty$  charge on cation anion
  - (I) Charge on cation  $\propto$  Polarisation (covalent character)

eg. NaCl	MgCl <sub>2</sub>	AICI <sub>3</sub>	SiCl <sub>4</sub>
Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Si <sup>4+</sup>

- Charge on cation increases
- Covalent character increases
- Ionic character decreases (M.P. decreases)

Charge on anion  $\propto$  polarisation  $\propto$  covalent nature  $\propto \frac{1}{MP}$ 

#### (d) Electronic configuration of cation : -

Polarisation capacity of cation having pseudo inert gas configuration is high. If the size of cations is same than that of cation having inert gas configuration.

CuCl (M.P. 442°C)  $\rightarrow$  Cu<sup>+</sup> 2, 8, 18 (Covalent)

NaCl (M.P. 800°C)  $\rightarrow$  Na<sup>+</sup> 2, 8 (lonic)

 $\rm Cu^+$  and Na^+ both the cation (Pseudo & inert) have same charge and size but polarising power of Cu^+ is more than Na^+ because –

 $Z_{eff}$  of ns<sup>2</sup>p<sup>6</sup> (inert) <  $Z_{eff}$  of ns<sup>2</sup>p<sup>6</sup>d<sup>10</sup> (pseudo)

(Ionic) (Covalent)

So CuCl has more covalent character than NaCl.



#### COVALENT BOND :

The **Lewis-Langmuir theory** can be understood by considering the formation of the chlorine molecule, Cl<sub>2</sub>. The Cl atom with electronic configuration, [Ne]<sup>10</sup> 3s2 3p5, is one electron short of the argon configuration. The formation of the Cl molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both

$$: \overset{\circ}{\Box} + : \overset{\circ}{\Box} \longrightarrow \underbrace{: \overset{\circ}{\Box} : \overset{\circ}{\Box} : \overset{\circ}{\Box} :}_{\text{or } \mathsf{Cl} - \mathsf{Cl}} \overset{\circ}{Be^{-}} \overset{\circ}{Be^{-}}$$

Covalent bond between two Cl atoms

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

#### **LEWIS OCTET RULE :**

- (I) Every atom has a tendency to complete its octet outermost.
- (II) H has the tendency to complete its duplet.
- (III) To acquire inert gas configuration atoms loose or gain electron or share electron.

(IV) The tendency of atoms to achieve eight electrons in their outer most shell is known as Lewis octet rule.



Obeys octet rule



Doesn't obeys octet rule

#### **EXCEPTION OF OCTET RULE :**

#### (a) Incomplete octet molecules : - or (electron defficient molecules)

Compound in which octet is not complete in outer most orbit of central atom. Examples - Halides of IIIA groups, BF<sub>3</sub>, AICl<sub>3</sub>, BCl<sub>3</sub>, hydride of III A/13<sup>th</sup> group etc.

In BCl<sub>3</sub> Boron has only 6 electrons

Other examples - BeCl<sub>2</sub> (4e<sup>-</sup>), ZnCl<sub>2</sub>(4e<sup>-</sup>), Ga(CH<sub>3</sub>)<sub>3</sub> (6e<sup>-</sup>)

#### (b) Expansion of octet or (electron efficient molecules)

Compound in which central atom has more than  $8e^-$  in outermost orbits. Example - In PCl<sub>5</sub>, SF<sub>6</sub>, IF<sub>7</sub>, the central atom P, S and I contain 10, 12, and 14 electrons respectively.



Electron dot formula of PCl<sub>5</sub>

- (c) I-Pseudo inert gas configuration : -
- (i) Cations of transition metals, which contains 18 electrons in outermost orbit Examples : Ga<sup>+3</sup>, Cu<sup>+</sup>, Ag<sup>+</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup>, Sn<sup>+4</sup>, Pb<sup>+4</sup> etc. Electronic configuration of Ga - 1s<sup>2</sup>, 2s<sup>2</sup>2p<sup>6</sup>, 3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>, 4s<sup>2</sup>4p<sup>1</sup>

Electronic configuration of Ga<sup>+3</sup> - 1s<sup>2</sup>, 2s<sup>2</sup> 2p<sup>6</sup>,  $\frac{3s^23p^63d^{10}}{18e^{-1}}$ 

#### (d) Odd electron molecules : -

Central atom have an unpaired electron or odd no (7e<sup>-</sup>,  $11e^-$  etc) of electrons in their outer most shell.

Examples : NO, NO<sub>2</sub> CIO<sub>2</sub> etc.





#### COORDINATE BOND (DATIVE BOND) :

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



#### FORMAL CHARGE :

Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :



#### Modern Theories of Covalent bond :

- (i) Valence bond theory (VBT)
- (ii) Valence shell electron pair repulsion (VSEPR) theory
- (iii) Molecular orbital theory (MOT)

#### VBT :

#### **Orbital Overlap Concept**

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

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

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

#### **Overlapping of Atomic Orbitals**

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

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





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

#### Types of Overlapping and Nature of Covalent Bonds

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

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

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



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





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CHEMICAL BONDING\_ADVANCED # 8

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



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



#### Figure

#### 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)

#### **BOND PARAMETERS**

- (I) Bond Lengthe (Bond distance) (II) Bond Angle (III) Bond Energy
- (I) Bond Lenght :- The average distance between the nucleus of two atoms is known as bond lenght, normally it is represented in Å. eg. A B
  - It depends mainly on electronegativilties of constituent atoms

**Case - I** Electronegativity difference is zero then-Bond length =  $r_A + r_B$ 

Or 
$$d_{A-B} = r_A + r_B$$

where  $_{\!A}$  is covalent radius of A

r<sub>B</sub> is covalent radius of A

 $X_{\mathsf{A}}$  is electronegativity of  $\mathsf{A}$ 

- $X_B$  is electronegativity of B
- $r_A = r_B$  then Bond length =  $2r_A$  or  $2r_B$

Electronegative difference is not equal to zero then-

Bond length is given by shomaker & Stevenson formula is Bond length =  $r_A + r_B - 0.09 (X_A - X_B)$ Difference in electronegativities

#### Factors affecting Bond Length :-

lf

Case II

- (a)  $\Delta$  electronegativity :- Bond lengh  $\propto \frac{1}{\Delta EN}$  (While B.E.  $\propto \Delta EN$ ) H-F < H-Cl < H-Br < H-I
- (b) bond order or number of bonds :- Bond length  $\propto \frac{1}{\text{Number of bond or bond order}}$ Bond energy  $\propto$  Number of bond e.g. C-C, C = C, C = C
  - Bond length 1.54 Å 1.34 Å 1.20 Å





Example : -	Compound	Hybridisation	Bond length
s	Ethane	sp <sup>3</sup> — sp <sup>3</sup>	1.54 Å
crease	⇒cc=	sp <sup>3</sup> —sp <sup>2</sup>	1.51 Å
cter in	->cc≡c	sp <sup>3</sup> — sp	1.47 Å
hara	C=C-C=C	sp <sup>2</sup> — sp <sup>2</sup>	1.46 Å
с v	C=C−C≡C	sp²— sp	1.42 Å
*	c≡c–c≡c	sp sp	1.37 Å

(II) Bond Angle :- The angle between any two adjacent bond is known as bond angle. It is represented in degree (°), min (') and second (")

180°

#### Factors affecting the bond angle-

120°

#### (b) Hybridisation :-

#### Case 1

When hybridisation is same, bonded atoms are same, central atom and lone pair are different.

Then bond angle  $\propto \frac{1}{\text{No.of lone pair}}$ 

Example :-	$CH_4$	<mark>й</mark> н <sub>з</sub>	H₂Ö
Hybridisation	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup>
Bond angle	109 >	107 >	105
No 1.p	. one 1.p. two 1.p.		



#### Case-II

When hybridisation is same, bonded atoms are same lone pair is same but central atom is different. Then bond angle  $\infty$  electrongativity of central atom

Exa	mple:-	NH <sub>3</sub>	PH <sub>3</sub>	ÅsH <sub>3</sub>				
Bon	d angle	107°	93°	91°				
			<ul> <li>Eletroneg</li> </ul>	ativity decreasi	ng			
			<ul> <li>Bond ang</li> </ul>	le will decreas	е			
Cas	e-III							
Whe	en hybridisa	ation is s	ame, lone p	oair are same, 0	Central at	om is same, t	onded atoms	are different.
	$sp_3$		OF <sub>2</sub>	103 – 105	0	Electroneg	ativity	
	$sp_3$		Cl <sub>2</sub> O	109 – 111	l°	of bonded	atom is	
	$sp_3$		Br <sub>2</sub> O	116 – 118	3°,	decreasing	I	
Here	e bond ang	$g = \infty \frac{1}{e e}$	ctrongativity	1 v of bonded ato	— ∝ size m	of side atom		
(III) Bo	nd Energy	/ (BE) :-	Bond energ	gy may be difin	ed as-			
	a) Bond fo) energy (	ormation e	energy:- Ene energy.	ergy released w	hen any b	ond is formed	is known as bo	ond formation
	(b) Bond di	ssociation	n energy :- E	nergy required	to dissocia	ite any bond is	known as bone	d dissociation
	Calculati	on of rele	eased energ	v is more diffcu	It than the	dissociation e	neray therefore	e dissociation
	energy of	of bond is	s calculated	and is assum	ed as bor	nd energy or l	cond formation	i energy.
Cas	e-I In (	diatomic	molecule :					
	Bo	nd energ	y = bond di	ssociation ene	rgy			
eg :	- N <sub>2</sub>	$> 0_2 >$	$H_{2} > F_{2}$					
Cas	e-II Foi	r polyator	mic molecul	e :-				
	Bo	nd energ	y ≀ Bond o	dissociation ene	ergy (D)			
		Η.						
eg;-	H–	–C—H E	Bond energy	y = per C—H b	oond is 99	.5 K. Cal/mol	le	
-		 H						
The	oritical valu	les of bo	nd dissociat	ion energy (D)	of individ	ual C—H bon	ds CH <sub>4</sub> are giv	en below-
	D (CH <sub>3</sub>	<sub>с</sub> —Н)	=	102 K Cal/mol	е			
	D (CH <sub>2</sub>	<u>-</u> H)	=	105 K Cal/mol	е			
	D (CH-	—H)	=	108 K Cal/mol	е			
	D (C—	H)	=	83 K Cal/mole				
Hen	ce bond er	nergy E p	oer C—H bo	ond in methane	$e = \frac{398}{4} =$	99.5 K Cal/m	ole.	
● Fact	Bond disso t <b>ors affect</b>	ociation e t <b>ing the</b>	nergy (D) is <b>bond energ</b>	s related to the <b>gy:-</b>	e state of	hybirdisation.		
	(a) ∆ Elect	tronegativ	vity (b) I	Bond order	(c) Ate	omic size	(d) Bond pol	arity
	(e) Resona	ance	(f) ⊢	lybridisation	(g) Lor	e pair electro	'n	
(a) ⊿	Electron	egativity	·:- Bond er	nergy ∞∆EN				
	eg. HF >	HCI > H	Br > HI					
(h)	Bond orde	r :- Bon	d energy or	Bond order				
(5)	ea. C—C		< onlongy ~	C = C <		С =	≡ C	
	79 K	Cal.	-	143.3 K. Ca	I	199	.0 K. Cal.	
		,			,	.00		



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(c) Atomic size :- Bond energy  $^{\infty}$ Atomic size

eg. C≡C C≡N < N≡N

Exception :- In case of halogen group, order of bond energy is-

CI - CI > Br - Br > F - F > I - I

Because of higher electron densityb and small size of F atoms, repulsion between of two F atom, weakens the bond energy.

Other ex. S - S > O - OC - C > Si - Si > Ge - Ge

- (d) Bond Polarity :- Bond energy  $\propto$  polarity eg. H—F > H—Cl > H—Br > H—I
- (e) Resonance :- Bond energy increases due to resonance In benzene bond energy of C—C increases due to  $\pi$  electrons of C = C. ea.
- (f) Hybridisation :- Bond energy  $\propto$  s-character in hybrid orbitals.

eq. sp—sp  $> sp^2 - sp^2 > sp^3 - sp^3$ s. character- 50% 33.3% 25%

$$-C - C - > N - N < - C - > N - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N < - N <- N <- N <-- N <--$$

Size of F and O atoms small so their bond energy should be high (small atomic radius) but it is actually less due to lone pair of electrons present on F and O atoms, which repells each other in F-F and -O-O- type of bonds.

1

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

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

#### The main postulates of VSEPR theory are as follows :

- (i) The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded] around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged. (ii)
- (iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum (iv) distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond (v) are treated as a single super pair.
- (vi) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

#### The repulsive interaction of electron pairs decreases in the order :

lone pair ( $\ell p$ ) - lone pair ( $\ell p$ ) > lone pair ( $\ell p$ ) - bond pair (bp) > bond pair (bp) - bond pair (bp)

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

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



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

Table





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

Та	ıbl	e

Molecule type	No.of bonding pairs	No.of Ione pairs	Arrangement of electron pairs	Shape	Examples
AB <sub>2</sub> E	2	1	і В В	Bent	SO <sub>2</sub> ,O <sub>3</sub>
AB₃E	3	1	і В В В	Trigonal pyramidal	$NH_3$
$AB_2E_2$	2	2	A B B	A Bent	
AB₄E	4	1		See saw	SF₄
$AB_3E_2$	3	2	B-A B	T–shape	CIF3
AB₅E	5	1	B A B B B	Square pyramidal	$BrF_{\mathfrak{s}}$
$AB_4E_2$	4	2	B B Square B B B		XeF <sub>4</sub>

#### **HYBRIDISATION:**

Consider an example of Be compound :-If it is formed without hybridisation then -

## $CI\frac{s-p}{Be}Be\frac{p-p}{CI}$

both the Be–CI bonds should have different parameters and p-p bond strength >s-p bond strength. Practically bond strength and distance of both the Be-CI bonds are same.

This problem may overcome if hybridisation of  $\boldsymbol{s}$  and p-orbital occurs.

#### Hybridisation :

- (I) It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.
- (II) Definition : Mixing of different shapes and approximate equal energy atomic orbitals, and redistribution of energy to form new orbitals, of same shape & same energy. These new orbitals are called hybrid orbitals. and the phenomenon is called hybridisation.

Now after considering s-p hybridisation in BeCl<sub>2</sub>

 $CI \xrightarrow{sp - sp} Be \xrightarrow{sp - p} CI$ 

bond strength of both the bonds will be equal.



#### Characteristic of Hybridisation :

- (I) Hybridisation is a mixing of orbitals and not electrons. Therefore in hybridisation full filled, half filled and empty orbitals may take part.
- (II) Number of the hybrid orbitals formed is always be equivalent to number of atomic orbital which have taken part in the process of hybridisation.

Structure of hybrid orbital

- (III) Each hybrid orbital having two lobes, one is larger and other is smaller. Bond will be formed from large lobe.
- (IV) The number of hybrid orbitals on central atom of a molecule or ion = number of  $\sigma$  bonds
  - + lone pair of electron.
  - (i) The 1<sup>st</sup> bond between two atoms will be sigma.
  - (ii) The other bond between same two atoms will be pi bond.
  - (iii) Maximum two pi bonds may be present on a single atom.
  - (iv) The electron pair of an atom which do not take part in bond formation called as lone pair of electron.

(v) One element can represent many hybridisation state depending on experimental conditions for example, C showing sp,  $sp^2$  and  $sp^3$  hybridisation in its compounds.

(vi) Hybrid orbitals are differentiated as **sp**, **sp**<sup>2</sup>, **sp**<sup>3</sup> etc.

(vii) The order of repulsion between lp & bp is : lp - lp > lp - bp > bp - bp

(viii) The directional properties in hybrid orbital is more than atomic orbitals. Therefore hybrid orbitals form stronger sigma bond. The directional property of different hybrid orbitals will be in following order.

#### $sp < sp^2 < sp^3 < sp^3d < sp^2d^2 < sp^3d^3$

#### Difference between hybridisation & overlapping

Overlapping	Hybridisation
<ul> <li>It occurs between orbitals of two atoms</li> </ul>	It occurs among orbitals of the same atom
<ul> <li>Only half filled orbitals takes part in overlapping</li> </ul>	<ul> <li>Any type of orbital can participates</li> </ul>
<ul> <li>It occurs during bond formation bond formed after hybridisation</li> </ul>	<ul> <li>Process, just before overlapping.</li> </ul>
<ul> <li>Orbital of different energies may participates in excited states.</li> </ul>	<ul> <li>It may takes place in ground or in excited state</li> <li>Inground state – NH<sub>3</sub>, NCl<sub>3</sub>, PH<sub>3</sub>, PCl<sub>3</sub>,</li> </ul>
<ul> <li>Molecular orbitals are formed</li> </ul>	<ul> <li>Hybridised orbitals are formed</li> </ul>

#### Determination of hybridisation state -

#### Method (I) :

- Count the following pair of e<sup>-</sup> arround the central atom :
- (a) Count all pure  $\sigma$  bonded electron pairs (or  $\sigma$  bonds)
- (c) Count Co ordinate bond

- (b) Count all lone pair of electron
- (d) Count negative charge



#### Method (II) :

To predict hybridisation following formula may be used :

No. of hybrid orbital =  $\frac{1}{2}$  [Total number of valence e<sup>-</sup> in the central atom + total number of monovalent atoms - charge on cation + charge on anion]  $\frac{1}{2}[5 + 4 - 1] = 4$  sp<sup>3</sup> hybridisation.  $NH_{4}^{+}$ eg. SF<sub>4</sub>  $\frac{1}{2}$ [6+4] = 5 sp<sup>3</sup>d hybridisation.  $\frac{1}{2}$ [6 + 2] = 4 sp<sup>3</sup> hybridisation.  $SO_4^{2-}$ ('O' is divalent so add only charge on anion)  $\frac{1}{2}[5 + 1] = 3$ sp<sup>2</sup> hybridisation. NO<sub>3</sub> If such type of e<sup>-</sup> pairs are hybridisation two sp sp<sup>2</sup> hybridisation three \_ sp<sup>3</sup> hybridisation four sp<sup>3</sup>d hybridisation five six sp<sup>3</sup>d<sup>2</sup> hybridisation

#### **DIPOLE MOMENT**

#### (Ionic Nature in Covalent Bond)

- (I) Polarity of any polar covalent bond or moleucule is measured in terms of dipole moment.
- (II) For measurement of extent of polarity, Pauling introduced the concept of dipole moment (μ). The product of positive or negative charge (q) and the distance (d) between two poles is called dipole moment.

hybridisation

#### Here - $\mu$ = q × d (magnitude of charge × distance)

seven -

(III) Dipole moment is a vector quantity i.e. it has both magnitude as well as direction.

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

(IV) Direction of dipole moment is represented by an arrow pointing from electro +ve to electro -ve element and from central atom to lone pair of electrons.

(V) Unit of dipole moment is Debye

u

1 Debye =  $1 \times 10^{-18}$  esu cm.

=  $1.6 \times 10^{-29}$  coulomb metre

(VI) In the diatomic molecule  $\mu$  depends upon difference of EN i.e.  $\mu \propto \Delta \text{EN}$ 

order of  $\mu$  : H-F > H-Cl > H-Br > H-I

$$L = 0$$
 for H–H, F–F, CI–CI, Br–Br, O–O

- (VII) For polyatomic molecules  $\boldsymbol{\mu}$  depends on the vector sum of dipole moments of all the covalent bonds.
- (VIII) For  $PCl_5$  and  $SF_6$ , etc.  $\mu = 0$  due to their regular geometry.
- (IX) Benzene, naphthalene, diphenyl have  $\mu = 0$  due to planar structure.
- (X) If the vector sum is zero, than compound is non-polar compound or symmetrical compound (and it is not essential that individual μ of every bond should be zero).

Example : (A)  $BX_3$ ,  $CCI_4$ ,  $SiCI_4$ ,  $CH_4$ ,  $CO_2CS_2$ ,  $PCI_5$ ,  $SiH_4$  etc.

In these examples the bond B–F, C–CI, C–H, C–O, P–CI etc. are polar even though compounds are non-polar.



(B)  $\ddot{\mathbf{N}}\mathbf{H}_3$   $\ddot{\mathbf{P}}\mathbf{H}_3$   $\ddot{\mathbf{N}}\mathbf{F}_3$ 



Total  $\mu = \mu_1 + \mu_2 + \mu_3 + \mu_4 = 1.47D$ 

(XI) Dipole moment of H<sub>2</sub>O is 1.85 D which is resultant  $\mu$  of two O-H bonds.



 $\mu$  of H<sub>2</sub>O  $\mu$  of H<sub>2</sub>S because electronegativity of oxygen is higher than sulphur.

(XII) Angular structure of molecule have greater dipole moment.

#### Application of dipole moment :

- (I) To determine polarity and geometry of molecule -
- (II) To calculate % ionic character :-

% lonic character =  $\frac{\text{Experimental value of }\mu}{\text{Theoritical value of }\mu} \times 100$ 

(III) To distinguish cis form or trans form:-Some important orders of diple moments-

$HF > H_2O > NH_3 > NF_3$	$H_2O > H_2S$
$CH_3CI > CH_3F > CH_3Br > CH_3I$	$BF_3 < NF_3 < NH_3$
$HF > H_2O > SO_2 > NH_3$	$PH_3 < PCI_3$
$NO_2^- > NO_2 > NO_2^+$	$H_2O < H_2O_2$

#### RESONANCE

- (I) The concept of resonance was introduced by heisen berg (1920), and later developed by pauling and ingold, to explain the properties of certain molecules,
- (II) 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 resonane hybrid and the different individual structures are called resonating structures or canonical forms. This phenomeni is called resonance.
- (III) Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O—O = 1.48Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



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

Bond order = Totalnumber of bonds in a molecule Resonating Structures



#### Some special bonding situations:

eg.

#### (a) Electron deficient bonding:

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



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

structure.

#### (b) Back Bonding :

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF<sub>3</sub> the boron atom completes its octet by accepting two 2p-electrons of fluorine into 2p empty orbital.



Decrease in B – F bond length is due to delocalised  $p\pi$ – $p\pi$  bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :

 $BF_3 > BCI_3 > BBr_3$ 

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

- O The extent of back bonding decreases if the atom having vacant orbitals is also having some non-bonded electron pairs on it. So among the atoms of third period the extent of back bonding follows the order Si > P > S > Cl
- **O** The extent of  $p\pi$ - $p\pi$  overlapping  $\propto \frac{1}{\text{Lewis acid character}}$



Ο

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

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



 $p\pi - d\pi$  overlap

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

#### VANDER WAAL'S FORCES

- (a) This type of attractive forces occurs in case of non polar molecules such as  $H_2$ ,  $O_2$ ,  $CI_2$ ,  $CH_4$ ,  $CO_2$  etc.
- (b) The existence of weak attractive forces among the nonpolar molecule was first proposed by dutch scientist J.D. Vander Waal
- (c) Vander waal force  $\infty$  molecular weight
  - ∞ Atomic weight
  - $\propto$  Boiling point

Types of Vander Waal's force : -

(i) Ion dipole attraction - This force is between an ion such as Na+ and a polar molecule such as HCI



(ii) Dipole Dipole attraction - It is again in between two polar molecules such as HF and HCI



(iii) lon induced dipole attraction - In this case a neutral molecule is induced by an ion as a dipole as shown in fig





after induction

(iv) Dipole - Induced dipole attraction : In this case a neutral molecule is induced as a dipole by another dipole as shown in fig.



HCI



e.g.

ETOOS ACADEMY Pvt. Ltd

(v) Induced dipole - induced dipole attraction or London dispersion force between two non polar molecules as in Cl<sub>2</sub>, He etc.



**Note:** The relative strength of various bonds is as follows Ionic bond > Covalent bond > Metallic bond > H-bond > Vander waal bond

#### HYDROGEN BOND

#### **Definintion**:

- (I) It is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electonegative atom (F, O, N)
- (II) It is not formed in ionic compounds
- (III) H-bond forms in polar covalent compouds, (not in non-polar)
- (IV) It is also known as dipole-dipole attraction

$$\mathsf{H}^{\delta_+} - \mathsf{F}^{\delta_-} \dots \mathsf{H}^{\delta_+} - \mathsf{F}^{\delta_-} \dots \mathsf{H}^{\delta_+} - \mathsf{F}^{\delta_-}$$

#### Main condition for H-bonding : -

- (I) H- should be covalently bonded with high electro-ve element like F, O, N
- (II) Atomic size of electro-ve element should be small.

Decreasing order of atomic size is- N > O > FDecreasing order of atomic size is- F > O > N(4.0) (3.5) (3.0)

- (III) Strength of H–bond  $\infty$  Electronegativity of Z (element)  $\infty \frac{1}{\text{atomic size of Z}}$
- (IV) Hydrogen bonding occurs in HCN, due to  $(-C \equiv N)$  triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.

$$H-C \equiv N....H-C \equiv N...H-C \equiv N$$



#### (A) Intermolecular H-bond

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

These are two types.

(i) Homointermolecular :- H-bond between molecules of same compounds.

eg.





(ii) **Hentro intermolecular :-** H–bond between molecules of different compounds. eg. alcohol, water



- (B) Intra molecula H-bond :- It takes place within the molecule.
  - (i) H-bonded with electronegative elements of a functional group, form H-bond with another electronegative element present on nearest position on the same molecule.
  - (ii) This type of H-bond is mostly occured in organic compounds.
  - (iii) It result in ring formation (Chelation).
    - eg.



#### Hydrolysis :

**Hydrolysis** means reaction with water molecules ultimately leading to breaking of O-H bond into H<sup>+</sup> and OH<sup>-</sup> ions. While the term **Hydration** means the surrounding of polar molecule or ions by polar molecules of water. In hydrolysis there is complex formation with water molecule or reaction with water molecule.

Hydrolysis in covalent compounds takes place generally by two mechanisms

(a) By Coordinate bond formation : Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbitals.

(b) By H-bond formation : For example in Nitrogen trihalides

(a) Hydrolysis via coordinate bond formation :

Hydrolysis of SiCl<sub>4</sub> (due to presence of vacant d-orbitals on silicon)



(b) By H-bond formation : Hydrolysis of NCl<sub>3</sub> (N has no vacant orbitals)

$$\begin{array}{c} H \rightarrow 0 \\ H \rightarrow 0 \\ H \\ H \end{array} \rightarrow NH_3 + HOCI$$

O By similar mechanism there will be hydrolysis of NBr<sub>3</sub> and NI<sub>3</sub> but NF<sub>3</sub> does not undergo hydrolysis mainly because it is a polar molecule and also the hydrolysis product FOH is an unstable compound.



#### Molecular Orbital Theory (MOT) :

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

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

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

Let us begin by discussing the case of molecular hydrogen. An approximate description of the molecular orbitals in H<sub>2</sub> can be obtained by considering them as Linear Combinations of Atomic Orbitals (LCAOs). Let us label the nuclei A and B. The lowest energy orbital associated with each nucleus is the 1s orbital, and each of these atomic orbitals may be represented by wave function  $\psi_A$  or  $\psi_B$ . Now each molecular orbital may also be represented by a wave function which is a suitable linear combination of atomic orbitals; since A and B are identical atoms their atomic orbitals obviously contribute equally to molecular orbitals. In this case we can write down two molecular orbitals derived by combining the 1s atomic orbitals, these being

 $\label{eq:presented by: } \psi_m = \ [\psi_A + \psi_B] \ ; \qquad \quad \psi_m^* = [\psi_A - \psi_B]$ 

The molecular wave functions  $\psi_m$  and  $\psi^*_m$  are bonding and antibonding molecular orbitals.

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

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

#### ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

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

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

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



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



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

#### ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR :

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

(i) The molecule is stable if  $N_b$  is greater than  $N_a$ , and

(ii) The molecule is unstable if N<sub>b</sub> is less than N<sub>a</sub>
 In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.
 N<sub>b</sub> is number of electrons in bonding molecular orbitals and N<sub>a</sub> is number of electrons in antibonding molecular orbitals.



#### **BOND ORDER**

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

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

#### NATURE OF THE BOND

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

#### **BOND-LENGTH**

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

#### **MAGNETIC NATURE**

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

#### Metallic bond :

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

#### **Electron-Sea Model**

Metals have ability to conduct electricity, ability to conduct heat, ease of deformation [that is, the ability to be flattened into sheets (malleability) and to be drawn into wires (ductility)] and lustrous appearance.

One over simplified model that can account for some of these properties is the electron-sea model. The metal is pictured as a network of positive ions immersed in a "sea of electrons". In lithium the ions would be Li<sup>+</sup> and one electron per atom would be contributed to the sea. These free electrons account for the characteristic metallic properties. If the ends of a bar of metal are connected to a source of electric current, electrons from the external source enter the bar at one end. Free electrons pass through the metal and leave the other end at the same rate.

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





# **PART - I : OBJECTIVE QUESTIONS**

* Mark	ed Questions are hav	ing more than one co	rrect option.					
Secti	on (A) : Ionic bond							
A-1.	Which of the following c (A) $CH_{3}CI$	ompound has electrovale (B) NaCl	ent linkage ? (C) CH <sub>3</sub> OH	(D) CH <sub>3</sub> COOH				
A-2.	<ul> <li>An ionic bond A<sup>+</sup> B<sup>−</sup> is most likely to be formed when :</li> <li>(A) the ionization energy of A is high and the electron affinity of B is low</li> <li>(B) the ionization energy of A is low and the electron affinity of B is high</li> <li>(C) the ionization energy of A and the electron affinity of B is high</li> <li>(D) the ionization energy of A and the electron affinity of B is low</li> </ul>							
A-3.	Select the correct order (A) $SrSO_4 < CaSO_4 < M$ (C) $Ba(OH)_2 > Sr(OH)_2 >$	of solubility (in water) fro $IgSO_4 < BeSO_4$ > Ca(OH) <sub>2</sub> > Mg(OH) <sub>2</sub>	m the following : (B) NaF < KF < RbF < (D) All of these	CsF				
A-4.	Anhydrous AIC $\ell_3$ is cova Lattice Energy = 5137 k $\Delta$ H hydration fo $\Delta$ H hydration fo identify the correct state (A) It will remain covaler (B) The solution will corr (C) The solution will corr (D) None of these	alent. From the data giver KJ/mol. or $A\ell^{3+} = -4665 KJ/mol$ or $C\ell^{-} = -381 KJ/mol$ ement. Int in aqueous solution insist of $A\ell^{3+} \& C\ell^{-}$ insist of hydrated $A\ell^{3+} \& C\ell^{-}$	n below ∶ℓ					
A-5.	Which is the most ionic (A) NaF	: ? (B) Na <sub>2</sub> O	(C) Na <sub>3</sub> N	(D) All same				
A-6.	The correct order of the (A) $BeBr_2 < MgBr_2 < Ca$ (C) $BeBr_2 < BaBr_2 < Mg$	increasing ionic character $Br_2 < BaBr_2$ $Br_2 < CaBr_2$	er is : (B) BeBr <sub>2</sub> < MgBr <sub>2</sub> < Ba (D) BaBr <sub>2</sub> < MgBr <sub>2</sub> < Ca	Br <sub>2</sub> < CaBr <sub>2</sub> aBr <sub>2</sub> < BeBr <sub>2</sub>				
A-7.	Which of the following c (A) PbCl <sub>2</sub>	compounds of elements i (B) PbCl <sub>4</sub>	n group IV is expected to (C) CCl <sub>4</sub>	be most ionic ? (D) SiCl <sub>4</sub>				
A-8.	Which of the following is	s in order of increasing co	valent character ?					
	(A) $CCI_4 < BeCI_2 < BC$	I <sub>3</sub> < LiCl	(B) LiCl < CCl <sub>4</sub> < BeCl <sub>2</sub>	$_2 < BCl_3$				
	(C) LiCl $<$ BeCl <sub>2</sub> $<$ BCl <sub>3</sub>	$< CCI_4$	(D) LiCl $<$ BeCl <sub>2</sub> $<$ CCl <sub>2</sub>	$_{\rm t}$ < BCl <sub>3</sub>				
A-9.	Least melting point is sl (A) PbCl <sub>2</sub>	hown by the compound : (B) SnCl <sub>4</sub>	(C) NaCl	(D) AICI <sub>3</sub>				
A-10.	<ul> <li>SnCl<sub>4</sub> is a covalent liquid because :</li> <li>(A) electron clouds of the Cl<sup>-</sup> ions are weakly polarized to envelop the cation.</li> <li>(B) electron clouds of the Cl<sup>-</sup> ions are strongly polarized to envelop the cation.</li> <li>(C) its molecules are attracted to one another by strong van der Waals forces.</li> <li>(D) Sn shows inert pair effect.</li> </ul>							
A-11.	Which of the following c (A) Fe <sup>2+</sup> , Br <sup>_</sup>	ombination of ion will hav (B) Ni <sup>4+</sup> , Br <sup>_</sup>	ve highest polarisation ? (C) Ni²+, Br−	(D) Fe, Br⁻				



### Section (B) : Covalent bond

B-1.	The maximum covalency for representative elements is equal to (excluding 1st and 2nd period) : (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.						
B-2.	Which of the following co (A) $CH_4$	ontains both elec (B) H <sub>2</sub> O <sub>2</sub>	trovalent	t and covalent bonds ? (C) NH <sub>4</sub> Cl	(D) none		
B-3.	Example of super octet (A) $SF_6$	molecule is : (B) PCI <sub>5</sub>		(C) IF <sub>7</sub>	(D) All of these		
B-4.	The octet rule is not obe	eyed in :					
	(A) CO <sub>2</sub>	(B) BCl <sub>3</sub>		(C) PCI <sub>5</sub>	(D) (B) and (C) both		
B-5.	To which of the following	g species octet ru	ile is not	applicable ?			
	(A) BrF <sub>5</sub>	(B) SF <sub>6</sub>		(C) IF <sub>7</sub>	(D) All of these		
B-6.	Which of the following s	pecies are hyperv	valent?				
	1. $CIO_4^{-}$ ,	2. BF <sub>3</sub> ,		3. SO <sub>4</sub> <sup>2-</sup> ,	4. $CO_3^{2-}$		
	(A) 1, 2, 3	(B) 1, 3		(C) 3, 4	(D) 1, 2		
B-7.	$NH_3$ and $BF_3$ combine re(A) a covalent bond	eadily because of (B) a hydrogen b	f the form oond	nation of : (C) a coordinate bond	(D) an ionic bond		
B-8.	Pick out among the follo (A) $N_3^-$	wing species iso (B) (CNO) <sup>_</sup>	electron	ic with CO <sub>2</sub> . (C) (NCN) <sup>2–</sup>	(D) All of these		
Sectio	on (C) : V.B.T., Hybr Which of the following h	idisation & V	SEPR	<b>theory</b> easing order of size of th	e hybrid orbitals ?		
	(A) $sp < sp^2 < sp^3$	(B) $sp^3 < sp^2 <$	sp	(C) $sp^2 < sp^3 < sp$	(D) $sp^2 < sp < sp^3$		
C-2.	Which of the following o (a) 2 $p_y + 2 p_y \rightarrow \pi 2 p_y$	verlaps is <u>incorr</u>	ect [ass	uming z-axis to be the in (b) 2 $p_z + 2 p_z \rightarrow \sigma 2 p_z$	ternuclear axis] ?		
	(c) $2 p_x + 2 p_x \rightarrow \pi 2 p_x$			(d) 1 s + 2 $p_y \rightarrow \pi$ (1 s-2	$2 p_y$ )		
	(A) 'a' & 'b'	(B) b & d		(C) only 'd'	(D) None of these		
C-3.	Effective overlapping wi	ll be shows by :					
	(A) ⊕⊖+⊕⊝	(B) ⊕+⊕		(C) ⊕⊖+⊝⊕	(D) All the above		
C-4.*	In which of the following, all the hybrid orbitals lie at same angle to one another ? (A) sp <sup>3</sup> – tetrahedral (B) sp <sup>3</sup> d – trigonal bipyramidal (C) sp <sup>2</sup> – trigonal planar (D) dsp <sup>2</sup> – square planar						
C-5.	In which of the following (A) $CIF_3$ , $CIF_3O$	pairs hybridisatic (B) CIF <sub>3</sub> O, CIF <sub>3</sub> O	on of the O <sub>2</sub>	central atom is different (C) $[CIF_2O]^+, [CIF_4O]^-$	? (D) [CIF₄O]⁻, [XeOF₄]		
C-6.	Identify the correct mate (i) $XeF_2$ (ii) $N_3^-$ (iii) $PCI_5$ (s) anion (iv) $I_2CI_6$ ( $\ell$ ) cation (A) (i – a), (ii – b), (iii – c	h. :), (iv – d)	(a) Cen (b) Cen (c) Cen (d) Cen	tral atom has sp <sup>3</sup> hybridi tral atom has sp <sup>3</sup> d <sup>2</sup> hybri tral atom has sp hybridis tral atom has sp <sup>3</sup> d hybric (B) (i – d), (ii – b), (iii – c)	sation and bent geometry. disation and octahedral. ation and linear geometry. disation and linear geometry. d), (iv – c)		



ETOOS ACADEMY Pvt. Ltd

F-106, Road No.2 Indraprastha Industrial Area, End of Evergreen Motor, BSNL Lane, Jhalawar Road, Kota, Rajasthan (324005) Tel. : +91-744-242-5022, 92-14-233303 C-7. Which of the following is true statement?

(A) All the carbon in  $H_2C = C - C \equiv C - C = CH_2$  are in sp<sup>2</sup> hybridisation.

- н н
- (B) In  $C_2H_2(CN)_2$  there are six ' $\sigma$ ' bonds.
- (C) In diamond C' is in sp<sup>2</sup> hybridisation.
- (D) In  $C_3O_2$  all the carbons are in sp hybridisation.
- **C-8.\*** Which of the following statements is/are correct about  $P_4O_{10}$  molecule ?
  - (A) Each 'P' atom can be considered to be sp<sup>3</sup> hybridised
  - (B) There are six POP bonds in the molecule
  - (C) There are two types of P— O bond lengths
  - (D) POP angle is 180°.
- C-10. Which among the following molecules have sp<sup>3</sup>d hybridisation with one lone pair of electrons on the central atom ?
  (i) SE (ii) IPCL It (iii) XoO E (iv) CIOE

(i) SF₄	(ii) [PCl₄] <sup>+</sup>	$(iii) XeO_2F_2$	(iv) CIOF <sub>3</sub>
(A) (i), (ii) and (iii) only		(B) (i), (iii) and (iv) only	0
(C) (i) and (iii) only		(D) (iii) and (iv) only.	

C-11.	Choose the molecules in which hybridisation occurs in the ground state ?					
	(a) BCl <sub>3</sub>	(b) NH <sub>3</sub>	(c) PCl <sub>3</sub>	(d) $BeF_2$		
	The correct answer is -	Ū	C C	-		
	(A) a, b, d	(B) a, b, c	(C) b, c	(D) c, d		

**C-12.** Number and type of bonds between two carbon atoms in  $CaC_2$  are : (A) one sigma ( $\sigma$ ) and one pi ( $\pi$ ) bond (B) one  $\sigma$  and two  $\pi$  bonds (C) one  $\sigma$  and one and a half  $\pi$  bond (D) one  $\sigma$  bond

**C-13.** The structure of  $IC\ell_2^+$  would be :



**C-14.** Which is the right structure of  $XeF_4$ ?



- **C-15.** In which of the following molecules number of lone pairs and bond pairs on central atom are not equal? (A)  $H_2O$  (B)  $I_3^-$  (C)  $O_2F_2$  (D)  $SCI_2$
- **C-16.** Which of the following species given below have shape similar to  $XeOF_4$ ?

(A)  $XeO_3$  (B)  $IOF_4^+$  (C)  $PCI_5$  (D)  $XeF_5^{\oplus}$ 



C-17.	The correct order of increasing $X - O - X$ bond a			angle is $(X = H, F \text{ or } CI)$ :			
	(A) $H_2O > CI_2O > F_2O$	(B) $CI_2O > H_2O$	$\mathbf{O} > \mathbf{F}_2\mathbf{O}$	(C) F <sub>2</sub> C	$O > Cl_2O$	$>H_2O$	(D) $F_2O > H_2O > Cl_2O$
C-18.	Consider the following n	nolecules ;	H₂O I	H₂S ∏	H₂Se ∭	H <sub>2</sub> Te	
	Arrange these molecule (A) I < II < III < IV	s in increasing o (B) IV < III < II <	rder of bo	ond angl (C) I <	es. II < IV < I	II	(D) II < IV < III < I
C-19.	Which has the smallest (A) $OSF_2$	bond angle (X – (B) OSCl <sub>2</sub>	S – X) in	the give (C) OS	en molec Br <sub>2</sub>	ules?	(D) OSI <sub>2</sub> .
C-20.	Consider the following id	odides :	PI <sub>3</sub> 102°		AsI <sub>3</sub> 100.2°		SbI <sub>3</sub> 99°
	The bond angle is maxi (A) due to small size of (C) due to less electron	mum in Pl <sub>3</sub> , whic phosphorus egativity of P	h is :	(B) due (D) Nor	to more ne of the	bp–bp r se	epulsion in PI <sub>3</sub>

#### Section (D) : Back bonding and hydrolysis

- **D-1.** Which of the following can not be completely hydrolysed in cold water at room temperature ? (A)  $BCI_3$  (B)  $PCI_3$  (C)  $BBr_3$  (D)  $CH_3CI$
- **D-2.** For  $BF_3$  molecule which of the following is true ?
  - (A) B-atom is sp<sup>2</sup> hybridised.
  - (B) There is a  $P\pi P\pi$  back bonding in this molecule.
  - (C) Observed B–F bond length is found to be less than the expected bond length.
  - (D) All of these
- D-3. Which of the following statements is not correct ?
  - (A)  $(CH_3)_3$  COH is less acidic than  $(CH_3)_3$  SiOH.
  - (B) Like CO, its analogue of Si is not stable.
  - (C) In phosgene, C O bond length is longer than expected while C–Cl bond length is shorter.
  - (D) None of these.
- D-4. Which of the following statement is false for trisilylamine ?
  - (A) Three sp<sup>2</sup> orbitals are used for  $\sigma$  bonding, giving a plane triangular structure.
  - (B) The lone pair of electrons occupy a p-orbital at right angles to the plane triangle and this overlaps with empty p–orbitals on each of the three silicon atoms resulting in  $\pi$  bonding.
  - (C) The N–Si bond length is shorter than the expected N–Si bond length.
  - (D) It is a weaker Lewis base than trimethyl amine.
- D-5. Which of the following statements is true ?
  - (A) In diborane, an sp<sup>3</sup> hybrid orbital from each boron atom overlaps with 1s orbital of the hydrogen atom to give a three centre two electron bond.
  - (B) The B–F bond length in  $Me_3N.BF_3$  is 1.35 Å, much longer than 1.30 Å in  $BF_3$ .
  - (C) Among the different trihalides of boron the order of ease of hydrolysis is  $BBr_{3} > BCl_{3} > BF_{3}$ .
  - (D) All of these.

# **D-6.** As the tendency to form $p\pi$ -d $\pi$ bond decreases the tendency for the polymerisation increases. So the correct order of tendency of polymerisation is :

- (A)  $SiO_4^{-} < PO_4^{-} < SO_4^{-} < CIO_4^{-}$ (C)  $CIO_4^{-} < SO_4^{-} < SiO_4^{-} < PO_4^{-}$
- (B)  $PO_4^{3-} < SiO_4^{4-} < SO_4^{2-} < CIO_4^{-}$ (D)  $SiO_4^{4-} > PO_4^{3-} > SO_4^{2-} > CIO_4^{-}$
- **D-7.**\*  $p\pi p\pi$  bonding occurs between oxygen and (A) Phosphorus in  $P_4O_{10}$  (B) Xenon in  $XeO_2F_2$  (C) N
  - (C) Nitrogen in  $N_2O_5$  (D) Sulphur in  $SO_2$



### Section (E) : Polarity of bond / Dipole moment

E-1. Which has maximum dipole moment?

	(A)	(B)	(C)	(D) ←→
E-2.	Which of the following s (A) The dipole moment (C) The dipole moment	tatements is true? of NF <sub>3</sub> is zero of NF <sub>3</sub> is more than NH <sub>3</sub>	(B) The dipole moment (D) The dipole moment	of NF $_3$ is less than NH $_3$ of NH $_3$ is zero
E-3.	The geometry of $H_2S$ ar (A) angular and non zer (C) linear and non zero	nd its dipole moment are : o	(B) angular and zero (D) linear and zero	
E-4.	Of the following molecu (A) $SiF_4$	les, the one, which has p (B) BF <sub>3</sub>	ermanent dipole moment (C) PF <sub>3</sub>	, is : (D) PF <sub>5</sub>
E-5.	Which of the following h (A) $CH_3CI > CH_3F > CH_3F$ (C) $CH_3CI > CH_3Br > CH_3Br$	as been arranged in orde H <sub>3</sub> Br > CH <sub>3</sub> I 'H <sub>3</sub> I > CH <sub>3</sub> F	r of decreasing dipole mo (B) $CH_3F > CH_3CI > CH$ (D) $CH_3F > CH_3CI > CH$	ment ? H <sub>3</sub> Br > CH <sub>3</sub> I H <sub>3</sub> I > CH <sub>3</sub> Br
E-6.	Which of the following h (A) $\mathrm{NF}_3$	as the least dipole mome (B) CO <sub>2</sub>	ent ? (C) SO <sub>2</sub>	(D) NH <sub>3</sub>
E-7.	Which of the following c (A) Benzene $(C_6H_6)$	ompounds possesses ze (B) Carbon tetrachloride	ro dipole moment? e (C) Boron trifluoride	(D) All of these
Sectio F-1.	<b>on (F) : Inter molecu</b> Which of the following is (A) HF	ular forces s least volatile ? (B) HCl	(C) HBr	(D) HI
F-2.	The critical temperature (A) fewer electrons than (C) V - shape	e of water is higher than the $O_2$	nat of O <sub>2</sub> because the H <sub>2</sub> (B) two covalent bonds (D) dipole moment	O molecule has :
F-3.	The correct order of boi (A) $H_2O < H_2S < H_2Se$ (C) $H_2O > H_2S > H_2Se$	ling point is : < H <sub>2</sub> Te > H <sub>2</sub> Te	(B) $H_2O > H_2Se > H_2Te$ (D) $H_2O > H_2Te > H_2Se$	> H <sub>2</sub> S > H <sub>2</sub> S
F-4.	Intermolecular hydroge (A) decrease in the attra (B) increase in the attra (C) decrease in the mol (D) increase in the effect	n bonding increases the e action between molecules ction between molecules ar mass of unassociated tive molar mass of hydrog	enthalpy of vaporization o s. liquid molecules. gen - bonded molecules.	f a liquid due to the :
F-5.	Which of the following c HF. CH	ompounds would have sig	gnificant intermolecular hy	/drogen bonding ?
	(A) HF, N <sub>2</sub> O <sub>4</sub>	(B) HF, CH <sub>4</sub> , CH <sub>3</sub> OH	(C) HF, CH <sub>3</sub> OH	$(D)CH_3OH,CH_4$
F-6.	Which one of the followi (A) $H_2O$	ng does not have intermo (B) o-nitro phenol	lecular H-bonding ? (C) HF	(D) CH <sub>3</sub> COOH
F-7.	Which of the following e (A) $CH_4$	xhibits H-bonding ? (B) H <sub>2</sub> Se	(C) N <sub>2</sub> H <sub>4</sub>	(D) H <sub>2</sub> S



F-8.	Which of the following m (A) metallic bonding (C) non-metallic covalen	nodels best descr t bonding	ibes the (D) van	bonding within a layer of (B) ionic bonding der Waals forces	the graphite structure ?
F-9.	Among the following, va (A) HBr	n der Waals force (B) LiBr	es are m	aximum in : (C) LiCl	(D) AgBr
F-10.	Which of the following b (A) Covalent bond	onds/forces is we (B) Ionic bond	eakest?	(C) Hydrogen bond	(D) London force
F-11.	Which of the following fa (A) Instantaneous dipole (B) Dipole-induced dipol (C) Dipole-dipole interac (D) All of these.	actor is responsibl e-induced dipole ir e interaction and tion and ion-induc	le for va nteractic ion-indu ced dipo	n der Waals forces ? on. ced dipole interaction. le interaction.	
F-12.	<ul> <li>Which of the following is</li> <li>(A) Van der Waals force</li> <li>(B) Branching lowers the bold of attraction.</li> <li>(C) In graphite, van der V</li> <li>(D) Boiling point of NH<sub>3</sub></li> </ul>	s false ? s are responsible poiling points of isor Waals forces act l is greater than Sb	for the f meric org betweer bH <sub>3</sub> .	formation of molecular cry ganic compounds due to rea n the carbon layers.	ystals. duction in the van der Waals force
F-13.	In which molecule is the (A) ICI	London dispersio (B) Br <sub>2</sub>	on force	likely to be most importa (C) $H_2S$	nt in determining boiling point ? (D) CO
F-14.	Iron is harder than sodiu (A) iron atoms are small (C) metallic bonds are s	im because : er. tronger in sodium	I.	(B) iron atoms are more (D) metallic bonds are st	closely packed. tronger in iron.
F-15.	Which of the following is (A) Mobile valence elect (C) Highly directed bond	observed in meta rons	allic bon	ds ? (B) Localised electrons (D) None of these	
Sectio	on (G) : MOT				
G-1.	Among the following spectrum (A) $B_2$	ecies, which has t (B) C <sub>2</sub>	he minii	mum bond length ? (C) F <sub>2</sub>	(D) O <sub>2</sub> -
G-2.	Number of antibonding (A) 4	electrons in N <sub>2</sub> is (B) 10	:	(C) 12	(D) 14
G-3.	Pick out the incorrect st (A) $N_2$ has greater disso (C) Bond length in $N_2^+$ is	atement. ciation energy tha s less than N <sub>2</sub>	an N <sub>2</sub> +	(B) O <sub>2</sub> has lower dissoci (D) Bond length in NO <sup>+</sup>	ation energy than O <sub>2</sub> + is less than in NO.
G-4.	Which of the following s (A) During $N_2^+$ formation (B) During $O_2^+$ formation (C) During $O_2^-$ formation (D) During CN <sup>-</sup> formation	tatement is incorr n, one electron is r n, one electron is r n, one electron is a n, one electron is	rect ? removed removed added to added t	I from the bonding molecu I from the antibonding mo o the bonding molecular o o the bonding molecular o	ular orbital of N <sub>2</sub> . ecular orbital of O <sub>2</sub> . orbital of O <sub>2</sub> . orbital of CN.
G-5.	Which of the following part (A) $N_2^+$ and $O_2^+$	airs have identica (B) F <sub>2</sub> and Ne <sub>2</sub>	l values	of bond order ? (C) O <sub>2</sub> and B <sub>2</sub>	(D) $C_2$ and $N_2$
G-6.	A simplified application (A) 2	of MO theory to th (B) 1.5	ne hypot	thetical 'molecule' OF wo (C) 1.0	uld give its bond order as : (D) 0.5



G-7.	Which of the following species is paramagnetic?				
	(A) NO-	(B) O <sub>2</sub> <sup>2-</sup>	(C) CN <sup>_</sup>	(D) CO	

(C) CN-

- G-8. During the formation of a molecular orbital from atomic orbitals of the same atom, probability of electron density is :

   (A) none zero in the nodal plane
   (B) maximum in the nodal plane
   (D) zero on the surface of the lobe
- G-9. According to Molecular orbital theory which of the following is correct ?
  (A) LUMO level for C<sub>2</sub> molecule is σ<sub>2px</sub> orbital
  (B) In C<sub>2</sub> molecules both the bonds are π bonds
  (C) In C<sub>2</sub><sup>2-</sup> ion there is one σ and two π bonds
  (D) All the above are correct
  G-10.\* Which of the following have bond order three ?

# **PART - II : MISCELLANEOUS QUESTIONS**

# **COMPREHENSION**

#### **COMPREHENSION #1**

 $(A) O_2^{2+}$ 

(B) NO<sup>+</sup>

Hybridisation is the chemists attempt to explain the observed molecular shape by constructing hybridised atomic orbitals with the appropriate inter orbital angles. The molecule for which deviation from normal bond angle is observed, VSEPR theory suggest electron pair repulsive interaction  $(\ell p - \ell p > \ell p - bp > bp - bp)$ . While from hybridisation point of view that is departure from normal hybridisation because the angle between any equivalent hybrid orbitals determine the fraction of s and p character of the hybrid and vice - versa.

(D) CN+

1. An element 'A' has outer shell configuration of  $5s^25p^6$ . If A forms covalent compound  $AF_2$  with fluorine. The orbitals used by 'A' for bonding are (A) d-orbitals (B) p-orbitals

(A) u-orbitais	(D) p-orbitais
(C) sp-hybridised orbital	(D) sp <sup>3</sup> d hybrid orbital

- 2. In which species number of lone pair on iodine and number of d orbitals used in hybridisation by iodine are same
  - (A)  $ICl_2^+$  (B)  $ICl_2^-$  (C)  $IF_7$  (D)  $ICl_4^-$
- 3. Which line of properties A, B, C or D correctly listed, properties of the given three compounds.  $XeF_4$   $CCI_4$   $Zn^{2+}$

(A)	Square planar	Non-planar	$\mu = \sqrt{8}$ BM
(B)	μ = 0	Tetrahedral	Diamagnetic
(C)	Non-planar	Polar	μ = Zero
(D)	Polar	Square planar	Total number of 12 electrons having m
			(Magnetic guantum number) = Zero

#### COMPREHENSION # 2

Hybridisation is a concept of mixing or merging of orbitals of same atom with slight differences in energies to redistribute their energies and give new orbitals of equivalent energy called 'Hybrid Orbitals'. Hybridisation is a hypothetical concept and never actually exists.

One should not be confused by common misconception that hybridisation is responsible for particular geometry. Geometry of a molecule is decided by energy factor not by hybridisation. It is the orbital (which may be half–filled, completely filled or empty) that undergoes hybridisation and not the electrons. The bond angles in hybridised orbitals are influenced by presence of lone pair, presence of multiple bonds, presence of one electron and electronegativity of atom.

An increase in s-character of hybridised orbitals results in decrease in size of orbitals. This results in decrease in bond length and increase in bond energy.



4. Which of the following statements is true ?

(A) The state of hybridisation of boron and oxygen atoms in boric acid are sp<sup>3</sup> and sp<sup>2</sup> respectively. (B) NH<sub>3</sub> and [BF<sub>4</sub><sup>-</sup>] have same bond angles of 109<sup>o</sup>.28<sup>'</sup>.

- (C) SF<sub>e</sub> and PF<sub>e</sub><sup>-</sup> both have undistorted octahedral structures.
- (D) The hybridisation of P in  $P_1$  molecule is the same as in S in SO<sub>2</sub> molecule.
- 5. Among the following which have the same molecular geometry?

(I) I <sub>5</sub> <sup>-</sup>	(II) $XeF_4$	(III) $BrF_4^{-}$	$(IV) XeO_2F_2$
(A) I, II and	IV only		(B) I , II , III and IV
(C) I , II , an	id III only		(D) II , III , and IV only

6. Which of the following statements is not true ?

(A) O – F bond length in OF<sub>2</sub> is less than O – F bond length in  $O_2F_2$ .

(B) In  $HCO_3^-$ , all C – O bond lengths are not identical.

(C) In diborane, two different B – H bond lengths are observed although the hybridisation of both boron atoms are same.

(D) In hydrazine , the N - N bond length is larger than normal N-N bond length.

#### Comprehension # 3

Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in electronegativity of two atoms. This means that every bond carries with it an electrical moment called the "bond moment". The dipole moment of a molecule is really the vectorial sum of the individual bond moment present in it. To compute the dipole moment it is necessary to find out the values of various bond moment. in the following table dipole moment of different bonds are as given.

Bond	H-C		$\overrightarrow{c=0}$
Bond moments	0.4 D	1.5 D	2.5 D

The group moments of few group as given

Group	NO <sub>2</sub>	ОН	CN	CH <sub>3</sub>
direction of dipole	toward N	towards O	toward N	away from CH <sub>3</sub>
Dipole moment	4D	1.6 D	3.8 D	0.4 D

7. The bond angle in H<sub>2</sub>S is 97° and its dipole moment is 1.5 D. The S – H bond distance is 0.15 nm There fore approximate percentage ionic character of S – H bond is (neglect the effect of dipole moment of lone pair on sulphur atom in H<sub>2</sub>S). (Given [cos 97° = -0.12] and  $\sqrt{0.88} = 0.94$ )

(1) 00 0/		$(\mathbf{O}) \mathbf{O} \mathbf{A} \mathbf{O}$	
(A) 32 %	(B) 16 %	((,) 84 %	(1)) 10 %

- 8. In CH<sub>3</sub>CCl<sub>3</sub> (I), CHCl<sub>3</sub> (II) and CH<sub>3</sub>Cl (III) the normal tetrahedral bond angle is maintained. Also given cos 70.5° = <sup>1</sup>/<sub>3</sub> Therefore dipole moments of the given compounds are. (given due to I effect of CI, the Bond moment of H—C bond directed toward the H in CHCl<sub>3</sub>)
  (A) I = 1.9 D, II = 1.9 D, III = 1.7 D
  (B) I = 1.9 D, II = 1.7 D, III = 1.9 D
  (C) I = 1.9 D, II = 1.7 D, III = 1.7 D
  (D) I = 1.9 D, II = 1.1 D, III = 1.9 D
- 9. In the acetone molecule considering the normal planer structure, the observed dipole moment of acetone molecule is –

(A) 2.9 D (B) 2.75 D (C) 3 D (D) None of these



#### **COMPREHENSION #4**

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

(A) Stability of molecule : The molecule is stable if number of bonding molecular orbital electrons (N,) is greater than the number of antibonding molecular orbital electrons (N) and vice-versa.

(B) Bond order :

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

A positive bond order means a stable molecule while a negative or zero bond order means an unstable molecule.

(C) Nature of the bond :

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

(D) Bond length :

Bond length decreases as bond order increases.

(E) Magnetic nature :

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

10. Which of the following statements is incorrect?

(A) Among  $O_2^+$ ,  $O_2^-$  and  $O_2^-$  the stability decreases as  $O_2^+ > O_2^- > O_2^-$ 

(B) He<sub>2</sub> molecule does not exit as the effect of bonding and anti-bonding molecular orbitals cancel each other (C)  $C_2$ ,  $O_2^{2-}$  and Li<sub>2</sub> are diamagnetic

(D) In F<sub>2</sub> molecule, the energy of  $\sigma 2 P_z$  is more than  $\pi_{2\text{pv}}$  and  $\pi_{2\text{Pv}}$ 

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

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

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

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

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

12. The following molecules / species have been arranged in the order of their increasing bond orders. Identify the correct order.

(I)  $O_2$ ; (II)  $O_2^{-}$ ; (III)  $O_2^{2-}$ ; (IV)  $O_2^{+}$ (C)III < II < IV < I(A)  $I\bar{I}I < II < \bar{I} < IV$ (B) IV < I I < I < I (D) I < I I < I < I V

 $N_2$  has greater bond dissociation energy than  $N_2^+$ , where as  $O_2$  has a lower bond dissociation energy than 13. O\_+ because:

(A) Bond order is reduced when  $O_2$  is ionized to  $O_2^+$  and bond order is increased when  $N_2$  is ionized to  $N_2^+$ 

- (B) Bond order is increased when  $O_2$  is ionized to  $O_2^+$  and bond order is decreased when  $N_2$  is ionized to  $N_2^+$  (C) Bond order is decreased when  $O_2^-$  is ionized to  $O_2^+$  and bond order is decreased when  $N_2^-$  is ionized to  $N_2^+$ (D) None of these.
- 14. Which the following molecules / species have identical bond order and same magnetic properties? (I)  $O_2^+$ ; (II) NO; (III)  $N_2^+$ (A) (I), (II) only (B) (I) and III only (C) (I), (II) and (III) (D) (II) and (III) only



# MATCH THE COLUMN

**15.** Match the species given in column-I with the type of hybridisation given in column-II.

Column-I Colum		
(A) $IO_2F_2^-$	(p) sp <sup>3</sup> d	
(B) F <sub>2</sub> SeO	(q) sp <sup>3</sup>	
(C) CIOF <sub>3</sub>	(r) sp <sup>2</sup>	
(D) XeF <sub>5</sub> <sup>+</sup>	(s) sp <sup>3</sup> d <sup>2</sup>	

16. Match the group of species in **Column I** with the correctly related characteristic(s) in **Column II**.

Column - I	Column - II
(A) CI $F_5^{}$ , $BrF_4^{+}$ , $IF_6^{-}$ , $PCI_2F_3^{}$	(p) All molecules/ions are polar in nature.
(B) $CIF_3$ , $BrF_2^+$ , $ICI_4^-$ , $NF_3$	(q) All molecules/ions have same number of lone pair(s) on the central atom and have same shape.
(C) $XeF_2$ , $ICI_2^-$ , $I_3^-$	(r) All molecules/ions have same oxidation state of central atoms
(D) CIOF <sub>3</sub> , CIF <sub>4</sub> <sup>+</sup> , IO <sub>2</sub> F <sub>2</sub> <sup>-</sup> , XeO <sub>4</sub> <sup>2-</sup>	(s) All molecules/ions have same hybridisation of central atoms

**17.** Match the species listed in column-I with hybridisation listed in column-II and bond angle listed in column-III.

	Column – I Column – II		Column – III			
	(Compound /species)	(Hybridisation)	(Bond angle)			
	(A) XeF <sub>5</sub> <sup>-</sup>	(p) sp <sup>3</sup>	(w) All angles same and 72°			
	(B) SPCI <sub>3</sub>	(q) sp <sup>2</sup>	(x) All bond angles less than the bond angle in water			
	(C) OF <sub>2</sub>	(r) sp <sup>3</sup> d <sup>3</sup>	(y) Axial bond angle $\approx 177^{\circ}$ and equatorial $\approx 104^{\circ}$			
	(D) SF <sub>4</sub>	(s) sp³d	(z) One angle more than 109°28' and other angle less than 109°28'.			
18.	18. Column-l		Column-II			
	(A) HCl < HF		(p) Strength of hydrogen bonding			
	(B) PH <sub>3</sub> < NH <sub>3</sub>		(q) Dipole moment			
	(C) $H_2O < D_2O$		(r) Boiling point			
	(D) $F_2 < Cl_2$		(s) Bond energy			
19.	Match each of the diato	mic molecules in <b>Colum</b> i	n I with its property/properties in Column II.			

Column I Column II Note : Concept of molecular orbital is to be used strictly.

(A) B <sub>2</sub>	(p) Paramagnetic
(B) N <sub>2</sub>	(q) Diamagnetic
(C) $O_2^{+}$	(r) Stability more than $O_2$ (thermodynamic stability)
(D) C <sub>2</sub>	(s) Bond order $\leq$ 2.
	(t) Contain two $\pi$ bonds.



# **ASSERTION / REASONING**

#### DIRECTIONS :

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

(A) Statement-1 is True, Statement-2 is True; 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.
- (E) Statement-1 and Statement-2 both are False.
- **20.** Statement-1 : In CH<sub>3</sub>NCO, the bond angles C N C and N C O are not identical. Statement-2 : N – atom has a lone pair of electrons which is involved in  $p\pi$ -d $\pi$  delocalisation where as C – atom does not have lone pair of electrons.
- Statement-1 : Amongst the oxo acids of halogens, HOCI, HOBr and HOI, the HOI is the most acidic acid.
   Statement-2 : The conjugate base stability is CIO<sup>-</sup> > BrO<sup>-</sup> > IO<sup>-</sup>
- 22. Statement-1 :  $[SiC\ell_6]^2$ -does not exist. Statement-2 : Interaction between lone pairs of chloride ions and Si<sup>4+</sup> is not very strong and six large chloride ions can not be accommodated around Si<sup>4+</sup> due to limitation of its size.
- **23. Statement-1 :** Molecular species like  $SF_6$ ,  $PF_5$ ,  $I_3^-$  and  $XeF_2$  violate the octet rule. **Statement-2 :** Compounds with an expanded octet are called hypervalent compounds.
- 24. Statement-1 : In tetrahedral hybridisation i.e., in sp<sup>3</sup> hybridisation all p-orbitals of valence shell are involved and no p-orbital is left for forming π-bonds.
   StatemENT-2 : Central atom can not form double bonds in the molecules or species having sp<sup>3</sup> hybridisation.
- **25.** Statement-1 : All F-S-F angles in  $SF_4$  are greater than 90° but less than 180°. Statement-2 : The bond pair-bond pair repulsion is weaker than lone pair-bond pair repulsion.
- Statement-1: NF<sub>3</sub> has little tendency to act as a donor molecule.
   Statement-2: The highly electronegative F atoms attract electrons and these moments partly cancel the moment from the lone pair.
- 27. Statement-1 : Si F , Si C $\ell$  and Si O bonds are stronger than the corresponding bonds with C.



- **28. Statement-1**: SiO<sub>2</sub> is solid while CO<sub>2</sub> is gas at room temperature. **Statement-2**: Si-O bonds are more stronger than C—O bonds.
- **29.** Statement-1 : In  $IOF_4^-$  a single lone pair is present on iodine atom trans to oxygen atom to have minimum repulsion between the I = O and the lone pair of electrons. Statement-2 : The VSEPR model considers double and triple bonds to have slightly greater repulsive effect than single bonds because of the repulsive effect of  $\pi$  electrons.
- **30.** Statement-1 : The dipole moment of  $C_3O_2$  and  $CO_2$  are zero. Statement-2 : Two more electronegative ends are in diametrically opposite direction in both cases.



# TRUE / FALSE

- **31.** Simple ionic compounds show isomerism and isomorphism due to the directional nature of the electrovalent bond.
- **32.** Covalent bond formed by hybrid orbitals are more stronger than those of formed by pure atomic orbitals.
- **33.** The number of lone pair(s) of electrons present on Xe in  $XeO_2F_2$ ,  $XeO_4$ ,  $XeO_3$  and  $XeO_4$  are 1, 1, 1 and 0 respectively.
- **34.** The correct order of bond angles in  $H_2S$ ,  $NH_3$ ,  $SiH_4$  and  $BF_3$  is  $BF_3 > SiH_4 > H_2S > NH_3$ .
- **35.** Hydrogen bond is an electrostatic force of attraction which exist between covalently bonded H–atom of one molecule and the most electronegative atom of another molecule.
- **36.**  $PC\ell_2F_3$  has trigonal bipyramidal shape and has some net dipole moment.
- **37.** The bond angle O I O in  $IO_2F_2^-$  is less than the bond angle F I O in  $IOF_3$ .
- **38.** In  $CO_3^{2-}$ , all C O bond lengths are identical but in  $HCO_3^{-}$  two different bond lengths are observed.
- **39.** According to molecular orbital theory, the LUMO level for  $C_2$  molecules is  $\pi 2P_x$  not  $\sigma 2P_z$ .
- **40.**  $P_4O_{10}$  does not have a single P–P bond and O–O bond.
- 41. In 1 chloropropene, cis form has higher dipole moment than trans-form.
- **42.** The decreasing orders of bond angle in  $NO_2^+$ ,  $NO_2^-$  and  $NO_2$  is  $NO_2^+ > NO_2 > NO_2^-$ .
- **43.** In  $C\ell F_3O$  and  $C\ell F_3O_2$  the hybridisation of the central atom is different.
- **44.** OF<sub>2</sub> and Cl<sub>2</sub>O both are SP<sup>3</sup> hybridised and bond angle in  $C\ell_2O$  is greater than 109°28'.
- 45. Dipole moment is the measure of the degree of polarity of a bond.
- **46.**  $B_2$  is found only in the gas phase and is diamagnetic.

## FILL IN THE BLANKS

- 47. When two atoms approach each other, potential energy \_\_\_\_\_\_ and a \_\_\_\_\_\_ is formed between them.
- **48.** Low ionization potential of electropositive element and high electron affinity of electronegative element favour the formation of \_\_\_\_\_\_ bond.
- **49.** NaCl is soluble in water due to its low \_\_\_\_\_\_ energy.
- **50.** The shape of [CH<sub>3</sub>]<sup>+</sup> is \_\_\_\_\_.
- **51.** The boiling point of  $CCI_{a}$  is \_\_\_\_\_\_ (higher/lower) than that of  $CHCI_{a}$ .
- **52.** The paramagnetic molecule is \_\_\_\_\_ (NO,  $H_2O$ ,  $SO_2$ ,  $CO_2$ ).
- **53.** \_\_\_\_\_\_is half of the difference in number of electrons in bonding and antibonding molecular orbitals.
- 54. In the species O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>--</sup>, \_\_\_\_\_\_ is diamagnetic and has a bond order \_\_\_\_





# **PART - I : MIXED OBJECTIVE**

# Single Choice Type

1.	When two atoms com (A) Energy is released (C) Energy is neither r	nbine to form a molecu I eleased nor absorbed	lle - (B) Energy is absorbed (D) Energy may either	d released or absorbed	
2.	Out of following which (A) NaF	has maximum value of (B) NaCl	lattice energy - (C) NaBr	(D) Nal	
3.	The crystal lattice of e (A) Atoms (C) Oppositely charged	lectrovalent compound d ions	is composed of - (B) Molecules (D) Both molecules and ions		
4.	lons are formed from (A) Loss of electron (C) Sharing of electror	neutral atoms by - ns	(B) Gain of electrons (D) Loss and gain of e	electrons	
5.	Compound with maxim (A) Na and Cl	num ionic character is fo (B) Cs and F	ormed from - (C) Cs and I	(D) Na and F	
6.	Out of the following wh (A) ZnCl <sub>2</sub>	hich one has the highes (B) CaCl <sub>2</sub>	t values of covalent cha (C) CdCl <sub>2</sub>	aracter - (D) CuCl	
7.	Compound having high (A) BeCl <sub>2</sub>	nest M.Pt. (B) MgCl <sub>2</sub>	(C) CaCl <sub>2</sub>	(D) SrCl <sub>2</sub>	
8.	AgCl is colourless whereas AgI is yellow, because of : (A) Ag <sup>+</sup> have 18 electron shell to screen the nuclear charge. (B) Ag <sup>+</sup> shows pseudo inert gas configuration. (C) distortion of I <sup>−</sup> is more pronounced than CI <sup>−</sup> ion. (D) existence of d – d transition.				
9.	Which follows octet rule (A) FeCl <sub>2</sub>	e - (B) AgCl	(C) CaCl <sub>2</sub>	(D) CuCl	
10.	Which is linear PH <sub>4</sub> <sup>+</sup> , H (A) Phosphonium ion (P (C) Nitronium ion (NO <sub>2</sub> <sup>+</sup>	H <sub>3</sub> S <sup>+</sup> or NO <sub>2</sub> <sup>+</sup> ? 'H <sub>4</sub> <sup>+</sup> ) ) .	(B) Sulphonium (H <sub>3</sub> S <sup>+</sup> ) (D) None of these		
11.	The ONO angle is maxi (A) $NO_3^-$	mum in : (B) NO <sub>2</sub> +	(C) N <sub>2</sub> O <sub>4</sub>	(D) NO <sub>2</sub>	
12.	In following which cent (A) Cl <sub>2</sub> O	tral atom has different h (B) OF <sub>2</sub>	ybridisation than other · (C) H <sub>2</sub> O	(D) SO <sub>2</sub>	
13.	In following hydrocarbo (A) C <sub>2</sub> H <sub>4</sub>	on which one has 75% (B) $C_2H_2$	p character and 25% s (C) CH <sub>4</sub>	s charater - (D) :CH <sub>2</sub>	



14.	<ul> <li>Which of the following statement in incorrect -</li> <li>(A) Non-bonding pairs occupy more space than bonding pairs</li> <li>(B) The bonding orbitals in a trigonal bipyramidal molecule are described as sp<sup>3</sup>d hybrid</li> <li>(C) SnCl<sub>2</sub> has linear shape</li> <li>(D) PCl<sub>4</sub><sup>+</sup> and AlCl<sub>4</sub><sup>-</sup> are isoelectronic</li> </ul>						
15.	Shape of $NH_3$ is very (A) $CH_4$	similar to - (B) CH <sub>3</sub>	(C) BH <sub>3</sub>	(D) CH <sub>3</sub> <sup>+</sup>			
16.	Which of the following (A) XeO <sub>3</sub>	has pyramidal shape- (B) XeF <sub>4</sub>	(C) XeF <sub>2</sub>	(D) XeF <sub>6</sub>			
17.	Which of the following (A) O – H	bonds is most polar - (B) P – H	(C) C – F	(D) S – CI			
18.	Bond length of HCl is (A) 100% ionic	1.275 Å (Charge = 4.8 (B) 83% covalent	× $10^{-10}$ e.s.u.) if $\mu = 1$ (C) 50% covalent	I.02 D, then HCI is - (D) 40% ionic			
19.	The dipole moment of (A) $3.08 \times 10^{-11} \text{ m}$	the ammonia molecule (B) 5 × $10^2$ m	is 1.48D. The length of (C) 308 m	the dipole is - (D) None			
20.	The geometry of SO3 and its dipole moment are :(A) pyramidal and non-zero.(B) trigonal planar and non-zero.(C) trigonal planar and zero.(D) T-shaped and zero.						
21.	Which one of the follow (A) H <sub>2</sub> O	wing does not have inter (B) o-Nitrophenol	rmolecular H-bonding - (C) HF	(D) CH <sub>3</sub>			
22.	Arrange in incresing of HF, HCl, HBr, HI Which order is correct (A)HCl < HBr < HI < H (C)HCl < HBr > HI < H	rder of their boiling point – HF HF	t- (B) HCl > HBr > HI > (D) None	HF			
23.	Correct order of bond er (A) $N_2 > N_2^+ > N_2^- > N_2^2$ (C) $N_2 > N_2^- = N_2^+ > N_2^2$	nergy is : - -	(B) $N_2^+ > N_2^- > N_2^{2-} > N_2$ (D) $N_2^- > N_2 = N_2^+ > N_2^{2-}$	-			
24.	Which of the following w (A) CH <sub>3</sub> CN	/ill be strongest Lewis bas (B) CH <sub>3</sub> NH <sub>2</sub>	se ? (C) N <sub>2</sub>	(D) None of these			
25.	<ul> <li>Which is <u>incorrect</u> statement ?</li> <li>(A) In CF<sub>2</sub> = C = CF<sub>2</sub> molecule all the four fluorine atoms are not in the same plane.</li> <li>(B) Ka<sub>2</sub> of fumaric acid is more than Ka<sub>2</sub> of maleic acid due to intra molecular hydrogen bonding in maleic acid.</li> <li>(C) The O – O bond length in O<sub>2</sub>[AsF<sub>4</sub>] is longer than KO<sub>2</sub>.</li> <li>(D) The bond angle order in belogen S = belogen is OSE = COSCI = COSPr</li> </ul>						
26.	A diatomic molecule has	s a dipole moment of 1.2	D. If its bond distance is e	equal to 1.0Å then the fraction of			
	(A) 25%	(B) 37%	(C) 52%	(D) 42%			
27.	Two elements X and Y X $1s^2$ , $2s^2$ , $2p^6$ ; $3s^2$ , Y $1s^2$ , $2s^2$ , $2p^6$ ; $3s^2$ , The expected compound (A) XY <sub>2</sub>	have following electroni $3p^6$ ; $4s^2$ $3p^5$ nd formed by combination (B) $X_5Y_2$	ic configuration- on of X and Y will be e (C) X <sub>2</sub> Y <sub>5</sub>	xpressed as- (D) XY <sub>5</sub>			



28.	An atom of element A has three electrons in its outer shell and B has six electrons in its outermost shell. The formula of the compound formed between these will be- (A) $A_6B_6$ (B) $A_2B_3$ (C) $A_3B_2$ (D) $A_2B$						
29.	The electronegativity on nature of HCI is/are	of H and CI are 2.1 and	3.0 respectively. The c	orrect statement (s) about the			
	(A) HCl is 17% ionic	(B) 83% ionic	(C) 50% ionic	(D) 100% ionic			
30.	The electronegativity of	f O.F.N. CI and H are 3.	5, 4.0, 3.0 and 2.1 respe	ctively. The strongest bond will			
	(A) F – O	(B) O – Cl	(C) N – H	(D) O – H			
31.	The ratio of $\sigma$ to $\pi$ box (A) 3	nds in mesitylene is (B) 7	(C) 5	(D) 6			
32.	In which solvent NaCl (A) H <sub>2</sub> O	has maximum solubility (B) C <sub>2</sub> H <sub>5</sub> OH	/: (C)CH <sub>3</sub> COCH <sub>3</sub>	(D) C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>			
33.	Which has maximum o (A) NaCl	covalent character ? (B) SiCl <sub>4</sub>	(C) AICI <sub>3</sub>	(D) MgCl <sub>2</sub>			
34.	The dipole moment of	HBr_ is 2.6 × 10 <sup>−30</sup> cm : Br_is-	and the interatomic space	cing is 1.41 Å. The percentage			
	(A) 10.5	(B) 11.5	(C) 12.5	(D) 13.5			
35.	Which of the following	hydrocarbons has the	lowest dipole moment :				
	(A) $\begin{array}{c} CH_3 \\ H \end{array} C = C \begin{array}{c} CH_3 \\ CH_3 \end{array}$	$(B) \ CH_3C \equiv CH_3$	$(C) \ CH_3 CH_2 C \equiv C$	(C) $CH_2 = CH-C \equiv CH$			
36.	Identify the correct se molecules :	quence of increasing r	number of $\pi$ -bonds in t	he structures of the following			
	(I) H <sub>2</sub> S <sub>2</sub> O <sub>6</sub> (A) I, II, III	(II) H <sub>2</sub> SO <sub>3</sub> (B) II, III, I	(III) H <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (C) II, I, III	(D) I, III, II			
37.	Enol form of acetone of (A) $9\sigma$ -bond, I $\pi$ -bond (B) $8\sigma$ -bond, 2 $\pi$ -bond (C) $10\sigma$ -bond, I $\pi$ -bond (D) $9\sigma$ -bond, 2 $\pi$ -bond	contains the following: and two lone pair of ele and two lone pair of el d and one lone pair of e and one lone pair of el	ectrons ectrons electrons lectrons				
38.	The decreasing order (A) AgI > AgBr > AgCl (C) AgCl > AgF > AgE	of solubility of silver hal I > AgF Br > AgI	lide is : (B) AgF > AgCl > AgB (D) AgBr > AgF > AgI	sr > Agl > AgCl			
39.	Where dative bond is r (A) Protonationof ether (C) Dimerisation of ber	not involved : nzoic acid	(B) dissolution of HCl (D) Formation of Be <sub>2</sub> C	in water I <sub>4</sub>			
40.	The atomic number of	Sn is 50. The shape o	f gaseous SnCl <sub>2</sub> molec	ule is :			
	(A) CI–Sn–Cl	(B) CI CI	$(C) \underbrace{\bigcirc}_{CI}^{CI}$	(D) Sn CI CI			
41.	In which case hydroge	n bond will not be obse	erved :				
	(A) H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	(B) H <sub>2</sub> O	(C) $H_5O_2^+$	(D) H <sub>3</sub> O <sup>+</sup>			



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CHEMICAL BONDING\_ADVANCED # 39

42.	Which of the following is (A) NaClO <sub>4</sub> < KClO <sub>4</sub>	correct order for solubili (B) NaBF <sub>4</sub> > NaF	ty in water ? (C) MgSO <sub>4</sub> < SrSO <sub>4</sub>	(D) all the above			
43.	In which of the following (a) Tetrahedral hybridisa (b) Hybridisation can be (c) All bond lengths are (A) $B_2H_6$	molecules/species all fol tion considered to have take identical i.e. all A – B bor (B) Al <sub>2</sub> Cl <sub>6</sub>	lowing characteristics are n place with the help of er id lengths are identical. (C) BeCl <sub>2</sub> (g)	e found ? npty orbital(s). (D) $BF_4^-$			
44.	Which of the following s (A) Hybridization is the n (B) sp <sup>2</sup> -hybrid orbitals a (C) dsp <sup>2</sup> -hybrid orbitals (D) d <sup>2</sup> sp <sup>3</sup> -hybrid orbitals	tatements is not correct of nixing of atomic orbitals of re formed from two p - at are all at 90° to one anot are directed towards the	? of large energy difference omic orbitals and one s- a her. corners of a regular octa	atomic orbitals. hedron.			
45.	Which of the following m (A) $SF_2$	olecules has two lone pair (B) $KrF_4$	rs and bond angle (need (C) ICl <sub>4</sub> <sup>-</sup>	not be all bond angles) < 109.5°? (D) All of these			
46.	What should be the corr (A) Central atom Xe has (B) It is square planar. (C) There are two non-be (D) It is an odd electron	ect statement with respe sp <sup>3</sup> d <sup>2</sup> hybridisation. onding electron pairs, one species.	ct to $XeF_{5}^{-}$ ?	other below the plane.			
47.	The correct order of hyb $NO_3^{-}$ is : (A) dsp <sup>2</sup> , sp <sup>3</sup> d , sp <sup>3</sup> , sp <sup>2</sup> (C) sp <sup>3</sup> , dsp <sup>2</sup> , sp <sup>3</sup> d, sp <sup>2</sup>	pridisation of the central a	tom in the following spec (B) dsp², sp³ , sp³d, sp² (D) dsp² , sp³d sp³, sp²	sies; [Ni (CN) <sub>4</sub> ] <sup>2–</sup> , XeO <sub>4</sub> , SF <sub>4</sub> and			
48.	Which of the following is (A) The O – O bond leng (B) The O – O bond leng (C) $O_2^-$ and $O_2^+$ species a (D) None	incorrect ? gth in $H_2O_2$ is larger than gth in $H_2O_2$ is very slightly are paramagnetic and ha	that in $O_2F_2$ . v smaller than in $O_2^{2-}$ ion. ve same number of unpai	ired electrons.			
49.	The common features o (A) bond order three and (C) bond order three but	f the species $N_2^{2-}$ , $O_2$ and isoelectronic. not isoelectronic.	d NO⁻ are : (B) bond order two and i (D) bond order two but r	soelectronic. not isoelectronic.			
50.	Which of the following statements is incorrect ? (A) Among $O_2^+$ , $O_2^-$ and $O_2^-$ the stability decreases as $O_2^+ > O_2^- > O_2^-$ (B) He <sub>2</sub> molecule does not exist as the effect of bonding and anti-bonding orbitals cancel each other . (C) $C_2^-, O_2^{-2-}$ and Li <sub>2</sub> are diamagnetic						
51.	The following molecules	/ species have been arrar	iged in the order of their in	creasing bond orders, Identify the			
	correct order. (I) $O_2$ ; (II) $O_2^-$ ; (III) $O_2$ (A) I I I < I I < I V	<sup>2-</sup> ; (IV) O <sub>2</sub> <sup>+</sup> (B) IV < I I I < I I < I	(C)111<11<1V<1	(D) I I < I I I < I < I V			
52.	Which the following mole (I) $O_2^+$ ; (II) NO; (III) N; (A) (I), (II) only	ecules / species have ide (B) (I) and I I I only	ntical bond order and sar (C) (I) ,(I I) and (I I I)	ne magnetic properties ? (D) (I I) and (I I I) only			
53.	The increasing order of t (i) O—HS (A) (i) < (ii) < (iv) < (iii)	the strength of hydrogen (ii) S—HO (B) (ii) < (i) < (iv) < (iii)	bond in the following men (iii) F—HF⁻ (C) (i) < (ii) < (iii) < (iv)	itioned linkages is : (iv) F—HO (D) (ii) < (i) < (iii) < (iv)			



54.	In the dichromate dianion (A) 4 Cr–O bonds are equ (C) All Cr–O bonds are eq	: : ivalent uivalent	(B) 6 Cr–O bonds are equivalent (D) All Cr–O bonds are non-equivalent			
55.	CH <sub>3</sub> Cl has more dipole moment than CH <sub>3</sub> F because : (A) electron affinity of chlorine is greater than that of fluorine. (B) the charge separation is larger in CH <sub>3</sub> Cl compared to CH <sub>3</sub> F. (C) the repulsion between the bond pairs and non-bonded pairs of electrons is greater in CH <sub>3</sub> Cl than CH <sub>3</sub> F. (D) chlorine has higher electronegativity than fluorine.					
56.	Amongst $NH_3$ , $PH_3$ , $AsH_3$ (A) $NH_3$ because of lower (C) $PH_3$ because of H-bor	and SbH <sub>3</sub> the one with h molecular weight nding	highest boiling point is : (B) SbH <sub>3</sub> because of higher molecular weight (D) AsH <sub>3</sub> because of lower molecular weight			
57.	<b>Consider the following</b> $S_1$ : The percentage of s-or respectively are same. $S_2$ : In SF <sub>4</sub> the bond angles between lone pair and bon $S_3$ : Aqueous H <sub>3</sub> PO <sub>4</sub> is sy $S_4$ : SiO <sub>2</sub> crystal may be alternate silicon and oxygo Of these :	statements. character in the orbital for s, instead of being 90° an nd pairs of electrons. rupy (i.e more viscous th considered as giant mo gen atoms.	rming S – S bonds and P - nd 180° are 89° and 177° re nan water) olecule in which eight-me	- P bonds in $S_8$ and $P_4$ molecules espectively due to the repulsions embered rings are formed with		
	(A) $S_1 \& S_4$ are correct on (C) $S_1, S_2, S_3 \& S_4$ are co	ıly. rrect.	(B) $S_2$ , $S_3 \& S_4$ are correction (D) $S_1$ , $S_2 \& S_3$ are correction	ect only. et only.		
58.	Which of the following is a <u>wrong</u> order with resp (A) $O_2^{2-} > O_2 > O_2^+$ [Paramagnetic moment] (C) $H_2 > H_2^+ > He_2^+$ [bond energy]		bect to the property mentioned against each ? (B) $(NO)^{-} > (NO) > (NO)^{+}$ [bond length] (D) $NO_{2}^{+} > NO_{2} > NO_{2}^{-}$ [bond angle]			
59.	Which of the following is $(A) S_3O_9 - \text{contains no S-}$ (C) $(\text{HPO}_3)_3 - \text{contains P}$	correct ? –S linkage. – P linkage	(B) $S_2O_6^{2-}$ – contains –O (D) $S_2O_8^{2-}$ contains S–S	–O– linkage. linkage		
More 60.	than one choice type The octet rule is not ob	<b>e</b> beyed in -				
	(A) $CO_2$	(B) BCI <sub>3</sub>	(C) PCI <sub>5</sub>	(D) $SIF_4$		
61.	Which of the following s (A) CO	pecies have a bond ord (B) CN <sup>–</sup>	ler of 3 ? (C) NO <sup>+</sup>	(D) O <sub>2</sub> <sup>+</sup>		
62.	Which of the following a (A) $C_2$	re diamagnetic ? (B) O <sub>2</sub> <sup>2–</sup>	(C) Li <sub>2</sub>	(D) N <sub>2</sub> +		
63.	CO <sub>2</sub> is isostructural with (A) HgCl <sub>2</sub>	h: (B) SnCl <sub>2</sub>	(C) C <sub>2</sub> H <sub>2</sub>	(D) NO <sub>2</sub>		
64.	Which of the following control $(A) \operatorname{NH}_4CI$	mpounds contain(s) both (B) KCN	n ionic and covalent bonds (C) CuSO <sub>4</sub> ·5H <sub>2</sub> O	s? (D) NaOH		
65.	Which of the following sta (A) BaO is more ionic that	atements is/are true for E an MgO.	BaO and MgO ? (B) MgO is more ionic th	an BaO.		

(C) BaO has a higher melting point than MgO. (D) MgO has a higher melting point than BaO.



66.	Most ionic compounds have : (A) high melting points and low boiling points (B) high melting points and non-directional bonds (C) high solubilities in polar solvents and low solubilities in nonpolar solvents (D) three-dimensional crystal structures, and are good conductors of electricity in the molten state								
67.	All bond : (A) dissociations are e (C) enthalpies are pos	exothermic itive	dissociations are endothermic enthalpies are negative						
68.	Which of the following (A) Low charge on ion (C) Large cation and s	factors do not favo s small anion	our electr	ovalency (B) Higl (D) Sma	? n charge on io all cation and	ons large anion			
69.	To which of the follow (A) $BrF_5$	ing species is the o (B) SF <sub>6</sub>	octet rule	not appl (C) IF <sub>7</sub>	icable ?	(D) CO <sub>2</sub>			
70.	Which statement(s) is (A) Polarising power r (B) Polarisability refer (C) Small cation is mo (D) Molecules in which	s/are correct ? efers to cation. s to anion. ore efficient to pola h cation having pse	rise anioi eudo ineri	n. t gas con	figuration are	more covalent.			
71.	In which of the followir (A) PCI <sub>5</sub>	ng molecules centr (B) SO <sub>4</sub> <sup></sup>	al atom i	nvolve ex (C) NO <sub>3</sub>	pansion of o	ctet ? (D) ClO <sub>3</sub> -			
72.	Which of the following $(A) SH_6$ (B) H	g do not exist ? FO <sub>4</sub>	(C) Fel <sub>3</sub>	3	(D) HCIO <sub>3</sub>				
73.	Which statement is co (A) In hybridisation or (B) In hybridisation ele (C) In hybridisation fu (D) Hybridised orbitals	orrect about hybrid bitals take part ectrons take part ılly filled , half filled s only contains bor	lization ? I or empty nd pair ele	y orbitals ectron	can take par	t			
74.	Which is true about O (A) Both are sp <sup>3</sup> hybrid (C) Bond angle in Cl <sub>2</sub> O	PF <sub>2</sub> & Cl <sub>2</sub> O ? dised D is greater than 10	)9°28'	(B) Bon (D) Bon	d angle in OF d angle in bot	$\frac{1}{2}$ less than 109 th cases are 10	°28' 9°28'		
75.	The halogen form comhalogen. Which of the (A) $XX'$ – Linear – pola (C) $XX'_5$ – square pyra	pounds among the following pairs repr ar amidal – polar	emselves resenting	with form their stru (B) XX' (D) XX'	ula XX′, XX′ <sub>3</sub> , ictures and be , – T-shaped – , – Pentagona	XX' <sub>5</sub> and XX' <sub>7</sub> w eing polar and no - polar Il bipyramidal — I	where X is the heavier on-polar are correct? non-polar		
76.	Which is true about N (A) Hybridization of N (C) Molecular geomet	H₂ <sup>-</sup> , NH₃ ,NH₄⁺ ? is same. ry (i.e. shape) is dii	fferent.	(B) No. (D) Bor	of lone pair of d angle is sar	f electron on N a me.	are same.		
77.	Which is/are in linear (A) $NO_2^+$	shape? (B) XeF <sub>2</sub>		(C) I <sub>3</sub> -		(D) I <sub>3</sub> +			
78.	Which combination of $(A)$ HgCl <sub>2</sub> - linear	the compounds a (B) XeF <sub>5</sub> + - squa	nd their g are pyran	jeometry nidal	/shape are co (C) CIF <sub>3</sub> - T-s	orrect ? shaped (D) ICl <sub>4</sub> -	square-planar		
79.	Correct order about be (A) $H_2O > H_2S > H_2Se$ (C) $SF_6 < NH_3 < H_2O$	ond angle is/are : e > H <sub>2</sub> Te < OF <sub>2</sub>		(B) C₂H (D) CIC	<sub>2</sub> > C <sub>2</sub> H <sub>4</sub> > CI <sub>2</sub> > H <sub>2</sub> O > H <sub>2</sub>	H <sub>4</sub> > NH <sub>3</sub> S > SF <sub>6</sub>			



80. Which is(are) true about VSEPR theory?

Identify the correct option(s).

81.

(A) Lone pair-lone pair repulsion is maximum.

(A)  $NH_4^+ > NH_3 > NH_2^-$  order of bond angle.

- (B) Lone pair and double bond occupy equatorial position in trigonal bipyramidal structure.
- (C) More electronegative atoms occupies axial position in trigonal bipyramidal structure.
- (D) Bigger atoms occupy axial positions in trigonal bipyramidal structure.
- (B)  $(CH_3)_3$  B is a trigonal planar molecule (not considering the H-atoms on 'C'). (C) In NH<sub>4</sub>Cl 'N' atom is in sp<sup>3</sup>d hybridisation. (D) In S<sub>8</sub> molecule a total of 16 electrons are left on all the 'S' atoms after bonding. 82. Which of the following statements is/are correct? (A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2 (B) The peroxide ion has a weaker bond than that of dioxygen molecule. (C) The peroxide ion as well as the dioxygen molecules are paramagnetic. (D) The bond length of the peroxide ion is greater than that of the dioxygen molecule. 83. The species which are paramagnetic is/are : (A) NO (B) NO<sub>2</sub>  $(C) CIO_{2}$  $(D) N_2 O_4$ 84. Among the following, the species with one unpaired electron are : (B) NO  $(D) B_{a}$  $(A) O_{2}^{+}$  $(C) O_{2}^{-}$ 85. Which of the following is/are correct statement(s) for dipole moment ? (A) Lone pair of electrons present on central atom can give rise to dipole moment. (B) Dipole moment is vector quantity. (C) CO<sub>2</sub> molecule has dipole moment. (D) Difference in electronegativities of combining atoms can lead to dipole moment. 86. Which of the following are polar? (A) XeF<sub>4</sub> (B) XeF<sub>6</sub> (C) XeOF<sub>4</sub> (D) XeF5-87. Which of the following is/are electron deficient compounds?

# **PART - II : SUBJECTIVE QUESTIONS**

(C) AICI

(D) LiAIH

 $\begin{array}{ll} \textbf{1.} & \mbox{Calculate the lattice energy of solid KF with the help of following data :} \\ & \Delta H^0{}_f(KF) = -562.6 \ \mbox{KJ mol}{}^{-1} \\ & \Delta H_{sub}(K) = 89.6 \ \mbox{kJ mol}{}^{-1} \\ & \Delta H_{IE1}(K) = 419.0 \ \mbox{kJ mol}{}^{-1} \\ & \Delta H_{diss}(F_2) = 158.2 \ \mbox{kJ mol}{}^{-1} \\ & \Delta H_{EA}(F) = a - 332.6 \ \mbox{kJ mol}{}^{-1} \end{array}$ 

 $(B) B_{2}H_{2}$ 

- **2.** Write the Lewis structure of the nitrite ion,  $NO_2^{-}$ .
- 3. What are the total number of  $\sigma \& \pi$  bonds in tetracyanomethane.
- 4. Use the VSEPR model to predict the geometry of the following : (a)  $XeF_2$  (b)  $CIO_3^-$
- 5. The triodide ion  $(I_3^-)$  in which the I atoms are arranged in a straight line is stable, but the corresponding  $F_3^-$  ion does not exist.



(A) NaBH

- 6. Ether R R and water H H have same hybridization at oxygen. What angle would you expect for them -
- 7. Discuss the bond angle in carbonyl halides COF<sub>2</sub>, COCl<sub>2</sub>, COBr<sub>2</sub>, COI<sub>2</sub>
- 8. Compare bond angle of  $OF_2$ ,  $CI_2O$  and  $Br_2O$ .
- **9.** The resultant dipole moment of water is 1.85 D ignoring the effects of lone pair. Calculate, the dipole moment of each OH bond (given that bond angle in  $H_2O = 104^\circ$ , cos  $104^\circ = -0.25$ ).
- **10.** For HCl molecule observed dipole moment is 1.03 D and bond length is 1.275 Å. Calculate % ionic character.
- 11. Why NH<sub>3</sub> is having more dipole moment than NF<sub>3</sub>.
- 12. Silyl isocyanate (SiH<sub>3</sub>NCO) is linear but methyl isocyanate (CH<sub>3</sub>NCO) is bent explain.
- 13. Arrange in order of increasing ionic radii in water and their mobility : Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>.
- 14.  $C_2H_2$  is not soluble in  $H_2O$  but it is highly soluble in acetone.
- **15.** Why SnCl<sub>2</sub>.2H<sub>2</sub>O readily loses one molecule of water at 80°C?
- **16.** Why crystalline sodium peroxide is highly hygroscopic in nature.
- 17. Explain that tetramethyl ammonium hydroxide is a stronger base than that of trimethyl ammonium hydroxide.
- **18.** Explain the hydrolysis in BCl<sub>3</sub> and BF<sub>3</sub>.
- **19.** Though O<sub>2</sub> molecule is paramagnetic yet it is a colourless gas. Why?
- 20. Why transition element have high heat of atomization.
- 21. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :
  (a) SiSi bond in Cl<sub>3</sub>SiSiCl<sub>3</sub>
  (b) SiCl bond in Cl<sub>3</sub>SiSiCl<sub>3</sub>
  (c) CaF bond in CaF<sub>2</sub>
  (d) NH bond in NH<sub>3</sub>
- 22. (a) Which one has highest and lowest melting point and why? NaCl KCl RbCl CsCl
  - (b) Why melting points of cesium halide (CsX) decrease in the order given below ? CsF > CsCl > CsBr > CsI.
- 23. Which of the compounds MgCO<sub>3</sub> and ZnCO<sub>3</sub> is thermally more stable ? Explain.
- 24. Why is anhydrous HCI predominantly covalent in the gaseous state but is ionic in aqueous solution?
- **25.** Which type of hybridisation is found in  $H_3O^+$ ?
- **26.** Why  $BeF_2$  has zero dipole moment whereas  $H_2O$  has some dipole moment?
- 27. Why crystals of hydrated calcium sulphate are soft and easily cleaved where as anhydrous calcium sulphate are very hard and very difficult to cleave ?
- 28. Super oxides are coloured and paramagnetic why?
- **29.** Of the species  $O_2^+, O_2^-, O_2$  and  $O_2^{2-}$  which would have the maximum bond strength ?



- **30.** The dipole moment of KCl is 3.336 × 10<sup>-29</sup> Coulomb meter. The interionic distance in KCl is 2.6Å. Find the % ionic character in KCl.
- **31.** The gaseous potassium chloride molecule has a measured dipole moment of 10.0 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is  $2.67 \times 10^{-8}$  cm. Calculate the percentage ionic character in KCI molecule.
- **32.** There will be three different fluorine-fluorine distances in molecule  $CF_2(C)_2 CF_2$ . Assuming ideal bond angles for a particular hybridisation (assume no distortion due to double bonds) find out the two smaller fluorine-fluorine distances and fill the result (in pm) in the increasing order in your answer sheet. Round off your answer to the nearest whole number.

(Given that C–F bond length = 134 pm, C = C bond length = 134 pm  $\sqrt{3}$  = 1.73)

**33.** For an ionic compound  $AX_3$  (s) formed between a metal A and a non-metal X (outermost shell configuration of  $X = ns^2 np^5$ ). Find the enthalpy of formation (magnitude) of  $AX_3$ (s) in k cal mol<sup>-1</sup> with the help of the following data. (Non-metal X is found to exist in nature as a diatomic gas)

$\Delta H_{Sublimation} A(s) = 100 \text{ Kcal/mol}$	$\Delta H_{IE_1} A(g) = 60 \text{ Kcal/mol}$
$\Delta H_{IE_2} A (g) = 150 \text{ Kcal/mol}$	$\Delta H_{IE_3} A(g) = 280 \text{ Kcal/mol}$
$\Delta H_{diss} X_2(g) = 80 \text{ Kcal/mol}$	$\Delta H_{e,q} X(g) = -110 \text{ Kcal/mol}$
$\Delta H_{\text{Lattice energy}} A X_3(s) = -470 \text{ Kcal/mol}$	Ŭ

- **34.** CO forms weak bonds to Lewis acid such as BF<sub>3</sub>. In contrast CO forms strong bonds to transition metals. Why explain ?
- **35.**  $(SiH_3)_3N$  is a weaker base than  $(CH_3)_3N$ .
- **36.** The dipole moment of  $NH_3$  is more than that of  $NF_3$
- **37.** o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzalehye is a high melting solid
- **38.** The central carbon-carbon bond in 1,3-butadiene is shorter than of n-butane
- **39.** Using VSEPR theory, draw the shape of  $PCI_5$  and  $BrF_5$ .
- **40.** Indicate the type of hybridization of each carbon atom in the following compounds(A)  $CH_3CN$ (B)  $CH_3CH = CH_2$ (C)  $H_3C-C \equiv C-CH_3$ (D)  $HC \equiv C-CH = CH_2$
- 41. Among the following compounds/species write the order O–O bond length in O<sub>2</sub>, O<sub>2</sub>[AsF<sub>4</sub>], K[O<sub>2</sub>]
- 42. BaSO<sub>4</sub> being an electrovalent compound and still it does not pass into solution state in water. Why
- **43.** Explain why NO<sup>+</sup> is more stable towards dissociation into its atoms than NO ?
- **44.** Arrange the following in the increasing order of their covalent character. (a) NaF, Na<sub>3</sub>N and Na<sub>2</sub>O (b) NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>, SiCl<sub>4</sub> and PCl<sub>5</sub>
- 45. SnCl<sub>4</sub> has melting point 15°C where as SnCl<sub>2</sub> has melting point 535°C. Why?
- **46.**  $SnCl_2$  is white but  $SnI_2$  is red. Why?



- **47.** Arrange the following in the increasing order of their solubility in water. (a) AgCl, AgBr, AgI, AgF (b)  $BeF_2$ ,  $BeCl_2$ ,  $BeBr_2$ ,  $Bel_2$ (c)  $PbF_2$ ,  $PbCl_2$ ,  $PbBr_2$ ,  $Pbl_2$ (d)  $Na_2SO_4$ ,  $MgSO_4$ ,  $Al_2(SO_4)_3$ (e) LiCl,  $BeCl_2$ ,  $BCl_2$
- **48.** Draw the Lewis structures of the following molecules and ions.  $PH_3$ ,  $H_2S$ ,  $BeF_2$ ,  $SiCl_4$ , HCOOH,  $N_2O_4$ ,  $H_2SO_4$ ,  $H_2S_2O_7$ ,  $O_2^{2-}$ ,  $F_2O$ ,  $CH_3COCI$ ,  $CrO_5$ ,  $C_3^{4-}$
- 49. Explain hybridisation of central atom in :

NH<sub>3</sub> NF<sub>3</sub>

50.

(7)

	, <b>,</b>								
(1)	XeF <sub>2</sub>		(2)	XeF₄	(3)	$PCI_3$		(4)	$PCl_5$
(5)	SF <sub>6</sub>		(6)	IF <sub>3</sub>	(7)	IF <sub>5</sub>		(8)	IF <sub>7</sub>
(9)	CH₄		(10)	CČl₄	(11)	SiCl₄		(12)	SiH₄
(13)	) H <sub>2</sub> O		(14)	NH3	(15)	$N_2O_5$		(16)	BrF <sub>5</sub>
(17)	) $N\overline{O}_{3}^{-}$		(18)	CO <sub>3</sub> <sup>2-</sup>	(19)	$NH_4^+$		(20)	
Wh	ich one has	s highest	and leas	st bond angle i	in the follov	ving ?			
(1)	$CH_4$	$PH_{3}$	AsH <sub>3</sub>	SbH <sub>3</sub>	(2)	H <sub>2</sub> O	$H_2S$	H <sub>2</sub> Te	$CO_2$
(3)	$PH_{3}$	$H_2O$	-	-	(4)	Cl <sub>2</sub> O		_	_
(5)	PF	PH			(6)	BF,	NF <sub>3</sub>		

**51.** PCI<sub>s</sub> has the shape of a trigonal bipyramidal where as  $IF_s$  has the shape of square pyramidal. Explain.

(8) PF PCI

- (a) PH<sub>5</sub> is not possible but PCI<sub>5</sub> is possible. Why ?
  (b) NCI<sub>5</sub> is not possible but PCI<sub>5</sub> is possible. Why ?
  (c) F<sub>3</sub><sup>-</sup> does not exist but I<sub>3</sub><sup>-</sup>, Br<sub>3</sub><sup>-</sup> exist. Why ?
  (d) SCI<sub>6</sub> does not exist but SF<sub>6</sub> exists. Why ?
- **53.** Explain the hybridisation in solid form of  $PCI_5$ ,  $N_2O_5$  and  $XeF_6$ .
- 54. Why  $CH_3 O H$  is having more dipole moment than  $CH_3 S H$ ?
- 55. Why CH<sub>3</sub>Cl is having higher dipole moment than CH<sub>3</sub>F?
- 56. trans–1, 2 dichloro ethene have zero dipole moment while its cis- form has some dipole moment. Explain.
- 57. Arrange in increasing order of dipole moment ; H<sub>2</sub>O, H<sub>2</sub>S, BF<sub>3</sub>.
- **58.** Why  $CCl_4$  have zero dipole moment but  $CHCl_3$  have some dipole moment?
- 59. Why glucose, fructose, sucrose etc. are soluble in water though they are covalent compounds?
- **60.** Benzene has zero dipole moment and therefore, experiences no dipole-dipole forces but it is a liquid rather than a gas at room temperature. Explain.
- 61. Br<sub>2</sub> and ICI have the same number of electrons but ICI has higher boiling point than Br<sub>2</sub>. Why, explain ?
- **62.** Why  $D_2O$  has higher viscosity than  $H_2O$ ?
- **63.** Explain the H-bonding in crystalline NaHCO<sub>3</sub> and KHCO<sub>3</sub>?
- 64. Ethanol has higher boiling point than diethyl ether. Why?
- **66.** Explain the structure, hybridisation and oxidation state of S in sulphuric acid, Marshall's acid, Caro's acid and oleum.
- **67.** The POCl<sub>3</sub> molecule has the shape of an irregular tetrahedron with the P atom located centrally. The Cl–P–Cl angle is found to be 103.5°. Give a qualitative explanation for the deviation of this structure from a regular tetrahedron.
- **68.** Write the geometry of  $XeF_4$  and  $OSF_4$  using VSEPR theory and clearly indicate the position of lone pair of electrons.



- **69.** Explain the structure of  $CIF_3$  on the basis of VSEPR theory.
- **70.** The dipole moment of HBr is 2.60 × 10<sup>-30</sup> Cm and the inter-atomic distance is 1.41 Å. What is the per cent ionic character of HBr ?
- 71. Out of trimethylamine and trimethyphosphine, which one has higher dipole moment?
- 72. Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character in LiF molecule Li—F bond length is 156 pm.
- **73.** A diatomic molecule has a dipole moment of 1.2 D. If bond length is 1.0 Å, what percentage of an electronic charge exists on each atom.
- 74. BF<sub>3</sub>(g) dissolves in diethyl ether forming a viscous liquid. Explain ?

Arrange the following (i)  $N_2$ ,  $O_2$ ,  $F_2$ ,  $O_2^+$ ; in increasing order of bond dissociation energy. (ii) O, S, F, CI, N; in increasing strength of hydrogen bonding (X – H – – – X). (iii)  $N_3^-$ ,  $BF_3$ ,  $NH_3$ ,  $XeF_4$ . in increasing bond angle.

**76.** Why  $[SiCl_{\beta}]^{2-}$  does not exist?

75.

- 77. CIO<sub>2</sub> does not forms dimer but NO<sub>2</sub> forms. Why?
- **78.** Discuss the hybridisation of C-atoms in allene  $(C_3H_4)$  and show the  $\pi$ -orbital overlaps.
- **79.** O<sub>2</sub>, N<sub>2</sub> are colourless gases but Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> are coloured gases. Explain on the basis of M.O. theory.
- **80.** BCl<sub>3</sub> is more acidic than BF<sub>3</sub>. Why?
- **81.** BF<sub>3</sub> exists but BH<sub>3</sub> does not. Why explain?
- **82.** In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine  $N(SiH_3)_3$  it has a planar geometry. Explain? Out of trimethylamine and trisilyamine which one is more basic and why?
- 83. Find out the bond order of : (a)  $H_2$  (b)  $H_2^+$  (c)  $He_2$  (d)  $Li_2$  (e)  $Be_2$  (f)  $B_2$
- **84.** Identify the molecules or atoms or ions from the following molecular orbital energy level formulations. The species should be selected from (B<sub>2</sub>, C<sub>2</sub>, O<sub>2</sub><sup>2+</sup>, O<sub>2</sub>, F<sub>2</sub>, N<sub>2</sub>)
  - (a) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \pi (2p_x)^1 \pi (2p_y)^1$
  - (b) KK  $\sigma$  (2s)<sup>2</sup>  $\sigma^{*}$  (2s)<sup>2</sup>  $\pi$  (2p<sub>x</sub>)<sup>2</sup>  $\pi$  (2p<sub>y</sub>)<sup>2</sup>
  - (c) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \sigma (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2$
  - (d) KK  $\sigma$  (2s)<sup>2</sup>  $\sigma^{*}$ (2s)  $\sigma$ (2p<sub>z</sub>)<sup>2</sup>  $\pi$ (2p<sub>x</sub>)<sup>2</sup>  $\pi$ (2p<sub>y</sub>)<sup>2</sup>  $\pi$ (2p<sub>x</sub>)<sup>1</sup> $\pi^{*}$ (2p<sub>y</sub>)<sup>1</sup>
  - (e) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \sigma (2p_z)^2 \pi (2p_x)^2 \pi (2p_y)^2 \pi (2p_x)^2 \pi^* (2p_y)^2$
  - (f) KK  $\sigma (2s)^2 \sigma^* (2s)^2 \pi (2p_y)^2 \pi (2p_x)^2 \sigma (2p_z)^2$
- **85.** What is the bond order of underlined species in  $\underline{NO}[BF_4]$ ?
- 86. At high temperatures sulphur vapour is predominantly in the form of  $S_2(gas)$  molecules. Assuming that the molecular orbitals for third row diatomic molecules (homonuclear) are analogous to those for second-row molecules. Answer the following questions by putting correct number in the boxes provided at the bottom.
  - P: The number of unpaired electrons in  $S_2$ .
  - Q: The bond order of  $S_2$ .
  - R: The number of  $\pi$  bond(s) in S<sub>2</sub>.
  - S: The bond order of  $S_2^{2-}$ , disulphide ion formed by the gain of two electrons.







# PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

#### Marked Questions are having more than one correct option.

1.	The hybridization of at (A) sp, sp <sup>3</sup> and sp <sup>2</sup> res (C) sp <sup>2</sup> , sp and sp <sup>3</sup> res	: ectively ectively	[JEE–2000, 1/35]		
2.	The number of P—O- (A) zero	—P bonds in tricyclic metap (B) two	phosphoric acid is : (C) three	(D) four	[JEE–2000, 1/35]
3.	Molecular shapes of S (A) the same with 2, 0 (B) the same with 1, 1 (C) different with 0, 1 a (D) different with 1, 0 a		[JEE–2000, 1/35]		
4.	Amongst $H_2O$ , $H_2S$ , $H$ (A) $H_2O$ because of $H_2C$ (C) $H_2S$ because of $H_2C$	<b>[JEE–2000, 1/35]</b> cular weight. cular weight.			
5.	Write the Molecular of	rbital electron distribution o	f O <sub>2</sub> . Specify its bond orde	er and m	agnetic property. [JEE–2000, 3/100]
6.	Draw the molecular st	ructures of $XeF_2$ , $XeF_4$ and	$XeO_2F_2$ , indicating the loc	ation of I	lone pair of electrons. [JEE–2000, 3/100]
7.	The number of S–S be (A) three	onds, in sulphur trioxide trir (B) two	ner (S <sub>3</sub> O <sub>9</sub> ) is : (C) one	(D) Zero	<b>[JEE–2001, 1/35]</b>
8.	The correct order of $BCl_3$ is : [ Atomic num (A) dsp <sup>2</sup> , dsp <sup>3</sup> , sp <sup>2</sup> ar (C) dsp <sup>2</sup> , sp <sup>2</sup> , sp <sup>3</sup> , ds	hybridisation of the centra mber Pt = 78 ] nd sp <sup>3</sup> p <sup>3</sup>	al atom in the following sp (B) sp³, dsp², dsp³, sp² (D) dsp², sp³, sp², dsp³	pecies;	NH <sub>3</sub> , [PtCl₄]²⁻, PCl₅ and <b>[JEE–2001, 1/35]</b>
9.	The common feature (A) bond order three a (C) bond order two an	of the species CN $$ , CO, No nd isoelectronic. d $\pi$ acceptor.	O⁺ are : (B) bond order three and (D) isoelectronic and we	l weak fi ak field l	<b>[JEE–2001, 1/35]</b> eld ligand. igands.
10.	<b>Assertion :</b> Between <b>Reason :</b> $SiCl_4$ is ionia (A) Both Assertion and (B) Both Assertion and (C) Assertion is true b (D) Assertion is false	SiCl <sub>4</sub> and CCl <sub>4</sub> only SiCl <sub>4</sub> re c and CCl <sub>4</sub> is covalent. d Reason are true and Rea d Reason are true but Reas ut Reason is false. but Reason is true.	eacts with H <sub>2</sub> O. son is the correct explana son is not correct explanat	ition of A tion of A	[JEE–2001, 1/35] Assertion. Ssertion.
11.	Specify the coordinati NH <sub>3</sub> . (A) N : tetrahedral sp <sup>3</sup> (C) N : pyramidal sp <sup>3</sup> ,	on geometry around and hy , B : tetrahedral sp <sup>3</sup> B : planar sp <sup>2</sup>	ybridisation of N and B ato (B) N : pyramidal sp³, B (D) N : pyramidal sp³, B	oms in a : pyarmi : tetrahe	1 : 1 complex of BCl <sub>3</sub> & [ <b>JEE–2002, 3/90]</b> idal sp <sup>3</sup> edral sp <sup>3</sup>



12.	Identify the correct order	r of boiling points of the fo	ollowing compounds :		[JEE-2002, 3/90]		
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl 1	H <sub>2</sub> OH CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C 2	HO CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C 3	ООН			
	(A) 1 > 2 > 3	(B) 3 > 1 > 2	(C) 1 > 3 > 2	(D) 3 >	2 > 1		
13.	Which of the following m (A) $N_2$	nolecular species has unp (B) F <sub>2</sub>	paired electron(s) ? (C) $O_2^-$	(D) O <sub>2</sub> <sup>2-</sup>	[JEE–2002, 3/90]		
14.	Which of the following $NO_3^{-}$ , $CO_3^{2-}$ , $O_3^{2-}$	are isoelectronic and is $CIO_3^-$ , $SO_3$ .	ostructural?		[JEE-2003, 3/84]		
	(A) NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	(B) $SO_3^-$ , $NO_3^-$	(C) ClO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>	(D) CO	<sub>3</sub> <sup>2–</sup> , SO <sub>3</sub> .		
15.	Among the following the (A) $CH_3CI$	Among the following the molecule with the highest dipole moment is : (A) $CH_3CI$ (B) $CH_3CI_2$ (C) $CHCI_3$ (D)					
16.	Which of the following re	<sup>2</sup> – sp – sp	from left to right.				
	(A) $H_2C = CH - C \equiv N$		(B) $HC \equiv C - C \equiv CH$		[022-2003, 3/04]		
	(C) $H_2C = C = C = CH_2$		(D) H <sub>2</sub> N				
17.	Using VSEPR theory, dr		[JEE-2003, 2/60]				
18.	Which one is more solul	Cl <sub>3</sub> ? Expla	ain in terms of bonding. [JEE–2003, 2/60]				
19.	The number of lone pair (A) 3	(s) of electrons in XeOF <sub>4</sub> (B) 2	is : (C) 1	(D) 4	[JEE–2004, 3/84]		
20.	Amongst the following the (A) $H_2 S_2 O_3$	ne acid having $-O-O-bc$ (B) $H_2S_2O_5$	ond is : (C) $H_2 S_2 O_6$	(D) H <sub>2</sub> S	<b>[JEE–2004, 3/84]</b> S <sub>2</sub> O <sub>8</sub>		
21.	According to molecular of is correct ? (A) It is paramagnetic an (B) It is paramagnetic an (C) It is diamagnetic and (D) It is diamagnetic and	orbital theory, which one o nd has less bond order th nd more bond order than d has less bond order tha d has more bond order tha	of the following statements an $O_2^{}$ $O_2^{}$ an $O_2^{}$ an $O_2^{}$	s about the	e molecular species O <sub>2</sub> + [ <b>JEE–2004, 3/84]</b>		
22.	Use VSEPR model to dr specify their geometry.	aw the structures of OSF	$F_4$ and XeF <sub>4</sub> (indicate the	lone pair(	(s) on central atom) and <b>[JEE–2004, 2/60]</b>		
23.	Arrange the following th	ree compounds in terms	of increasing O — O bor	nd length	:		
	Justify your answer base compounds.	ed on the ground state ele	ctronic configuration of th	e dioxyge	n species in these three [JEE–2004, 2/60]		
24.	$AIF_3$ is insoluble in anh addition of $BF_3$ , $AIF_3$ is p	ydrous HF but when little precipitated. Write the ba	e KF is added to the cor lanced chemical equation	mpound i ns.	t becomes soluble. On [JEE-2004, 2/60]		
25.	In which of the following	the maximum number o	f lone pairs is present on	the centra	al atom ?		
	(A) [CIO <sub>3</sub> ] <sup>_</sup>	(B) XeF <sub>4</sub>	(C) SF <sub>4</sub>	(D) I <sub>3</sub> -	[JEE−2003, 3/84]		



26.	Which of the following silicate is formed when three oxygen atoms of [SiO <sub>4</sub> ] <sup>4-</sup> tetrahedral units are shared? [JEE-2005, 3/84]										
	(A) She	et silicat	te			(B) Pyrosilicate	)		• • •		
	(C) Thr	ee dimer	nsional s	ilicate		(D) Linear chai	n silicate				
27.	Predict (i) NMe	whether	the follo (ii) N(Si	wing molecule: Me <sub>3</sub> ) <sub>3</sub>	s are iso-s	tructural or not.	Justify your a	Inswei	r. <b>[JEE–2005, 2/60]</b>		
28.	Write tl	he struct	ure of $P_2$	O <sub>10</sub> .					[JEE–2005, 1/60]		
29.	The sp (A) NO	ecies hav	ving bon (B) NO <sup>-</sup>	d order differen	t from that (C) CN	in CO is :	(D) N <sub>2</sub>		[JEE–2007, 3/162]		
30.	Among (A) Na <sub>2</sub>	the follo O <sub>2</sub>	wing, the	e paramagnetic (B) O <sub>3</sub>	compoun	d is : (C) N <sub>2</sub> O	(D)	) KO <sub>2</sub>	[JEE–2007, 3/162]		
31.	The pe (A) 25	rcentage	of p-cha	aracter in the or (B) 33	rbitals forn	ning P – P bonds (C) 50	s in P <sub>4</sub> is : (D)	) 75	[JEE–2007, 3/162]		
32.	Statem Statem (A) Stat (B) Stat (C) Sta (D) Sta	nent-1 : E nent-2 : T tement-1 tement-1 tement-1 tement-1	Boron alv The smal is True, is True, is True, is False	vays forms cov I size of B <sup>3+</sup> fav Statement-2 is Statement-2 is Statement-2 is e, Statement-2 is	alent bond ours forma True; Stat True; Stat False. s True.	l, <b>because</b> ation of covalent rement-2 is a co ement-2 is NOT	bond. rrect explana a correct ex	ation fo	[JEE–2007, 3/162] or Statement-1. tion for Statement-1.		
33.	Statem Statem (A) Stat (B) Stat (C) Stat (D) Stat	tement-1 : E tement-2 : 7 tement-1 tement-1 tement-1 tement-1	Band gap The ener is True, is True, is True, is False	o in germanium gy spread of ea Statement-2 is Statement-2 is Statement-2 is a, Statement-2 is	is small, I ach germa True; Stat True; Stat False s True	<b>Decause</b> nium atomic ene rement-2 is a co ement-2 is NOT	ergy level is ir rrect explana a correct ex	nfinite ation fo	simally small. [ <b>JEE–2007, 3/162]</b> or Statement-1. tion for Statement-1		
34.	Match	each of t <b>Colum</b>	he diato <b>n I</b>	mic molecules	in <b>Columı</b>	n I with its prope Column II	s in <b>C</b>	olumn II. [JEE–2009, 8/160]			
	(A)	B <sub>2</sub>			(p)	Paramagnetic					
	(B)	N <sub>2</sub>			(q)	Undergoes oxic	lation				
	(C)	0			(r)	Undergoes red	uction				
	(D)	0,			(s)	Bond order $\geq 2$					
		L			(t)						
35.*	The nit (A) N <sub>2</sub> C	rogen ox )	ide(s) tha (B) N <sub>2</sub> O	at contain(s) N-	–N bond(s (C) N <sub>2</sub> O	s) is(are) : 4	(D) N <sub>2</sub> O <sub>5</sub>		[JEE–2009, 4/160]		
36.	Thenu	mber of v	vater mo	lecule (s) direct	ly bonded	to the metal cen	tre in CuSO <sub>4</sub> .	5H <sub>2</sub> O	is : <b>[JEE–2009, 4/160]</b>		
37.	Based on VSEPR theory, the number of 90 degree F–Br–F angles in BrF <sub>5</sub> is : [,								[JEE–2010, 3/163]		
38.	Assum (A) 1 ar (C) 1 ar	ing that H nd diama nd param	Hund's ru gnetic agnetic	ule is violated, t	he bond o	rder and magne (B) 0 and diama (D) 0 and paran	tic nature of agnetic nagnetic	the dia	atomic molecule B <sub>2</sub> is : [ <b>JEE–2010, 5/163]</b>		
39.*	The co (A) O-C (C) O <sub>3</sub> i	rrect stat ) bond le is diamaç	ement(s ngths ar gnetic in	) about O <sub>3</sub> is(ar e equal nature	re) :	(B) Thermal de (D) O <sub>3</sub> has a be	composition ent structure	of O <sub>3</sub> i	[JEE–2013, P-2] s endothermic		



# PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

1.	Increasing order of bond (1) $O_2^+ < O_2 < O_2^- < O_2^2$ (3) $O_2^- < O_2^{2-} < O_2^+ < O_2^{2-}$	d strength of O <sub>2</sub> , O <sub>2</sub> <sup>-</sup> , O <sub>2</sub> <sup>2-</sup>	and $O_2^+$ is : (2) $O_2 < O_2^+ < O_2^- < O_2^{-2}$ (4) $O_2^{-2} < O_2^- < O_2^- < O_2^{-2}$	[AIEEE-2002]					
2.	The number of lone pair	s on Xe in XeF <sub>2</sub> , XeF <sub>4</sub> and	I XeF <sub>6</sub> respectively are :		[AIEEE-2002]				
	(1) 3, 2, 1	(2) 2, 4, 6	(3) 1, 2, 3	(4) 6, 4, 2					
3.	The hybridisation of the (1) AIH <sub>3</sub> changes to AIH <sub>4</sub> (3) $NH_3$ changes to $NH_4$	underline atom changes ,- ,-	in : (2) $H_2O$ changes to $H_3O$ (4) in all cases	+	[AIEEE-2002]				
4.	<ul> <li>Select correct statement.</li> <li>(1) When a covalent bond is formed, transfer of electrons takes place.</li> <li>(2) Pure H<sub>2</sub>O does not contain any ion.</li> <li>(3) A bond is formed when attractive forces overcome repulsive forces.</li> <li>(4) HF is less polar then HBr.</li> </ul>								
5.	Bond angle of 109º 28' i (1) NH <sub>3</sub>	s found in: (2) H <sub>2</sub> O	(3) CH <sub>3</sub> <sup>+</sup>	(4) NH <sub>4</sub> <sup>+</sup>	[AIEEE-2002]				
6.	<ul> <li>In the anion HCOO<sup>-</sup> the two C – O bonds are found to be of equal length. What is the rest</li> <li>(1) Electronic orbits of carbon atom are hybridised.</li> <li>(2) The C = O bond is weaker than the C – O bond.</li> <li>(3) The anion HCOO<sup>-</sup> has two resonating structures.</li> <li>(4) The anion is obtained by removal of a proton from the acid molecule.</li> </ul>								
7.	Which of the following c (1) SO <sub>2</sub>	ompounds has the small (2) H <sub>2</sub> O	est bond angle in its mole (3) H <sub>2</sub> S	ecule ? (4) NH <sub>3</sub>	[AIEEE-2003]				
8.	An ether is more volatile than an alcohol having the same molecular formula. This is due (1) dipolar character of ethers. (3) inter-molecular hydrogen bonding in ethers. (4) inter-molecular hydrogen bonding i								
9.	The pair of species have $(1) \operatorname{CF}_4, \operatorname{SF}_4$	ng identical shapes for m (2) $XeF_2$ , $CO_2$	nolecules of both species (3) $BF_3$ , PCI $_3$	is : (4) PF <sub>5</sub> , IF <sub>5</sub> .	[AIEEE-2003]				
10.	Which of the following p	air of molecules will have	permanent dipole mome	nts for both mem	oers? [AIEEE-2003]				
	(1) SiF <sub>4</sub> and NO <sub>2</sub>	(2) $NO_2$ and $CO_2$	(3) $NO_2$ and $O_3$	(4) SiF $_4$ and CO	2				
11.	The maximum number of (1) dsp <sup>3</sup>	of 90° angles between bon (2) sp³d	d pair–bond pair of electro (3) dsp²	ons is observed in (4) sp³d²	: <b>[AIEEE-2004]</b>				



12.	The correct order of bot (1) $H_2S < SiH_4 < NH_3 <$ (3) $H_2S < NH_3 < SiH_4 <$	nd angles (smallest first) BF <sub>3</sub> BF <sub>3</sub>	in $H_2S$ , $NH_3$ , $BF_3$ and $SiH_4$ (2) $NH_3 < H_2S < SiH_4 <$ (4) $H_2S < NH_3 < BF_3 < SiH_3 < S$	[AIEEE-2004]						
13.	The bond order in NO i species?	s 2.5 while that in NO $^{+}$ is	3. Which of the following	statements is tro	ue for these two [AIEEE-2004]					
	<ol> <li>Bond length in NO<sup>+</sup></li> <li>Bond length in NO<sup>+</sup></li> </ol>	is greater than in NO is equal to that in NO	<ul><li>(2) Bond length in NO is</li><li>(4) Bond length is unpresented</li></ul>	s greater than in l edictable	NO <sup>+</sup>					
14.	The states of hybridizati (1) sp² and sp²	on of boron and oxygen a (2) sp² and sp³	toms in boric acid (H <sub>3</sub> BO <sub>3</sub> (3) sp <sup>3</sup> and sp <sup>2</sup>	) are respectively (4) sp <sup>3</sup> and sp <sup>3</sup>	: [AIEEE-2004]					
15.	Which one of the following has the regular tetrahedral structure ? (Atomic number : B = 5, S = 16, Ni = 28, Xe = 54)									
	(1) XeF <sub>4</sub>	(2) SF <sub>4</sub>	(3) BF <sub>4</sub> <sup>-</sup>	(4) [Ni(CN) <sub>4</sub> ] <sup>2-</sup>						
16.	Which one of the follow (1) Acetone	ing does not have sp² hyb (2) Acetic acid	oridized carbon? (3) Acetonitrile	(4) Acetamide	[AIEEE-2004]					
17.	The structure of diborar (1) four 2c–2e bonds an (3) two 2c–2e bonds an	ne (B <sub>2</sub> H <sub>6</sub> ) contains : d four 3c–2e bonds d four 3c–2e bonds	(2) two 2c–2e bonds an (4) four 2c–2e bonds ar	[AIEEE-2005] ds ds						
18.	Lattice energy of an ion (1) charge on the ions c (3) packing of ions only	ic compound depends up only	oon : (2) size of the ions only (4) charge on the ion ar	, nd size of the ion	[AIEEE-2005]					
19.	Based on lattice energy and other considerations, which one of the following alkali me expected to have the highest melting point ?									
	(1) LiCl	(2) NaCl	(3) KCI	(4) RbCl						
20.	The molecular shapes of (1) the same with 2, 0 a (2) the same with 1, 1 a (3) different with 0, 1 an (4) different with 1, 0 an	of $SF_4$ , $CF_4$ and $XeF_4$ are : nd 1 lone pairs of electro nd 1 lone pair of electron d 2 lone pairs of electron d 2 lone pairs of electron	ns on the central atom, re s on the central atom, re s on the central atom, res s on the central atom, res	espectively. spectively. spectively. spectively.	[AIEEE-2005]					
21.	Which one of the follow (1) He,*	ing species is diamagnet (2) H <sub>a</sub>	ic in nature ? (3) H <sub>a</sub> +	(4) H <sub>a</sub>	[AIEEE-2005]					
22.	The number and type o (1) one sigma, one pi	f bonds between two carb (2) one sigma, two pi	oon atoms in calcium carl (3) two sigma, one pi	bide are : (4) two sigma, t	<b>[AIEEE-2005]</b> wo pi					
23.	Which of the following n $(1) O^{2}$	nolecules/ions does not c	ontain unpaired electrons	s?	[AIEEE-2006]					
	$(1) U_2^{2^-}$	(2) B <sub>2</sub>	(3) $N_2^+$	$(4) O_2$						
24.	A metal, M forms chlori chlorides is correct ? (1) $MCl_2$ is more volatile (3) $MCl_2$ is more ionic th	des in + 2 and + 4 oxidati than $MCl_4$ han $MCl_4$	<ul> <li>ion states. Which of the f</li> <li>(2) MCl<sub>2</sub> is more soluble</li> <li>(4) MCl<sub>2</sub> is more easily</li> </ul>	nts about these [AIEEE-2006] hanol than MCl <sub>4</sub> MCl <sub>4</sub>						



25.	Which of the following s	[AIEEE	-2007, 3/120]							
	(1) O <sub>2</sub> <sup>2-</sup>	(2) O <sub>2</sub> <sup>+</sup>	(3) O <sub>2</sub>	(4) NO						
26.	Which of the following h	ydrogen bonds is the stro	ongest?	[AIEEE	-2007, 3/120]					
	(1) O – H O	(2) O – H F	(3) F – H H	(4) F – H F						
27.	The charge/ size ratio c represents the increasir	f a cation determines its ng order of the polarizing	polarizing power. Which power of these cationic s	one of the follov species, K <sup>+</sup> , Ca <sup>24</sup> [AIEEE	ving sequences <sup>•</sup> , Mg <sup>2+</sup> , Be <sup>2+</sup> ? <b>-2007, 3/120]</b>					
	(1) K <sup>+</sup> < Ca <sup>2+</sup> < Mg <sup>2+</sup> < E (3) Mg <sup>2+</sup> < Be <sup>2+</sup> < K <sup>+</sup> < C	3e <sup>2+</sup> Ca <sup>2+</sup>	(2) Ca <sup>2</sup> < Mg <sup>2+</sup> < Be <sup>2+</sup> < (4) Be <sup>2+</sup> < K <sup>+</sup> < Ca <sup>2+</sup> < N	- K+ 1g²+	· -					
28.	In which of the following changed ?	and the magnet [AIEEE	ic behaviour has <b>-2007, 3/120]</b>							
	(1) $O_2 \longrightarrow O_2^+$	(2) $N_2 \longrightarrow N_2^+$	$(3) \operatorname{C}_2 \longrightarrow \operatorname{C}_2^+$	$(4) \text{ NO} \longrightarrow$	NO⁺					
29.	Which one of the followi (1) CN⁻ and CN⁺	ng pairs of species has th (2) $O_2^-$ and $CN^-$	ne same bond order? (3) NO⁺ and CN⁺	[AIEEE (4) CN <sup>-</sup> and NC	-2008, 3/105] ⁺					
30.	The bond dissociation energy of B – F in BF <sub>3</sub> is 646 kJ mol <sup>-1</sup> whereas that of C – F in CF <sub>4</sub> is 515 kJ mol <sup>-1</sup> . The correct reason for higher B – F bond dissociation energy as compared to that of C – F is : <b>[AIEEE-2009, 4/144]</b> (1) stronger $\sigma$ bond between B and F in BF <sub>3</sub> as compared to that between C and F in CF <sub>4</sub> . (2) significant $p\pi - p\pi$ interaction between B and F in BF <sub>3</sub> whereas there is no possibility of such interaction									
	(3) lower degree of $p\pi$ - (4) smaller size of B - at	$p_{\pi}$ interaction between B om as compared to that	and F in $BF_3$ than that be of C - atom.	tween C and F i	n CF₄.					
31.	Using MO theory predict (1) $O_2^+$	which of the following sp $(2) O_2^{-}$	ecies has the shortest bo (3) $O_2^{2-}$	nd length ? <b>[AIEI</b> (4) O <sub>2</sub> <sup>2+</sup>	EE-2009, 4/144]					
32.	Among the following the (1) FeCl <sub>2</sub>	maximum covalent char (2) SnCl <sub>2</sub>	acter is shown by the con (3) AICI <sub>3</sub> (4) MgC	npound : Cl <sub>2</sub>	[AIEEE - 2011]					
33.	The hybridisation of orb	itals of N atom in $NO_3^-$ , N	$O_2^+$ and $NH_4^+$ are respecti	vely :	[AIEEE - 2011]					
	(1) sp, sp <sup>2</sup> , sp <sup>3</sup>	(2) sp <sup>2</sup> , sp, sp <sup>3</sup>	(3) sp, sp <sup>3</sup> , sp <sup>2</sup>	(4) sp <sup>2</sup> , sp <sup>3</sup> , sp	)					
34.	The structure of IF <sub>7</sub> is : (1) square pyramid (3) octahedral		(2) trigonal bipyramid (4) pentagonal bipyramid	ł	[AIEEE - 2011]					
35.*	Which one of the followi	ng molecule is expected	to exhibit diamagnetic be	haviour?	[AIEEE - 2013]					
	(1) C <sub>2</sub>	(2) N <sub>2</sub>	(3) O <sub>2</sub>	(4) S <sub>2</sub>						
36.	In which of the following (1) $H_2^+$ , $He_2^{2-}$	pairs molecules/ions, bo (2) $H_2^-$ , $He_2^{2-}$	oth the species are not lik (3) $H_2^{2+}$ , $He_2$	ely to exist ? (4) $H_2^-$ , $He_2^{2+}$	[AIEEE - 2013]					



# NCERT QUESTIONS

- 1. Explain the formation of a chemical bond.
- 2. Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.
- 3. Write Lewis symbols for the following atoms and ions : S and S<sup>2-</sup> ; AI and AI<sup>3+</sup> ; H and H<sup>-</sup>
- 4. Draw the Lewis structures for the following molecules and ions :  $H_2S$ , SiCl<sub>4</sub>, BeF<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, HCOOH
- 5. Define octet rule. Write its significance and limitations.
- 6. Write the favourable factors for the formation of ionic bond.
- 7. Discuss the shape of the following molecules using the VSEPR model :  $BeCl_2$ ,  $BCl_3$ ,  $SiCl_4$ ,  $AsF_5$ ,  $H_2S$ ,  $PH_3$
- 8. Although geometries of  $NH_3$  and  $H_2O$  molecules are distorted tetrahedral, bondangle in water is less than that of ammonia. Discuss.
- 9. How do you express the bond strength in terms of bond order?
- **10.** Define the bond length.
- **11.** Explain the important aspects of resonance with reference to the  $CO_3^{2-}$  ion.
- **12.**  $H_3PO_3$  can be represented by structures 1 and 2 shown below. Can these twostructures be taken as the canonical forms of the resonance hybrid representing  $H_3PO_3$ ? If not, give reasons for the same.



- **13.** Write the resonance structures for  $SO_3$ ,  $NO_2$  and  $NO_3^-$ .
- 14. Use Lewis symbols to show electron transfer between the following atoms to formcations and anions :(a) K and S(b) Ca and O(c) Al and N.
- **15.** Although both  $CO_2$  and  $H_2O$  are triatomic molecules, the shape of  $H_2O$  molecule isbent while that of  $CO_2$  is linear. Explain this on the basis of dipole moment.
- **16.** Write the significance/applications of dipole moment.
- 17. Define electronegativity. How does it differ from electron gain enthalpy?
- **18.** Explain with the help of suitable example polar covalent bond.



- **19.** Arrange the bonds in order of increasing ionic character in the molecules :  $\text{LiF}, \text{K}_2\text{O}, \text{N}_2, \text{SO}_2 \text{ and } \text{CIF}_3.$
- **20.** The skeletal structure of  $CH_3COOH$  as shown below is correct, but some of thebonds are shown incorrectly. Write the correct Lewis structure for acetic acid.



- **21.** Apart from tetrahedral geometry, another possible geometry for  $CH_4$  is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why  $CH_4$  is not square planar?
- 22. Explain why BeH, molecule has a zero dipole moment although the Be-H bonds arepolar.
- 23. Which out of NH, and NF, has higher dipole moment and why?
- 24. What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp<sup>2</sup> and sp<sup>3</sup> hybrid orbitals.
- **25.** Describe the change in hybridisation (if any) of the AI atom in the following reaction.  $AICI_3 + CI^- \rightarrow AICI_4^-$
- 26. Is there any change in the hybridisation of B and N atoms as a result of the following reaction ? BF<sub>3</sub> + NH<sub>3</sub>  $\rightarrow$  F<sub>3</sub>B.NH<sub>3</sub>
- 27. Draw diagrams showing the formation of a double bond and a triple bond betweencarbon atoms in  $C_2H_4$  and  $C_2H_2$  molecules.
- 28. What is the total number of sigma and pi bonds in the following molecules ? (a)  $C_2H_2$  (b)  $C_2H_4$
- 29. Considering x-axis as the internuclear axis which out of the following will not forma sigma bond and why? (a) 1s and 1s (b) 1s and 2px ; (c) 2py and 2py (d) 1s and 2s.
- **30.** Which hybrid orbitals are used by carbon atoms in the following molecules ?  $CH_3 - CH_3$ ; (b)  $CH_3 - CH = CH_2$ ; (c)  $CH_3 - CH_2 - OH$ ; (d)  $CH_3 - CHO$  (e)  $CH_3COOH$
- **31.** What do you understand by bond pairs and lone pairs of electrons ? Illustrate bygiving one exmaple of each type.
- **32.** Distinguish between a sigma and a pi bond.
- **33.** Explain the formation of H<sub>2</sub> molecule on the basis of valence bond theory.
- 34. Write the important conditions required for the linear combination of atomic orbitalsto form molecular orbitals.
- **35.** Use molecular orbital theory to explain why the Be<sub>2</sub> molecule does not exist.
- **36.** Compare the relative stability of the following species and indicate their magnetic properties :  $O_2, O_2^+, O_2^-$  (superoxide),  $O_2^{2-}$  (peroxide)
- 37. Write the significance of a plus and a minus sign shown in representing the orbitals.
- 38. Describe the hybridisation in case of PCI<sub>5</sub>. Why are the axial bonds longer ascompared to equatorial bonds?
- 39. Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?
- 40. What is meant by the term bond order ? Calculate the bond order of :  $N_2$ ,  $O_2$ ,  $O_2^+$  and  $O_2^-$



						Ansv	VERS						
					ΕX	ERC	ISE ‡	<u> </u>					
						PAR	T # I						
A-1.	(B)	A-2.	(B)	A-3.	(D)	A-4.	(C)	A-5.	(A)	A-6.	(A)	A-7.	(A)
A-8.	(C)	A-9.	(B)	A-10.	(B)	A-11.	(B)	B-1.	(D)	B-2.	(C)	В-3.	(D)
B-4.	(D)	B-5.	(D)	B-6.	(B)	B-7.	(C)	B-8.	(D)	C-1.	(A)	C-2.	(C)
C-3.	(C)	C-4.*	(ACD)	C-5.	(C)	C-6.	(D)	C-7.	(D)	C-8.*	(ABC)	C-9.	(A)
C-10.	(B)	C-11.	(C)	C-12.	(B)	C-13.	(D)	C-14.	(C)	C-15.	(B)	C-16.	(D)
C-17.	(B)	C-18.	(B)	C-19.	(A)	C-20.	(B)	D-1.	(D)	D-2.	(D)	D-3.	(D)
D-4.	(B)	D-5.	(D)	D-6.	(D)	D-7.*	(CD)	E-1.	(A)	E-2.	(B)	E-3.	(A)
E-4.	(C)	E-5.	(A)	E-6.	(B)	E-7.	(D)	F-1.	(A)	F-2.	(D)	F-3.	(D)
F-4.	(B)	F-5.	(C)	F-6.	(B)	F-7.	(C)	F-8.	(C)	F-9.	(D)	F-10.	(D)
F-11.	(D)	F-12.	(D)	F-13.	(B)	F-14.	(D)	F-15.	(A)	G-1.	(B)	G-2.	(A)
G-3.	(C)	G-4.	(C)	G-5.	(A)	G-6.	(B)	G-7.	(A)	G-8.	(C)	G-9.	(D)
G-10.*	(ABC)	•	(-)		( )		(-)		( )		(-)		(-)
	PART - I												
1.	(D)	2.	(D)	3.	(B)	4.	(C)	5.	(C)	6.	(D)	7.	(B)
8.	(D)	9.	(A)	10.	(D)	11.	(D)	12.	(A)	13.	(B)	14.	(C)
15.	(A) p ;	(B) q;(	(C) p ; (E	0) s		16.	(A) p, r	; (B) p, r	; (C) q,	s ; (D) p	, q, s		( )
17.	(A) r, w	, x ; (B)	p, z ; (C)	) p, x ; ([	D) s, y	18.	(A) p, q	, r, s ; (E	8) p, q, r,	s ; (C) p	o, q, r, s	; (D) r, s	
19.	(A) p, s	; (B) q,	r, t ; (C)	p, r, t ; (	D) q, r, s	, t	20.	(A)	21.	(D)	22.	(A)	
23.	(B)	24.	(C)	25.	(D)	26.	(A)	27.	(A)	28.	(B)	29.	(A)
30.	(A)	31.	F	32.	т	33.	Т	34.	F	35.	Т	36.	Т
37.	F	38.	Т	39.	F	40.	Т	41.	F	42.	Т	43.	F
44.	T	45. 50	T	46.	F	47.	decreas	ses, bono	d	48. 50	electrov	alent	
49. 50	lattice	<b>50.</b>	planar t	riangulai		51.	Higner.			52.	NO		
53.	bond or	aer	54.	$0_2^{}.0$	ne	<b>-</b>							
						Exerci	se # 2						
						PAR	T - I						
1.	(A)	2.	(A)	3.	(C)	4.	(D)	5.	(B)	6.	(A)	7.	(D)
8.	(C)	9.	(C)	10.	(C)	11.	(B)	12.	(D)	13.	(C)	14.	(C)
15.	(B)	16.	(A)	17.	(C)	18.	(B)	19.	(A)	20.	(C)	21.	(B)
22.	(A)	23.	(A)	24.	(B)	25.	(C)	26.	(A)	27.	(A)	28.	(B)
29.	(A)	30.	(D)	31.	(B)	32.	(A)	33.	(B)	34.	(B)	35.	(B)
36.	(B)	37.	(A)	38.	(B)	39.	(C)	40.	(D)	41.	(D)	42.	(B)
43.	(D)	44.	(A)	45.	(D)	46.	(C)	47.	(B)	48.	(D)	49.	(B)
50.	(D)	51.	(A)	52.	(C)	53.	(B)	54.	(B)	55.	(B)	56.	(B)
57.	(C)	58.	(A)	59.	(A)	60.	(BC)	61.	(ABC)	62.	(ABC)	63.	(AC)
64.	(ABCD)	65.	(AD)	66.	(BCD)	67.	(BC)	68.	(BD)	69.	(ABC)		
70.	(ABCD)	) 71.	(ABD)	72.	(ABC)	73.	(AC)	74.	(ABC)	75.	(ABCD)		
76.	(AC)	77.	(ABC)	78.	(ABCD)	79.	(ABD)	80.	(ABC)	81.	(AB)		
82.	(ABD)	83.	(ABC)	84.	(ABC)	85.	(ABD)	86.	(BC)	87.	(BC)		



### PART - II

- 1. Lattice energy of KF =  $817.7 \text{ kJ mol}^{-1}$
- 2. Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron).

N 
$$(2s^2 2p^3)$$
, O  $(2s^2 2p^4)$ 

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

**Step 2.** The skeletal structure of  $NO_2^-$  is written as : O N 0

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

$$\begin{bmatrix} \ddot{\Omega} :: N : \ddot{\Omega} : \end{bmatrix} Or \begin{bmatrix} \ddot{\Omega} = \ddot{N} - \ddot{\Omega} : \end{bmatrix} Or \begin{bmatrix} : \ddot{\Omega} - \ddot{N} = \ddot{\Omega} \end{bmatrix}$$

3. 
$$N = C - C = N$$
 (in triple bond  $\underline{=}_{\pi}^{\pi}$ )

N

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

4. Species Structure



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

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

- $F_3^-$  and  $I_3^-$  are of same group. Iodine can expand its octet but F cannot and thus, in  $I_3^-$  octet rule is not violated, but in  $F_3^-$  octet rule is violated. 5.
- In H<sub>2</sub>O bond angle is less than 109°28' due to lone pair and bond pair repulsion. But in ether, due 6. to strong mutual repulsion between two alkyl groups bond angle becomes greater then 109°28'
- 7.



Double bonds require more room than single bonds. Hence C = O group compresses the molecule and bond angle decrease maximum in COF<sub>2</sub> as bond pairs of electrons are more closer to the fluorine atoms because of high electronegativity of fluorine. As size of halogen atoms increase and their electronegativity decreases repulsion between bond pairs increases and therefore  $\theta$  increase.

**8.** 
$$OF_2$$

 $O^{\cdot}$   $O^{\circ$ 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 F—O—F bond angle decreases to 102° from 109.5°. In Cl<sub>2</sub>O, the bond pair are more closer to the oxygen atom because of the high electronegativity of oxygen. So the bp - bp repulsion is more than ℓp - ℓp. Thus the bond angle CI—O—CI increases to ≈111° due to bp - bp repulsion and repulsion between larger Cl atoms.

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

9. x = 1.51 D



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

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

**11.** In  $\ddot{N}H_3$  molecule Nitrogen is more electronegative than Hydrogen. So the net dipole moment is towards. Nitrogen atom but in NF<sub>3</sub> molecule. Fluorine is more electronegative than. Nitrogen so the net dipole moment is towards. Fluorine atoms. In NH<sub>3</sub> the bond pair moments and lone pair moments are in the same direction while in NF<sub>3</sub> the lone pair moment and bond pair moments are in opposite direction.



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

(i) Size ∞ 1/degree of hydration (i.e. with increase in size, number of water molecules around central metal ions decrease). So order of increasing radii is Sr<sup>2+</sup> < Ca<sup>2+</sup> < Mg<sup>2+</sup> < Be<sup>2+</sup>.
(ii) Heavily hydrated ions move slowly so the order of increasing mobility is Be<sup>2+</sup> < Mg<sup>2+</sup> < Ca<sup>2+</sup> < Sr<sup>2+</sup>.

12.

$$CH_{3}$$
  
 $C = O: ---- H - C = C - H$   
 $(sp)$ 

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

- **15.** One water molecule is coordinated to lone pair of electrons on SnCl<sub>2</sub> and the other is hydrogen bonded to coordinated water molecules.
- **16.**  $Na_2O_2$  forms stable hydrates on account of H-bonding.

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

**17.** 
$$\begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{H}_{3} \\ \mathsf{H}_{3} \\ \mathsf{CH}_{3} \end{array} \overset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{CH}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\overset{\mathsf{H}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{H}_{3}}{\underset{\mathsf{C}}{\underset{\mathsf{H}_{3}}{\underset{1$$

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

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





 $BF_3 + 3H_2O \longrightarrow B(OH)_3 + 3HF$ But the HF produced will react with the reactant  $BF_3$  to form  $BF_4^-$  ion  $BF_3 + HF \longrightarrow H^+[BF_4]^-$ ; hydrogen tetrafluoroborate (III) (stable species)

- **19.** It is because the energy gap between HOMO and LUMO levels in  $O_2$  molecule is so large that radiations of visible light cannot excite a e<sup>-</sup> from HOMO to LUMO. In fact  $O_2$  gas shows absorption in UV zone. So it is colourless.
- **20.** Transition metals may use inner -d-electrons along with the outer s-electrons for bonding as (n–1) d and ns have nearly same energy. So in them number of metallic bonds per atoms is quite large (more than two always). Hence element have high heat of atomization.
- **21.** (a) Covalent, due to identical electronegativity.
  - (b) Covalent, due to less electronegativity difference.
  - (c) Ionic, due to more electronegativity difference.
  - (d) Covalent, due to nearly similar electronegativity.
- (a) NaCl will have highest lattice energy on account of the smaller Na<sup>+</sup> while CsCl has lowest lattice energy on account of the larger Cs<sup>+</sup>. Hence NaCl has highest melting point and CsCl has lowest melting point.
   (b) As size of anions increase their polarisability increases thus their covalent character increases and melting point decrease.
- 23. Mg<sup>+2</sup> has less polarising power due to inert gas configuration while Zn<sup>+2</sup> has higher polarising power due to pseudo inert gas configuration. A cation i.e. Zn<sup>2+</sup> with a greater, polarising power exercise a strong pull on the electron cloud of the neighbouring O-atom of the  $CO_3^{2-}$  ion and as such the metal carbonate (ZnCO<sub>3</sub>) gets readily decomposed into  $CO_2$  and the oxide of the metal, ZnO. Thus ZnCO<sub>3</sub> is less stable than MgCO<sub>3</sub>.
- 24. It exists as HCI (bond formed by equal sharing of electrons) but in aqueous solution ionises as  $H^+$  (or  $H_3O^+$ ) and  $CI^-$  due to polarity of HCI.
- 25. According to steric no. rule Steric number = Number of bond pair(s) + number of lone pair(s) at central atom

$$H \xrightarrow{\bullet \bullet}_{I} \xrightarrow{\bullet}_{H^+} H^+$$
 So, steric number = 3 + 1 = 4.

Thus the hybridisation of oxygen in  $H_3O^+$  is sp<sup>3</sup>.

**26.**  $BeF_2$  has linear molecule and  $H_2O$  has bent molecule.





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CHEMICAL BONDING\_ADVANCED # 59

- 27. With in the Ca<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> layer the ions are held together by strong electrovalent bonds but these separated Ca<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> layers are linked by relative weak H–bond. The weak H-bonds link SO<sub>4</sub><sup>2-</sup> ion in the intermediate region.
- **28.** Super oxides contain one unpaired electron in anti bonding molecular orbital and are coloured due to transition of HOMO orbital electron within visible region.
- **29.**  $O_2^+$  has higher bond order i.e. 2.5 than  $O_2(2)$  and  $O_2^-(1.5)$  and bond strength is directly proportional to bond order.
- **30.** The theoretical dipole moment in KCI =  $e \times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29}$  C meter % ionic character =  $\frac{exp \text{ erimental dipole moment}}{theoretical dipole moment} \times 100 = (3.336 \times 10^{-29}/4.1652 \times 10^{-29}) \times 100$
- **31.** Dipole moment of compound would have been completely ionic =  $(4.8 \times 10^{-10} \text{ esu}) (2.67 \times 10^{-8} \text{ cm}) = 12.8 \text{ D}$

So % ionic character = 
$$\frac{10.0}{12.8}$$
 × 100% = 78.125 %  $\sim$  78% Ans.

 $d_2 = 134 \times 3 + 2 \times 134 \cos 60^\circ \text{ pm} = 536 \text{ pm}$  Ans.



$$\begin{array}{ccc} A(s) & & +\frac{3}{2}X_{2}(g) \longrightarrow A X_{3}(s) \\ & & \downarrow \Delta H_{sub} & & \begin{vmatrix} \frac{3}{2}\Delta H_{diss} \\ A(g) & 3X(g) \\ \Delta H_{IE_{1}} + \Delta H_{IE_{2}} + \Delta H_{IE_{3}} \\ & & \downarrow & & \downarrow 3 \Delta H_{e.g} \\ A^{3*}(g) & 3X^{-}(g) \end{array}$$

$$\Delta H_{f} = \Delta H_{sub} + \Delta H_{I.E_{1}} + \Delta H_{I.E_{2}} + \Delta H_{I.E_{3}} + \frac{3}{2} \Delta H_{diss} + 3 \Delta H_{e.g} + \Delta H_{L.E}$$
  
= 100 + 60 + 150 + 280 +  $\frac{3}{2}$  × 80 - 3 × 110 - 470 = 100 + 60 + 150 + 280 + 120 - 330 - 470  
= - 90 Kcal/mol Ans.

**34.** CO  $\leftarrow_{\sigma}$  BF<sub>3</sub>

/

Transition metal  $\overleftarrow{\sigma}$  CO

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

- **35.** Lone pair of electrons on nitrogen in  $(SiH_3)_3N$  are used up in  $p\pi$ -d $\pi$  back bonding while in  $(CH_3)_3N$  such a  $p\pi$ -d $\pi$  bonding is not possible due to absence of vacant d-orbitals in carbon. therefore  $(CH_3)_3N$  is more basic than  $(SiH_3)_3N$ .
- **36.** The dipole moment of  $NH_3$  acts in the directions  $H \rightarrow N$  and thus moment due to unshared pair of electron will naturally increase the moment of the  $NH_3$  molecule while in the case of  $NF_3$ , the dipole moment acts in the direction  $N \rightarrow F$  and thus unshared electron pair will partially neutralizwe the dipole moment, causin ga lower moment of  $NF_3$  relative of  $NH_3$





**37.** o-Hydroxy benzaldehyde show intramolecular H-bonding or chelation, which are weaker than intermolecular H-bonding in p-hydroxy benzaldehyde.



**38.** Buta 1-3-diene, i.e.,  $CH_2 = CH-CH=CH_2$  has  $sp^2-sp^2$  (C-C) bond length more is s-character in hybridisation lesser is bond length.



**40.** (A) sp<sup>3</sup> and sp (B) sp<sup>3</sup>, sp<sup>2</sup>, sp<sup>2</sup> (C) sp<sup>3</sup>, sp, sp, sp<sup>3</sup> (D) sp, sp, sp<sup>2</sup>, sp<sup>2</sup>

**41.** O<sub>2</sub>

 $O^2 [AsF_4] \text{ or } O_2^+ [AsF_4]^-$ 

 $K[O_2]$  or  $K^+O_2^-$ 

The bond length decreases with increasing bond order

Species	02	$O_2^+$		0 <sub>2</sub>	
Bond order	2.0	2.5	1.5		
Bond length	$O_{2}^{+}$	< 0 <sub>2</sub>	<	$O_2^-$	

- **42.** Bigger  $SO_4^{2-}$  ions covers  $Ba^{2+}$  ions, therefore,  $Ba^{2+}$  ion attracts less number of water molecules and thus have low hydration energy. The compound is soluble when hydration energy > lattice energy. As  $BaSO_4$  has lower hydration energy than lattice energy, it is insoluble in water.
- **43.** NO<sup>+</sup> and NO are derivative of N<sub>2</sub>; so NO<sup>+</sup> bond order = 3 and NO bond order = 2.5; B.O.  $\propto$  bond strength.
- 44. According to Fajan's rule as size of anion increases and charge on anion increases polarisability of anions increases and thus covalent character increases. Hence they follow the following order.
  (a) NaF < Na<sub>2</sub>O < Na<sub>3</sub>N
  (b) NaCl < MgCl<sub>2</sub> < AlCl<sub>3</sub> < SiCl<sub>4</sub> < PCl<sub>5</sub>
- **45.** According to Fajan's rule, as charge on cation increases its polarising power increases resulting in to the greater polarisation of anion. Thus covalent character increases and melting point decreases.
- **46.** Bigger anion has higher polarisability; more polarisation greater is the intensity of colour (valence shell electrons are loosely bound with the nucleus).
- 47. (a) Agl < AgBr < AgCl < AgF size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.</li>
  (b) Bel<sub>2</sub> < BeBr<sub>2</sub> < BeCl<sub>2</sub> < BeF<sub>2</sub> size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.
  (c) Pbl<sub>2</sub> < PbBr<sub>2</sub> < PbCl<sub>2</sub> < PbF<sub>2</sub> size of anion increases, polarisation increases, covalent character increases and so solubility in water decreases.
  (d) Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> < MgSO<sub>4</sub> < Na<sub>2</sub>SO<sub>4</sub> charge on cation increases, polarisation increases, covalent character increases and so solubility in water decreases.

(e)  $BCI_3 < BeCI_2 < LiCI - charge on cation increases, polarisation increases, covalent character increases and so solubility in water decreases.$ 



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CHEMICAL BONDING\_ADVANCED # 62

 $\rightarrow sp^3$ 



**51.** In PCI<sub>5</sub> there are 5 electron pairs around central phosphorus atom and all are bond pairs. The hybridisation of phosphorus is thus sp<sup>3</sup>d. To have minimum repulsions between bp-bp it acquires trigonal bipyramidal shape as shown below.



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



- (a) With hydrogen which is less electronegative phosphorous does not undergo sp<sup>3</sup>d hybridisation as there is large difference in the size of s, p and d orbitals. In PCl<sub>5</sub> the chlorine is more electronegative and therefore produces positive charge on the phosphorous atom. As a result of this, the size of d orbitals decreases much more as compared to s and p orbitals. Hence phosphorus atom undergoes sp<sup>3</sup>d hybridisation.
  - (b) This is because of the absence of d-orbitals in nitrogen for  $sp^3d$  hybridisation.
  - (c) Because of the absence of d-orbitals in fluorine it can not expand its covalency.
  - (d) Bigger size of chlorine can not be accommodated around sulphur atom because of steric crowding.
- **53.** Solid PCl<sub>5</sub> exists as  $[PCl_4]^+$  (sp<sup>3</sup>) and  $[PCl_6]^-$  (sp<sup>3</sup>d<sup>2</sup>); N<sub>2</sub>O<sub>5</sub> as NO<sub>2</sub><sup>+</sup> (sp) and NO<sub>3</sub><sup>-</sup> (sp<sup>2</sup>); XeF<sub>6</sub> as XeF<sub>5</sub><sup>+</sup> (sp<sup>3</sup>d<sup>2</sup>) and F<sup>-</sup> (as bridging ion).



50.

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54.  $CH_3 - O - H$  is having more dipole moment than  $CH_3SH$  because in  $CH_3OH$  the central oxygen atom is more electronegative then sulphur atom. So net dipole moment is more in  $CH_3OH$ .



**55.** Dipole moment is product of charge and the bond length. In CH<sub>3</sub>F the charge is higher but due to greater bond length in CH<sub>3</sub>Cl the dipole moment comes out to be higher (remember as a fact)

56.



- **57.**  $BF_3$ ,  $\mu = 0$  (trigonal planar);  $H_2S$ ,  $\mu = 0.95$  (bent with 2 lone pair);  $H_2O$ ,  $\mu = 1.85$  (bent with 2 lone pair). So the increasing order of dipole moment is  $BF_3 < H_2S < H_2O$ .
- **58.**  $CCI_4$  is a symmetrical and non polar molecule while  $CHCI_3$  is an unsymmetrical and polar molecule.
- **59.** These compounds contain polar–OH groups which can form H-bonds with water.
- 60. Benzene molecules are held together by dispersion London forces (a type of van der Waal's forces)
- **61.** ICl has dipole dipole attraction due to polar nature but Br<sub>2</sub> being non-polar experiences very weak dispersion London forces.
- **62.** Deuterium is more electropositive than hydrogen. Therefore, stronger H-bonding is found in  $D_2O$  than in  $H_2O$ .  $D_2O$  is also denser than  $H_2O$ .
- **63.** Inter molecular H–bonding in both but  $KHCO_3$  forms dimers through H–bonding and NaHCO<sub>3</sub> form infinite long chains through H–bonding.
- **64.** In ethanol, there is H-bonding but in diethyl ether, there is no H-bonding (because O-atom is attached to C-atom) but there exists weak dipole-dipole attraction in diethyl ether.

#### 66. Sulphuric acid $(H_2SO_4)$

$$H-O-S-O-H$$
 S.No. = 4, Hybridisation = sp<sup>3</sup>, Oxidation state of Sulphur = + 6

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

 $\cap$ 



Caro's acid (H,SO,)

$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$H - O - O - S - O - H$$
  
$$O xidation state of sulphur = +6$$

Oleum  $(H_2S_2O_7)$ 

$$H - O - S - O - S - O - H$$
  
Sp<sup>3</sup> Oxidation state of both sulphur atoms = +6

67.

7.  $CI \sim CI \sim CI$ , double bond occupies large area and has large electron density. So there is intrinsic repulsion

between P = O and P - CI bond pairs. To minimize this repulsion bond angle decrease from 109.5° to 103.5°.



Square planar

Trigonal bipyramidal

69. 
$$F$$
,  $F$   
 $B7.5^{\circ}$  F nearly 'T' shaped.

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

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

71. Nitrogen is more electronegative than phosphorus.



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



- **72.** 84.5%
- **73.** 25%
- **74.** In diethyl ether oxygen atom has two lone pairs of electrons and  $BF_3(g)$  has vacant 2p-orbital in valence shell.  $BF_3$  being electron deficient compensates its deficiency by accepting a lone pair of electrons from diethyl ether forming a complex as given below.

- **75.** (i) Bond order of  $N_2 = 1/2 (10 4) = 3$ Bond order of  $O_2 = 1/2 (10 - 6) = 2$ Bond order of  $F_2 = 1/2 (10 - 8) = 1$ 
  - Bond order of  $O_2^+ = 1/2 (10 5) = 2.5$

Bond order is directly proportional to the bond strength and so, the increasing order of their bond dissociation energies is :

$$F_2 < O_2 < O_2^+ < N_2^-$$

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



So, the increasing order of bond angles is  $XeF_4 < NH_3 < BF_3 > N_3^-$ 

- (i) Interaction between lone pair of electrons of chloride ion and Si<sup>4+</sup> is not very strong and
   (ii) Six large chloride ions can not be accommodated around Si<sup>4+</sup> due to limitation of its size.
- **77.** Unpaird electron on CI atom is delocalised in 'd' orbtial. So CIO<sub>2</sub> will not form dimer while in NO<sub>2</sub>, the unpaired electron is localised on N atom and thus easily form dimer.



The  $\pi$ - bonds between  $C_1$  and  $C_2$  are perpendicular to that of  $C_2$  and  $C_3$  by  $p\pi - p\pi$  overlapping. Therefore, the hydrogen attached to  $C_1$  and those attached to  $C_2$  are in different planes (i.e., perpendicular).  $\sigma$ -bonds between  $C_1 - C_2$  and  $C_2 - C_3$  are sp<sup>2</sup> - sp and sp - sp<sup>2</sup> overlapping on their axes.

- **79.** In  $O_2$  and  $N_2$  energy gap between HOMO and LUMO is large so electronic excitation is not possible with visible light. But for halogens, the electronic excitation can be done with visible light because energy difference between HOMO and LUMO is small.
- **80.** In BF<sub>3</sub> vacant p-orbital of boron undergoes  $2p\pi 2p\pi$  back bonding with fluorine atom, which is stronger than  $2p\pi 3p\pi$  back bonding in BCl<sub>3</sub>. So BCl<sub>3</sub> is more electron deficient than BF<sub>3</sub>. Thus BCl<sub>3</sub> is more acidic than BF<sub>3</sub>.



- 81. BF, molecule being electron deficient gets stabilised through  $P\pi - P\pi$  back bonding. where as BH, removes its electron deficiency through dimerisation and thus exists as B<sub>a</sub>H<sub>a</sub>.
- 82. The lone pair of electrons on N atom in trisilyl amine undergoes  $p\pi$ -d $\pi$  delocalisation. Thus this lone pair of electron is not easily available for the donation. On the other hand, in trimethyl amine it is easily available for donation as carbon does not have d-orbital for  $p\pi$ -d $\pi$  delocalisation.

(a) Hydrogen molecule :  $H_2: (\sigma 1s)^2$  Its bond order, therefore, is  $= \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$ (b) Cation of hydrogen molecule :  $H_2^+: (\sigma 1s)^1$  Its bond order, therefore, is = 1/2 (1 - 0) = 1/283. (c) Helium molecule : He<sub>2</sub>:  $(\sigma 1s)^2 (\sigma^* 1s)^2$ Its bond order, therefore, is  $\frac{1}{2}(2-2) = 0$ (d) Lithium molecule (Li<sub>2</sub>) :  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$ Its bond order, therefore, is 1/2(4-2) = 1. (e) **Beryllium (Be**<sub>2</sub>):  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma^2 s)^2 (\sigma^* 2s)^2$ Its bond order, therefore, is 1/2(4-4) = 0. (f) **Boron** (**B**<sub>2</sub>):  $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x^1 = \pi 2p_y^1) (\sigma p_z^{0})^0$ Its bond order, therefore, is 1/2(6-4) = 1.

- 84. (a)  $B_2$  (b)  $C_2$  (c)  $O_2^{2+}$  (d)  $O_2$  , (e)  $F_2$  (f)  $N_2$
- 85. Complex exists as NO<sup>+</sup> and [BF<sub>4</sub>]<sup>-</sup>. NO<sup>+</sup> is isoelectronic with N<sub>2</sub>; so  $\sigma$ 1s<sup>2</sup>,  $\sigma$ \*1s<sup>2</sup>,  $\sigma$ 2s<sup>2</sup>,  $\sigma$ \*2s<sup>2</sup>,  $\pi$ 2p<sup>2</sup><sub>x</sub> =

$$\pi 2p_y^2$$
,  $\sigma 2p_z^2$ , then its bond order is  $\frac{10-4}{2} = 3$ 

#### Exercise # 3 PART - I

- 1. (B) 2. (C) (D) 4. (A) 3.
- 5. Molecular orbital electronic configuration of  $O_2$  is as follows (Z is taken as molecular axis).

$$\sigma_{1s^{2}} \sigma_{1s^{2}}^{*} \sigma_{2s^{2}}^{*} \sigma_{2s^{2}}^{*} \sigma_{2p_{z}^{2}}^{*} \pi_{2p_{x}^{2}}^{*} = \pi_{2p_{y}^{2}}^{*} \pi_{2p_{x}^{1}}^{*} = \pi_{2p_{y}^{1}}^{*}$$

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

As it contains two unpaired electrons in bonding  $\pi$  molecular orbitals O<sub>2</sub> is paramagnetic.

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

6. According to VSEPR theory

> XeF<sub>2</sub> Number of electron pairs = 5, Xe (linear) Number of bond pairs = 2, So, Number of lone pairs = 3Thus XeF<sub>2</sub> is linear with 3 lone pairs occupying 3 equatorial positions of trigonal bipyramidal so as to minimize the repulsions.

Number of electron pairs = 6, (square planar) F F A Number of bond pairs = 4, So, Number of lone pairs = 2Thus XeF, is linear with 2 lone pairs occupying 2 axial positions of octahedral pyramidal so as to minimize the repulsions. XeO<sub>2</sub>F<sub>2</sub> Number of electron pairs (including super electron pairs) = 5, Number of bond pairs = 4, So, Number of lone pairs = 1 Thus XeO<sub>2</sub>F<sub>2</sub> is see-saw with 1 lone pairs occupying one equatorial position and two double bonds occupying other

two equatorial positions of trigonal bipyramidal so as to minimize the repulsions.



(see-saw)

XeF<sub>4</sub>

7.	(D)	8.	(B)	9.	(A)	10.	(C)	11.	(A)	12.	(B)	13.	(C)
14.	(A)	15.	(A)	16.	(A)								

17. There are 5 electron pairs and all are bonds pairs in PCI<sub>5</sub>. So to have the minimum repulsions between bond pairs it acquires trigonal bipyramidal shape. In BrF<sub>5</sub>, there are 6 electrons pairs out of which one lone pair and rest all are bond pairs. So to have the minimum repulsions between bond pairs and lone pairs it acquires square pyramidal shape.



PCI<sub>5</sub> (trigonal bipyramidal),



BrF<sub>5</sub> (square pyramidal)

In diethyl ether (C<sub>2</sub>H<sub>5</sub>—Ö—C<sub>2</sub>H<sub>5</sub>) oxygen atom has two lone pairs of electrons, thus acts as lewis base while 18. in anhydrous AICI<sub>3</sub> aluminium has vacant 3p-orbital of valence shell and thus acts as Lewis acid. AICI<sub>3</sub>

accepts a lone pair of electrons from diethyl ether to complete its octet forming a complex  $C_2H_3$ .

Hence, anhydrous AICl<sub>3</sub> is more soluble in diethyl ether by means of solvolysis in comparison to hydrous AICI<sub>3</sub> (i.e., AICI<sub>3</sub> . 6H<sub>2</sub>O). Hydrous AICI<sub>3</sub> is a polar compound, while ether is non-polar, so on basis of Thumb's rule, like dissolve in like solvents. Hence hydrous AICI<sub>3</sub> is least soluble in ether.

- 19. (C) 20. (D) 21. (B)
- 22. According to VSEPR theory two lone pairs out of six electron pairs are trans to each other to have minimum repulsion. The shape of XeF<sub>4</sub> is square planar and geometry is octahedral with sp<sup>3</sup>d<sup>2</sup> hybridisation. The molecule looks like :



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

The structure looks like:



23. The electronic configuration of O<sub>2</sub> will be:

 $O_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p^2_{z} \pi 2p^2_{x} = \pi 2p^2_{y} \pi^* 2p^1_{x} = \pi^* 2p^1_{y}$ 

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

Where,  $N_{h} =$  Number of electrons in bonding orbitals

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

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



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CHEMICAL BONDING\_ADVANCED # 68

N<sub>a</sub> = Number of electrons in antibonding orbitals

Bond order =  $\frac{10-7}{2} = \frac{3}{2} = 1.5$ In O<sub>2</sub> [AsF<sub>4</sub>]<sup>-</sup>, O<sub>2</sub> is O<sub>2</sub><sup>+</sup>.

The electronic configuration of  $O_2^+$  will be

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi^2 p_x^2, = \pi 2p_y^2 \pi^* 2p_x^1 \implies \text{bond order} = \frac{10-5}{2} = 2.5$$

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

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

 $\mathsf{AIF}_3 + \mathsf{KF} \longrightarrow \mathsf{K}_3[\mathsf{AIF}_6].$ 

 $BF_3$  is more acidic than  $AIF_3$  because of the small size of B than that of AI. Thus  $BF_3$  pulls out F<sup>-</sup> from  $[AIF_6]^{3-}$  forming  $[BF_4]^-$  and  $AIF_3$ . Hence  $AIF_3$  is precipitated on adding  $BF_3$  to  $[AIF_6]^{3-}$ .

$$\mathsf{K}_3[\mathsf{AIF}_6] + \mathsf{3BF}_3 \longrightarrow \mathsf{3K}[\mathsf{BF}_4] + \mathsf{AIF}_3 \downarrow$$
 .

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

(ii) In N( $Me_3$ ), there is no such  $p\pi$ -d $\pi$  delocalisation of lone pair of electrons on N atom as carbon does not have vacant d-orbital. So N(Me)<sub>3</sub> with steric number four is trigonal pyramidal with a lone pair at the apex.



Hence both are not isostructural.



29. 34.	(A) <b>(A) - p</b>	30. , q, r, t	(D) ; <b>(B) - q</b>	31. , r, s, t ;	(D) (C) - p, q	32. , r ; (D)	(A) - p, q, r	33. , s	(C)				
35.*	(ABC)	36.	4	37.	0 or 8	38.	(A)	39.*	(ACD	)			
						PA	RT - II						
1.	(4)	2.	(1)	3.	(1)	4.	(3)	5.	(4)	6.	(3)	7.	(3)
8.	(4)	9.	(2)	10.	(3)	11.	(4)	12.	(3)	13.	(2)	14.	(2)
15.	(3)	16.	(3)	17.	(4)	18.	(4)	19.	(2)	20.	(4)	21.	(2)
22.	(2)	23.	(1)	24.	(3)	25.	(1)	26.	(4)	27.	(1)	28.	(4)
29.	(4)	30.	(2)	31.	(4)	32.	(3)	33.	(2)	34.	(4)	35.*	(1, 2)
36.	(3)												



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