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CHEMICAL BONDING AND MOLECULAR STRUCTURE

INTRODUCTION

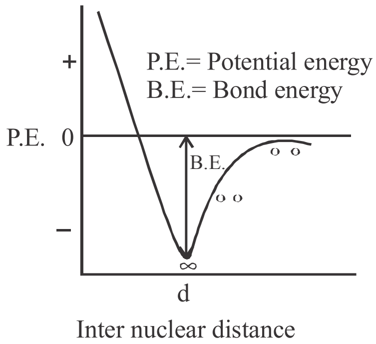
* The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

* Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability.

* When two atoms approaches to each other, two types of interaction become operative

- The force of attraction between the nucleus of one atom and electrons of the other atom.
- The forces of repulsion among the nuclei of reacting atoms and electrons of the reacting atoms.

* If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.



* No decrease in potential energy → No bonding exists.

* The internuclear distance (d) (point of minimum energy or maximum stability) is called bond length.

* The amount of energy released (i.e. decrease in potential energy) is known as bond energy (enthalpy of formation).

* From the curve it is apparent that greater the decrease in potential energy. Stronger will be the bond formed and viceversa.

$$\text{Attraction} \propto \frac{1}{\text{Energy of molecule}} \propto \text{Stability}$$

* Bond formation is an exothermic process.

* Molecules having two identical atoms like H_2, O_2, Cl_2, N_2 etc. are called as homonuclear diatomic molecules.

* Molecules containing two different atoms like CO, HCl, NO, HBr etc., are called as heteronuclear diatomic molecules.

* Molecules containing identical but many atoms bonded together such as P_4, S_8 etc., are called as homonuclear polyatomics.

* In most of the molecules, more than two atoms of different kinds are bonded such as in molecules like NH_3, CH_3COOH, SO_2, HCHO and they are called as heteronuclear polyatomics.

* Chemical bonds are basically classified into three types consisting of (i) ionic or electrovalent bond (ii) covalent bond and (iii) coordinate-covalent bond.

* Mostly, valence electrons in the outer energy level of an atom take part in the chemical bonding.

* Atoms having 8 electrons in their outermost shell are stable and chemically inert.

* An atom can acquire 8 electrons in outermost shell (i) by losing or accepting electrons (ionic bonding) (ii)by sharing electrons (covalent bonding)

VALENCY

* It is originated from latin word. "Valentia" means capacity or power.

* Each element have a valency equal to its combining capacity.

* Valency is termed as the number of chemical bonds formed by an atom in a molecule.

* The modern concept believes that outer most shell electrons of atom are responsible for chemical bonding. So these electrons are known as valence electrons.

KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

* Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons.

Lewis dot symbols

* A Lewis dot symbol consists of the symbol of an element and one dot for each valence electron in an atom of the element.

* For example, Li is a Group 1A (1) element and has one dot for one valence electron; Be, a Group 2A (2) element, has two valence electrons (two dots); and so on.

$$\cdot\mathbf{Li},\ \cdot\mathbf{Be}\cdot,\ \cdot\dot{\mathbf{B}}\cdot,\ \cdot\underset{\cdot}{\dot{\mathbf{C}}}\cdot$$

* Elements in the same group have similar outer electron configurations and hence similar Lewis dot symbols.

* The transition metals, lanthanides, and actinides all have incompletely filled inner shells, and in general, we cannot write simple Lewis dot symbols for them.

* Kossel, in relation to chemical bonding, drew attention to the following facts:

(i) In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases.

(ii) The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.

(iii) The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, ns^2np^6.

(iv) The negative and positive ions are stabilized by electrostatic attraction. For example, the formation of NaCl from sodium and chlorine:

$Na \rightarrow Na^+ + e^-$
$[Ne]\,3s^1 \quad [Ne]$
$Cl + e^- \rightarrow Cl^-$
$[Ne]\,3s^2\,3p^5 \quad [Ne]\,3s^2\,3p^6$ or $[Ar]$
$Na^+ + Cl^- \rightarrow NaCl$ or $Na^+\,Cl^-$

* The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion.

LEWIS OCTET RULE

(Tendency to acquire noble gas configuration)

* It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.

* It means that these atoms must be having stable electronic configurations.

* These elements (noble gases) have 8 electrons ($ns^2\ np^6$) except helium having 2es$^-$ ($1s^2$) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most configuration	$2s^22p^6$	$3s^23p^6$	$4s^24p^6$	$5s^25p^6$	$6s^26p^6$

* It is therefore concluded that s^2p^6 configuration in the outer energy level constitutes a structure of maximum stability or of minimum energy

* "The tendency of atoms to achieve eight electrons in their outermost shell is known as Lewis octet rule". To acquire inert gas configuration atoms lose or gain electron or share electron.

Limitations of the Octet rule :

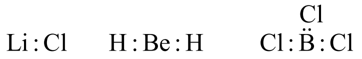
* The octet rule, though useful, is not universal.

* It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table.

* There are three types of exceptions to the octet rule.

(i) The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.



$Li:Cl \qquad H:Be:H \qquad Cl:\overset{Cl}{\ddot{B}}:Cl$

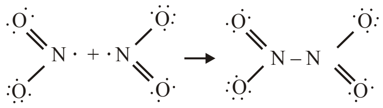
Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

(ii) Odd-electron molecules : In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms.

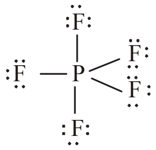
$\dot{N}=\ddot{O} \qquad \ddot{O}=\dot{N}^+-\ddot{O}:^-$

Odd-electron molecules are sometimes called radicals. Many radicals are highly reactive. The reason is that there is a tendency for the unpaired electron to form a covalent bond with an unpaired electron on another molecule.

For example, when two nitrogen dioxide molecules collide, they form dinitrogen tetroxide in which the octet rule is satisfied for both the N and O atoms:

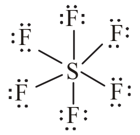


(iii) The expanded octet : Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom. In addition to the 3s and 3p orbitals, elements in the third period also have 3d orbitals that can be used in bonding. These orbitals enable an atom to form an expanded octet. Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.



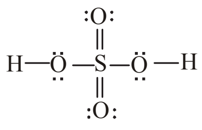
PF_5

10 electrons around the P atom



SF_6

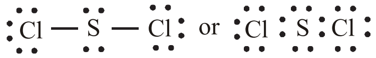
12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

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



Other drawbacks of the octet theory

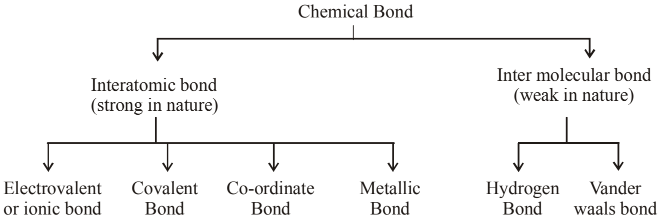
* It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.

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

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

CLASSIFICATION OF CHEMICAL BONDS

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



Bonds	Energy permole
Ionic, Covalent, Co-ordinate :	≈ 200 kJ
Hydrogen bonding :	10 – 40 kJ
Vander–waals :	2 – 10 kJ

ELECTROVALENT OR IONIC BOND

- * 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 ionic or electrovalent bond.
- * Electropositive atom loses electrons (group IA to IIIA)
- * Electronegative atom gains electron (group IVA to VII A)
- * Electronegativity difference $\propto$ strength of ionic bond.
- * IA and VII A group elements form strong ionic compound.

$$\underset{2,8,1}{Na} + \underset{2,8,7}{Cl} \longrightarrow \underset{2,8}{Na^+} + \underset{2,8,8}{Cl^-}$$

(Ne configuration) (Ar configuration)

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

Example :

(1) $Mg^{2+} + O^{2-} \rightarrow MgO$ or $Mg^{2+}O^{2-}$

$$\underset{2,8}{Mg^{+2}} \longleftarrow \underset{2,8,2}{Mg} \qquad \underset{2,6}{O} \longrightarrow \underset{2,8}{O^{-2}}$$

electrovalency of Mg = 2

electrovalency of O = 2

(2) $Ca^{2+} + 2Cl^- \rightarrow CaCl_2$ or $Ca^{2+}(Cl^-)_2$

$$\underset{2,8,8}{Ca^{+2}} \longleftarrow \underset{2,8,8,2}{Ca} \qquad \underset{2,8,7}{Cl} \longrightarrow \underset{2,8,8}{Cl^-}$$

electrovalency of Ca = 2

electrovalency of Cl = 1

(3) $Ca + O \longrightarrow CaO$

$$\underset{2,8,8}{Ca^{+2}} \longleftarrow \underset{2,8,8,2}{Ca} \qquad \underset{2,6}{O} \rightarrow \underset{2,8}{O^{-2}}$$

electrovalency of Ca = 2 ; electrovalency of O = 2

- * Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond. The force of attraction is equal in all direction so ionic bond is non–directional.
- * A definite three dimensional structure is formed called crystal lattice. Energy released during the formation of one mole crystal lattice is called lattice energy.

Ex. $6.023 \times 10^{23} Na^+ + 6.023 \times 10^{23} Cl^- \longrightarrow 6.023 \times 10^{23} NaCl + 788$ kJ (Lattice energy).

- * Ionic compound do not have molecular formula. It has only empirical formula.

Ex. NaCl is empirical formula of sodium chloride.

- * Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two nonmetallic elements) is an exception.

Factor favouring in formation of Ionic bond :

(A) Ionisation energy (IE) :

- * Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. [energy absorbed so endothermic process]

$$M + I.E. \rightarrow M^+ + e^-$$

- * Lesser Ionisation energy → Greater tendency to form cation.

$Na^+ > Mg^{+2} > Al^{+3}$
$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$
} Cation formation tendency

(B) Electron affinity : Amount of energy released when an electron is added to an isolated gaseous atom to form –ve ion (anion) [energy released so exothermic process]

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

Higher electron affinity → Greater tendency to form anion

$Cl^- > F^- > Br^- > I^-$
$F^- > O^{-2} > N^{-3}$
} Anion formation tendency

Ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy.

(C) Lattice energy : [Energy released so exothermic processes]

Higher lattice energy → High stability of Ionic compound

- * Due to the strong electrostatic attraction between the ions, formation of the crystal results in release of energy.
- * Higher the lattice energy greater will be the ease of formation of the ionic compound.

Factors influencing magnitude of lattice energy are:

- * **Size of ions :** Smaller the size of the ions, lesser is the internuclear distance consequently the inter ionic attraction will be high and lattice energy will also be large.
- * **Charge on ions :** Larger the magnitudes of charge on the ions, greater will be the attractive forces between the ions. Consequently the lattice energy will be high.

Types of ions :

(a) Ions having inert gas configuration :

The atoms of representative elements of group I, II & III by complete loss of their valence electron and the elements of group V, VI and VII by gaining 3, 2 and 1 electrons respectively form ions either with ns^2 configuration or ns^2p^6 configuration (**Example :** Na^+, Ca^{2+}, Cl^-, O^{-2})

(b) Ions with pseudo inert gas configuration :

The Zn^{2+} ion is formed when zinc atom loses its outer 4s electrons. The outer shell configuration of Zn^{2+} ion is $3s^2$ $3p^6$ $3d^{10}$,

Example : Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^+, Ag^+, Au^+, Ga^{3+} etc.

(c) Ions with ns^2 configuration :

Heavier member of group III, IV and V lose p–electrons only to form ions with ns^2 configuration Ti^+, Sn^{2+}, Pb^{2+}, Bi^{3+} are the examples of this type. These are stable ion.

(d) Polyatomic ions :

The ions which are composed of more than one atom are called polyatomic ions. These ions move as such in chemical reactions, some common polyatomic ions are :

NH_4^+ (Ammonium) : NO_3^- (Nitrate)
PO_4^{3-} (Phosphate) : SO_4^{2-} (Sulphate)
CO_3^{2-} (Carbonate) : SO_3^{2-} (Sulphite) etc.

Energy steps involved in ionic bond formation :

* **Formation of cation :**

(a) $M_{(s)}$ + Sublimation energy $\rightarrow M_{(g)}$ $\Delta H = +SE$

(b) $M_{(g)} + IP \rightarrow M^+_{(g)} + e^-$ $\Delta H = +IP$

* **Formation of anion :**

(a) $\frac{1}{2}X_{2(g)} + \frac{1}{2}$ Dissociation energy $\rightarrow X_{(g)}$; $\Delta H = +D/2$

(b) $X_{(g)} + e^- \rightarrow X^-_{(g)}$ + Electron affinity ; $\Delta H = -EA$

* **Formation of ionic bond :**

$M^+ + X^- \rightarrow M^+X^-$ + Lattice energy

ΔH = –Lattice energy

* **Born – Harber equation :**

$$\text{Total }\Delta H = \underbrace{\text{S.E.} + \text{I.P.} + \text{D/2}}_{\text{Energy absorbed}} - \underbrace{\text{E.A.} - \text{L.E.}}_{\text{Energy released}}$$

Ionic bond is formed if –

Total ΔH = –ve (energy released)

More the –ve value, more will be the strength of ionic bond

E.A. + L.E. > I.P. + S.E. + D/2

(Electron affinity + Lattice energy) > (Ionisation potential + Sublimation energy + Dissociation energy)

Characteristics of ionic compound :

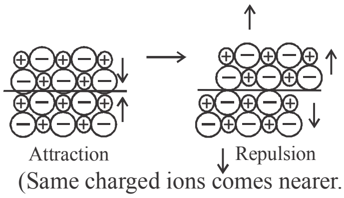
(i) Physical state :

* Electrovalent compounds are generally crystalline, hard and brittle in nature.

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

* Electrovalent compounds exist as three dimensional solid aggregates.

* Normally each ions surrounded by a number of oppositively charged ions and this number is called as coordination number.



(Same charged ions comes nearer. So they repel each other)

(ii) Boiling point and melting point :

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

(iii) Electrical 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 electricity.

(iv) Ionic reaction :

* Ionic compounds show ionic reaction & covalent compounds shows molecular reaction.

* Ionic reactions are fast reactions.

* **Example :** When NaCl is added in $AgNO_3$ solution, white ppt of AgCl is formed at once.

$Ag^+NO_3^- + Na^+Cl \rightleftharpoons Na^+NO_3^- + AgCl\downarrow$
white ppt.

(v) Isomorphism :

* Two compounds are said to be isomorphous if they have similar number of electrons i.e. similar configuration of their cation and anion.

* They have similar crystal structure

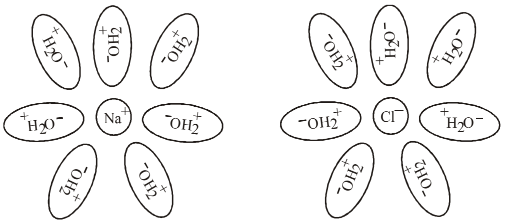
Example :	Na^+	F^-	Mg^{+2}	O^{-2}
Valency	+1	–1	+2,	–2
Electronic configuration	2, 8	2, 8	2, 8	2, 8
similarly	Ca^{+2}	Cl^{-1}	K^{+1}	S^{-2}
	2, 8, 8	2,8,8	2,8,8	2,8,8

(vi) Solubility

* Highly soluble in water (Polar solvents)

* **Example :** NaCl in water

* The Na^+ ions get associates with negatively charged 'O' of water and Cl^- ions associates with positively charged 'H' of water.



Oxygen atom of H_2O give its electron to Na⊕

H atom of H_2O gain electron from Cl⊖

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

* The energy released due to interaction between solvent and solute is called solvation energy.

* If water used as solvent it is called hydration energy.

* For an ionic compound to be soluble in water

Hydration energy > Lattice energy

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

$$\text{Hydration energy} \propto \text{Solubility}$$

$$\text{Hydration energy (H)} \propto \frac{1}{r^+} + \frac{1}{r^-}$$

(r^+ & r^- radius of cation and anion)

- * Hydration energy mainly depends on the cation radius because the value of $\frac{1}{r^-}$ is negligible in compared to $\frac{1}{r^+}$.
- * Down the group both the lattice energy and hydration energy decreases. If decrease in lattice energy is greater than hydration energy solubility increases down the group and viceversa.

Factor affecting solubility

(i) Dielectric constant –

- * The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant.
- * It is represented by **ε.**
- * Water has maximum dielectric constant ($\varepsilon = 80$)

$(\varepsilon_{CH_3OH} = 35)$, $(\varepsilon_{Acetone} = 21)$

$(\varepsilon_{C_2H_5OH} = 27)$, $(\varepsilon_{Ether} = 4.1)$, $(\varepsilon_{Benzene} = 2.3)$

$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

- * Ionic compounds are more soluble in the solvents, having high dielectric constant. H_2SO_4 and H_2O_2 have high dielectric constant but these are not good solvent due to oxidising nature.

(ii) Size of ion :

- * Keeping size of cation constant, the lattice energy decreases with the increase of anionic radius hence order of solubility of LiX in water is

$LiF < LiCl < LiBr < LiI$

As $\text{Solubility} \propto \frac{1}{\text{lattice energy}}$

- * In LiI covalent nature is more according to Fajan's rule but hydration energy > lattice energy therefore LiI is more soluble in water.
- * Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. Order of solubility of MSO_4 will be :

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

(Exception of Fajan's rule)

- * If size of cation and anion is very large, solubility decreases from top to bottom.
- * Solubility decreases in a period (as ionic nature decreases and covalent nature increases)

$NaCl > MgCl_2 > AlCl_3$

(iii) Polarisation of anion : Polarisation capacity is maximum in pseudo inert gas configuration

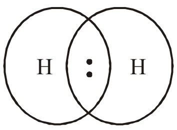
$\text{Solubility} \propto \frac{1}{\text{polarisation}}$

$$\underrightarrow{AgF > AgCl > AgBr > AgI}$$

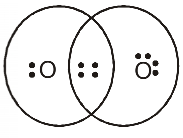
– Polarisation increases
– Covalent character increases.
– Solubility decreases.

COVALENT BOND

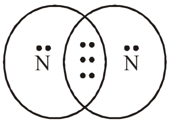
- * Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term covalent bond.
- * A covalent bond may be defined as the bond formed by mutual sharing of electrons between the combining atoms of comparable electronegativity.



H_2 molecule
H—H



O_2
O = O



N_2
N≡N

Covalency :

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

Formation of a covalent bond :

It is favoured by –

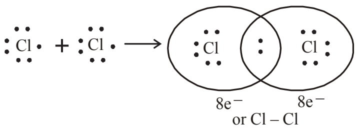
- * High ionisation enthalpy of the combining elements.
- * Nearly equal electron gain enthalpy and equal electronegativities of combining elements.
- * High nuclear charge and small atomic size of the combining elements.

Lewis structure and covalent bond :

- * Structures in which valence electrons are represented by dots are called lewis structures.
- * All atoms in a formula will have a total number of eight electrons by sharing in the valence shell in the center of skeleton structure. Other atoms surround it to complete the octet.
- * Lewis dot formulae show only the no. of valence electron, the number and kinds of bonds, but do not depict the three dimensional shapes of molecules and polyatomic ions.

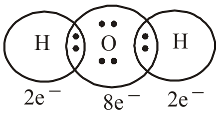
Single covalent bond : A covalent bond formed by the mutual sharing of one pair of electrons

Formation of the chlorine molecule, Cl_2 : The Cl atom with electronic configuration, $[Ne]3s^2\,3p^5$, is one electron short of the argon configuration. Each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

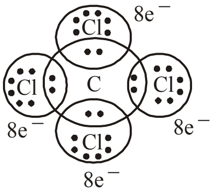


Covalent bond between two Cl atoms

- In water and carbon tetrachloride molecules, formation of covalent bonds can be represented as:

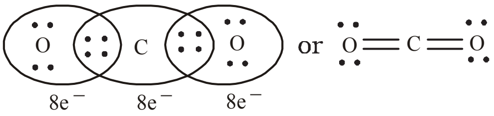


H-atoms attain a duplet of electrons and O, the octet.



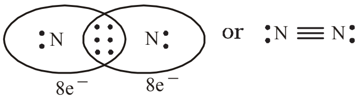
Each of the four Cl atoms along with the C atom attains octet of electrons.

- **Double covalent bond :** A covalent bond formed by the mutual sharing of two pair of electrons E.g. O = O, O=C= O etc. In the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

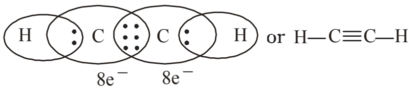


Double bonds in CO_2 molecule

- **Triple covalent bond :** A covalent bond formed by the mutual sharing of three pair of electrons E.g. N ≡ N, H – C ≡ C – H etc. In the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.



N_2 molecule



C_2H_2 molecule

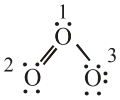
Formal charge :

- 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.
- Formal charge can be calculated as follows:

  Formal charge

$$= \begin{bmatrix}\text{total number of valence}\\ \text{electrons in the free}\\ \text{atom}\end{bmatrix} - \begin{bmatrix}\text{total number of non}\\ \text{bonding (lone pair)}\\ \text{electrons}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{total number of}\\ \text{bonding (shared)}\\ \text{electrons}\end{bmatrix}$$

- For example, The formal charges on ozone



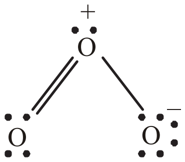
The central O atom marked 1 $= 6 - 2 - \frac{1}{2}(6) = +1$

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

The end O atom marked 3

$= 6 - 6 - \frac{1}{2}(2) = -1$

O_3 along with the formal charges :



- Formal charges do not indicate real charge separation within the molecule.
- Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.
- Generally the lowest energy structure is the one with the smallest formal charges on the atoms.
- The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

Characteristics of covalent compounds :

(i) Physical state :

- Under the normal conditions of temperature and pressure, these exist as gases or liquid state of low boiling points.
- This is due to the fact that very weak forces of attraction (vander walls forces) exist between discrete molecules.
- Some exist as soft solids if their molecular masses are high ex. Sulphur, phosphorus, iodine are soft solids.

(ii) Crystal structure :

- **Covalent solid –** In this type of structure every atom is bonded to four other atom by single covalent bonds resulting in the formation of giant structure e.g. SiC, AlN and diamond these crystals are very hard and posses high melting point.

  Diamond – sp^3 hybridized carbon atom forms tetrahedral structures.

  Graphite – sp^2 hybridized carbon atoms form hexagonal shaped layer which can slide over each other due to weak vander waals forces of attraction distance between C–C atom 1.42 Å distance between layers is 3.6 Å. Graphite is more stable than diamond due to high value of change in enthalpy.
- **Molecular solids :** When one atom combine with another with covalent bond and then the molecule combines with another similar molecule with the help of vander waal force of attraction or hydrogen bond

  Example :– CH_4(Solid), dry ice (CO_2), ice

(iii) Melting and boiling points :

- With the exception of few which have giant three dimensional structures such as diamond, carborundum (SiC), Silica (SiO_2), others have relatively low melting and boiling points. This is due to the presence of weak attractive forces between the molecules.

(iv) Electrical conductivity :

- In general covalent substances are bad conductors of electricity.
- Substances which have polar character like HCl in solution, can conduct electricity.

* The graphite can conduct electricity since electrons can pass from one layer to the other.

* Some show conductivity due to self ionisation example Liq NH_3
$NH_3 + NH_3 \longrightarrow NH_4^+ + NH_2^-$
$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$

(v) Chemical reactions :

* Covalent substances show molecular reactions.

* The reaction rates are usually low because it involves two steps (i) breaking of covalent bonds of the reactants and (ii) establishing of new bonds, while the ionic reactions only regrouping of ions.

(vi) Solubility :

* Nonpolar compounds are soluble in non polar solvent. Nonpolar solvent are CCl_4, Benzene, CS_2 etc.

* Polar compounds are soluble in polar solvent (i.e. ΔEN 0.9 to 1.8). Polar solvent are H_2O, $CHCl_3$, Alcohol etc.

(vii) Isomerism :

* As the covalent bonds are rigid and directional. On account of this there is a possibility of different arrangement of atoms in space.

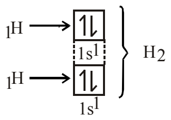
* Covalent compounds can thus shows isomerism (structural and space)

Orbital concept of covalent bond :

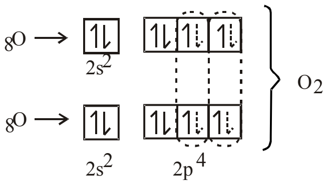
* One orbital can accommodate at the most 2 electrons with opposite spins $\boxed{\uparrow\downarrow}$

* Half filled orbital or unpaired electron orbital accepts one electron from another atom to complete its orbital.

* Tendency to completer orbital or to pair the electron is an essential condition of covalent bond.
No.of bonds = No. of unpaired es^- (Half filled orbitals) in outer most orbit.
Example : In H_2 molecule only single bond formed



In O_2 molecule, 2 bonds formed

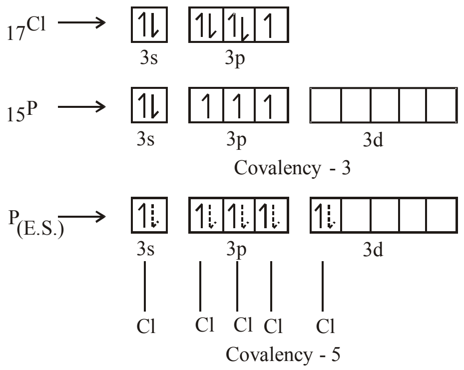


* If the outermost orbit has empty orbitals then covalent bonds are formed in excited states.

* Paired electrons get excited in the subshell of the same shell to form the maximum number of unpaired electrons. Maximum covalency is shown in excited state.

* The energy required for excitation of electrons is called promotion energy.

Example : In PCl_5 molecule



COORDINATE COVALENT BOND

* This type of bond is formed by one sided sharing of pair of electron between atoms.

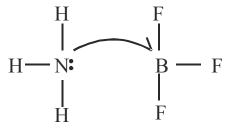
* Electron pair of one atom is shared between two atoms.

* Necessary conditions for the formation of Coordinate bond are
(i) Octet of one atom should be complete and should have atleast one lone pair of electron.
(ii) Other atom should have a deficiency of at least one pair of electron.

Example : $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}: \longrightarrow \overset{\times\times}{\underset{\times\times}{Y}}\overset{\times}{\underset{\times}{}}$ or $X \longrightarrow Y$

* Atom which provide electron pair for sharing is called donor.

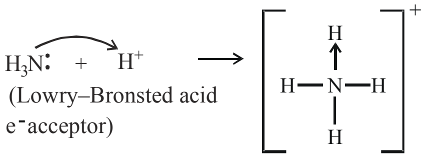
* Other atom which accepts electron pair is called acceptor. That is why it is called donor–acceptor or dative bond.



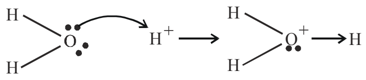
$\rightarrow NH_3 \rightarrow BF_3$

BF_3 is electron defficient compound

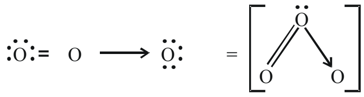
* A coordinate covalent bond is represented by an arrow (→) pointing towards the acceptor atom.
Example : NH_4^+ :



H_3O^+ :



O_3 :



N_2O :

Characteristic of co–ordinate bond

Coordinate compounds have properties between ionic & covalent compounds.

* They may be gaseous, liquids or solids.

* Melting point and boiling point are lower than ionic but higher than covalent compounds.

* They are semiconductor of electricity.

COVALENT CHARACTER IN IONIC COMPOUNDS – FAJAN'S RULE

* Although in an ionic compound like M^+X^- the bond is considered to be 100% ionic, but it has some covalent character.

* Likewise, a covalent bond has some ionic character.

* The partial covalent character of an ionic bond has been explained by Fazan.

* When a cation approaches an anion, the electron cloud of the anion is attracted towards the cation and hence gets distorted, the effect is called polarisation of the anion.

* The power of the cation to polarised the anion is called its polarising power.

* The tendency of the anion to get polarised is called its polarisability.

Fajan's rule : (Factors)

(a) Size of cation : Polarisation of the anion increases as the size of cation decreases. Polarisation $\propto \dfrac{1}{\text{size of cation}}$

Ex. : In a group : $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$

* Size of cation increases
- Covalent character decreases
- Ionic character increases

* Greatest polarising power of Be^{2+}, shows its maximum covalent character

In a period – $Na^+ \quad Mg^{+2} \quad Al^{+3} \quad Si^{+4}$

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Cation size decreases
– Covalent character increases

(b) Size of anion –

* If the size of the anion increases for a given cation, the covalent character increases.

Example : Polarisation $\propto$ size of anion

$CaF_2 < CaCl_2 < CaBr_2 < CaI_2$

* Size of anion increases
- Covalent character increases
- Ionic character decreases

(c) Charge on cation and anion :

* Polarisation $\propto$ charge on cation or anion

* Charge on cation $\propto$ Polarisation (covalent character).

Example :

$$\begin{array}{cccc} NaCl & MgCl_2 & AlCl_3 & SiCl_4 \\ Na^+ & Mg^{++} & Al^{+++} & Si^{++++} \end{array}$$

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

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

$SnCl_2 < SnCl_4$
$PbCl_2 < PbCl_4$
$Mn^{+2} < Mn^{+3} < Mn^{+4} < Mn^{+7}$; $FeO < FeO_3$

(Charge on cation $\propto$ polarisation power $\propto$ covalent character $\propto$ 1/M.P.)

* Charge of anion $\propto$ Polarisation

Example: $F^- \quad O^{2-} \quad N^{-3}$

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

– Charge increases
– Covalent character increases

$AlN > Al_2O_3 > AlF_3$

(d) Electronic configuration of cation :

Polarisation capacity of pseudo inert gas configuration cation > Polarisation capacity of inert gas configuration cation. **Example :**

CuCl (M.P. 442ºC) $\rightarrow Cu^+$ 2, 8, 18 (Covalent)
NaCl (M.P. 800ºC) $\rightarrow Na^+$ 2, 8 (Ionic)

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^2p^6 (inert) < Z_{eff} of $ns^2p^6d^{10}$ (pseudo)
Na^+ (Ionic) < Cu^+ (Covalent)

So CuCl has more covalent character than NaCl.

Application of the concept of polarisation :

Polarisation power of a cation is usually called ionic potential

$$\text{Ionic potential } \phi = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

1. To determine covalent and ionic character of molecule :

Covalent character $\propto \phi$
Ionic character $\propto 1/\phi$

From left (larger size) to right (smaller size) in a period ϕ increase so covalent character increases.

$Na^+ \quad Mg^{++} \quad Al^{+++} \quad Si^{++++}$

$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

$$\left.\begin{array}{l} \text{– charge increases} \\ \text{– size decreases} \end{array}\right\} \phi \text{ increases}$$

– Covalent character increases

From top to bottom in a group ϕ decreases so covalent character decreases.

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$

* Size increases (charge is fix)
- ϕ decreases
- Hence covalent character decreases

2. To determine nature of oxide :

$\sqrt{\phi} < 2.2$ (Basic oxides)

$\sqrt{\phi} = 2.2$ to 3.2 (Amphoteric oxides)

(Amphoteric oxides (Al_2O_3 etc.) reacts with acid and base.)

$\sqrt{\phi} > 3.2$ (Acidic oxide)

Example : $Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O$

$\longrightarrow$

$\sqrt{\phi}$ decreases Basic character increases

3. **To determine conductivity of metal halides (MX) :**

If $\sqrt{\phi} < 2.2$ MX – ionic nature – good conductor of electricity.

If $\sqrt{\phi} > 2.2$ MX – covalent nature – bad conductor of electricity.

4. **Formation of complex compounds :**

* Smaller the cation, more will be the tendency of forming complex compounds.

* High value of ϕ shows high tendency of forming complex compounds.

* If ϕ is low → No tendency of forming complex compounds.

* s–block metals (larger size) doesn't have the tendency to form complex compounds.

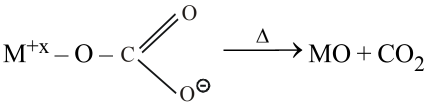
* **Exceptions –** Li, Be, Mg (small size)

* d–block metals have the tendency to form complex compounds (small in size)

5. **Thermal stability of metal carbonates :**

* $\text{Stability} \propto \frac{1}{\phi\,(\text{covalent nature})}$

*



(x is no. of +ve charge)

* More smaller the size of metal cation, its polarisation capacity increases – strength of M–O bond increases and C – O bond decreases.

* From top to bottom thermal stability of carbonates increases (as size of cation increase)
(Ionic character increases or covalent character decreases)
$BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

* Size of cation increases
- ϕ decreases (covalent character decreases)
- Thermal stability increases.

6. **Colour of compounds :** More the covalent character, more will be the colour intensity.

Colour intensity $\propto \phi$ (Covalent character)

Example :

AgF	AgCl	AgBr	AgI
(Colourless)	(White)	(Light yellow)	(Dark yellow)

$\longrightarrow$

BOND PARAMETERS

1. **Bond Length :** The average distance between the nucleus of two bonded atoms in a molecule is known as bond length, normally it is represented in Å. eg. A——B
It depends mainly on electronegativities of constituent atoms.

Case I : Electronegativity difference is zero then
Bond length = $r_A + r_B$
where r_A is covalent radius of A,
r_B is covalent radius of B
If $X_A = X_B$ (X_A is electronegativity of A and X_B is electronegativity of B)
$r_A = r_B$ then Bond length = $2r_A$ or $2r_B$
Example : Cl–Cl

Case II : Electronegativity difference is not equal to zero then – Bond length is given by Shomaker & Stevenson formula is –

Bond length = $r_A + r_B - 0.09(X_A - X_B)$

($X_A - X_B$ = Difference in electronegativities)

Trends in Bond Lengths

* The more electrons two atoms share, the shorter the covalent bond
- $C \equiv C$ (120 pm) < $C = C$ (134 pm) < $C - C$ (154 pm)
- $C \equiv N$ (116 pm) < $C = N$ (128 pm) < $C - N$ (147 pm)

* Decreases from left to right across period
$C - C$ (154 pm) > $C - N$ (147 pm) > $C - O$ (143 pm)

* Increases down the column
$F - F$ (144 pm) > $Cl - Cl$ (198 pm) > $Br - Br$ (228 pm)

* In general, as bonds get longer, they also get weaker

Factor influencing Bond length :

(a) Δ Electronegativity :

$\text{Bond length} \propto \frac{1}{\Delta EN}$ (While B.E. $\propto \Delta EN$)

Example :– H—F < H—Cl < H—Br < H—I

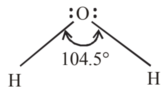
(b) Bond order or number of bonds :

$\text{Bond length} \propto \frac{1}{\text{Number of bonds or bond order}}$

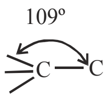
Bond energy $\propto$ Number of bond
For example bond length decreases in the order
$C - C > C = C > C \equiv C$.

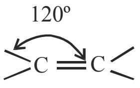
2. **Bond Angle :** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.

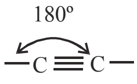
For example H – O – H bond angle in water can be represented as under :



Bond angle $\propto$ Number of bonds (Bond order)







3. Bond Energy (B.E) : Bond energy may be defined as –

(a) Bond formation energy : Energy released when any bond is formed is known as bond formation energy or bond energy.

(b) Bond dissociation energy : Energy required to dissociate any bond is known as Bond dissociation energy.

Calculation of released energy is more difficult than the dissociation energy therefore dissociation energy of bond is calculated and is assumed as bond energy or bond formation energy.

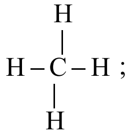
Case I : In diatomic molecule :

Bond energy = bond dissociation

Example : $N_2 > O_2 > H_2 > F_2$

Case II : For polyatomic molecule :

Bond energy ≈ Bond dissociation energy (D)

Example : In  ;

$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H}$$

Bond energy per C–H bond is 99.5 Kcal/mole.

Theoretical values of bond dissociation energy (D) of individual C–H bonds in CH_4 are given :

$D(CH_3\text{–}H)$ = 102 K Cal/mole
$D(CH_2 – H)$ = 105 K Cal/mole
D(CH–H) = 108 K Cal/mole
D(C—H) = 83 K Cal/mole

Hence mean bond energy E per C–H bond in methane

$$= \frac{398}{4} = 99.5 \text{ K Cal/mole.}$$

Factors affecting the bond energy :

(i) Δ Electronegativity :– Bond energy ∝ ΔEN

Example : HF > HCl > HBr > HI

(ii) Bond order : Bond energy ∝ Bond order

Example : C — C < C = C < C ≡ C

79 kcal, 143.3kcal., 199.0 Kcal.

(iii) Atomic size : Bond energy ∝ 1/(Atomic size)

Example : C ≡ C < C ≡ N < N ≡ N

Exception :– In case of halogen group, order of bond energy is Cl—Cl > F—F > Br—Br > I—I

Because of higher electron density and small size of F atoms, repulsion between electrons of two F–atoms, weakens the bond energy.

Example : S—S > O—O

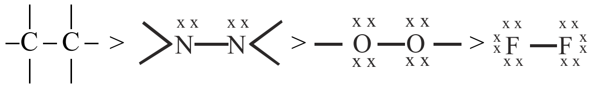
C—C > Si—Si > Ge—Ge

(iv) Bond Polarity : Bond energy ∝ Bond polarity

Example : H—F > H—Cl > H—Br > H—I

(v) Lone pair of electrons :

$$\text{Bond energy} \propto \frac{1}{\text{Lone pair of electrons}}$$



Size of F and O atoms are 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.

4. Bond Order :

* In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule.

* Isoelectronic molecules and ions have identical bond orders; for example, F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

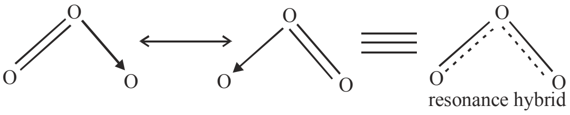
* With increase in bond order, bond enthalpy increases and bond length decreases.

5. Resonance :

* It has been found that the observed properties of certain compounds cannot be satisfactorily structures, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecules.

* The actual structure is in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical forms. This phenomenon is called resonance.

* Let us discuss resonance in ozone, according to its resonance structure it should have one single bond (O–O = 1.48 Å) and one double bond (O = O = 1.21 Å) but experiments show that both the bonds are same which can be proved by its resonance hybrid as shown below.



Conditions for writing resonance structures.

* All resonating structures must have the same arrangement of atomic nuclei

* The resonating structures must have the same number of paired and unpaired electrons. However they differ in the way of distribution of electrons.

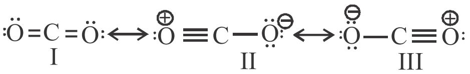
* The energies of the various contributing structures must be same or nearly the same.

* Resonating structures the like charges should not reside on adjacent atoms.

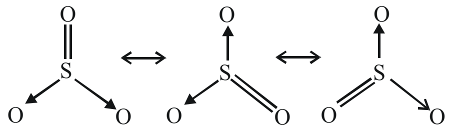
* Structures of ion should be so written that negative charge is present on an electron negative atom and positive charge an electropostive atom.

Examples of resonance structure of some molecule

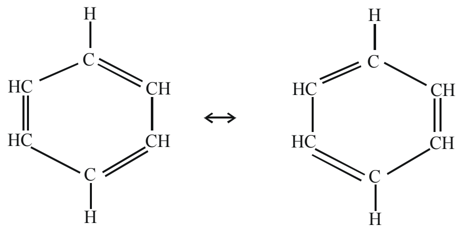
* **CO :** 

* **CO_2 :** 

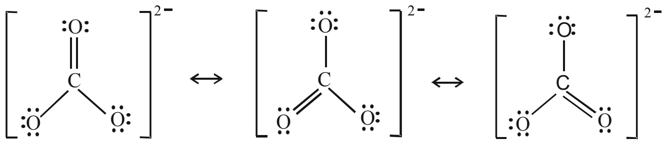
- **Sulphur Trioxide (SO_3) :**



- **Benzene (C_6H_6) :**



- **CO_3^{2-}**



Characteristic features of resonance hybrid.

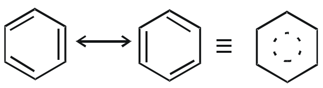
- The resonance hybrid is more stable (i.e. has less energy) than any one of the various resonating structures.
- For example, the total energy of the benzene hybrid is lower than the total energy of either of the two kekule structures by about 152.0kJ/mol.
- The difference in energy between the hybrid and the most stable canonical structure is referred to as the resonance energy of the molecule.
- The resonance energy of a resonance hybrid is the difference between the theoretical and experimental heats of hydrogenation of the compound. Thus.

  Resonance energy = Theoretical heat of hydrogenation
  – Experimental heat of hydrogenation
- In a resonance hybrid, the bond lengths are different from those in the contributing structure.

  Example (i) : Benzene

  C—C bond length 1.54 Å

  C = C bond length 1.34 Å



but bond length is between

single & double bond is = 1.39 Å

(ii) Bond length of C–O in CO_2 is 1.15Å

Resonance occurs in CO_2 a follows –

$\longleftrightarrow O^{-}—C\equiv O^{+} \longleftrightarrow O^{+}\equiv C—O^{-}$

Bond length = 1.15 Å (Between double & triple bond)

- In benzene bond energy of C—C increases due to π electrons of C = C.

- **Bond order :** Bond order can be defined as the number of covalent bonds formed in molecule.
- Stability of molecule ∝ bond order :
- $$\text{Bond order} = \frac{\text{Total covalent bonds between two certain atoms in each resonating structure}}{\text{Total number of resonating structure}}$$

For example,

In CO_3^{--} : Total resonating structure = 3

Total covalent bonds between C – O in all resonating structure = 4

Bond order = 4/3 = 1.33

DIPOLE MOMENT

- Polarity of any polar covalent bond is measured by dipole moment.
- We know that in a polar molecule, one end of the molecule is negative and the other is positive, in other words, there are two poles present in the molecule Hence the molecule is said to possess an electric dipole.
- The product of magnitude of negative or positive charge (q) and the distance (d) between the centres of positive and negative charges is called dipole moment. It is usually denoted by μ. $\mu = q \times d$
- The charge 'q' is of the order of 10^{-10} e.s.u. and the internuclear distance 'd' is of the order of 10^{-8} cm (Å) therefore, the dipole moment 'μ' is of the order of $10^{-10} \times 10^{-8} = 10^{-18}$ e.s.u. cm. This quantity is known as one Debye.

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

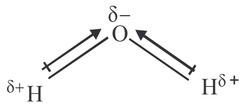
  $1\,D = 3.33564 \times 10^{-30}$ C-m

Diatomic molecules :

- Dipole moment is a vector quantity i.e., it has magnitude as well as direction.
- It is often represented by an arrow with its tail at the positive centre and head pointing towards the negative end (+ → –).
- As a polar diatomic molecule posses only one polar bond, the dipole moment of that molecule is equal to the dipole moment of the polar bond e.g. in case of HCl, the molecular dipole moment is equal to the dipole moment of H–Cl bond i.e. 1.03 D. Thus. $\overset{+\delta}{H} \Longrightarrow \overset{-\delta}{Cl}$ $\mu = 1.03$ D

Polyatomic molecules

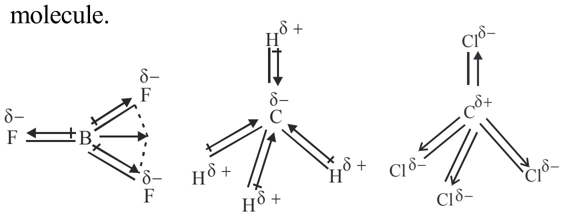
- As a polyatomic molecule has more than one polar bond, the dipole moment is equal to the resultant dipole moment of all the individual bonds.
- For example dipole moment of H_2O is 1.84 D which is equal to the resultant dipole moment of two O–H bonds.



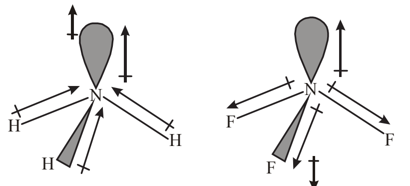
μ = 1.84D

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

* Again in case of symmetrical molecules such as BF_3, CH_4 and CCl_4 the molecular dipole moment is found to be zero. This is again because of the fact that individual dipole moments cancels out on account of the symmetry of the molecule.



* **Comparison of NH_3 and NF_3 molecule :** Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom.
Although fluorine is more electronegative than nitrogen, the resultant dipole moment of $_3$ (4.90×10^{-30} Cm) is greater than that of NF_3 (0.8×10^{-30} Cm). This is because, in case of NH_3 the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in NF_3 the orbital dipole is in the direction opposite to the resultant dipole moment of the three N – F bonds.
The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of NF_3 as represented :



Resultant dipole moment in $NH_3 = 4.90 \times 10^{-30}$ Cm

Resultant dipole moment in $NF_3 = 0.80 \times 10^{-30}$ Cm

Applications of dipole moment

(i) In determining the polarity of bonds :

* As $\mu = q \times d$. obviously, greater is the magnitude of dipole moment, higher will be the polarity of the bond.

* But in the strict sense, this concept is applicable to molecules containing only one polar bond.

* Further in case of non polar molecules like H_2, O_2, N_2 etc. the dipole moment is found to be zero. This is because there is no charge separation in these molecules.

(ii) In the calculation of ionic character :

* A covalent bond develops a polar character due to the difference in the electronegative of the atoms forming the bond.

* If the electronegativity difference between two atoms is large, the bond will be highly polar

* It has been observed that when the electronegativity difference is 1.7, the bond existing between two atoms is 50% ionic and 50% covalent.

* The percentage of ionic character of a bond can be calculated from the ratio of the observed dipole moment of the calculate dipole moment (considering 100% ionic character).
% ionic character

$$= \frac{\text{Observed dipole moment}}{\text{Dipole moment considering 100\% ionic character}} \times 100$$

* In A—B molecule
Ionic nature $\propto X_A - X_B$ i.e. ionic nature of molecule depends on electronegativity difference of A–B.

Hannay and Smith formula

% Ionic character = $[16 (X_A - X_B) + 3.5(X_A - X_B)^2$

% Ionic character = 0, when $X_A = X_B$ (100% covalent bond)

% Ionic character = 0 – 15% Non polar covalent

% Ionic character = 15 – 50% Polar covalent

% Ionic character = > 50% Ionic bond

(iii) Shape or symmetry of molecule :

* Dipole moment is an important factor in determining the shape of molecules containing three or more atoms.

* For instance if any molecule possesses two or more polar bonds.

- It will not be symmetrical if it possesses some molecular dipole moment as in case of water (μ = 1.84D) and ammonia (μ = 1.49 D).
- But if a molecule contains a number of similar atoms linked to the central atom and the overall dipole moment of the molecule is found to be zero. This will imply that the molecule is symmetrical e.g. CH_4, CCl_4 etc.

* **Dipole Moments of Selected Molecules**

Type of Molecule	Dipole Moment, μ(D)	Geometry
Molecule (AB)		
HF	1.78	linear
HCl	1.07	linear
HBr	0.79	linear
HI	0.38	linear
H_2	0	linear
Molecule (AB_2)		
H_2O	1.85	bent
H_2S	0.95	bent
CO_2	0	linear
Molecule (AB_3)		
NH_3	1.47	trigonal-pyramidal
NF_3	0.23	trigonal-pyramidal
BF_3	0	trigonal-planar
Molecule (AB_4)		
CH_4	0	tetrahedral
$CHCl_3$	1.04	tetrahedral
CCl_4	0	tetrahedral

TIPS

- * Second-period elements cannot have an expanded octet.
- * Third-period elements and beyond can have an expanded octet.
- * The noble gases usually only have an expanded octet.
- * The greater the charge on the cation, the greater the covalent character of the ionic bond.
- * For cations of the same size and charge, the one, with electronic configuration $(n-1)\ d^n ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, ns^2np^6, typical of alkali and alkaline earth metal cations.
- * The increasing order of electronegativity is $C < N < O < F$ and $I < Br < Cl < F$.
- * The covalent bond is directed in space.
- * Ionic bond is formed by the transfer of electrons from a less electronegative atom to an atom with more electron affinity.
- * **The strength of ionic bond :**
  - (a) $NaF > MgF_2 > AlF_3$
  - (b) $CsF > RbF > KF > NaF > LiF$
  - (c) $KF > KCl > KBr > KI$
  - (d) $AlF_3 > Al_2O_3 > Al_3N_3$.

TRY IT YOURSELF-1

Q.1 Calculate formal charge of S in SCl_2.

Q.2 Calculate the lattice energy of $CaCl_2$. If S is the enthalpy of sublimation of Ca(s), IE is the ionization enthalpy to form Ca^{2+} from Ca, EA is the electron affinity of Cl, H_a is the enthalpy of atomization of Cl_2 and ΔH_f is the enthalpy of formation.

Q.3 Which of the following has the highest dipole moment?
(A) CO_2 (B) HI
(C) H_2O (D) SO_2

Q.4 In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is
(A) + 1 (B) – 1
(C) – 0.75 (D) + 0.75

Q.5 If the electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$, the four electrons involved in chemical bond formation will be_____.
(A) $3p^6$ (B) $3p^6, 4s^2$
(C) $3p^6, 3d^2$ (D) $3d^2, 4s^2$

Q.6 Which will form more stable ionic bond ?
(i) Na and Cl (ii) Ca and Cl

Q.7 Calculate the bond order of N – O bond in NO_3^- ion.

Q.8 Can a non-polar molecule have polar covalent bond?

Q.9 The dipole moment of LiH is 1.964×10^{-29} cm and the inter-atomic distance between Li and H in the molecule is 1.59Å. Calculate % covalent character in the molecule.

Q.10 Arrange LiCl, NaCl, KCl, RbCl, CsCl in decreasing order of covalent character.

Q.11 Arrange $MgCl_2$, NaCl, $AlCl_3$ in decreasing order of covalent character.

ANSWERS

(1) 0 **(2)** $S + IE + H_a - 2 \times EA - \Delta H_f$

(3) (C) **(4)** (B) **(5)** (D)

(6) (ii) **(7)** 1.33 **(8)** Yes

(9) 23.2% **(10)** $LiCl > NaCl > KCl > RbCl > CsCl$
(size of cation increases)

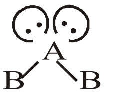
(11) $AlCl_3 > MgCl_2 > NaCl$ (charge of cation decreases)

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- * Proposed by Sidgwick and Powell in 1940.
- * Redefined by Nyholm and Gillespie (1957).

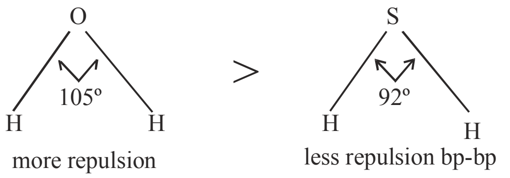
The main postulates of VSEPR theory are :

- * 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.
- * 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 distance from one another.
- * A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- * 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 decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp).
- * If on central atom number of lone pair of electron are equal then bond angle will depend on electronegativities of A & B.

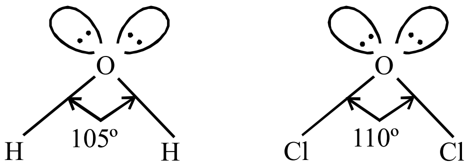


As electronegativity of A increases bond angle increases because bond pair of electron comes to 'A' and hence repulsion between bp-bp will be more. If electronegativity of 'B' increases then bond angle will decreases.

Examples: Electronegativity of 'O'> Electronegativity of 'S'



Bond angle $PCl_3 < PBr_3 < PI_3$ (EN of central atom increases)
$NH_3 > PH_3 > AsH_3$ (EN of central atom decreases)



Bond angle depends on size of side atom
Here Cl > H so bond angle of
$ClO_2 > H_2O$

Prediction of geometrical shapes of molecules with the help of VSEPR theory :

* We can predict the geometry of molecules (and ions) in a systematic way. For this purpose, it is convenient to divide molecules into two categories, according to whether or not the central atom has lone pairs.

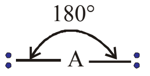
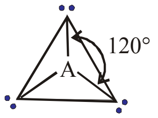
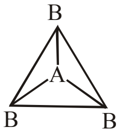
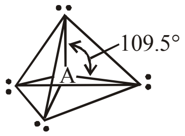
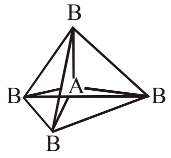
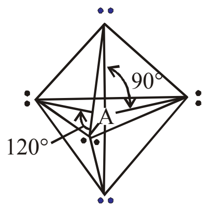
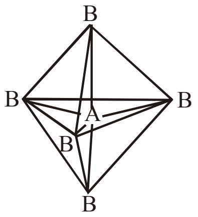
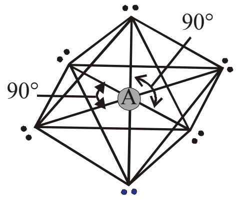
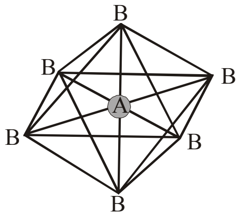
1. Molecules in which the central atom has no lone pairs :

* For simplicity we will consider molecules that contain atoms of only two elements, A and B, of which A is the central atom.

* These molecules have the general formula AB_x, where x is an integer 2, 3,.... (If x = 1, we have the diatomic molecule AB, which is linear by definition.)

* In the vast majority of cases, x is between 2 and 6.

Table : Arrangement of electron pairs about a central atom (A) in a molecule and geometry of some simple molecules and ions in which the central atom has no lone pairs

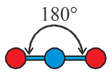
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

- * Table shows five possible arrangements of electron pairs around the central atom A. As a result of mutual repulsion, the electron pairs stay as far from one another as possible.
- * Note that the table shows arrangements of the electron pairs but not the positions of the atoms that surround the central atom. Molecules in which the central atom has no lone pairs have one of these five arrangements of bonding pairs.
- * Using Table as a reference, let us take a close look at the geometry of molecules with the formulas AB_2, AB_3, AB_4, AB_5, and AB_6.

AB_2 : Beryllium Chloride ($BeCl_2$)

The Lewis structure of beryllium chloride in the gaseous state is $:\ddot{Cl}-Be-\ddot{Cl}:$

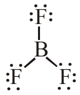
- * Because the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, the ClBeCl angle is predicted to be 180°, and the molecule is linear. The "ball-and-stick" model of $BeCl_2$ is



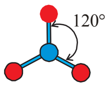
$BeCl_2$

AB_3 : Boron Trifluoride (BF_3)

- * Boron trifluoride contains three covalent bonds, or bonding pairs.
- * In the most stable arrangement, the three BF bonds point to the corners of an equilateral triangle with B in the center of the triangle:



According to Table, the geometry of BF_3 is trigonal planar because the three end atoms are at the corners of an equilateral triangle that is planar:

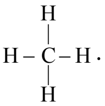


BF_3

Thus, each of the three FBF angles is 120°, and all four atoms lie in the same plane.

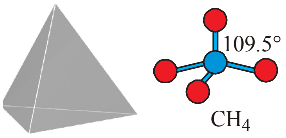
AB_4: Methane (CH_4)

- * The Lewis structure of methane is



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H\,.$$

- * Because there are four bonding pairs, the geometry of CH_4 is tetrahedral. A tetrahedron has four sides (the prefix tetra means "four"), or faces, all of which are equilateral triangles. In a tetrahedral molecule, the central atom (C in this case) is located at the center of the tetrahedron and the other four atoms are at the corners. The bond angles are all 109.5°.

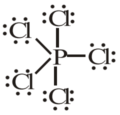


CH_4

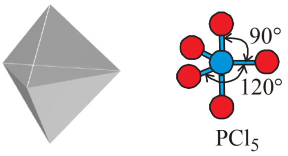
Tetrahedral

AB_5 : Phosphorus Pentachloride (PCl_5)

- * The Lewis structure of phosphorus pentachloride (in the gas phase) is



- * The only way to minimize the repulsive forces among the five bonding pairs is to arrange the PCl bonds in the form of a trigonal bipyramid. A trigonal bipyramid can be generated by joining two tetrahedrons along a common triangular base:



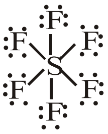
PCl_5

Trigonal bipyramidal

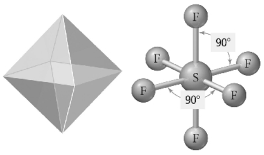
- * The central atom (P in this case) is at the center of the common triangle with the surrounding atoms positioned at the five corners of the trigonal bipyramid.
- * The atoms that are above and below the triangular plane are said to occupy axial positions, and those that are in the triangular plane are said to occupy equatorial positions.
- * The angle between any two equatorial bonds is 120°; that between an axial bond and an equatorial bond is 90°, and that between the two axial bonds is 180°.

AB_6: Sulphur Hexafluoride (SF_6)

- * The Lewis structure of sulphur hexafluoride is



- * The most stable arrangement of the six SF bonding pairs is in the shape of an octahedron, shown in Table. An octahedron has eight sides (the prefix octa means "eight").
- * It can be generated by joining two square pyramids on a common base. The central atom (S in this case) is at the center of the square base and the surrounding atoms are at the six corners. All bond angles are 90° except the one made by the bonds between the central atom and the pairs of atoms that are diametrically opposite each other. That angle is 180°. Because the six bonds are equivalent in an octahedral molecule, we cannot use the terms "axial" and "equatorial" as in a trigonal bipyramidal molecule.



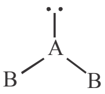
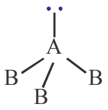
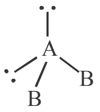
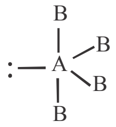
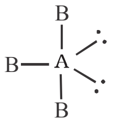
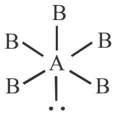
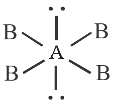
Octahedral

2. Molecules in which the central atom has one or more lone pairs

- * Determining the geometry of a molecule is more complicated if the central atom has both lone pairs and bonding pairs.

* In such molecules there are three types of repulsive forces—those between bonding pairs, those between lone pairs, and those between a bonding pair and a lone pair.
* In general, according to the VSEPR model, the repulsive forces decrease in the following order:
  lone-pair vs. lone-pair repulsion > lone-pair vs. bonding pair repulsion > bonding-pair vs. bonding pair repulsion
* Electrons in a bond are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less "spatial distribution" than lone pairs; that is, they take up less space than lone-pair electrons, which are associated with only one particular atom.
* Because lone-pair electrons in a molecule occupy more space, they experience greater repulsion from neighboring lone pairs and bonding pairs.
* To keep track of the total number of bonding pairs and lone pairs, we designate molecules with lone pairs as AB_xE_y, where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both x and y are integers; x = 2, 3, ... , and y = 1, 2, ... Thus, the values of x and y indicate the number of surrounding atoms and number of lone pairs on the central atom, respectively.
* The simplest such molecule would be a triatomic molecule with one lone pair on the central atom and the formula is AB_2E.

Table : Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E).

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramid	NH_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4

* As the following examples show, in most cases the presence of lone pairs on the central atom makes it difficult to predict the bond angles accurately.

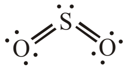
AB_2E : Sulphur Dioxide (SO_2)

The Lewis structure of sulphur dioxide is : $\underset{\cdot\cdot}{\ddot{O}}=\ddot{S}=\underset{\cdot\cdot}{\ddot{O}}$

* Because VSEPR treats double bonds as though they were single, the SO_2 molecule can be viewed as consisting of three electron pairs on the central S atom.

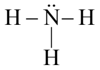
* Of these, two are bonding pairs and one is a lone pair. In Table we see that the overall arrangement of three electron pairs is trigonal planar. But because one of the electron pairs is a lone pair, the SO_2 molecule has a "bent" shape.

* Because the lone-pair versus bonding-pair repulsion is greater than the bonding-pair versus bonding-pair repulsion, the two sulphur-to-oxygen bonds are pushed together slightly and the OSO angle is less than 120°.



AB_3E : Ammonia (NH_3)

The ammonia molecule contains three bonding pairs and one lone pair:



$H-\ddot{N}-H$ with H bonded below N

As Table shows, the overall arrangement of four electron pairs is tetrahedral. But in NH_3 one of the electron pairs is a lone pair, so the geometry of NH_3 is trigonal pyramidal (so called because it looks like a pyramid, with the N atom at the apex).

* Because the lone pair repels the bonding pairs more strongly, the three NH bonding pairs are pushed closer together:

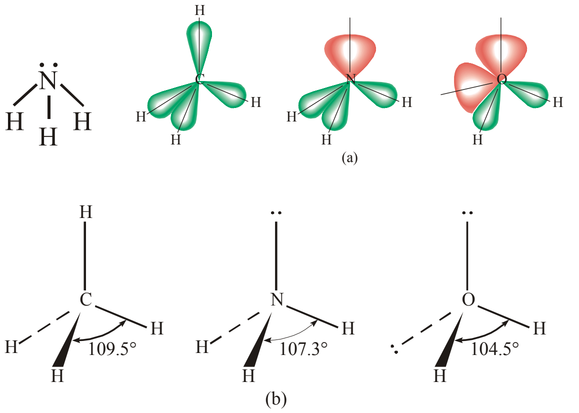


Figure : (a) The relative sizes of bonding pairs and lone pairs in CH_4, NH_3, and H_2O. (b) The bond angles in CH_4, NH_3, and H_2O. Note that the dashed lines represent a bond axes behind the plane of the paper, the wedged lines represent a bond axes in front of the plane of the paper, and the thin solid lines represent bonds in the plane of the paper.

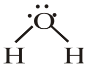
* Thus, the HNH angle in ammonia is smaller than the ideal tetrahedral angle of 109.5° (Figure).

AB_2E_2: Water (H_2O)

* A water molecule contains two bonding pairs and two lone pairs: $H-\underset{\cdot\cdot}{\ddot{O}}-H$

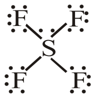
* The overall arrangement of the four electron pairs in water is tetrahedral, the same as in ammonia. However, unlike ammonia, water has two lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible.

* Consequently, the two OH bonding pairs are pushed toward each other, and we predict an even greater deviation from the tetrahedral angle than in NH_3. As Figure shows, the HOH angle is 104.5°. The geometry of H_2O is bent:



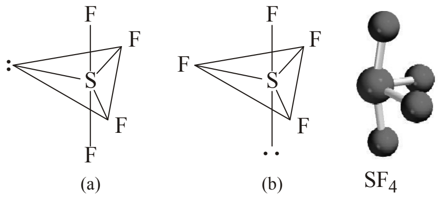
AB_4E : Sulphur tetrafluoride (SF_4)

* The Lewis structure of SF_4 is



* The central sulphur atom has five electron pairs whose arrangement, according to Table, is trigonal bipyramidal.

* In the SF_4 molecule, however, one of the electron pairs is a lone pair, so the molecule must have one of the following geometries:



* In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position. The axial position has three neighboring pairs at 90° and one at 180°, while the equatorial position has two neighboring pairs at 90° and two more at 120°. The repulsion is smaller for (a), and indeed (a) is the structure observed experimentally. This shape is sometimes described as a seesaw (if you turn the structure 90° clockwise to view it). The angle between the axial F atoms and S is 173°, and that between the equatorial F atoms and S is 102°.

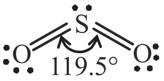
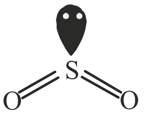
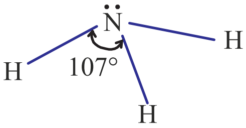
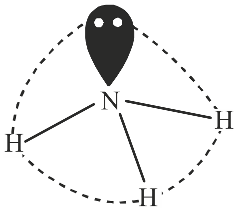
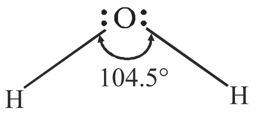
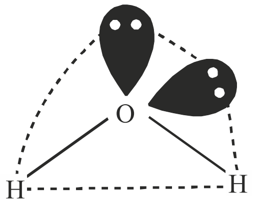
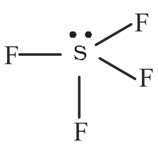
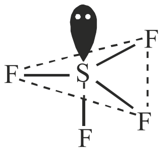
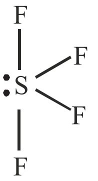
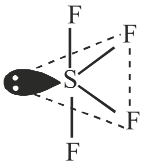
Guidelines for applying the VSEPR model :

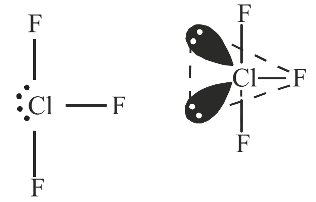
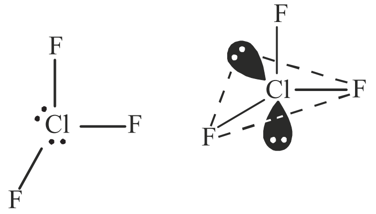
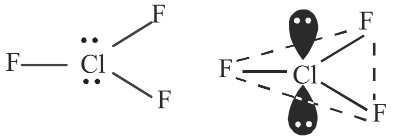
Having studied the geometries of molecules in two categories (central atoms with and without lone pairs), let us consider some rules for applying the VSEPR model to all types of molecules:

1. Write the Lewis structure of the molecule, considering only the electron pairs around the central atom (that is, the atom that is bonded to more than one other atom).
2. Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double and triple bonds as though they were single bonds. Refer to Table to predict the overall arrangement of the electron pairs.
3. In predicting bond angles, note that a lone pair repels another lone pair or a bonding pair more strongly than a bonding pair repels another bonding pair. Remember that in general there is no easy way to predict bond angles accurately when the central atom possesses one or more lone pairs.

The VSEPR model generates reliable predictions of the geometries of a variety of molecular structures. Chemists use the VSEPR approach because of its simplicity. Although there are some theoretical concerns about whether "electron-pair repulsion" actually determines molecular shapes, the assumption that it does leads to useful (and generally reliable) predictions.

Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	2	1	 	Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1	 	Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.
AB_2E_2	2	2	 	Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB_4E	4	1	(a)   (b)   (More stable)	See-saw	In (a) the lp is present at axial position so there are three lp-bp repulsions at 90. In(b) the lp is in an equatorial position, and there are two lp-bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw.

AB_3E_2	3	2	T-shape (a)  (b)  (c) 	In (a) the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped).

TIPS

- * If the central atom has only two bond pairs, the molecule or ion will be linear in shape. Examples are $BeCl_2$, CO_2, C_2H_2, HCN etc.
- * If the central atom has only three bond pairs, the molecule or ion will be trigonal planar. Examples are BCl_3 , C_2H_2 , SO_3 etc.
- * If the central atom has only four bond pairs, the molecule or ion is expected to be tetrahedral in shape. Examples are CH_4, C_2H_6, CCl_4, CBr_4, $SiCl_4$, NH_4^+, SO_4^{2-} , ClO_4^-, BF_4^- etc.
- * If there are five bond pairs only at the central atom, the molecule or ion will be trigonal planar. Examples are PCl_5, PF_5 etc.
- * If there are only six bond pairs at the central atom, the molecule or ion will be octahedral in shape. Examples are SeF_6, SF_6, TeF_6 etc.
- * If the central atom has only seven bond pairs, the molecule or ion is pentagonal bipyramidal in shape. Example is IF_7.
- * If the central atom has two bond pairs and one lone pair, the molecule or ion will be angular, bent or V-shaped. Examples are SO_2, $SnCl_2$, $PbCl_2$
- * If the central atom has three electron pairs and one lone pair the molecule or ion will be pyramidal in shape. Examples are : NH_3, NF_3, PCl_3, H_3O^+, ClO_3^- etc.
- * If the central atom has two electron pairs and two lone pairs the molecule or ion will be angular. Examples are ClO_2^- , H_2O.
- * If there are four bonded pairs and one lone pair, the molecule or ion will be distorted tetrahedral. Examples are $TeCl_4$, SCl_4, SF_4 etc.

WAVE MECHANICAL CONCEPT OF CHEMICAL BONDING

- * To explain the nature of covalent bond two theories based on quantum mechanics have been proposed.

(A) Valence bond theory (VBT)
(B) Molecular orbital theory (MOT)

- * Valence bond (VB) theory assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms. It enables us to retain a picture of individual atoms taking part in the bond formation.
- * The second theory, called molecular orbital (MO) theory, assumes the formation of molecular orbitals from the atomic orbitals.

VALENCE BOND THEORY (VBT)

- * It was presented by Heitter & London to explain how a covalent bond is formed and It was extended by Pauling & stater.

The main points of theory :

(i) Overlapping occurs between half filled valence shell orbitals of the two atoms.

(ii) Resulting bond acquired a pair of electrons with opposite spins to get stability.

(iii) Orbitals come closer to each other from the direction in which there is maximum overlapping

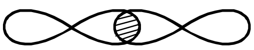
(iv) Covalent bond has directional character.

(v) Extent of overlapping ∝ strength of chemical bond

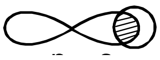
(vi) **Extent of overlapping depends on two factors.**

(a) **Nature of orbitals :** p, d and f are directional orbitals → more overlapping
s–orbital is non directional → less overlapping

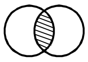
(b) **Nature of overlapping :**
Co–axial overlapping → extent of overlapping more.
Collateral overlapping → extent of overlapping less
In Co–axial overlapping extent of overlapping is
$p - p > s - p > s - s$



p–p



p–s



s–s

(vii) As the value of n increases, bond strength decreases.

$1-1 > 1-2 > 2-2 > 2-3 > 3-3$

(viii) If n is same $2p-2p > 2s-2p > 2s-2s$

$1s-2p > 2s-2p > 3s-3p$

(ix) Electron which is already paired in valency shell can enter into bond formation, if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same energy shell.

This point can explain the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus etc.

(x) **Two types of bonds are formed on account of overlapping.**

(A) **Sigma bond :**

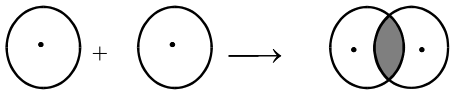
* This type of covalent bond is formed by the end to end overlapping of bonding orbitals along the internuclear axis.

* The overlap is known as head on overlap or axial overlap.

* The sigma bond is formed by any one of the following types of combinations of atomic orbitals.

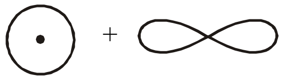
(i) **s–s overlapping :** In this type two half filled s–orbitals overlap along the internuclear axis as shown below

e.g. : H_2

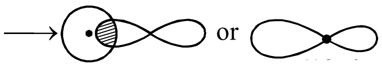


s–orbital s–orbitals s–s overlapping

(ii) **s–p overlapping :** It involves the overlapping of half filled s–orbital of one atom with the half filled p–orbital of other atom example : formation of H–F molecule involves the overlapping of 1s orbital of H with the half filled $2p_z$ orbital of Fluorine

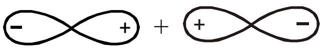


1s–orbital of H–atom 2p–orbitals of F atom



s–p overlapping in H–F molecule M.O. of HF

(iii) **p–p overlapping :** It involves the coaxial overlapping between p–orbitals of one atom with the p–orbitals of the other Example; formation of F_2 molecule in which $2p_z$ orbital of one F atom overlap coaxially with the $2p_z$ orbitals of second F atom as shown



$2p_z$–orbitals of F atom $2p_z$ orbitals of F atom

p–p coaxial overlapping in F_2 molecule M.O. of F_2

(iv) Bond between two hybrid orbitals $sp^3–sp^3$, $sp^2–sp^2$, $sp^3–sp^2$, $sp^3–sp$, $sp^2–sp$, sp–sp etc. overlapping of orbitals form σ bond

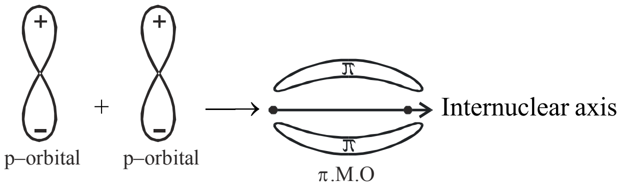
(B) **Pi (π) bond :**

* This type of covalent bond is formed by the side wise (or lateral) overlapping of half filled atomic orbitals of bonding atoms.

* The orbitals involved in overlap must be parallel and perpendicular to the internuclear axis

* It is always accompanied by a σ bond and consists of two charge clouds i.e. above and below the plane of sigma bond

* For example,



* Since overlapping takes place on both sides of the internuclear axis, free rotation of atoms around a π bond is not possible.

* Further more, formation of a π bond shortens the bond distance between the two atoms involved example C–C, C=C and C≡C, bond lengths are 1.54 Å, 1.34 Å and 1.20 Å respectively.

HYBRIDISATION

* Consider an example of Be compound : $BeCl_2$

* If it is formed without hybridisation then –

$\text{Cl}\overset{\text{s-p}}{\overline{\qquad}}\text{Be}\overset{\text{p-p}}{\overline{\qquad}}\text{Cl}$

both the Be–Cl bonds should have different parameters and **p–p bond strength > s–p bond strength**.

Practically bond strength and distance of both the Be–Cl bonds are same. This problem may overcome if hybridisation of s and p–orbital occurs.

* It is introduced by pauling, to explain equivalent nature of covalent bonds in a molecule.

* 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 $BeCl_2$

$\text{Cl}\ \underline{\text{ p-sp }}\ \text{Be}\ \underline{\text{ sp-p }}\ \text{Cl}$

bond strength of both the bonds will be equal.

Characteristics of hybridisation :

* Only orbitals of almost similar energies and belonging to the same atom or ion under hybridisation.

* Hybridisation is of orbitals only, not of electron.

* The number of hybrid orbitals produced is equal to the number of pure orbitals mixed during hybridisation, e.g. four hybrid orbitals are produced by mixing one s and three p (p_x, p_y and p_z) pure orbitals.

* In the excited state, the number of unpaired electrons must correspond to the oxidation state of the central atom in the molecule.

* Both half filled orbitals or fully filled orbitals of equivalent energy can involve in hybridisation s–orbital of equivalent energy always participate.

- * Most of the hybrid orbitals are similar in shape, size & energy.
- * Orbitals involved in π bond formation do not participate in hybridisation.
- * Hybridisation never takes place in an isolated atom but it occurs only at the time of bond formation.
- * The hybrid orbitals are distributed in space as apart as possible resulting in a definite geometry of molecule.
- * Hybridised orbitals provide efficient overlapping than overlapping by pure s, p and d–orbitals
- * Hybridised orbitals possess lower energy

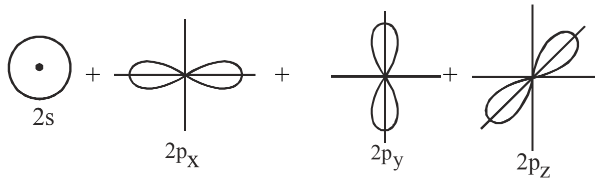
Types of hybridisation :

Depending upon the type and number of orbitals involved in intermixing, the hybridisation can be of various types namely sp, sp^2, sp^3, sp^3d, dsp^2, sp^3d^2, sp^3d^3.

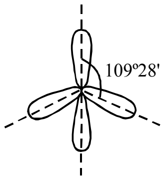
1. Tetrahedral or sp^3 hybridisation :

- * When one s and three p–orbitals belonging to the same shell of an atom mix together to form four new equivalent orbitals the type of hybridisation is called sp^3 or tetrahedral hybridisation.
- * The new orbitals are called sp^3 orbitals.
- * These are directed towards the four corners of a regular tetrahedron and make an angle of 109º28' with one another.
- * Each sp^3 hybrid orbital has 25% s–character and 75% p–character.

Example : H_2O, NH_3, CH_4, OF_2, Cl_2O, BF_4^- SO_4^{-2} etc.



sp^3 hybridisation



Four sp^3 hybrid orbitals

2. Trigonal or sp^2 hybridisation

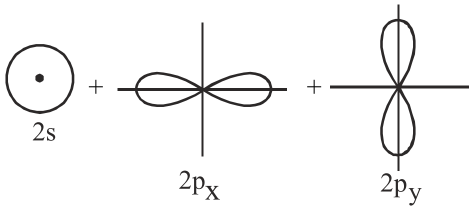
(a) When one s and two p–orbitals of the same shell of an atom mix to form three new equivalent orbitals, the type of hybridisation is called sp^2 hybridisation or trigonal hybridisation.

(b) The new orbitals formed are called sp^2 hybrid orbitals

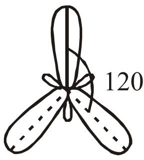
(c) All the three hybrid orbitals remain in the same plane making an angle of 120º with one another as shown in fig.

(d) Each of the hybrid orbitals formed has 33% s character and 67% p–character.

Example : C_2H_4, BX_3, BeF_3^-, $SnCl_2$, CO_3^{-2}, $AlCl_3$, Benzene, etc.



sp^2 hybridisation



Three sp^2 hybrid orbitals

3. Diagonal or sp hybridisation :

- * When one s and one p orbital belonging to the same main shell of an atom mix together to form two new equivalent orbitals, the type of hybridisation is called sp hybridisation or diagonal hybridisation.
- * The new orbitals formed are called sp hybrid orbitals.
- * They are collinear with an angle of 180º as shown in figure
- * Each orbital has 50% s–character and 50% p–character.

Example : C_2H_2, $BeCl_2$, CO_2, CS_2, $HgCl_2$, NO_2^+ etc.

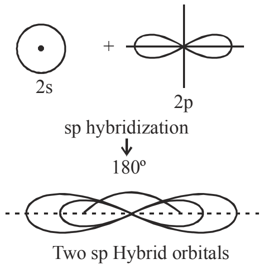


Figure : sp hybridisation in C_2H_2

4. sp^3d hybridisation :

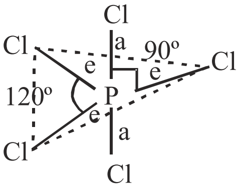
- * There are five orbitals : One s, three $p(p_x, p_y, p_z)$ and one (dz^2 – orbital) which are singlyfilled.
- * These orbitals hybridize to yield a set of five sp^3d hybrid orbitals.
- * The resultant shape of trigonal bipyramidal
- * There are two sets of equivalent hybrid orbitals : one set consists of three coplanar (120º) equivalent equatorial 'e' sp^2 orbitals and the other consisting of two equivalent axial 'a' sp^3d orbitals. This can be understood taking example of PCl_5.
- * Electronic configuration of phosphorous in ground state is $3s^2$, $3p_x^1$, $3p_y^1$, $3p_z^1$

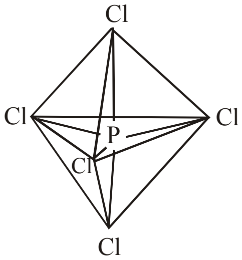
3s	3p			3d				
↑↓	↑	↑	↑					

Excited state of P is –

3s	3p			3d				
↑	↑	↑	↑	↑				

on sp^3d Hybridisation



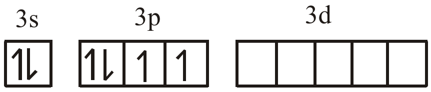


Trigonal bipyramidal geometry of PCl_5 molecule

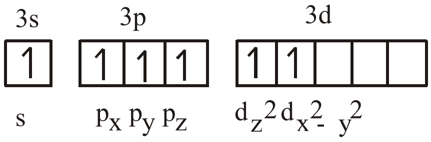
Shape of PCl_5 molecule (Trigonal bipyramidal)
Other example PF_5

5. sp^3d^2 Hybridisation :

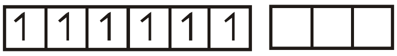
- * It involve the intermixing and redistribution of six atomic orbitals namely one s.
- * Three p and two d orbitals forming sp^3d^2 hybridized orbitals.
- * Geometry : Octahedral
- * This is explained by taking case of SF_6
- * Ground state configuration of S is $3s^2 3p^4 3d^0$



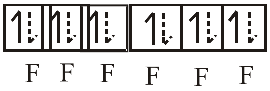
- * In excited state of S two electrons (one 3s and one 3p) are promoted to empty d_{z^2} and $d_{x^2-y^2}$ orbitals.



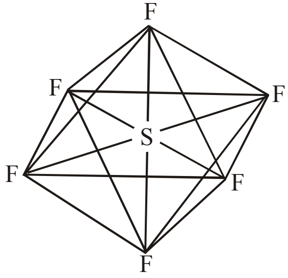
- * Sulpur in SF_6 during sp^3d^2 hybridised state



sp^3d^2 hybridised orbitals



- * These orbitals yield a set of six sp^3d^2 hybridised orbitals directed towards the corners of a regular octahedron as

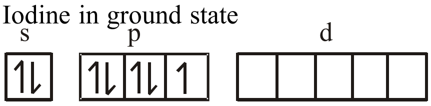


Octahedral geometry of SF_6 molecule

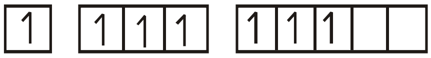
- * All the six S–F bonds in SF_6 have same bond length.

6. sp^3d^3 hybridisation :

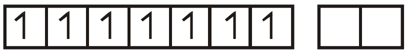
- * It involves the intermixing and redistribution of seven atomic orbitals namely one s, three p and three d–orbitals forming sp^3d^3 hybridized orbitals.
- * Geometry : Pentagonal bipyramid
- * This can be discussed taking example of IF_7
- * Iodine in ground state



Iodine in excited state

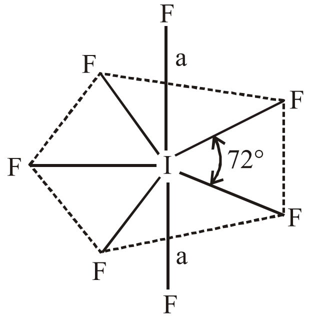


- * Iodine in sp^3d^3 hybridized state in the form of IF_7



sp^3d^3 hybridized orbitals

- * All seven hybridized orbitals overlap with 2p orbitals of fluorine to form IF_7 molecule having pentagonal bipyramid geometry as shown



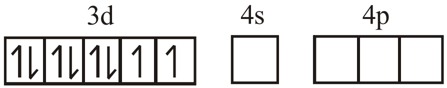
Pentagonal bipyramidal geometry of IF_7 molecular.

- * In this geometry, the five I–F bonds lie in one plane at an angle of 72°, these are equatorial bonds. The two I–F bonds lie perpendicular to the plane of equatorial bonds. These are axial bonds (marked as a). The axial bonds are relatively longer than equatorial bonds.

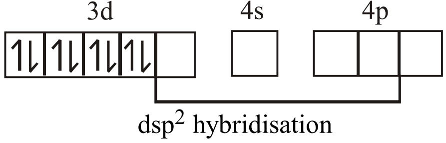
7. dsp^2 hybridisation :

- * In this hybridisation one s, two p orbitals and one (n – 1) d orbital are mixed to give four hybrid orbitals known as dsp^2 hybrid orbitals.
- * These four hybrid orbitals are equivalent in shape and energy and they are at angle 90°
- * The shape of molecule or ion obtained from dsp^2 hybrid orbitals will be square planar.
- * Example, $[Ni(CN)_4]^{-2}$, showing dsp^2 hybridisation

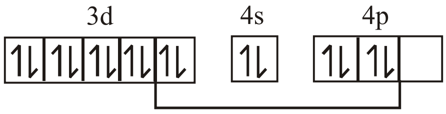
Ni^{2+} (ground state)



Ni^{2+} (excited state)

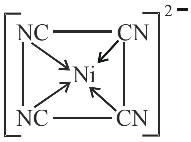


Ni^{2+} accepts 8e



dsp^2 hybridised

* The above four empty dsp^2 hybrid orbitals form coordinate bonds with four CN^- ions.



Structure of $[Ni(CN)_4]^{-2}$

Other examples : $[Ni(NH_3)_4]^{2+}$, $[Pt(Cl)_4]^{2-}$

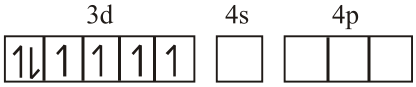
8. d^2sp^3 hybridisation :

* In this hybridisation inner two d–orbitals, one s–orbital and three p–orbitals will mix to give six new hybrid orbitals known as d^2sp^3 hybrid orbitals which are arranged in symmetrical octahedral.

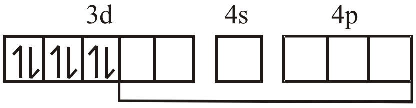
* The bond angle between them will be 90º.

* Example, $[Fe(CN)_6]^{-4}$, $[Co(NH_3)_6]^{+3}$, $[Fe(H_2O)_6]^{+2}[Cr(NH_3)_6]^{+3}$

Fe^{2+} (ground state)

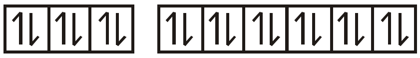


Fe^{+2} (excited state)



d^2sp^3 hybridisation

Fe^{2+} (after hybridisation)



d^2sp^3 hybridised orbitals

Determination of Hybridisation state :

Count the following four points on central atom :

(Total no. of σ bond)

* Count all pure σ bonds

* Count all lone pair, (Consider one lone pair = 1 σ bond)

* Count all co–ordinate bond (1 co–ordinate = 1 σ bond)

* Count multiple bonds (i.e. double or triple bond = 1 σ bond)

Consider few examples :

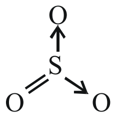
SO_2 : Central atom 'S' having –

$$O = \overset{x\,x}{S} \rightarrow O$$

One lone pair of e^- = 1σ bond
One co–ordinate bond = 1σ bond
One double bond = 1σ bond
Total = 3σ bonds

As SO_2 having 3σ bonds so its hybridisation will be sp^2.

SO_3 :



Total 3σ bonds

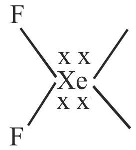
Hybridisation sp^2

Cl_2O : $Cl-\overset{x\,x}{\underset{x\,x}{O}}-Cl$

Central atom 'O' having 2 lone pair of e^- = 2σ bond and two pure σ bond.

Total 4σ bonds so hybridisation sp^3

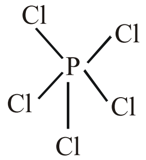
XeF_4 :



4 pure σ bonds
2 lone pair of e^-

Total 6σ bonds, so hybridisation state of central atom Xe will be sp^3d^2

PCl_5 :



5 σ b
so hybridization = sp^3d

(Here 5σ bonds means total five orbitals are hybridised (one s + three p + one d)

Anions : Ex. NO_2^- (nitrite ion), ClO^-, ClO_2^-, ClO_3^-, ClO_4^-, I_3^-, SO_4^{-2}, PO_4^{-3} etc.

Count number of negative charge.

No. of negative charge = No. of electrons

Add these extra electrons with central atom now determine hybridisation state of central atom

Example :

NO_2^- : 5 electrons in valence shell of N

Add one more electron of one negative charge on NO_2^-

$$O = \overset{xx}{N} \rightarrow O$$

No. of σ bonds are 3 so hybridisation state of N is sp^2

ClO^- : $:\ddot{\underset{\cdot\cdot}{Cl}}—O^-$

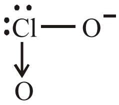
Central atom Cl have 3 lone pair of e^- = 3σ bonds

1 covalent bond = 1σ bond

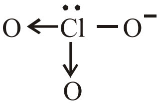
Total 4 σ bonds so hybridisation state of N is sp^3.

Similarly :

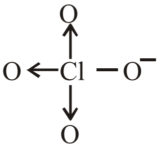
ClO_2^- ClO_3^- ClO_4^-



(4σ bonds)



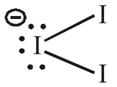
(4σ bonds)



(4σ bonds)

Hybridisation state of Cl in above examples will be sp^3.

I_3^- : Central atom is I having 7 valences shell e^- + 1 negative charge and side atoms are also I



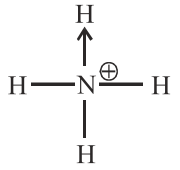
2 pure σ bonds with two side atoms of I

3 lone pair of electrons

Total 5σ bond $\quad sp^3d$ hybridisation

Cations : Example : NH_4^+, NO_2^+, H_3O^+ etc.
Count no. of positive charge. Deduct one electron of each positive charge from valence electrons of central atoms. Now determine hybridisation state of central atom as per points discussed earlier.

NH_4^+ : Valence e^- on central atom N = 5.
Deduct one electron of positive charge i.e.
Total 4 electrons remaining in valence shell of N



4σ bonds

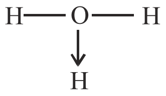
So, hybridisation state of N is sp^3

NO_2^+ : 5 valence e^- – 1 positive charge = 4e^- N atom.

$$O=\overset{\oplus}{N}=O$$

2σ bonds
So, hybridisation state of N is sp

H_3O^+: Central atom O having
6 valence e^- – 1 positive charge = 5e^-



Total 4σ bonds

So hybridisation state of O will be sp^3

Alternatively, hybridisation state can be find using

For simple molecule : $X = SA + \frac{1}{2}(G - V)$

For polyatomic anion : $X = SA + \frac{1}{2}(G - V + a)$

For polyatomic cation : $X = SA + \frac{1}{2}(G - V - c)$

where, SA means number of atoms/groups surrounding the central atom,
G means valence electrons of central atom from its atomic number.,
V means, valency of the central atom in the species, a means charge on the anion and c means charge on cation.
If X = 2 then hybrid state of central atom is sp.
If X = 3 then hybrid state of central atom is sp^2.
If X = 4 then hybrid state of central atom is sp^3.
If X = 5 then hybrid state of central atom is sp^3d.
If X = 6 then hybrid state of central atom is sp^3d^2.
If X = 7 then hybrid state of central atom is sp^3d^3.

Example :
S in SO_4^{2-} : Here, SA = 4, G = 6, V = 8, a = 2

$$X = 4 + \frac{1}{2}(6 - 8 + 2) = 4$$

Hybrid state of S is sp^3.
N in NH_4^+ : Here, SA = 4, G = 5, V = 4, c = 1

$$X = 4 + \frac{1}{2}(5 - 4 - 1) = 4$$

Hybrid state of N is sp^3.

SHAPE OF MOLECULE

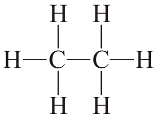
It was given by Sizwick & Powl. According to them the shape of covalent compound depends on total pairs of electron (bonded or non bonded) present on the central atom which is given as:

S.N.	Total pair of electrons	Shape	Hybridisation
1.	Two	Linear	sp
2.	Three	Coplanar trigonal (Triangular)	sp^2
3.	Four	Tetrahedral	sp^3
4.	Five	Trigonal bipyramidal	sp^3d
5.	Six	Octahedral (Square bipyramidal)	sp^3d^2
6.	Seven	Pentagonal bipyramidal	sp^3d^3

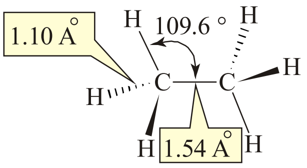
BONDING IN SOME ORGANIC COMPOUNDS

1. Bonding in Ethane

The two carbon atoms in ethane are tetrahedral. Each carbon uses four sp^3 orbitals to form four covalent bonds:



ethane

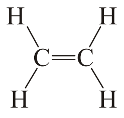


Perspective formula of ethane

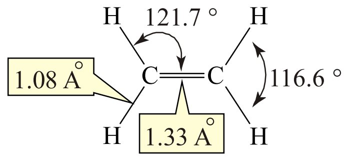
Ethane, like methane, is a nonpolar molecule.
All the bonds in methane and ethane are sigma (σ) bonds because they are all formed by the end-on overlap of atomic orbitals. All single bonds found in organic compounds are sigma bonds.

2. Bonding in Ethene: A double bond

Each of the carbon atoms in ethene (also called ethylene) forms four bonds, but each is bonded to only three atoms:



ethene (ethylene)



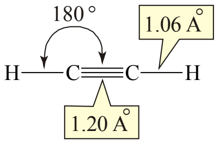
A double bond consists of one σ bond and one π bond

3. Bonding in Ethyne: A triple bond

The carbon atoms in ethyne (also called acetylene) are each bonded to only two atoms—a hydrogen and another carbon:

$H-C\equiv C-H$

ethyne (acetylene)



A triple bond consists of one σ bond and two π bonds

TIPS

* **Hybridisation and Bond length**

$$\text{Bond length} \propto \frac{1}{\text{'s' character}}$$

s-character increase ↓

Compound	Hybridisation	Bond length
Ethane	$sp^3 - sp^3$	1.54 Å
$>\!\!-$C - C =	$sp^3 - sp^2$	1.51 Å
$>\!\!-$C - C ≡	$sp^3 - sp$	1.47 Å
= C - C =	$sp^2 - sp^2$	1.46 Å
= C - C ≡	$sp^2 - sp$	1.42 Å
≡ C - C ≡	sp - sp	1.37 Å

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

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

Example :	CH_4	$\ddot{N}H_3$	$H_2\ddot{O}:$
Hybridisation	sp^3	sp^3	sp^3
Bond angle	109°28' >	107.5° >	104.5°
	No ℓ.p.	one ℓ.p.	two ℓ.p.

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

Then Bond angle ∝ Electronegativity of central atom

Example :	$\ddot{N}H_3$	$\ddot{P}H_3$	$\ddot{A}sH_3$
Bond angle	107°	93°	91°

⟶

Electronegativity decreasing.
Bond angle decreasing.

* When hybridisation is same, lone pair are same, Central atom is same, bonded atoms are different.

sp^3	OF_2	103 – 105°
sp^3	Cl_2O	109° – 111°
sp^3	Br_2O	116 – 118°

↓ Electronegativity of bonded atom is decreasing

$$\text{Bond angle} \propto \frac{1}{\text{electronegativity of bonded atom}}$$

$\propto$ size of side atom

* Bond energy ∝ % s–character in hybrid orbitals.

Example :	sp—sp >	$sp^2 - sp^2$ >	$sp^3 – sp^3$
s.character –	50%	33.3%	25%

MOLECULAR ORBITAL THEORY

* There is another approach to chemical bonding known as molecular orbital theory (MOT) developed by Mulliken (1932) and Hund which explains the bonding characteristics in a better way.

* The molecular orbital theory considers the entire molecule as a unit with all the electrons moving under the influence of all the nuclei present in the molecule.

* This approach recognizes that each electron belongs to the molecule as a whole and may move with in the entire molecule.

Important features of M.O.T. :

* Like an A.O. Which is around the nucleus of an atom there are M.O. which are around the nuclei of a molecule.

* The molecular orbitals are entirely different from the atomic orbitals from which they are formed.

* The valence electrons of the constituent atoms are considered to be moving under the influence of nuclei of participating atoms in the molecular orbital.

* The molecular orbitals possess different energy levels like atomic orbitals in an isolated atom.

* The shape of molecular orbitals are dependent upon the shapes of atomic orbitals from which they are formed.

* Molecular orbitals are arranged in order of increasing energy just like atomic orbitals.

* The number of molecular orbitals formed is equal to the number of atomic orbitals combining in bond formation.

* Like atomic orbitals, the filling of electrons in molecular orbitals is governed by the three principles such as Aufbau principle, Hund's rule and Pauli's exclusion principle.

Molecular orbitals :

* When the atoms to be bonded come close together, the orbitals of the bonded atoms lose their individual character and fuse (overlap) to form larger orbitals called molecular orbitals.

* Like atomic orbitals, there are molecular orbitals in a molecule.

* The only difference is that in atomic orbitals, electrons move under the influence of only one nucleus (i.e. AO' are monocentric), while in molecular orbitals, electrons move under the influence of many nuclei (i.e. MO's are polycentric)

* Molecular orbitals may, therefore be defined as " the regions in space associated with all the nuclei of the molecule where the probability of finding a particular electron in maximum.

* It may be noted that electrons in M.O., are not confined to an individual atom they belong to the entire molecule and are said to be delocalized with respect to the individual atoms.

Conditions for atomic orbitals to form M.O.

* The combining A.O. should be of a comparable energy

* The combining atomic orbitals must overlap to a large extent, greater the overlap stable is the molecule formed.

Formation of bonding and antibonding molecular orbitals (LCAO method) :

* An electron in an atom is described by a wave function Ψ called an atomic orbitals. Similarly, the behavior of an electron in a molecule is described by a molecular wave function called molecular orbitals.

* The most convenient way of working out the wave functions for molecular orbitals is to adopt the method of linear combination of atomic orbitals (LCAO).

* Quantum mechanics shows that linear combination of two functions gives, two combination and hence two molecular orbitals; a bonding orbital and an antibonding orbital.

(a) Combination by addition :

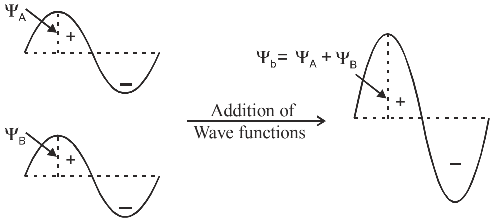
When the two electron waves are in phase i.e., they have the same sign, they will add up to give a new wave function expressed as Ψ_b

Wave function for bonding molecular orbital is

$$\Psi_b = \Psi_A + \Psi_B$$

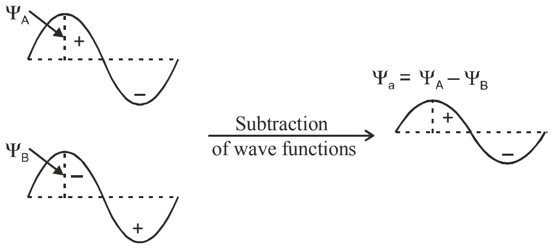
Ψ_A = wave function of atom A

Ψ_B = wave function of atom B



Addition of wave functions

(b) Combination by subtraction : When the two electron waves are out of phase i.e., they have opposite sign of the wave functions, then they will combine by subtraction and the resulting wave function Ψ_a



Subtraction of wave functions

Wave function for antibonding molecular orbital is :

$$\Psi_a = \Psi_A - \Psi_B$$

(c) We know that the probable electron density is given by Ψ^2 and not by Ψ. On squaring we get :

$$\Psi_b^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$$
$$\Psi_a^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

Here Ψ_A^2 and Ψ_B^2 represent the probable electron density in the two atomic orbitals where as Ψ^2 and Ψ^{*2} indicate the electron density in the two molecular orbitals. It may be noted that the molecular orbitals resulting from the addition of the wave functions is known as **bonding molecular orbital (Ψ_b^2)** whereas the orbital arising from the subtraction of the wave functions is called **antibonding molecular orbital (Ψ_a^2).**

$\Psi_b^2 = (\Psi_A + \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B$

i.e. there are Ψ_b^2 increases by $2\Psi_A\Psi_B$.This represents that larger overlap of atomic orbital, greater will be charge density between the nuclei & hence more stable is the bond. (Additive property of wave) or bonding molecular orbital. For antibonding molecular orbital,

$\Psi_a^2 = (\Psi_A - \Psi_B)^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$

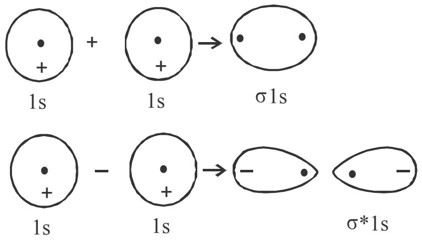
The area Ψ_a^2 decrease by $2\Psi_A\Psi_B$. This represents that low overlap of atomic orbital, lesser will be charge density between the nuclei and hence less stable is the bond (Subtractive property of wave) or antibonding molecular orbital.

* Such an orbital obviously cannot lead to the formation of a chemical bond and is therefore, termed as an antibonding M.O. combination of atomic orbitals – sigma (σ) and Pi (π) molecular orbitals

* In the M.O. theory, orbitals are identified as σ or π depending upon the type of the symmetry of the molecular orbital

* A sigma (σ) M.O. is one that has cylindrical symmetry around the internuclear axis, i.e. it does not show any change of sign on rotation through 180° about the axis.

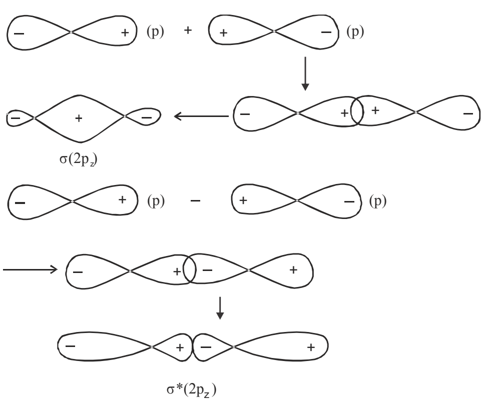
* It can be said that a sigma M.O. has no nodal plane (in which the electron density is zero) along the inter nuclear axis.



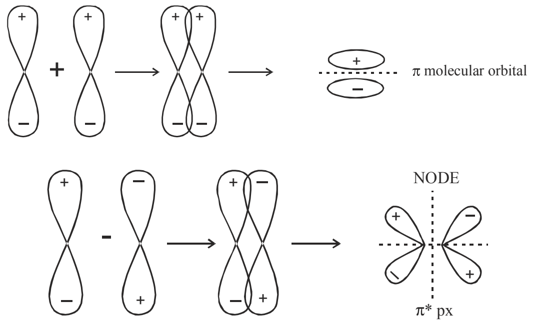
Formation of σ1s and σ*1s is bonding and anti bonding M.O.

* The bonding orbital is designated simply as σ orbital and antibonding as σ*.

* Such a sigma (σ) orbital is also formed when any two p–atomic orbitals overlap in end on (along their axis) position.



* Since the energy of a molecular orbital is directly related to the number of nodal planes, the π–orbital is more energetic than the σ–orbital. This explains why a π–bond is a weaker bond than a σ–bond.

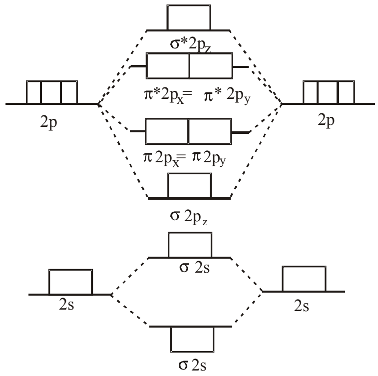


Comparison of bonding molecular orbital & antibonding molecular orbital :

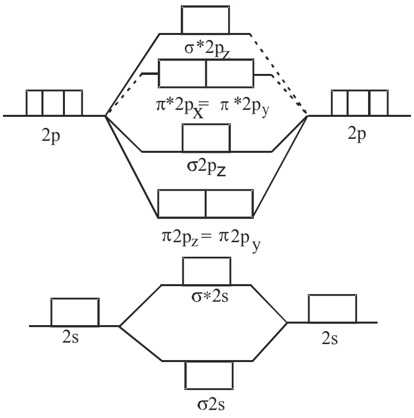
S.N.	Bonding molecular orbital (BMO)	Antibonding molecular orbital (ABMO)
1.	Bonding MO is the result of the linear combination of AO when their wave function are added $\Psi_b = \Psi_A + \Psi_B$	ABMO is result of linear combination of AO when their wave function are subtracted $\Psi_a = \Psi_A - \Psi_B$
2.	It does not have node.	It always have a node between two nuclei bonded atom.
3.	Charge density increases between two nuclei resulting attraction between two atoms.	Charge density decreases in between two nuclei leads to repulsion between two atoms.
4.	Energy of BMO is less, hence stable.	Energy of ABMO is high, hence unstable.

Relative energies of M.O. and filling of electron

* Two general criteria, which determine the energy of the molecular orbitals are
  (a) Initial energy of the atomic orbitals
  (b) The extent of the overlap of the atomic orbitals.
* It is obvious that molecular orbitals formed from lower energy atomic orbitals have lower energy than the molecular orbitals formed from higher energy atomic orbitals.
* The sequence in the order of increasing energy is given below (i.e., for more than N_2.)
  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
* It has been found experimentally that in same of the diatomic molecules $\sigma 2p_z$ M.O. is higher in energy than $\pi 2p_y$ and $\pi 2p_x$ M.O's. Therefore, the order of increasing energy of these M.O's changes to (i.e. upto N_2).
  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
* Energy diagram is shown



* The main difference between the two types of sequences in energy level is that for molecules O_2, F_2 and Ne (Hypothetical) The $\sigma 2p_z$ M.O.is lower in energy than $\pi 2p_x$ and $\pi 2p_y$
* In case of molecule of Li_2, Be_2 (hypothetical) B_2, C_2 and N_2 molecules, the $\sigma 2p_z$ MO has higher energy than $\pi 2p_x$ and $\pi 2p_y$MO's
* The new energy diagram is shown



M.O. energy diagram for Li_2, Be_2, B_2, C_2 and N_2 Molecule

* The filling of electrons in various M.O. follows similar rules to those for filling A.O. similar M.O. belongs to entire molecule the total number of electrons are taken into consideration.

Bond order :

* Bond order = 1/2 [No. of electrons in bonding orbitals – No. of electrons in antibonding orbitals] = 1/2 $[N_b - N_a]$
* The bond order of 1, 2 and 3 corresponds to single, double and triple bonds respectively it may be mentioned that according to M.O. theory, even a fractional bond order is possible.
* If the value of bond order is positive (i.e., $N_b > N_a$), it indicates a stable molecule and if the value of bond order is negative or zero (i.e., $N_b < N_a$ or $N_b = N_a$), it means that the molecule is unstable and is not formed.
* Dissociation energy of the molecule is directly proportional to the bond order of the molecule. In other words, greater the bond order, greater is the bond dissociation energy.

* Bond length of the molecule is inversely proportional to the bond order of the molecule. In other words, greater the bond order, shorter will be the bond length.

* Bond order of a molecule is equal to the number of covalent bond between the atoms in the molecule.

Magnetic property :

* If all the electrons in a molecule are paired than substance is diamagnetic, on the other hand if there are unpaired electrons in the molecule the substance is paramagnetic.

* More the number of unpaired electron in the molecule greater is the paramagnetism of the substance.

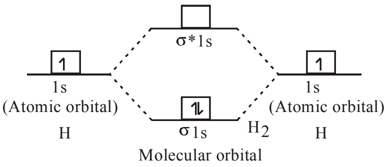
* If the bond order is fractional, the molecule will definitely be paramagnetic (attracted by magnetic field). However, if the bond order is whole number, the molecule mayor may not be paramagnetic.

Bonding in molecules :

(1) Hydrogen molecule (H_2) :

* Having two H atoms with one electron each ($1s^1$)

* M.O. configuration of $H_2 = (\sigma\ 1s)^2\ (\sigma^*\ 1s)^o$

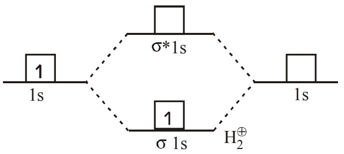


* Bond order $= \frac{1}{2}\ [N_b - N_a] = \frac{1}{2}\ [2-0] = 1$ i.e. single bond.

* Having paired electron so diamagnetic.

* Stability → quite stable (having single bond)

(2) H_2^+ ion :



* Configuration of $H_2^+ = (\sigma\ 1s)^1\ (\sigma^*1s)^o$

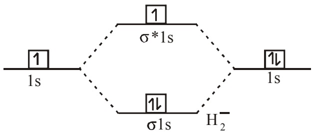
* One electron in bonding molecular orbital.

* Paramagnetic

* Bond order $= \frac{1}{2}\ [1-0] = \frac{1}{2}$

* Less stable than H_2 molecule

(3) H_2^- anion :



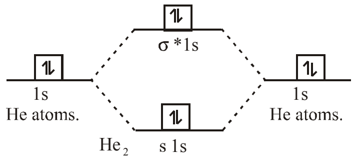
* M.O. configuration – $(\sigma\ 1s)^2\ (\sigma^*1s)^1$

* Paramagnetic

* Bond order $= \frac{1}{2}\ [2-1] = \frac{1}{2}$

* Stability is equal to $[H_2^+]$

(4) Helium molecule (He_2) –



* M.O. configuration – $(\sigma 1s)^2\ (\sigma^*1s)^2$

* Diamagnetic

* Bond order $= \frac{1}{2}\ [2-2] = 0$ (zero)

* Bond order zero indicates no linkage between Hence He_2 molecule does not exists.

* Stability (He_2) highly unstable molecule

(5) Helium molecule ion (He_2^+) –

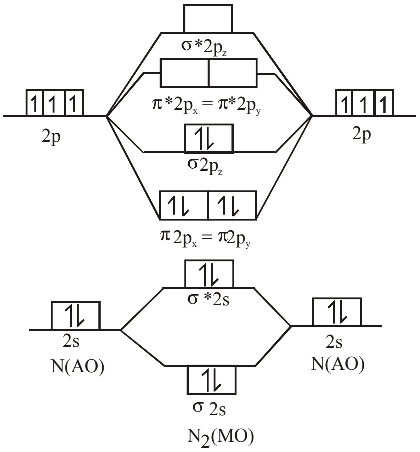
* M.O configuration–$(\sigma 1s)^2(\sigma^*1s)^1$

* Paramagnetic

* Bond order $= \frac{1}{2}[2-1] = \frac{1}{2}$

* As the bond order is positive this ion is formed.

(6) Nitrogen Molecule (N_2) :



M.O. Energy level diagram for N_2 molecule

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

* Diamagnetic

* Bond order $= \frac{1}{2}[10-4] = 3$

* N_2 molecule has three bonds one sigma and two pi

(7) Nitrogen Molecule cation(N_2^+) :

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

* Paramagnetic

* Bond order $= \frac{1}{2}[9-4] = 2.5$

* Since bond order of N_2^+ is smaller than bond order of N_2, therefore, it will have larger bond length and smaller bond dissociation energy than N_2 molecule.

(8) Oxygen molecule (O_2) :

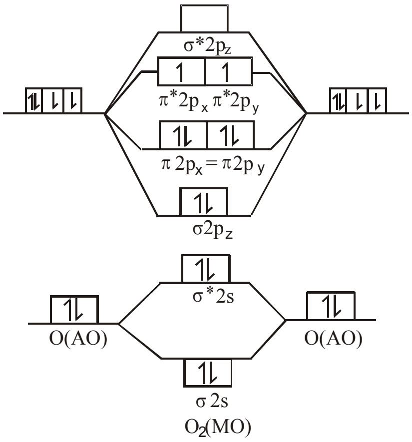
* M.O. configuration

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

* Paramagnetic

* Bond order $= \frac{1}{2}[8-4] = 2$

* In oxygen molecule atoms are held by a double bond.



M.O. Energy level diagram for O_2 molecule

* In oxygen molecule, atoms are held by a double covalent bond.

* The bond dissociation energy of O_2 molecule has been found to be 495 kJ/mole and bond length 121 pm.

* From the molecular orbital diagram of O_2 molecule, it may be noted that it contains two unpaired electrons in π^*2p_x and π^*2p_y molecular orbitals. O_2 molecule has paramagnetic nature.

* In this way, the M.O. theory successfully explains the paramagnetic nature of oxygen.

* The VB theory failed to explain the paramagnetic nature of oxygen.

(9) O_2^+(Oxygen molecule cation) :

* M.O. configuration

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

* Paramagnetic

* Bond order $= \frac{1}{2}[8-3] = 2.5$

* Since bond order of O_2^+ is greater than the bond order of O_2, therefore it will have smaller bond length and larger bond dissociation energy than O_2 molecule.

(10) O_2^- (Super oxide ion) :

* M.O. configuration

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

* Paramagnetic

* Bond order $= \frac{1}{2}[8-5] = 1.5$

* Since bond order of O_2^- is smaller than bond order of O_2 therefore it will have larger bond length and smaller bond dissociation energy than O_2 molecule.

(11) Peroxide ion (O_2^{2-}) :

* M.O. configuration

O_2^{2-} : $(\sigma 1s)^2\,(\sigma^*1s)^2\,(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2(\pi^*2p_x)^2\,(\pi^*2p_y)^2$

* Diamagnetic

* Bond order $= \frac{10-8}{2} = \frac{2}{2} = 1$

* Since bond order of O_2^{2-} ion is less than that of O_2 molecule, therefore, it will have longer bond length and smaller bond dissociation energy than that of O_2 molecule. Since there is no unpaired electron in it, it is diamagnetic in nature.

(12) Fluorine Molecule (F_2) :

* M.O. configuration

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

* Bond order $= \frac{1}{2}\,(10-8) = 1.$

* It is diamagnetic since it has no unpaired electrons.

(13) Neon (Ne_2) :

* M.O. configuration

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

* Bond order $= \frac{1}{2}\,(10-10) = 0$

* Since bond order of Ne_2 comes out to be zero, hence it is unstable and does not exist.

TIPS

* Bond orders of some molecules are:

$H_2 = 1.0$, $He_2 = 0$, $Be_2 = 0$, $C_2 = 2$, $N_2 = 3$,

$O_2 = 2$, $O_2^+ = 2.5$, $O_2^- = 1.5$, $O_2^{2-} = 1.0$,

$NO = 2.5$, $NO^+ = 3.0$, $NO_2^+ = 2.5$, $NO^- = 2$, $H_2^+ = 0.5$,

$H_2^- = 0.5$ and $He_2^+ = 0.5$.

* As the bond order or number of covalent bonds increases the bond length decreases.

* The larger the s-character, shorter is the orbital and shorter is the bond length of the bond formed by it. The s- character of sp, sp^2 and sp^3 hybrid orbitals is 50%, 33.3% and 25% respectively.

* Be_2 molecule does not exist.

TRY IT YOURSELF-2

Q.1 The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be

(A) sp, sp^3 and sp^2
(B) sp, sp^2 and sp^3
(C) sp^2, sp and sp^3
(D) sp^2, sp^3 and sp

Q.2 Which of the following species has tetrahedral geometry?
(A) BH_4^- (B) NH_2^-
(C) CO_3^{2-} (D) H_3O^+

Q.3 Which of the following angle corresponds to sp^2 hybridisation?
(A) 90° (B) 120°
(C) 180° (D) 109°

Q.4 Which of the following order of energies of molecular orbitals of N_2 is correct?
(A) $(\pi 2p_y) < (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(B) $(\pi 2p_y) > (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(C) $(\pi 2p_y) < (\sigma 2p_z) > (\pi^* 2p_x) \approx (\pi^* 2p_y)$
(D) $(\pi 2p_y) > (\sigma 2p_z) < (\pi^* 2p_x) \approx (\pi^* 2p_y)$

Q.5 Which of the following attain the linear structure:
(A) $BeCl_2$ (B) NCO^+
(C) NO_2 (D) CS_2

Q.6 Which of the following species have the same shape?
(A) CO_2 (B) CCl_4
(C) O_3 (D) NO_2^-

Q.7 Based on VSEPR theory, the number of 90 degree F – Br – F angles is BrF_5 is :

Q.8 The shape of XeO_2F_2 molecule is –
(A) Trigonal bipyramidal (B) Square planar
(C) tetrahedral (D) see-saw

ANSWERS

(1) (B) **(2)** (A) **(3)** (B)
(4) (A) **(5)** (AD) **(6)** (CD)
(7) 8 **(8)** (D)

HYDROGEN BONDING

- It is an electrostatic force of attraction between covalently bonded hydrogen atom of one molecule and an electronegative atom (F,O, N).
- It is not formed in ionic compounds. H–bond forms in polar covalent compounds, (not in non-polar).
- It is very weak bond (strength 2–10Kcal/mol.) but stronger than vander waal's force.
- It is also known as dipole–dipole attraction.
  $H^{\delta+} - F^{\delta-} .... H^{\delta+} - F^{\delta-} .... H^{\delta+} — F^{\delta-}$

Main condition for H–bonding :

- H–should be covalently bonded with high electro –ve element like F, O, N.
- Atomic size of electronegative element should be small.
- Decreasing order of atomic size is N > O > F
- Decreasing order of electronegativity is –
  F (4.0) > O (3.5) > N (3.0)
- Strength of H–bond ∝ Electronegativity of

$$Z\ (\text{element}) \propto \frac{1}{\text{Atomic size of Z}}$$

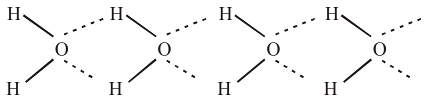
- Hydrogen bonding occurs in HCN, due to (–C ≡ N) triple bond (sp hybridisation), electronegativities of carbon and nitrogen increases.
  H—C ≡ N ....H—C≡ N .... H—C ≡ N

Types of hydrogen bonding :

(a) Intermolecular H–bond :
H–bond formation between two or more molecules of either the same or different compounds known as Inter molecular H-bonding. These are of two types :

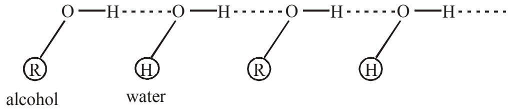
(i) Homo intermolecular : H–bond between molecules of same compounds

Example :– H—F.....H—F........H—F



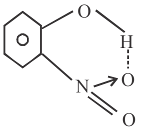
(ii) Hetero intermolecular : H–bond between molecules of different compounds

Example :– Alcohol, water

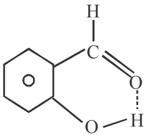


(b) Intramolecular H–bond :

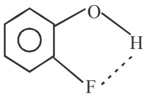
- It takes place within the molecule.
- H–bonded with electronegativity element of a functional group, form H–bond with another electronegative element present on nearest position on the same molecule.
- This type of H–bond is mostly occurred on organic compounds.
- It results in ring formation (Chelation). **Example :**



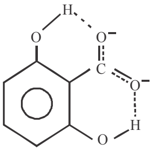
O-nitrophenol



Salicylaldehyde



O-fluorophenol



2-6 dihydroxyl benzoate

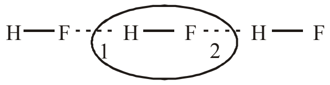
Effect of H–bond on physical properties :

1. Physical states : H_2O is liquid while H_2S is gas.

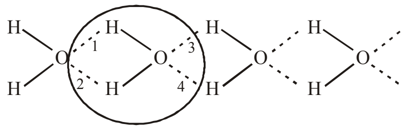
For water and Ice : Both have H–bonding even then density of ice is less than water.

Volume of ice is more because of open cage crystal structure of ice.

HF is liquid as it can form a only two H–bond.

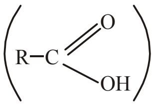


While H_2O becomes solid due to four hydrogen bond among water molecule are formed in tetrahedral manner.

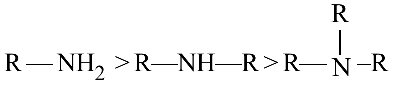


2. Melting point and boiling point :

- Due to intermolecular H-bond melting point and boiling point of compounds increases.
  $H_2O > CH_3OH > CH_3\text{–}O\text{–}CH_3$
  Trihydric alcohol > dihydric alcohol > Monohydric alcohol

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

* Decreasing order of melting point and boiling point :
1° – amine > 2° – amine > 3° – amine



$R—NH_2 > R—NH—R > R—\overset{R}{\overset{|}{N}}—R$

(no hydrogen with nitrogen atom)

* Boiling points of VA, VIA, VIIA hydrides decreases on decreasing molecular weights.

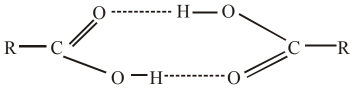
$PH_3 < AsH_3 < SbH_3 < NH_3$
$H_2S < SeH_2 < TeH_2 < H_2O$
$HI < HBr < HCl < HF$

But sudden increase in boiling point of NH_3, H_2O and HF is due to H–bonding.

$H_2O > HF > NH_3$
$PH_3 < H_2S < HCl$

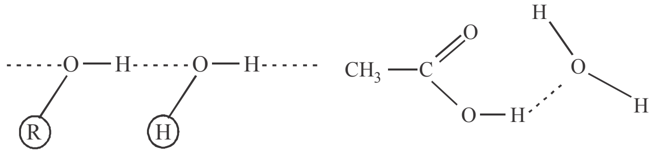
* Intramolecular H–bonding gives rise to ring formation, so the force of attraction among these molecule are vander waal force. So melting point and boiling point are low.

3. **Molecular weight :** Increases by H–bonding molecular wt. of CH_3COOH is double of its molecular formula, due to dimer formation occur by H–bonding.



4. **Solubility :**

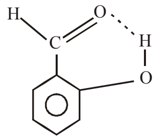
(a) Inter molecular H–bonding –Few organic compounds (Non–polar) are soluble in water (Polar solvent) due to H–bonding.



Alcohol Water Acetic acid Water

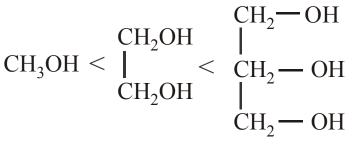
Other examples–Glucose, Fructose etc. dissolve in water. Ketone, ether, alkane etc. are insoluble (no H–bond). dimethyl ether is soluble in water while diethyl ether is partially soluble, due to bulky ethyl groups H–bonding interupts. Solubility order : $CH_3OCH_3 < CH_3OH$
Primary amine > secondary amine > tertiary amine

(b) **Intra molecular H–bonding :** It decreases solubility as it form chelate by H–bonding, so H– is not free for other molecule. It can not form H–bond with water molecule so cannot dissolves.



(Salicylaldehyde) O-Hydroxy benzaldehyde

5. **Viscosity –** H–bond associates molecules together so viscosity increases



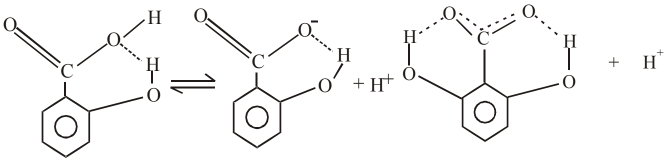
$$CH_3OH < \begin{array}{c}CH_2OH\\|\\CH_2OH\end{array} < \begin{array}{l}CH_2—OH\\|\\CH_2—OH\\|\\CH_2—OH\end{array}$$

H_2O > CH_3OH > $CH_3–O–CH_3$
Water Alcohol Ether

6. **Base strength :** CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ for H–bond with water. So less hydrolysis occurs. ie. it gives less OH^- ions .
While $(CH_3)_4N^+OH^-$ (ammonium compound) will give OH^- ion in large amount due to no H–bonding.

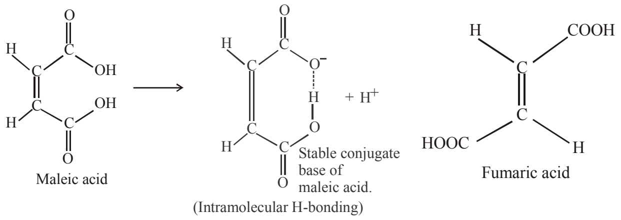
Effect of intramolecular H–bonding :

Strength of acid : The formation of intramolecular H–bonding in the conjugate base gives extra stability to conjugate base and hence acid strength increases
eg. Salicylic acid is stronger than benzoic acid and 2, 6–dihydroxy benzoic acid > salicylic acid.



Salicylic Acid Conjugate base 2, 6-dihydroxy benzoate ion.

C_2H_5SH is more acidic than C_2H_5OH.
In C_2H_5OH, H–bond forms so H^+ is not free.
HF weaker acid than HI, due to H–bond in H–F, H^+ is not free (due to H–bonding)
Maleic acid(cis) is stronger acid than fumaric acid (trans)



No Intramolecular H–bonding

TRY IT YOURSELF-3

Q.1 Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3 . The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is :
(A) $HF > H_2O > NH_3$ (ii) $H_2O > HF > NH_3$
(C) $NH_3 > HF > H_2O$ (iv) $NH_3 > H_2O > HF$

Q.2 In which substances will hydrogen bond be strongest?
(A) HCl (B) H_2O
(C) HI (D) H_2S

Q.3 The bond energy (in kcal mol^{-1}) of a C – C single bond is approximately –

(A) 1	(B) 10
(C) 100	(D) 1000

Q.4 Hydrogen bonding plays a central role in the following phenomena –
(A) Ice floats in water.
(B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions.
(C) Formic acid is more acidic than acetic acid.
(D) Dimerisation of acetic acid in benzene.

Q.5 Hydrogen bond is weaker or stronger than the van der Waals forces?

Q.6 Molecules of carboxylic acids are supposed to exist as dimers because of hydrogen bonding. [True/False]

Q.7 Ethanol has higher boiling point than that of dimethyl ether. [True/False]

Q.8 C = C bond length is greater than the C – C bond length value. [True/False]

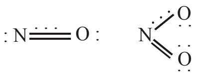
ANSWERS

(1) (B)	**(2)** (B)	**(3)** (C)	**(4)** (ABD)
(5) stronger	**(6)** True	**(7)** True	**(8)** False

SOME OTHER TYPE OF CHEMICAL BONDS

Odd electron bond :

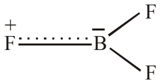
* These include one electron bond and three electron bond.
* The example of one electron bond is H_2^+.
* The one electron bond also exist in ferromagnetic metals.
* The bond is only half as strong as a shared electron pair bond.
* The three electron bond concept was given by Pauling.
* NO and NO_2 are the examples of odd molecule having three electron bonds e.g.



* The three electron bond is formed when the two atoms are identical or have nearly same electronegativity.

Back bonding :

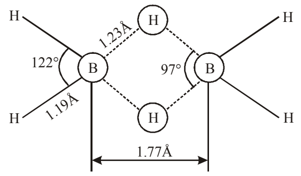
* This type of bonding occurs between atoms in a compound in which one atom has lone pair of electron and the other has vacant orbital placed adjacent to each other.
* A compound with back bonding has pi-bonding character since it results after formation of sigma bond.
* Back bonding allows the molecule to stable as it completes its octet.
* Back bonding results in a decrease in bond length and increase in bond order.
* In compounds like BF_3, the boron atom has an incomplete octet. The fluorine atom on its side has a lone pair which it can donate to boron. But, flurorine is also a very electronegative element. So, it also has a tendency to take back the electrons that it had donated to boron. This way, the lone pair of electrons keep jumping between fluorine and boron. This is called **back bonding**. This provides the lone pair of electrons more number of exchange positions (which simply means more space). As a result, the molecule becomes more stable.



* The order of acidity is as follows : $BF_3 < BCl_3 < BBr_3$

Banana bonding :

* This type of bonding is present in B_2H_6. A bridge structure for diborane was proposed by Dilthey in 1921.
* This structure shows that there are two types of hydrogen atoms-Terminals and bridging.



* 4-terminals hydrogen atoms can easily be replaced by methyl groups but when two bridging hydrogen atoms are attacked, the molecule is ruptured.
* The three centre two electron bonds are also known as **banana bond**.

IMPORTANT POINTS

* $\% \text{ ionic character} = \dfrac{\text{Actual dipole moment}}{\text{Calculated dipole moment}} \times 100$

* $\text{Percentage ionic character} = \dfrac{\Delta EN}{1.7} \times 50$

If $\Delta EN > 1.7$ then ionic character more than 50%
If $\Delta EN = 1.7$ then ionic character equal to 50%
If $\Delta EN < 1.7$ then ionic character less than 50%

* Fajan's Factors : Following factors are helpful in bringing covalent character in Ionic compounds
(a) Small cation (b) Big anion
(c) High charge on cation (d) High charge on anion
(e) Cation having pseudo inert gas configuration ($ns^2p^6d^{10}$) e.g. Cu^+, Ag^+, Zn^{+2}, Cd^{+2}
(f) Coming of colour or darkness of colour in compounds formed with colourless ions.

* M.O. theory :

(a) $\text{Bond order} = \dfrac{1}{2}(N_b - N_a)$

(b) Higher the bond order, higher is the bond dissociation energy, greater is the stability, shorter is the bond length.

(c)

Species	Bond order	Magnetic properties
H_2	1	Diamagnetic
H_2^+	0.5	Paramagnetic
Li_2	1	Diamagnetic

* Relative Bond Strength : $sp^3d^2 > dsp^2 > sp^3 > sp^2 > sp > p$-p (Co-axial) > s - p > s - s > p - p (Co-lateral)

* Bond angle :
(a) $NH_3 > PH_3 > AsH_3$ (b) $H_2O > H_2S > H_2Se$
(c) $NH_3 > NF_3$ (d) $Cl_2O > OF_2$

- The paramagnetic behaviour of O_2 is shown by M.O. theory.
- The bond length decreases with the increase in multiplicity of the bond. Thus
  $CH \equiv CH\,(1.20 Å) < CH_2{=}CH_2\,(1.34 Å) < CH_3{=}CH_3\,(1.54 Å)$.
- Order of stability is $O_2^+ > O_2 > O_2^- > O_2^{2-}$
-

BCl_3	$\Rightarrow sp^2$,	trigonal planar
$BrCl_3$	$\Rightarrow sp^3d$,	T-shaped
NH_3	$\Rightarrow sp^3$,	pyramidal
NO_3^-	$\Rightarrow sp^2$,	trigonal planar
NF_3	$\Rightarrow sp^3$,	pyramidal
BF_3	$\Rightarrow sp^2$,	trigonal planar
BF_4^-	$\Rightarrow sp^3$,	tetrahedral
NH_4^+	$\Rightarrow sp^3$,	tetrahedral

SOLVED EXAMPLES

Example 1 :

Indicate the type of hybridisation 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) $HC\equiv C-CH=CH_2$

Sol. (a) sp^3 and sp (b) sp^3, sp^2, sp^2

(c) sp^3, sp, sp, sp^3 (d) sp, sp, sp^2, sp^2

Example 2 :

Among the following compounds/species, write the order of O – O bond length in O_2, $O_2[AsF_4]$, $K[O_2]$

Sol. O_2 ; $O_2[AsF_4]$ or $O_2^+[AsF_4]^-$

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

The bond length decreases with increasing bond order.

Species	O_2	O_2^+	O_2^-
Bond order	2.0	2.5	1.5
Bond length	$O_2^+ < O_2 < O_2^-$		

Example 3 :

Two elements X and Y have following electronic configuration X : $1s^2, 2s^2, 2p^6 ; 3s^2, 3p^6 ; 4s^2$

Y : $1s^2, 2s^2, 2p^6 ; 3s^2 , 3p^5$

The expected compound formed by combination of X and Y will be expressed as :

(A) XY_2 (B) X_5Y_2

(C) X_2Y_5 (D) XY_5

Sol. **(A).** Valency of element X is 2 (2 electrons in the outermost shell) while that of element Y is 1 (1 electron required in the outermost shell to complete octet) so the formula of the compound between X and Y is XY_2.

Example 4 :

An atom of an 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 two will be –

(A) A_6B_6 (B) A_2B_3

(C) A_3B_2 (D) A_2B

Sol. **(B).** In this case the valence electron in the atom A is three and hence its valency is generally 3. In the atom B the number of valence electron is six. Hence its valency is usually 2. Hence the formula of the molecule formed from A and B could be A_2B_3. An example of two such elements are Al and O and the formula of Aluminium oxide is Al_2O_3.

Example 5 :

The electronegativity of H and Cl are 2.1 and 3.0 respectively. The nature of HCl is

(A) HCl is 17% ionic (B) 83% ionic

(C) 50% ionic (D) 100% ionic

Sol. **(A).** % ionic character $= 16\,(X_A - X_B) + 3.5\,(X_A - X_B)^2$

$= 16\,(3.0 - 2.1) + 3.5\,(3.0 - 2.1)^2$

$= 14.4 + 2.835 = 17.235 \approx 17\%$

Example 6 :

Which has maximum covalent character?

(A) NaCl (B) $SiCl_4$

(C) $AlCl_3$ (D) $MgCl_2$

Sol. **(B).** Polarisation in the molecule increases with increase of charge and decreases in size of the cation when the anion is same.

Example 7 :

The dipole moment of HBr is 2.6×10^{-30} cm and the interatomic spacing is 1.41 Å. The percentage of ionic character in HBr is –

(A) 10.5 (B) 11.5

(C) 12.5 (D) 13.5

Sol. **(B).** % ionic character $= \dfrac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$

Theoretical dipole moment of a 100% ionic character

$= e \times d = (1.6 \times 10^{-19}\,C) \times (1.41 \times 10^{-10}\,m)$

$= 2.256 \times 10^{-29}$ Cm.

$$\% \text{ ionic} = \frac{2.6 \times 10^{-30}}{2.256 \times 10^{-29}} \times 100 = 11.5\%$$

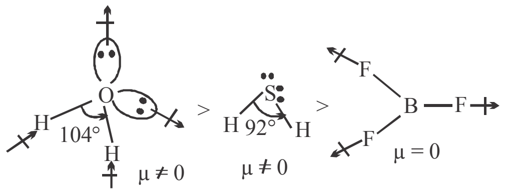
Example 8 :

Arrange the following in decreasing order of –

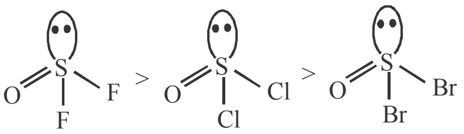
(i) Dipole moment – BF_3, H_2S, H_2O

(ii) bond energy – $OSCl_2$, OSF_2, $OSBr_2$.

Sol. (i) $H_2O > H_2S > BF_3$



(ii) B.E. $OSF_2 > OSCl_3 > OSBr_2$



QUESTION BANK

CHAPTER 4 : CHEMICAL BONDING AND MOLECULAR STRUCTURE

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART-1 : KOSSEL-LEWIS APPROACH TO CHEMICAL BONDING

Q.1 Lewis postulated that atoms achieve the stable octet when they are linked by
(A) only ionic bonds (B) only covalent bonds
(C) only coordinate bonds (D) chemical bonds

Q.2 Which type of bond is formed between similar atoms
(A) Ionic (B) Covalent
(C) Coordinate (D) Metallic

Q.3 Which of the following statements regarding covalent bond is not true
(A) The electrons are shared between atoms.
(B) The bond is non-directional.
(C) The strength of the bond depends upon the extent of overlapping.
(D) The bond formed may or may not be polar.

Q.4 $Ca^{2+} + 2F^- \rightarrow CaF_2$ or $Ca^{2+}(F^-)_2$
Choose the correct statement –
(A) Calcium is assigned a positive electrovalence of two
(B) Calcium is assigned a positive electrovalence of one.
(C) Calcium is assigned a negative electrovalence of two.
(D) None of these

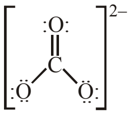
Q.5 According to Lewis and Kossel approach, for the ammonium ion (NH_4^+), the charge indicates
(A) loss of one electron from neutral atom.
(B) gain of one electron from neutral atom.
(C) no loss, no gain.
(D) All of the above

Q.6 Which of the following shows the Lewis dot formula for CO_2?
(A) $:\ddot{O}::C::\ddot{O}:$ (B) $:\ddot{O}:\ddot{C}::\ddot{O}:$
(C) $:\ddot{O}::C:\underset{\cdot\cdot}{\ddot{O}}:$ (D) $:\underset{\cdot\cdot}{\ddot{O}}:C:\underset{\cdot\cdot}{\ddot{O}}:$

Q.7 How many number of electrons are involved in the formation of a nitrogen molecule?
(A) Three (B) Four
(C) Eight (D) Six

Q.8 What is the formal charge on carbon atom in the following two structures:

$:\ddot{S}=C=\ddot{S}:$



(A) 0, –2 (B) 0, 0
(C) +2, –2 (D) +1, –1

Q.9 The important condition(s) for Lewis dot structure of covalent compounds is/are –
(A) each bond is formed as a result of sharing of an electron pair between the atoms.
(B) each combining atom contributes at least one electron to the shared pair.
(C) the combining atoms attain the outer shell noble gas configurations as a result of the sharing of electrons.
(D) All of the above

Q.10 Choose the correct statement –
(A) The octet rule is not universal.
(B) In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms.
(C) In LiCl, BeH_2 and BCl_3 number of electrons surrounding the central atom is less than eight.
(D) All of these

Q.11 In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
(A) 2, 2 (B) 3, 1
(C) 1, 3 (D) 4, 0

Q.12 What are the exceptions of the octet rule?
(A) The incomplete octet of central atom.
(B) An odd number of electrons on central atom.
(C) Expanded octet of the central atom.
(D) All of these.

Q.13 Which one of the following noble gases has a duplet of electrons in its outer shell?
(A) Neon (B) Argon
(C) Helium (D) Xenon

Q.14 Which of the following molecules has a triple bond?
(A) CO_2 (B) C_2H_4
(C) C_2H_2 (D) None of these

PART-2 : IONIC OR ELECTROVALENT BOND

Q.15 In which of the following species the bond is non-directional?
(A) NCl_3 (B) RbCl
(C) $BeCl_2$ (D) BCl_3

Q.16 The crystal lattice of electrovalent compound is composed
(A) Atoms
(B) Molecules
(C) Oppositely charged ions
(D) Both molecules and ions

Q.17 Electrovalent bond formation depends on
(A) Ionization energy (B) Electron affinity
(C) Lattice energy (D) All the three above

Q.18 An atom of sodium loses one electron and chlorine atom accepts one electron. This result the formation of sodium chloride molecule.This type of molecule will be
(A) Coordinate (B) Covalent
(C) Electrovalent (D) Metallic bond

Q.19 Electrovalent compounds do not have
(A) High melting point and Low boiling point.
(B) High dielectric constant
(C) High melting point and High boiling point.
(D) High polarity

Q.20 Sodium chloride has a crystalline structure made up of Na^+ and Cl^- ions. Why NaCl does not conduct electricity in solid state?
(A) Solids do not conduct electricity.
(B) The ions of NaCl become mobile only in molten state and are not free to move in solid state.
(C) The crystalline structure does not have ions.
(D) When a bond is formed between ions they lose their charge.

PART-3 : BOND PARAMETERS

Q.21 Which of the following bonds is most polar -
(A) O – H (B) P – H
(C) C – F (D) S – Cl

Q.22 Bond length of HCl is 1.275 Å (Charge = 4.8×10^{-10} e.s.u.) if $\mu = 1.02$ D, then HCl is -
(A) 100% ionic (B) 83% covalent
(C) 50% covalent (D) 40% ionic

Q.23 The dipole moment of the ammonia molecule is 1.48D. The length of the dipole is -
(A) 3.08×10^{-11}m (B) 5×10^2 m
(C) 308 m (D) None

Q.24 The interatomic distances in H_2 and Cl_2 molecules are 74 and 198 pm respectively. The bond length of HCl is
(A) 272 pm (B) 136 pm
(C) 124 pm (D) 248 pm

Q.25 Which bond angle θ would result in the maximum dipole moment for the triatomic molecule YXY
(A) $\theta = 90°$ (B) $\theta = 120°$
(C) $\theta = 150°$ (D) $\theta = 180°$

Q.26 The dipole moment of HBr is 1.6×10^{-30}Cm and interatomic spacing is 1Å. The % ionic character of HBr is –
(A) 7 (B) 10
(C) 15 (D) 27

Q.27 Identify the non-polar molecule in the set of compounds given : HCl, HF, H_2, HBr –
(A) H_2 (B) HCl
(C) HF, HBr (D) HBr

Q.28 Two electrons of one atom A and two electrons of another atom B are utilized to form a compound AB. This is an example of –
(A) Polar covalent bond
(B) Non-polar covalent bond
(C) Polar bond
(D) Dative bond

Q.29 Both polar and non-polar bonds are present in
(A) C_2H_6 (B) NH_4Cl
(C) HCl (D) $AlCl_3$

Q.30 For the formation of covalent bond, the difference in the value of electronegativities should be
(A) Equal to or less than 1.7
(B) More than 1.7
(C) 1.7 or more
(D) None of these

Q.31 The covalent compound HCl has the ionic character as
(A) The electronegativity of hydrogen is greater than that of chlorine.
(B) The electronegativity of hydrogen is equal to that of chlorine.
(C) The electronegativity of chlorine is greater than that of hydrogen.
(D) Hydrogen and chlorine are gases.

Q.32 The dipole moment is zero for the molecule
(A) Ammonia (B) Boron trifluoride
(C) Sulphur dioxide (D) Water

Q.33 Which of the following is non-polar
(A) H_2S (B) NaCl
(C) Cl_2 (D) H_2SO_4

Q.34 The ICl molecule is
(A) Purely electrovalent
(B) Purely covalent
(C) Polar with negative end on iodine
(D) Polar with negative end on chlorine

Q.35 Correct order of Bond energy –
(A) C – C < Si – Si (B) F – F > Cl – Cl
(C) O – O < S – S (D) All of them

Q.36 Which of the following molecules does not show any resonating structures?
(A) NH_3 (B) CO_3^{2-}
(C) O_3 (D) SO_3

Q.37 Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?
(A) CO_2 (B) HI
(C) H_2O (D) SO_2

Q.38 The correct sequence of bond length in single bond, double bond and triple bond of C is
(A) $(C-C) = (C=C) = (C\equiv C)$
(B) $C\equiv C < C=C < C-C$
(C) $C-C < C=C < C\equiv C$
(D) $C=C < C\equiv C < C-C$

Q.39 In water molecule, the two O – H bonds are oriented at an angle of 104.5°. In BF_3, the three B–F bonds are oriented at an angle of 120°. In BeF_2, the two Be–F bonds are oriented at an angle of 180°. Which of the following will have highest dipole moment?
(A) BeF_2 (B) BF_3
(C) H_2O (D) same for all

Q.40 Which of the following will be the strongest bond?
(A) F – O (B) O – Cl
(C) N – H (D) O – H

Q.41 Consider the following statements,
I. The canonical forms have no real existence.
II. The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.

III. There is no such equilibrium between the canonical forms as we have between tautomeric forms (keto & enol; in tautomerism.

IV. The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be depicted by a single Lewis structure.

Which of the above are correct?

(A) I and II (B) III and IV

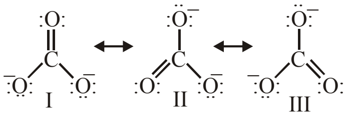
(C) II and III (D) I, II, III and IV

Q.42 Arrange the following in order of increasing dipole moment: H_2O, H_2S, BF_3.

(A) $BF_3 < H_2S < H_2O$ (B) $H_2S < BF_3 < H_2O$

(C) $H_2O < H_2S < BF_3$ (D) $BF_3 < H_2O < H_2S$

Q.43 The given structures I, II&III of carbonate ion represent



(A) hybrid structures (B) isomeric structures

(C) canonical structures (D) dipole structures

PART-4 : VSEPR THEORY

Q.44 According to VSEPR theory,

(A) the shape of the molecule depends upon bonded electron pairs.

(B) pair of electrons attract each other in valence shells.

(C) the pairs of electrons tend to occupy such positions that minimise repulsions.

(D) the pairs of electrons tend to occupy such positions that minimise distances from each other.

Q.45 Why do the deviations occur from idealised shape of H_2O, NH_3 etc., molecules?

(A) Due to same hybridisation

(B) Due to different hybridisation

(C) Due to repulsion effect

(D) None of the above

Q.46 Which of the following statements is correct regarding the structure of PCl_5?

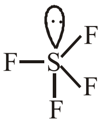
(A) Three P–Cl bonds lie in one plane and two P–Cl bonds lie above and below the equatorial plane.

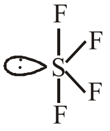
(B) Five P – Cl bonds lie in the same plane.

(C) The bond angle in all P– Cl bonds is 90°.

(D) The bond length of all P – Cl bonds is same.

Q.47 Which of the following shapes of SF_4 is more stable–


(i)


(ii)

(A) (i), due to 3 lp-bp repulsions at 90°.

(B) (ii), due to 2 lp-bp repulsions.

(C) Both are equally stable due to 2 lp-bp repulsions.

(D) Both are unstable since SF_4 has tetrahedral shape.

Q.48 The VSEPR theory is able to predict geometry of the compounds of ____ accurately.

(A) s-block elements (B) p-block elements

(C) d-block elements (D) f-block elements

Q.49 Few examples of the compounds formed by chemical bonding are given below. Mark the incorrect example.

(A) A molecule with central atom devoid of octet– BF_3

(B) A molecule with linear shape – CO_2.

(C) A non-polar covalent compound between two different atoms – CH_4

(D) A molecule which is V-shaped with a bond angle 104.5° – NH_3.

Q.50 In a bonded molecule, the order of repulsion between the bonded and non-bonded electrons is

(A) lone pair–lone pair > bond pair – bond pair > lone pair – bond pair

(B) bond pair–bond pair > lone pair – lone pair > lone pair – bond pair

(C) lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

(D) bond pair–bond pair > lone pair– bond pair > lone pair – lone pair.

Q.51 The shape of water molecule which should be tetrahedral has a bent or distorted tetrahedral shape with a bond angle 104.5°. What could be the reason for this?

(A) lp-lp repulsion is more than lp-bp repulsion.

(B) lp-bp repulsion is more than lp-lp repulsion.

(C) lp-lp repulsion is equal to lp-bp repulsion.

(D) Presence of lone pair does not affect the bond angle.

PART-5 : VALENCE BOND THEORY

Q.52 Which is not true according to VBT -

(A) A covalent bond is formed by the overlapping of orbitals with unpaired electrons of opposite spins.

(B) A covalent bond is formed by the over lapping of orbitals with unpaired electrons of same spin.

(C) The greater the extent of overlapping the stronger is the bond.

(D) Overlapping takes place only in the direction of maximum electron density of the orbital.

Q.53 Which type of overlapping is shown by p (p_x, p_y and p_z) orbitals?

(A) Two end to end and one sidewise overlap.

(B) Two sidewise and one end to end overlap

(C) Three sidewise overlaps

(D) Three end to end overlaps

Q.54 How many sigma and pi bonds are present in toluene?

(A) 10σ and 3π bonds (B) 12σ and 3π bonds

(C) 15σ and 3π bonds (D) 6σ and 3π bonds

Q.55 Which of the following orbitals will not form sigma bond after overlapping?

(A) s-orbital and s-orbital (B) s-orbital and p_z-orbital

(C) p_z-orbital and p_z-orbital (D) p_x-orbital and p_x-orbital

PART-6 : HYBRIDISATION

Q.56 In following hydrocarbon which one has 75% p character and 25% s charater -
(A) C_2H_4 (B) C_2H_2
(C) CH_4 (D) $:CH_2$

Q.57 The hybridisation of carbon atoms ion C – C single bond of $H-C\equiv C-CH=CH_2$ is -
(A) sp^3-sp^3 (B) sp^2-sp
(C) sp-sp^2 (D) sp^3-sp

Q.58 Hybridisation involves –
(A) Addition of an electron pair
(B) Mixing up of atomic orbitals
(C) Removal of an electron pair
(D) Separation of orbitals

Q.59 As the p-character increases, the bond angle in hybrid orbitals formed by s and atomic orbitals
(A) Decreases (B) Increases
(C) Doubles (D) Remains unchanged

Q.60 The compounds which is polar and has central atom with sp^2 hybridisation is –
(A) H_2CO_3 (B) BF_3
(C) SiF_4 (D) $HClO_2$

Q.61 In formation of ethene, the bond formation between s and p-orbitals takes place in the following manner.
(A) sp^2 hybridised orbitals form sigma bond while the unhybridised (p_x or p_y) overlaps sidewise to form π-bond.
(B) sp^2 hybridised orbitals form π-bond while the unhybridised (p_z) overlaps to form σ-bond.
(C) sp^2 hybridised orbitals overlap with s-orbitals of H atoms while unhybridised orbitals form C–C bond.
(D) sp^2 hybridised orbitals form sigma bonds with H atoms while unhybridised orbitals form π-bonds between C atoms.

Q.62 Which of the following pairs are isostructural?
(A) SO_4^{2-} and BF_4^- (B) NH_3 and NH_4^+
(C) CO_3^{2-} and CO_2 (D) CH_4 and BF_3

Q.63 Order of size of sp, sp^2 and sp^3 orbitals is
(A) $sp^3 < sp^2 < sp$ (B) $sp < sp^2 < sp^3$
(C) $sp^2 < sp < sp^3$ (D) $sp^2 < sp^3 < sp$

Q.64 Which type of hybridisation is shown by carbon atom from left to right in the given compound: $CH_2=CH-C\equiv N$?
(A) sp^2, sp^2, sp (B) sp^2, sp, sp
(C) sp, sp^2, sp^3 (D) sp^3, sp^2, sp

Q.65 Which of the followings is not an essential condition for hybridisation?
(A) The orbitals present in the valence shell of the atom are hybridised.
(B) The orbitals undergoing hybridisation should have almost equal energy.
(C) Promotion of electron is essential condition prior to hybridisation.
(D) It is not necessary that only half-filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Q.66 Atomic orbitals of carbon in carbon dioxide are
(A) sp^2-hybridised (B) sp^3d-hybridised
(C) sp-hybridised (D) sp^3-hybridised

PART-7 : MOLECULAR ORBITAL THEORY

Q.67 Which of the following statements is not true regarding molecular orbital theory?
(A) The atomic orbitals of comparable energies combine to form molecular orbitals.
(B) An atomic orbital is monocentric while a molecular orbital is polycentric.
(C) Bonding molecular orbital has higher energy than antibonding molecular orbital.
(D) Molecular orbitals like atomic orbitals obey Aufbau principle for filling of electrons.

Q.68 Which of the following facts regarding bond order is not valid?
(A) Bond order is given by the number of bonds between the two atoms in a molecule.
(B) With increase in bond order, bond enthalpy of the molecule decreases.
(C) Isoelectronic molecules and ions have identical bond orders.
(D) With increase in bond order, bond length decreases.

Q.69 What will be the bond order of the species with electronic configuration $1s^2\ 2s^2\ 2p^5$?
(A) One (B) Two
(C) Three (D) Zero

Q.70 Which of the following bond orders is indication of existence of a molecule?
(A) Zero (B) Negative
(C) Positive (D) All of these

PART-8 : BONDING IN SOME DIATOMIC MOLECULES

Q.71 The electronic configuration of four elements are given in brackets L $(1s^2, 2s^2 2p^1)$; M $(1s^2, 2s^2 2p^5)$
Q $(1s^2, 2s^2 2p^6, 3s^1)$; R $(1s^2, 2s^2 2p^2)$
The element that would most readily form a diatomic molecule is
(A) Q (B) M
(C) R (D) L

Q.72 Which molecule/ion out of the following does not contain unpaired electrons?
(A) N_2^+ (B) O_2
(C) O_2^{2-} (D) B_2

Q.73 The increasing order of energies of various molecular orbitals of N_2 is given below:

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

The above sequence is not true for the molecule.

(A) C_2 (B) B_2
(C) O_2 (D) Be_2

Q.74 Which of the following statements is **not** correct from the view point of molecular orbital theory?

(A) Be_2 is not a stable molecule.
(B) He_2 is not stable but He_2^+ is expected to exist.
(C) Bond strength of N_2 is maximum amongst the homo nuclear diatomic molecules belonging to the second period.
(D) The order of energies of molecular orbitals in molecule is $\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

Q.75 Which of the following species have a double bond is made up of only two pi bonds?

(A) He_2 (B) Li_2
(C) C_2 (D) O_2

Q.76 Choose the correct statement –

(A) O_2 is paramagnetic.
(B) Helium is diamagnetic.
(C) Nitrogen is diamagnetic.
(D) All of these

Q.77 Oxygen molecule is paramagnetic because

(A) no. of bonding electrons > no. of antibonding electrons.
(B) no. of bonding electrons < no. of antibonding electrons.
(C) no. of bonding electrons = no. of antibonding electrons
(D)presence of unpaired electrons in molecular orbitals.

PART-9 : HYDROGEN BONDING

Q.78 Though covalent in nature, methanol is soluble in water, why?

(A) Methanol is transparent like water.
(B) Due to hydrogen bonding between methanol and water molecules.
(C) Due to van der Waals' forces between methanol and water.
(D) Due to covalent attraction forces.

Q.79 Which one of the following does not have intermolecular H-bonding -

(A) H_2O (B) o-Nitrophenol
(C) HF (D) CH_3

Q.80 Hydrogen bond between two atoms is formed due to –

(A) displacement of electrons towards more electronegative atom resulting in fractional positive charge on hydrogen.
(B) displacement of electrons towards hydrogen atom resulting in a polar molecule.
(C) formation of a bond between hydrogen atoms of one molecule and the other.
(D) existence of an attractive force which binds hydrogen atoms together.

Q.81 Which of the following has strongest bond?

(A) HF (B) HCl
(C) HBr (D) HI

Q.82 In which of the following substances will hydrogen bond be strongest?

(A) HCl (B) H_2O
(C) HI (D) H_2S

Q.83 Which of the following observations can be explained on the basis of hydrogen bonding?

(i) H–F has higher boiling point than other halogen acids.
(ii) H_2O has highest boiling point among hydrides of group 16 elements.
(iii) NH_3 has lower boiling point than PH_3.

(A) (i), (ii) and (iii) (B) (i) and (iii)
(C) (ii) and (iii) (D) (i) and (ii)

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 The hybridisation and geometry of BrF_3 molecule are -

(A) sp^3d and distorted trigonal bipyramidal
(B) sp^3d^2 and Tetragonal
(C) sp^3d and bent
(D) None

Q.2 In following which central atom has different hybridisation than other –

(A) Cl_2O (B) OF_2
(C) H_2O (D) SO_2

Q.3 Which of the following statement is incorrect -

(A) Non-bonding pairs occupy more space than bonding pairs.
(B) The bonding orbitals in a trigonal bipyramidal molecule are described as sp^3d hybrid.
(C) $SnCl_2$ has linear shape.
(D) PCl_4^+ and $AlCl_4^-$ are isoelectronic.

Q.4 Shape of NH_3 is very similar to -

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

Q.5 Which of the following has pyramidal shape-

(A) XeO_3 (B) XeF_4
(C) XeF_2 (D) XeF_6

Q.6 In PO_4^{3-} ion, the formal charge on the oxygen atom of P– O bond is

(A) + 1 (B) –1
(C) – 0.75 (D) + 0.75

Q.7 Arrange in increasing order of their boiling point-HF, HCl, HBr, HI. Which order is correct –

(A) HCl < HBr < HI < HF (B) HCl > HBr > HI > HF
(C) HCl < HBr > HI < HF (D) None

Q.8 C – C bond in C_2H_6 undergoes heterolytic fission, the hybridisation of carbon is/are -
(A) sp^2
(B) sp^3
(C) sp^2, sp^3
(D) sp, sp^2

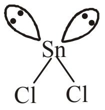
Q.9 The enolic form of actone contain σ bond (a), π bond (b) and lone pair (c). Possible values of a,b & c
(A) 9, 1, 2
(B) 8, 2, 2
(C) 10, 1, 1
(D) 9, 2, 1

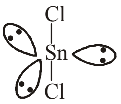
Q.10 The bond order of N_2^{-} anion is -
(A) 1
(B) 2
(C) 2.5
(D) 3

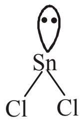
Q.11 Which of the following has maximum bond strength –
(A) O_2
(B) O_2^{+}
(C) O_2^{-}
(D) O_2^{2-}

Q.12 The atomic number of Sn is 50. The shape of gaseous $SnCl_2$ molecule is :

(A) Cl – Sn – Cl

(B)


(C)


(D)


Q.13 The compound which contains both covalent and co-ordinate bond is -
(A) C_2H_5NC
(B) C_2H_5CN
(C) HCN
(D) None

Q.14 The type of bond present in N_2O_5 are -
(A) Only covalent
(B) Only ionic
(C) Ionic and covalent
(D) Covalent and coordinate

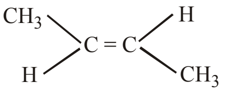
Q.15 Number of covalent and co-ordinate bond in pyrosulphuric acid are -
(A) 6, 4
(B) 6, 6
(C) 4, 4
(D) 4, 6

Q.16 Allyl cyanide has -
(A) 9 sigma bonds and 4 Pi bonds
(B) 9 sigma bonds, 3 pi bonds and 1 lone pairs
(C) 8 sigma bonds and 5 pi bonds
(D) 8 sigma bonds, 3 pi bonds an 4 non-bonding electrons

Q.17 The electronegativity of O, F, N, Cl and H are 3.5, 4.0, 3.0, 3.0 and 2.1 respectively. The strongest bond will be –
(A) F – O
(B) O – Cl
(C) N – H
(D) O – H

Q.18 In which solvent NaCl has maximum solubility?
(A) H_2O
(B) C_2H_5OH
(C) CH_3COCH_3
(D) $C_2H_5OC_2H_5$

Q.19 Which of the following hydrocarbons has the lowest dipole moment :

(A)


(B) $CH_3C\equiv CH_3$
(C) $CH_3CH_2C\equiv CH$
(D) CH_2=CH–C$\equiv$CH

Q.20 The decreasing order of solubility of silver halide is –
(A) AgI > AgBr > AgCl > AgF
(B) AgF > AgCl > AgBr > AgI
(C) AgCl > AgF > AgBr > AgI
(D) AgBr > AgF > AgI > AgCl

Q.21 Where dative bond is not involved –
(A) Protonation of ether
(B) Dissolution of HCl in water
(C) Dimerisation of benzoic acid
(D) Formation of Be_2Cl_4

Q.22 Which follows octet rule -
(A) $FeCl_2$
(B) AgCl
(C) $CaCl_2$
(D) CuCl

Q.23 Which of the following is most covalent -
(A) AlF_3
(B) $AlCl_3$
(C) $AlBr_3$
(D) AlI_3

Q.24 Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character follows the order -
(A) LiCl < $BeCl_2$ > BCl_3 > CCl_4
(B) LiCl > $BeCl_2$ < BCl_3 < CCl_4
(C) LiCl < $BeCl_2$ < BCl_3 < CCl_4
(D) LiCl > $BeCl_2$ > BCl_3 > CCl_4

Q.25 In compound X, all the bond angles are exactly 109°28', X is –
(A) Chloromethane
(B) Iodoform
(C) Carbon tetrachloride
(D) Chloroform

Q.26 Oxygen molecule is formed by
(A) one axial s-s overlap & one p-p axial overlap
(B) two p-p axial overlaps
(C) two p-p sidewise overlaps
(D) one p-p axial and one p-p sidewise overlap.

Q.27 Formula of a metallic oxide is MO. The formula of its phosphate will be –
(A) $M_2(PO_4)_2$
(B) $M(PO_4)$
(C) M_2PO_4
(D) $M_3(PO_4)_2$

Q.28 Compounds show high melting and boiling points
(A) Electrovalent compounds
(B) Covalent compounds
(C) Coordinate compounds
(D) All the three types of compounds have equal melting and boiling points.

Q.29 If a molecule X_2 has a triple bond, then X will have the electronic configuration
(A) $1s^2\ 2s^2\ 2p^5$
(B) $1s^2\ 2s^2\ 2p^3$
(C) $1s^2\ 2s^1$
(D) $1s^2\ 2s^2\ 2p^1$

Q.30 Among the species : CO_2, CH_3COO^-, CO, CO_3^{2-}, HCHO which has the weakest carbon- oxygen bond –
(A) CO_2
(B) CH_3COO^-
(C) CO
(D) CO_3^{2-}

Q.31 Which type of bond is present in H_2S molecule
(A) Ionic bond
(B) Covalent bond
(C) Co-ordinate
(D) All of three

Q.32 Number of electrons in the valence orbit of nitrogen in an ammonia molecule are –
(A) 8
(B) 5
(C) 6
(D) 7

Q.33 The compound containing co-ordinate bond is
(A) O_3 (B) SO_3
(C) H_2SO_4 (D) All of these

Q.34 Which of the following has $p\pi - d\pi$ bonding
(A) NO_3^- (B) CO_3^{2-}
(C) BO_3^{-3} (D) SO_3^{-3}

Q.35 In a regular octahedral molecule, MX_6, the number X – M – X bonds at 180° is –
(A) Six (B) Four
(C) Three (D) Two

Q.36 Among the compounds, BF_3, NCl_3, H_2S, SF_4 and $BeCl_2$, identify the ones in which the central atom has the same type of hybridisation –
(A) BF_3 and NCl_3 (B) H_2S and $BeCl_2$
(C) BF_3, NCl_3 and H_2S (D) NCl_3 and H_2S

Q.37 Which of the following is non-linear molecule –
(A) CO_3^{2-} (B) CO_2
(C) CS_2 (D) $BeCl_2$

Q.38 Point out incorrect statement about resonance
(A) Resonance structures should have equal energy.
(B) In resonance structures, the constituent atoms should be in the same position.
(C) In resonance structures, there should not be the same number of electron pairs.
(D) Resonance structures should differ only in the location of electrons around the constituent atoms.

Q.39 In the following which substance will have highest boiling point
(A) He (B) CsF
(C) NH_3 (D) $CHCl_3$

Q.40 Which of the following has zero dipole moment
(A) CH_2Cl_2 (B) CH_4
(C) NH_3 (D) PH_3

Q.41 Which shows the least dipole moment
(A) CCl_4 (B) $CHCl_3$
(C) CH_3CH_2OH (D) CH_3COCH_3

Q.42 Polarisibility of halide ions increases in the order
(A) F^-, I^-, Br^-, Cl^- (B) Cl^-, Br^-, I^-, F^-
(C) I^-, Br^-, Cl^-, F^- (D) F^-, Cl^-, Br^-, I^-

Q.43 The bond in the formation of fluorine molecule will be
(A) Due to s – s overlapping
(B) Due to s – p overlapping
(C) Due to p – p overlapping
(D) Due to hybridisation

Q.44 Which type of overlapping results the formation of a π bond
(A) Axial overlapping of s – s orbitals
(B) Lateral overlapping of p – p orbitals
(C) Axial overlapping of p – p orbitals
(D) Axial overlapping of s – p orbitals

Q.45 The bond angle in ethylene is
(A) 180° (B) 120°
(C) 109° (D) 90°

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

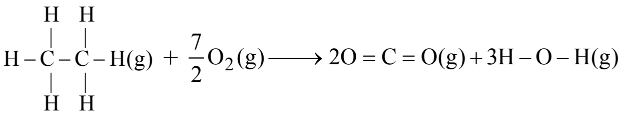
Q.1 How many $d_\pi - p_\pi$ bonds are present in ClO_3^-.

Q.2 Find out the total number of all $2C - 2e^{Q}$ and $3C - 4e^{Q}$ bonds in $BeCl_2$.

Q.3 The H – O – H bond angle in the water molecule is 105°, the O – H bond length being 0.94 Å. The dipole moment for H_2O molecule is 1.85 D. The fraction of electronic charge on the oxygen atom is 1/A. Find the value of A.

Q.4 The bond order of the He_2^+ ion is 1/A. Find the value of A.

Q.5 Estimate | ΔH | (in kJ) for the following reaction (where we explicitly show the bonds involved in the reactants and products) :



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H(g) + \frac{7}{2}O_2(g) \longrightarrow 2O=C=O(g) + 3H-O-H(g)$$

[Given : Average bond enthalpies, C – H = 413 kJ, C – C = 348 kJ, O_2 = 495 kJ, C = O = 799kJ, O – H = 463 kJ]

Q.6 The hybridization of the central atom in IF_5 is sp^xd^y. Find the value of x + y.

Q.7 Based on VSEPR theory, the number of 90 degree F – Br – F angles is BrF_5 is :

Q.8 The percentage of p-character in the orbitals forming P – P bonds in P_4 is –

Q.9 The bond energy (in kcal mol^{-1}) of a C – C single bond is approximately –

Q.10 Assuming that Hund's rule is violated, the bond order of the diatomic molecule B_2 is –

EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]

Q.1 In which of the following species is the underlined carbon having sp^3-hybridisation? **[AIEEE-2002]**
(A) $CH_3–\underline{C}OOH$ (B) $CH_3\underline{C}H_2NH_2$
(C) $CH_3\underline{C}OCH_3$ (D) $CH_2=\underline{C}H–CH_3$

Q.2 Which of the follwing statements is true? **[AIEEE-2002]**
(A) HF is less polar than HBr
(B) Water does not contain any ions
(C) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion.
(D) In covalent cond, transfer of electrons takes place

Q.3 A square planar complex is formed by hybridisation of which atomic orbital? **[AIEEE-2002]**
(A) s, p_x, p_y, d_{yz} (B) $s, p_x, p_y, d_{x^2-y^2}$
(C) s, p_x, p_y, d_{z^2} (D) $s, p_x\ p_y, d_{xy}$

Q.4 The reason for double helical structure of DNA is operation of: **[AIEEE-2003]**
(A) dipole-dipole interaction (B) hydrogen bonding
(C) electrostatic attraction (D) vander Wall's forces

Q.5 Which one of the following pairs of molecules will have permanent dipole moments for both members:
(A) NO_2 and CO_2 (B) NO_2 and O_3 **[AIEEE-2003]**
(C) SiF_4 and CO_2 (D) SiF_4 and NO_2

Q.6 The pair of species having identical shapes for molecules of both species is: **[AIEEE-2003]**
(A) XeF_2, CO_2 (B) BF_3, PCl_3
(C) PF_5, IF_5 (D) CF_4, SF_4

Q.7 The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is: **[AIEEE-2004]**
(A) $H_2S < NH_3 < SiH_4 < BF_3$ (B) $NH_3 < H_2S < SiH_4 < BF_3$
(C) $H_2S < SiH_4 < NH_3 < BF_3$ (D) $H_2S < NH_3 < BF_3 < SiH_4$

Q.8 The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species?
(A) Bond length in NO^+ is equal to that in NO
(B) Bond length in NO is greater than in NO^+
(C) Bond length in NO^+ is greater than in NO
(D) Bond length is unpredictable **[AIEEE-2004]**

Q.9 The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively: **[AIEEE-2004]**
(A) sp^3 and sp^2 (B) sp^2 and sp^3
(C) sp^2 and sp^2 (D) sp^3 and sp^3

Q.10 Which has the regular tetrahedral structure
(A) BF_4^- (B) SF_4 **[AIEEE-2004]**
(C) XeF_4 (D) $[Ni(CN)_4]^{2-}$
(Atomic nos. : B = 5, S = 16, Ni = 28, Xe = 54)

Q.11 The maximum number of 90° angles between bond pair-bond pair of electrons is observed in: **[AIEEE-2004]**
(A) dsp^2 (B) sp^3d hybridization
(C) dsp^3 hybridization (D) sp^3d^2 hybridization

Q.12 Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in **[AIEEE-2004]**
(A) Forming covalent halides
(B) Forming polymeric hydrides
(C) Exhibiting maximum covalency in compound
(D) Exhibiting amphoteric nature in their oxides

Q.13 Which one of the following species is diamagnetic in nature? **[AIEEE-2005]**
(A) He_2^+ (B) H_2
(C) H_2^+ (D) H_2^-

Q.14 Lattice energy of an ionic compound depends upon: **[AIEEE-2005]**
(A) charge on the ion only (B) size of the ion only
(C) packing of the ion only (D) charge and size of the ion

Q.15 The molecular shapes of SF_4, CF_4 and XeF_4 are: **[AIEEE-2005]**
(A) the same with 2, 0 & 1 lone pair of electrons on the central atom, respectively.
(B) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively.
(C) different with 0, 1 and 2 lone pair of electrons on the central atoms, respectively.
(D) different with 1, 0 and 2 lone pair of electrons on the central atoms, respectively.

Q.16 Of the following sets which one does not contain isoelectronic species? **[AIEEE-2005]**
(A) $PO_4^{3-}, SO_4^{2-}, CIO_4^-$ (B) CN^-, N_2, C_2^{2-}
(C) $SO_3^{2-}, CO_3^{2-}, NO_3^-$ (D) $BO_3^{3-}, CO_3^{2-}, NO_3^-$

Q.17 The number and type of bond between two carbon atom in calcium carbide are: **[AIEEE-2005]**
(A) One sigma, one pi bond (B) One sigma, two pi bond
(C) Two sigma, one pi bond (D) Two sigma, two pi bond

Q.18 Which of the following molecules\ions does not contain unpaired electrons? **[AIEEE-2006]**
(A) N_2^+ (B) O_2
(C) O_2^- (D) B_2

Q.19 Among the following mixtures, dipole-dipole as the major interaction, is present in: **[AIEEE-2006]**
(A) KCl and water
(B) benzene and carbon tetrachloride
(C) benzene and ethanol
(D) acetonitrile and acetone

Q.20 A metal, M foms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[AIEEE-2006]**
(A) MCl_2 is more ionic than MCl_4
(B) MCl_2 is more easily hydrolysed than MCl_4
(C) MCl_2 is more volatile than MCl_4
(D) MCl_2 is more soluble in anhydrous ethanol than MCl_4

Q.21 In which of the following molecules/ions are all the bonds not equal? **[AIEEE-2006]**
(A) XeF_4 (B) BF_4^-
(C) SF_4 (D) SiF_4

Q.22 The decreasing value of bond angles from NH_3 (106)° to SbH_3 (101)° down group-15 of the periodic table is due **[AIEEE-2006]**
(A) decreasing lp – bp repulsion
(B) increasing electronegativity
(C) increasing bp – bp repulsion
(D) increasing p–orbital character in sp^3

Q.23 In which of the following ionizion processes, the bond order has increased and the magnetic behaviour has changed **[AIEEE-2007]**
(A) $NO \rightarrow NO^+$
(B) $O_2 \rightarrow O_2^+$
(C) $N_2 \rightarrow N_2^+$
(D) $C_2 \rightarrow C_2^+$

Q.24 Which of the following hydrogen bonds is the strongest **[AIEEE-2007]**
(A) F – H .... F
(B) O – H ..... O
(C) O – H .... F
(D) O – H .... N

Q.25 Which of the following species exhibits the diamagnetic behaviour – **[AIEEE-2007]**
(A) O_2^+
(B) O_2
(C) NO
(D) O_2^{2-}

Q.26 The charge/size ratio of a cation determines its polarzing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{+2} Mg^{+2}, Be^{+2} **[AIEEE-2007]**
(A) $Be^{+2} < K^+ < Ca^{+2} < Mg^{+2}$
(B) $K^+ < Ca^{+2} < Mg^{+2} < Be^{+2}$
(C) $Ca^{+2} < Mg^{+2} < Be^{+2} < K^+$
(D) $Mg^{+2} < Be^{+2} < K^+ < Ca^{+2}$

Q.27 Which one of the following constitutes a group of the isoelectronic species? **[AIEEE-2008]**
(1) C_2^{2-}, O_2^-, CO, NO
(B) NO^+, C_2^{2-}, CN^-, N_2
(C) CN^-, N_2, O_2^{2-}, C_2^{2-}
(D) N_2, O_2^-, NO^+, CO

Q.28 Which one of the following pairs of species have the same bond order? **[AIEEE-2008]**
(A) CN^- and NO^+
(B) CN^- and CN^+
(C) O_2^- and CN^-
(D) NO^+ and CN^+

Q.29 The bond dissociation energy of B – F in BF_3 is 646 kJ mol^{-1} whereas that of C – F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B – F bond dissociation energy as compared to that of C – F is – **[AIEEE-2009]**
(A) lower degree of $p\pi$–$p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4.
(B) smaller size of B atoms as compared to that of C atom.
(C) stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4
(D) significant $p\pi$–$p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4.

Q.30 Using MO theory predict which of the following species has the shortest bond length? **[AIEEE-2009]**
(A) O_2^{2-}
(B) O_2^{2+}
(C) O_2^+
(D) O_2^-

Q.31 The energy required to break one mole of Cl – Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single Cl – Cl bond is –
($c = 3 \times 10^8$ ms^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1}) **[AIEEE 2010]**
(A) 594 nm
(B) 640 nm
(C) 700 nm
(D) 494 nm

Q.32 Among the following the maximum covalent character is shown by the compound : **[AIEEE 2011]**
(A) $FeCl_2$
(B) $SnCl_2$
(C) $AlCl_3$
(D) $MgCl_2$

Q.33 The hybridisation of orbitals of N atom in NO_3^-, NO_2^+ and NH_4^+ are respectively – **[AIEEE 2011]**
(A) sp, sp^2, sp^3
(B) sp^2, sp, sp^3
(C) sp, sp^3, sp^2
(D) sp^2, sp^3, sp

Q.34 The structure of IF_7 is – **[AIEEE 2011]**
(A) square pyramid
(B) trigonal bipyramid
(C) octahedral
(D) pentagonal bipyramid

Q.35 In which of the following pairs the two species are not isostructural ? **[AIEEE 2012]**
(A) CO_3^{2-} and NO_3^-
(B) PCl_4^+ and $SiCl_4$
(C) PF_5 and BrF_5
(D) AlF_6^{3-} and SF_6

Q.36 In which of the following pairs of molecules/ions, both the species are not likely to exist ? **[JEE MAIN 2013]**
(A) H_2^+, He_2^{2-}
(B) H_2^-, He_2^{2-}
(C) H_2^{2+}, He_2
(D) H_2^-, He_2^{2+}

Q.37 Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of – **[JEE MAIN 2013]**
(A) $Li_2 < Li_2^+ < Li_2^-$
(B) $Li_2^- < Li_2^+ < Li_2$
(C) $Li_2 < Li_2^- < Li_2^+$
(D) $Li_2^- < Li_2 < Li_2^+$

Q.38 Which one of the following molecules is expected to exhibit diamagnetic behaviour ? **[JEE MAIN 2013]**
(A) C_2
(B) N_2
(C) O_2
(D) S_2

Q.39 The correct statement for the molecule, CsI_3 is – **[JEE MAIN 2014]**
(A) it contains Cs^{3+} and I^- ions.
(B) it contains Cs^+, I^- and lattice I_2 molecule.
(C) it is a covalent molecule.
(D) it contains Cs^+ and I_3^- ions.

Q.40 The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is **[JEE MAIN 2015]**
(A) Ion-dipole interaction
(B) London force
(C) Hydrogen bond
(D) Ion-ion interaction

Q.41 The species in which the N atom is in a state of sp hybridization is : **[JEE MAIN 2016]**
(A) NO_2^-
(B) NO_3^-
(C) NO_2
(D) NO_2^+

Q.42 Which of the following species is not paramagnetic?
(A) B_2
(B) NO **[JEE MAIN 2017]**
(C) CO
(D) O_2

Q.43 Total number of lone pair of electrons in I_3^- ion is **[JEE MAIN 2018]**
(A) 9
(B) 12
(C) 3
(D) 6

Q.44 Which of the following compounds contain(s) no covalent bond(s)? KCl, PH_3, O_2, B_2H_6, H_2SO_4 **[JEE MAIN 2018]**
(A) KCl
(B) KCl, B_2H_6
(C) KCl, B_2H_6, PH_3
(D) KCl, H_2SO_4

Q.45 According to molecular orbital theory, which of the following will not be a viable molecule? **[JEE MAIN 2018]**

(A) H_2^- (B) H_2^{2-}
(C) He_2^{2+} (D) He_2^+

Q.46 According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^- ? **[JEE MAIN 2019 (JAN)]**

(A) Both are unstable
(B) Li_2^+ is unstable and Li_2^- is stable
(C) Li_2^+ is stable and Li_2^- is unstable
(D) Both are stable.

Q.47 The ion that has sp^3d^2 hybridization for the central atom, is : **[JEE MAIN 2019 (APRIL)]**

(A) $[ICl_2]^-$ (B) $[IF_6]^-$
(C) $[ICl_4]^-$ (D) $[BrF_2]^-$

Q.48 Among the following molecules / ions, $C_2^{2-}, N_2^{2-}, O_2^{2-}, O_2$, which one is diamagnetic and has the shortest bond length? **[JEE MAIN 2019 (APRIL)]**

(A) C_2^{2-} (B) N_2^{2-}
(C) O_2 (D) O_2^{2-}

Q.49 The correct statement about ICl_5 and ICl_4^- is **[JEE MAIN 2019 (APRIL)]**

(A) ICl_5 is trigonal bipyramidal and ICl_4^- is tetrahedral.
(B) ICl_5 is square pyramidal and ICl_4^- is tetrahedral.
(C) ICl_5 is square pyramidal and ICl_4^- is square planar.
(D) Both are isostructural.

Q.50 Among the following, the molecule expected to be stabilized by anion formation is : C_2, O_2, NO, F_2 **[JEE MAIN 2019 (APRIL)]**

(A) NO (B) C_2
(C) F_2 (D) O_2

Q.51 Among the following species, the diamagnetic molecule is **[JEE MAIN 2019 (APRIL)]**

(A) O_2 (B) NO
(C) B_2 (D) CO

Q.52 During the change of O_2 to O_2^-, the incoming electron goes to the orbital : **[JEE MAIN 2019 (APRIL)]**

(A) σ^*2p_z (B) $\pi\ 2p_y$
(C) π^*2p_x (D) $\pi\ 2p_x$

Q.53 The theory that can completely/properly explain the nature of bonding in $[Ni(CO)_4]$ is : **[JEE MAIN 2020 (JAN)]**

(A) Werner's theory
(B) Crystal field theory
(C) Valence bond theory
(D) Molecular orbital theory

Q.54 The dipole moments of CCl_4, $CHCl_3$ and CH_4 are in the order : **[JEE MAIN 2020 (JAN)]**

(A) $CHCl_3 > CCl_4 = CH_4$ (B) $CHCl_3 > CCl_4 > CH_4$
(C) $CCl_4 > CHCl_3 > CH_4$ (D) $CCl_4 = CH_4 > CHCl_3$

Q.55 Bond order and magnetic nature of CN^- are respectively **[JEE MAIN 2020 (JAN)]**

(A) 3, diamagnetic (B) 3, paramagnetic
(C) 2.5, paramagnetic (D) 2.5, diamagnetic

Q.56 Correct bond energy order of following is **[JEE MAIN 2020 (JAN)]**

(A) C–Cl > C–Br > C–I > C–F
(B) C–F < C–Cl < C–Br < C–I
(C) C–F > C–Cl > C–Br > C–I
(D) C–I < C–Br < C–F < C–Cl

EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)

Choose one correct response for each question.

Q.1 The correct sequence of increasing covalent character is represented by – **[AIPMT 2005]**

(A) $LiCl < NaCl < BeCl_2$
(B) $BeCl_2 < LiCl < NaCl$
(C) $NaCl < LiCl < BeCl_2$
(D) $BeCl_2 < NaCl < LiCl$

Q.2 Which of the following would have a permanent dipole moment – **[AIPMT 2005]**

(A) SiF_4
(B) SF_4
(C) XeF_4
(D) BF_3

Q.3 Which of the following molecules has trigonal planar geometry – **[AIPMT 2005]**

(A) BF_3
(B) NH_3
(C) PCl_3
(D) IF_3

Q.4 Which of the following species has a linear shape **[AIPMT 2006]**

(A) SO_2
(B) NO_2^+
(C) O_3
(D) NO_2^-

Q.5 Which of the following is not isostructural with $SiCl_4$? **[AIPMT 2006]**

(A) SO_4^{2-}
(B) PO_4^{3-}
(C) NH_4^+
(D) SCl_4

Q.6 Which of the following is not a correct statement **[AIPMT 2006]**

(A) The canonical structures have no real existence.
(B) Every AB_5 molecule does in fact have square pyramidal structure.
(C) Multiple bonds are always shorter than corresponding single bonds.
(D) The electron deficient molecules can act as Lewis acids.

Q.7 In which of the following pairs, the two species are isostructural – **[AIPMT 2007]**

(A) SO_3^{2-} and NO_3^-
(B) BF_3 and NF_3
(C) BrO_3^- and XeO_3
(D) SF_4 and XeF_4

Q.8 The correct order of C – O bond length among CO, CO_3^{2-} CO_2 is – **[AIPMT 2007]**

(A) $CO < CO_3^{2-} < CO_2$
(B) $CO_3^{2-} < CO_2 < CO$
(C) $CO < CO_2 < CO_3^{2-}$
(D) $CO_2 < CO_3^{2-} < CO$

Q.9 Four diatomic species are listed below in different sequences. Which of these presents the correct order of their increasing bond order ? **[AIPMT 2008]**

(A) $He_2^+ < O_2^- < NO < C_2^{2-}$
(B) $O_2^- < NO < C_2^{2-} < He_2^+$
(C) $NO < C_2^{2-} < O_2^- < He_2^+$
(D) $C_2^{2-} < He_2^+ < NO < O_2^-$

Q.10 The correct order of increasing bond angles in the following triatomic species is: **[AIPMT 2008]**

(A) $NO_2^+ < NO_2^- < NO_2$
(B) $NO_2^- < NO_2^+ < NO_2$
(C) $NO_2^- < NO_2 < NO_2^+$
(D) $NO_2^+ < NO_2 < NO_2^-$

Q.11 What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas? **[AIPMT 2009]**

(A) Dipole-dipole interaction
(B) Covalent bonds
(C) London dispersion force
(D) Hydrogen bonding

Q.12 According to MO theory which of the following lists ranks the nitrogen species in terms of increasing bond order? **[AIPMT 2009]**

(A) $N_2^{2-} < N_2^- < N_2$
(B) $N_2 < N_2^{2-} < N_2^-$
(C) $N_2^- < N_2^{2-} < N_2$
(D) $N_2^{2-} < N_2 < N_2^{2-}$

Q.13 In which of the following pairs of molecules/ions, the central atoms have sp^2 hybridisation ? **[AIPMT 2009, AIPMT (PRE) 2010]**

(A) NO_2^- and NH_3
(B) BF_3 and NO_2^-
(C) NH_2^- and H_2O
(D) BF_3 and NH_2^-

Q.14 Which one of the following species does not exist under normal conditions ? **[AIPMT (PRE) 2010]**

(A) Be_2^+
(B) Be_2
(C) B_2
(D) Li_2

Q.15 In which one of the following species the central atom has the type of hybridisation which is not the same as that present in the other three? **[AIPMT (PRE) 2010]**

(A) SF_4
(B) I_3^-
(C) $SbCl_5^{2-}$
(D) PCl_5

Q.16 In which of the following molecules, the central atom does not have sp^3 hybridisation? **[AIPMT (MAINS) 2010]**

(A) CH_4
(B) SF_4
(C) BF_4^-
(D) NH_4^+

Q.17 Choose the correct properties for NO_3^- and H_3O^+. **[AIPMT (MAINS) 2010]**

(A) Dissimilar in hybridisation for the central atom with different structures.
(B) Isostructural with same hybridisation for the central atom
(C) Isostructural with different hybridisation for the central atom.
(D) Similar in hybridisation for the central atom with different structures.

Q.18 Which of the following has the minimum bond length? **[AIPMT (PRE) 2011]**

(A) O_2
(B) O_2^+
(C) O_2^-
(D) O_2^{2-}

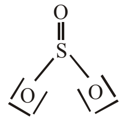
Q.19 Which of the two ions from the list given below that have the geometry that is explained by the same hybridisation of orbitals, NO_2^-, NO_3^-, NH_2^-, NH_4^+, SCN^- ? **[AIPMT (PRE) 2011]**

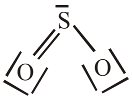
(A) NO_2^- and NH_2^-
(B) NO_2^- and NO_3^-
(C) NH_4^+ and NO_3^-
(D) SCN^- and NH_2^-

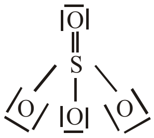
Q.20 The correct order of increasing bond length of C – H, C – O, C – C and C = C is **[AIPMT (PRE) 2011]**

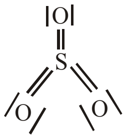
(A) $C-H < C-O < C-C < C=C$
(B) $C-H < C=C < C-O < C-C$
(C) $C-C < C=C < C-O < C-H$
(D) $C-O < C-H < C-C < C=C$

Q.21 Which of the following structures is the most preferred and hence of lowest energy for SO_3 ? **[AIPMT (MAINS) 2011]**

(A)


(B)


(C)


(D)


Q.22 The pairs of species of oxygen and their magnetic behaviours are noted below. Which of the following presents the correct description **[AIPMT (MAINS) 2011]**

(A) O_2^-, O_2^{2-} – Both diamagnetic
(B) O^+, O_2^{2-} – Both paramagnetic
(C) O_2^+, O_2 – Both paramagnetic
(D) O, .O_2^{2-} – Both paramagnetic

Q.23 Which one of the following pairs is isostructural (i.e. having the same shape and hybridisation) ? **[AIPMT (PRE) 2012]**

(A) [BCl_3 and $BrCl_3$]
(B) [NH_3 and NO_3^-]
(C) [NF_3 and BF_3]
(D) [BF_4^- and NH_4^+]

Q.24 Bond order of 1.5 is shown by : **[AIPMT (PRE) 2012]**

(A) O_2^+
(B) O_2^-
(C) O_2^{2-}
(D) O_2

Q.25 Which of the following species contains three bond pairs and one lone pair around the central atom ? **[AIPMT (PRE) 2012]**

(A) H_2O
(B) BF_3
(C) NH_2
(D) PCl_3

Q.26 The pair of species with the same bond order is **[AIPMT (PRE) 2012]**

(A) O_2^{2-}, B_2
(B) O_2^+, NO^+
(C) NO, CO
(D) N_2, O_2

Q.27 During change of O_2 to O_2^- ion, the electron adds on which one of the following orbitals ? **[AIPMT (MAINS) 2012]**

(A) π* orbital
(B) π orbital
(C) σ* orbital
(D) σ orbital

Q.28 Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them: **[AIPMT (MAINS) 2012]**

(A) $NO < O_2^- < C_2^{2-} < He_2^+$
(B) $O_2^- < NO < C_2^{2-} < He_2^+$
(C) $C_2^{2-} < He_2^+ < O_2^- < NO$
(D) $He_2^+ < O_2^- < NO < C_2^{2-}$

Q.29 Which of the following is electron-deficient ?

(A) PH_3
(B) $(CH_3)_2$ **[NEET 2013]**
(C) $(SiH_3)_2$
(D) $(BH_3)_2$

Q.30 XeF_2 is isostructural with – **[NEET 2013]**

(A) $BaCl_2$
(B) TeF_2
(C) ICl_2^-
(D) $SbCl_3$

Q.31 Which of the following is a polar molecule **[NEET 2013]**

(A) XeF_4
(B) BF_3
(C) SF_4
(D) SiF_4

Q.32 Which of the following is paramagnetic ? **[NEET 2013]**

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

Q.33 Dipole induced dipole interactions are present in which of the following pairs – **[NEET 2013]**

(A) SiF_4 and He atoms
(B) H_2O and alcohol
(C) Cl_2 and CCl_4
(D) HCl and He atoms

Q.34 Molecules with maximum dipole moment? **[AIPMT 2014]**

(A) CO_2
(B) CH_4
(C) NH_3
(D) NF_3

Q.35 Which one of the following species has plane triangular shape? **[AIPMT 2014]**

(A) N_3
(B) NO_3^-
(C) NO_2^-
(D) CO_2

Q.36 Which of the following pairs of ions are isolectronic and isostructural ? **[AIPMT 2015]**

(A) ClO_3^-, CO_3^{2-}
(B) SO_3^{2-}, NO_3^-
(C) ClO_3^-, SO_3^{2-}
(D) CO_3^{2-}, SO_3^{2-}

Q.37 The correct bond order in the following species is : **[AIPMT 2015]**

(A) $O_2^{2+} < O_2^- < O_2^+$
(B) $O_2^+ < O_2^- < O_2^{2+}$
(C) $O_2^- < O_2^+ < O_2^{2+}$
(D) $O_2^{2+} < O_2^+ < O_2^-$

Q.38 Maximum bond angle at nitrogen is present in which of the following ? **[AIPMT 2015]**

(A) NO_2^-
(B) NO_2^+
(C) NO_3^-
(D) NO_2

Q.39 Decreasing order of stability of O_2, O_2^-, O_2^+ and O_2^{2-} is **[RE-AIPMT 2015]**

(A) $O_2 > O_2^+ > O_2^{2-} > O_2^-$
(B) $O_2^- > O_2^{2-} > O_2^+ > O_2$
(C) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
(D) $O_2^{2-} > O_2^- > O_2 > O_2^+$

Q.40 In which of the following pairs, both the species are not isostructural ? **[RE-AIPMT 2015]**

(A) NH_3, PH_3
(B) XeF_4, XeO_4
(C) $SiCl_4$, PCl_4^+
(D) Diamond, silicon carbide

Q.41 Consider the molecules CH_4, NH_3 and H_2O. Which of the given statements is false? **[NEET 2016 PHASE 1]**

(A) The H – C – H bond angle in CH_4, the H – N – H bond angle in NH_3, and the H – O – H bond angle in H_2O are all greater than 90°.
(B) The H – O – H bond angle in H_2O is larger than the H – C – H bond angle in CH_4.
(C) The H – O – H bond angle in H_2O is smaller than the H – N – H bond angle in NH_3.
(D) The H – C – H bond angle in CH_4 is larger than the H – N – H bond angle in NH_3.

Q.42 Predict the correct order among the following – **[NEET 2016 PHASE 1]**

(A) lone pair - lone pair > lone pair - bond pair > bond pair - bond pair
(B) lone pair - lone pair > bond pair- bond pair > lone pair - bond pair
(C) bond pair - bond pair > lone pair-bond pair > lone pair - lone pair
(D) lone pair - bond pair > bond pair-bond pair > lone pair - lone pair

Q.43 Which one of the following compounds shows the presence of intramolecular hydrogen bond? **[NEET 2016 PHASE 2]**

(A) H_2O_2 (B) HCN

(C) Cellulose (D) Concentrated acetic acid

Q.44 The hybridisations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are **[NEET 2016 PHASE 2]**

(A) sp, sp^3 and sp^2 (B) sp^2, sp^3 and sp

(C) sp, sp^2 and sp^3 (D) sp^2, sp and sp^3

Q.45 Which of the following pairs of ions is isoelectronic and isostructural? **[NEET 2016 PHASE 2]**

(A) CO_3^{2-}, NO_3^- (B) ClO_3^-, CO_3^{2-}

(C) ClO_3^-, SO_3^{2-} (D) Both (A) and (C)

Q.46 Which of the following pairs of compounds is isoelectronic and isostructural ? **[NEET 2017]**

(A) TeI_2, XeF_2 (B) IBr_2^-, XeF_2

(C) IF_3, XeF_2 (D) $BeCl_2$, XeF_2

Q.47 The species, having bond angles of 120° is **[NEET 2017]**

(A) ClF_3 (B) NCl_3

(C) BCl_3 (D) PH_3

Q.48 Which of the following pairs of species have the same bond order ? **[NEET 2017]**

(A) O_2, NO^+ (B) CN^-, CO

(C) N_2, O_2^- (D) CO, NO

Q.49 In the structure of ClF_3, the number of lone pair of electrons on central atom 'Cl' is **[NEET 2018]**

(A) Four (B) Two

(C) One (D) Three

Q.50 Consider the following species : CN^+, CN^-, NO and CN. Which one of these will have the highest bond order?

(A) CN^+ (B) CN^- **[NEET 2018]**

(C) NO (D) CN

Q.51 Which of the following diatomic molecular species has only π bonds according to Molecular Orbital Theory?

(A) O_2 (B) N_2 **[NEET 2019]**

(C) C_2 (D) Be_2

Q.52 Identify the **INCORRECT** statement related to PCl_5 from the following: **[NEET 2019]**

(A) Three equatorial P–Cl bonds make an angle of 120° with each other.

(B) Two axial P–Cl bonds make an angle of 180° with each other.

(C) Axial P–Cl bonds are longer than equatorial P–Cl bonds.

(D) PCl_5 molecule is non-reactive.

ANSWER KEY

EXERCISE - 1

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
A	D	B	B	A	A	A	D	B	D	D	D	D	C	C	B	C	D	C	A	B	C	B	A	B	A
Q	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
A	B	A	A	B	A	C	B	C	D	C	A	C	B	C	D	D	A	C	C	C	A	B	B	D	C
Q	**51**	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**	**61**	**62**	**63**	**64**	**65**	**66**	**67**	**68**	**69**	**70**	**71**	**72**	**73**	**74**	**75**
A	A	B	B	C	D	C	C	B	A	A	A	A	B	A	C	C	C	B	A	C	B	C	C	D	C
Q	**76**	**77**	**78**	**79**	**80**	**81**	**82**	**83**																	
A	D	D	B	B	A	A	B	D																	

EXERCISE - 2

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
A	A	D	C	B	A	C	A	C	A	C	B	D	A	D	A	B	D	A	B	B	C	C	D	C	C
Q	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**					
A	D	D	A	B	D	B	B	D	D	C	D	A	C	B	B	A	D	C	B	B					

EXERCISE -3

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
A	2	2	3	2	1416	5	8	75	100	1

EXERCISE - 4

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
A	B	C	B	B	B	A	A	B	B	A	D	C	B	D	D	C	B	C	D	A	C	D	A	A	D
Q	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**
A	B	B	A	D	B	D	C	B	D	C	C	B	B	D	C	D	C	A	A	B	D	C	A	C	B
Q	**51**	**52**	**53**	**54**	**55**	**56**																			
A	D	C	D	A	A	C																			

EXERCISE - 5

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
A	C	B	A	B	D	B	C	C	A	C	D	A	B	B	C	B	A	B	B	B	D	C	D	B	D	A
Q	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**	**51**	**52**
A	A	D	D	C	C	C	D	C	B	C	C	B	C	B	B	A	C	C	D	B	C	B	B	B	C	D

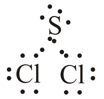
CHEMICAL BONDING AND MOLECULAR STRUCTURE

TRY IT YOURSELF-1

(1) First of all depic Lewis dot structure of SCl_2, then calculate formal charge by using following formula:

Formal charge = Valence electrons – Total e^- in lone pairs

$-\frac{1}{2}$ (number of shared electrons)



Formal charge on S atom $= 6 - 4 - \frac{1}{2} \times 4 = 0$

(2) ΔH_f = Algebraic sum of S, I.E., EA and lattice energy

$\Delta H_f = S + IE + H_a - 2 \times EA -$ lattice energy

$$\text{Lattic energy} = \underbrace{S + IE + H_a}_{\substack{\text{Energy required}\\ \text{therefore positive}}} \ \underbrace{-\ 2 \times EA - \Delta H_f}_{\substack{\text{Energy required}\\ \text{therefore negative}}}$$

E.A. is multiplied by two because 2 Cl atoms are present.

(3) (C) **(4)** (B) **(5)** (D)

(6) (ii) **(7)** 1.33 **(8)** Yes

(9) 23.2%

(10) LiCl > NaCl > KCl > RbCl > CsCl
(size of cation increases)

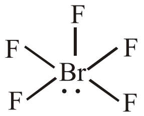
(11) $AlCl_3 > MgCl_2 > NaCl$ (charge of cation decreases)

TRY IT YOURSELF-2

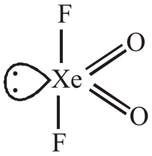
(1) (B) **(2)** (A) **(3)** (B)

(4) (A) **(5)** (AD) **(6)** (CD)

(7) **8.**



(8) (D).



TRY IT YOURSELF-3

(1) (B)

(2) (B)

(3) **(C).** $E_{C-C} \cong 100$ Kcal/mole

(4) **(ABD).**

In ice water molecules are excessively H-bonded giving a cage-like structure which is lighter than water.

Primary amines are more basic than tertiary amines in aqueous solution mainly due to H-bonding with water molecules. Dimerisation of acetic acid in benzene is due to intermolecular H-bonding.

(5) Hydrogen bonds are stronger than Van der Walls forces since hydrogen bonds are regarded as an extreme form of dipole-dipole interaction.

(6) True

(7) True

(8) **False.** C = C bond length is less than the C – C bond length value.

CHAPTER-4 : CHEMICAL BONDING AND MOLECULAR STRUCTURE

EXERCISE-1

(1) **(D).** The atoms can achieve the stable octet to linked by chemical bonds. It was postulated by Lewis.

(2) **(B).** Similar atoms form covalent bond.

(3) **(B).** Covalent bond is directional.

(4) **(A).** $Ca \rightarrow Ca^{2+} + 2e^-$

Calcium is assigned a positive electrovalence of two.

(5) **(A).** According to Lewis and Kossel approach, loss of one electron from neutral atom indicated the one positive charge on ammonium ion.

(6) **(A).** **Step I :** Skeleton OCO

Step II : $A = 1 \times 4$ for $C + 2 \times 6$

for $O = 4 + 12 = 16$ electrons

Step III : Total no. of electrons needed to achieve noble gas configuration (N)

$N = 1 \times 8 + 2 \times 8 = 24$

Step IV : Shared electrons,

$S = N - A = 24 - 16 = 8$ electrons

Step V : $O::C::O$

Step VI: $:\ddot{O}::C::\ddot{O}: = :\ddot{O}=C=\ddot{O}:$

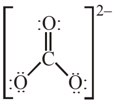
(7) **(D).** $:N\vdots\vdots N:$ Number of electrons involved in bonding is 6.

(8) **(B).** $:\ddot{S}=C=\ddot{S}:$

Formal charge on C atom = Valence electrons

$$- \text{Lone pair of electrons} - \frac{1}{2} \times \text{Bonding electrons}$$

$$= 4 - 0 - \frac{1}{2} \times 8 = 0$$

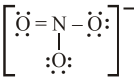
Formal charge on C atom = 0 

(9) **(D).**

(10) **(D).** The incomplete octet of the central atom :

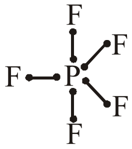
In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3.

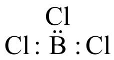
Odd-electron molecules : In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms.

(11) **(D).** The Lewis representation of NO_3^- is 

Thus, N atom has 4 bond pairs and 0 lone pairs of electrons.

(12) **(D).** According to octet rule, the central atom must have 8 electrons but in some compounds the number of electrons is more than 8, or less than 8 or an odd number of electrons is left on the central atom e.g., PCl_5, BF_3, NO.





$$\overset{Cl}{Cl:\ddot{B}:Cl}$$

$\ddot{N}=\ddot{O}$

10 electrons around P   6 electrons around B   Odd electrons around N

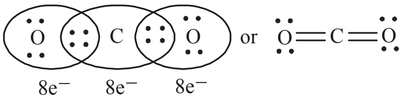
(13) **(C).** Neon = 2, 8 (octet)

Argon = 2, 8, 8 (octet)

Helium = 2(duplet)

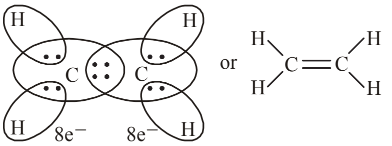
Xenon = 2, 8, 18, 8 (octet).

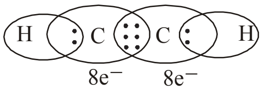
(14) **(C).** CO_2 :



Double bonds in CO_2 molecule

C_2H_4 :



C_2H_2 :  or H—C≡C—H

(15) **(B).** RbCl is an electrovalent compound.

(16) **(C).** It is the fact that electovalent compounds are made of ions.

(17) **(D).** Electrovalent bond formation depends on ionization energy of cation, electron affinity of anion and on lattice energy.

(18) **(C).** NaCl is formed by electrovalent bonding.

(19) **(A).** Electrovalent compounds generally have high melting point and high boiling point due to stronger coulombic forces of attractions.

(20) **(B).** Due to electrostatic force of attraction, the ions do not move when electric current is applied in solid state. The ions become mobile when melted or dissolved in a polar solvent and conduct electricity.

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

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

$$= \frac{\text{observed}\ \mu}{\text{theoritical}\ \mu} \times 100 = \frac{1.02}{1.275 \times 4.8} \times 100$$

= 17% ionic = 83% covalent

(23) **(A).** $M = 1.48 \times 3.33 \times 10^{-30}\ cm = 4.93 \times 10^{-30}\ cm.$

$q = 1.6 \times 10^{-19} C$

$$\ell = \frac{\mu}{q} = \frac{4.93 \times 10^{-30}}{1.6 \times 10^{-19}} = 3.08 \times 10^{-11}\ m = 0.0308\ nm$$

The NH_3 molecule can not have the shape of an equilateral triangle because in the case its dipole moment would equal zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

(24) **(B).** Middle length of $H_2 = 74$ pm

$$\text{Length of } H = \frac{74}{2} = 37\text{pm}$$

Middle length of $Cl_2 = 198$pm

$$\text{Length of Cl} = \frac{198}{2} = 99\,\text{pm}$$

Bond length of HCl = Length of H + Length of Cl = 37 + 99 = 136 pm

(25) **(A).** The dipole moment of two dipoles inclined at an angle θ is given by the equation

$$\mu = \sqrt{X^2 + Y^2 + 2XY\cos\theta}$$

$\cos 90° = 0$.

Since the angle increases from 90 – 180, the value of $\cos\theta$ becomes more and more – ve and hence resultant decreases. Thus, dipole moment is maximum when $\theta = 90°$.

(26) **(B).** Charge of $e^- = 1.6 \times 10^{-19}$

Dipole moment of $HBr = 1.6 \times 10^{-30}$

Inter atomic spacing $= 1Å = 1 \times 10^{-10}$m

% of ionic character in

$$HBr = \frac{\text{dipole moment of HBr} \times 100}{\text{inter spacing distance} \times q}$$

$$= \frac{1.6 \times 10^{-30}}{1.6 \times 10^{-19} \times 10^{-10}} \times 100$$

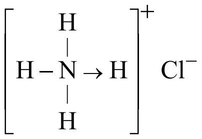
$$= 10^{-30} \times 10^{29} \times 100 = 10^{-1} \times 100$$

$$= 0.1 \times 100 = 10\%$$

(27) **(A).** Polarity create due to the difference in electronegativity of both atom in a molecule except H_2 all other molecule have the different atom so they will have the polarity while H_2 will be non polar.

(28) **(A).** When two atoms shares two electrons it is an example of covalent bond. This covalent bond may be polar or may be non-polar depends on the electronegativity difference. In given example formula is AB. So it is polar.

(29) **(B).** NH_4Cl has both types of bonds polar and non-polar.



$$\left[\begin{array}{c} H \\ | \\ H-N\rightarrow H \\ | \\ H \end{array}\right]^+ Cl^-$$

(30) **(A).** Covalent bond forms when electronegativity difference of two atom is equal to 1.7 or less than 1.7

(31) **(C).** HCl has ionic character yet it has covalent compound because electronegativity of chlorine is greater than that of hydrogen.

(32) **(B).** BF_3 has zero dipole moment.

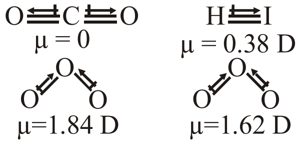
(33) **(C).** When two identical atoms form a bond, bond is non-polar.

(34) **(D).** Due to the electronegativity difference.

(35) **(C).** $Si-Si < C-C$; $Cl-Cl > F-F$
$S-S > O-O$; $P-P > N-N$

(36) **(A).** NH_3 does not show any resonating structure due to the absence of double bond.

(37) **(C).**

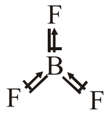


Thus, H_2O has highest dipole moment.

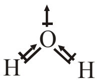
(38) **(B).** Bond order $\propto \dfrac{1}{\text{Bond length}}$

(39) **(C).** $BeF_2 : \mu = 0$

$BeF_3 : \mu = 0$



$H_2O : \mu = 1.84\,D$

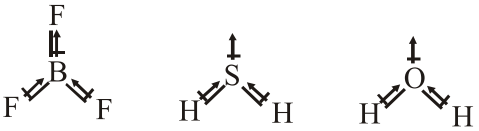


(40) **(D).** Bond strength $\propto$ Difference in electro negativity of atoms.

(41) **(D).**

- The canonical forms have no real existence.
- The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.
- There is no such equilibrium between the canonical forms as we have between tautomeric forms (keto and enol) in tautomerism.
- The molecule as such has a single structure which is the resonance hybrid of the canonical forms and which cannot as such be depicted by a single Lewis structure.

(42) **(A).** In BF_3, dipole moment is zero due to its symmetrical structure. Summations of all dipoles is zero.



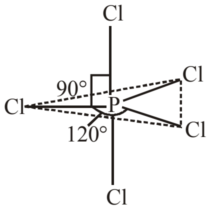
In H_2S and H_2O due to unsymmetrical structure net +ve dipole is there. H_2O has higher dipole due to higher electronegativity of oxygen than sulphur.

(43) **(C).** The structures represent canonical or resonating structures of carbonate ion.

(44) **(C).** The pairs of electrons tend to occupy such positions that place them farthest from each other and minimise repulsions.

(45) **(C).** 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 deviation from idealised shapes and alterations in bond angles in the molecules.

(46) **(A).** In PCl_5, three axial and two equatorial bonds are present.



The bond length of all P – C bonds is not same.

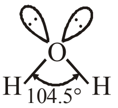
(47) **(B).** In structure (ii), lp-bp repulsions are minimum.

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

(49) **(D).** The correct example is H_2O. NH_3 is pyramidal and bond angle is 104.5°.

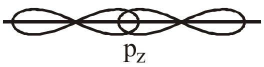
(50) **(C).** lp - lp repulsions > lp - bp repulsions > bp - bp repulsions

(51) **(A).** Due to presence of lone pairs, the repulsion is more which changes the bond angle to 104.5°.



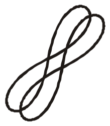
(52) **(B).** Electrons of same spin never combine to form a bond. Other facts are true for VBT.

(53) **(B).** p_z orbital by convention undergoes end to end overlapping and p_x, p_y undergo sidewise overlapping.



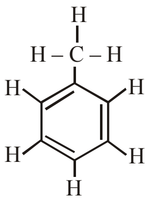
p_z

p_x



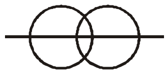
p_y

(54) **(C).** Toluene is $C_6H_5CH_3$.

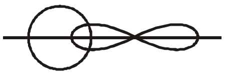


No. of σ bonds is 15.
No. of π bonds is 3.

(55) **(D).**

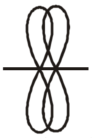


s-s overlapping (σ)



s-p_z overlapping (σ)

p_z-p_z overlapping (σ)



p_x-p_x overlapping (π)

(56) **(C).** CH_4 because it has sp^3 hybridisation.

(57) **(C).** As the first carbon has triple bond and second one has double bond with other two carbon atom.

(58) **(B).** Merging (mixing) of dissimilar orbitals of different energies to form new orbitals is known as hybridisation and the new orbital formed are known as hybrid oribitals. They have similar energy.

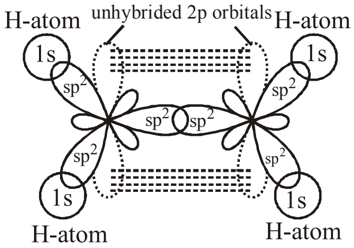
(59) **(A).** As p-character increases the bond angle decreases.
In sp - p-character 1/2, bond angle-180°

In sp^2- p-character $\frac{2}{3}$, bond angle-120°

In sp^3 - p-character $\frac{3}{4}$, bond angle-109°

(60) **(A).** In H_2CO_3 and BF_3 central atom are in sp^2 hybridisation but in H_2CO_3 due to the ionic character of O – H bond it will be polar (High electronegativity of oxygen).

(61) **(A).**



(62) **(A).** SO_4^{2-} and BF_4^- have sp^3 hybridisation and are tetrahedral in shape.

(63) **(B).** The percentage of s-character in sp^3, sp^2 and sp is 25%, 33% and 50% respectively. Order of size of orbitals is $sp < sp^2 < sp^3$.

(64) **(A).** $\overset{sp^2}{CH_2} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv N$

(65) **(C).** Promotion of electron is not essential condition prior to hybridisation.

(66) **(C).** $C_{\text{excited state}} = 2s^1\ 2p_x^{\ 1}\ p_y^{\ 1}\ p_z^{\ 1}$
$O_{\text{ground state}} = 2s^2\ 2p_x^{\ 2}\ p_y^{\ 1}\ p_z^{\ 1}$
In the formation of CO_2 molecule, hybridisation orbitals of carbon occurs only to a limited extent involving only one s and one p orbital and gives rise sp hybridisation.

(67) **(C).** Bonding molecular orbital has lower energy than the antibonding molecular orbital.

(68) **(B).** Higher the bond order, higher is the bond enthalpy.

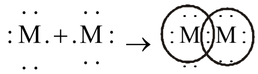
(69) **(A).** Electronic configuration of atom: $1s^2\ 2s^2\ 2p^5$
M.O. configuration:
$(\sigma 1s^2)\ (\sigma^* 1s^2)\ (\sigma 2s^2)\ (\sigma^* 2s^2)$
$(\sigma\ 2p_z^{\ 2})\ (\pi\ 2p_x^{\ 2} = \pi\ 2p_y^{\ 2})\ (\pi^*\ 2p_x^{\ 2} = \pi^*\ 2p_y^{\ 2})$

$$B.O. = \frac{1}{2} \times (10 - 8) = 1$$

(70) **(C).** A molecule exists only if the bond order is positive. If bond order is zero or negative, the molecule does not exist.

(71) **(B).** Non-metals readily form diatomic molecules by sharing of electrons.

Element M ($1s^2\ 2s^2\ 2p^5$) has seven electrons in its valence shell and thus needs one more electron to complete its octet. Therefore, two atoms share one electron each to form a diatomic molecule



(72) **(C).** N_2^+ (13) : $\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2,$

$\pi\, 2p_x^{\ 2} = \pi\, 2p_y^{\ 2}, \sigma\, 2p_z^{\ 1}$

O_2 (16) : $\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2,$

$\sigma\, 2p_z^{\ 2}, \pi\, 2p_x^{\ 2} = \pi\, 2p_y^{\ 2}, \pi^*2p_x^{\ 1} = \pi^*\, 2p_y^{\ 1}$

O_2^{2-} (18) : $\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2,$

$\sigma\, 2p_z^{\ 2}, \pi\, 2p_x^{\ 2} = \pi\, 2p_y^{\ 2}, \pi^*2p_x^{\ 2} = \pi^*\, 2p_y^{\ 2}$

B_2 (10) : $\sigma\, 1s^2, \sigma^*1s^2, \sigma\, 2s^2, \sigma^*2s^2,$

$\pi\, 2p_x^{\ 1} = \pi\, 2p_y^{\ 1}$

Thus, O_2^{2-} does not contain unpaired electrons.

(73) **(C).** For all elements which have atomic number more than 7 (beyond nitrogen) the energy of $\sigma\, 2p_z$ is lower than $\pi 2p_x$ and $\pi 2p_y$-orbitals.

(74) **(D).** The correct order of energies of molecular orbitals in N_2 molecule is

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

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

(75) **(C).** Double bond of C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals.

(76) **(D).**

(i) O_2 is paramagnetic because of unpaired electrons.

(ii) Helium is diamagnetic.

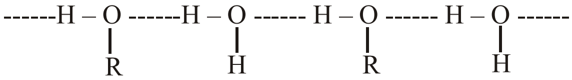
(iii) Nitrogen is diamagnetic as the electrons are paired.

(77) **(D).** M.O. configuration of O_2 :

$(\sigma 1s^2)\ (\sigma^*1s^2)\ (\sigma 2s^2)\ (\sigma^*2s^2)$

$(\sigma\, 2p_z)^2\ (\pi\, 2p_x^{\ 2} = \pi\, 2p_y^{\ 2})\ (\pi^*\, 2p_x^{\ 1} = \pi^*\, 2p_y^{\ 1})$

(78) **(B).**

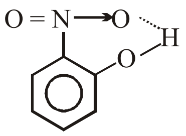


$$\text{------}\underset{\textstyle R}{H-O}\text{------}\underset{\textstyle H}{H-O}\text{------}\underset{\textstyle R}{H-O}\text{------}\underset{\textstyle H}{H-O}\text{------}$$

In methanol, R is $-CH_3$ group.

Hydrogen bonding between methanol and water.

(79) **(B).** Nitrophenol has intermolecular H bonding as shown below



(80) **(A).** Hydrogen bonding occurs when H atom is linked to an electronegative atom like F, O or N. It is the force of attraction between small positive charge developed on H atom and small negative charge developed on electronegative atom due to displacement of electrons towards more electronegative atom.

(81) **(A).** Due to largest difference in electronegativity, H – F bond is strongest.

(82) **(B).** Only H_2O forms H-bonding while other substances HCl, HI and H_2S do not form H-bonding.

(83) **(D).** Statement (iii) is not true since NH_3 has higher boiling point than PH_3 due to hydrogen bonding.

EXERCISE-2

(1) **(A).** One s, three p and one d orbital.

(2) **(D).** Because it has sp^2 hybridisation other three have sp^3 hybridisation.

(3) **(C).** $SnCl_2$ is a bent shape molecule due to presence of lone pair of electron other choices are correct.

(4) **(B).** Both have the same state of hybridisation with one lone pair of e^- each.

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

(6) **(C).** In PO_4^{3-} ion, the formal charge on each O atom of P – O bond

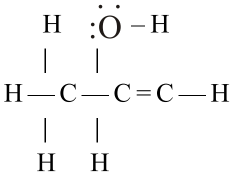
$$= \frac{\text{Total charge}}{\text{No. of O atoms}} = \frac{-3}{4} = -0.75$$

(7) **(A).** HCl < HBr < HI < HF

Due to strong hydrogen bonding in HF.

(8) **(C).** During heterolytic fission there will be formation of CH_3^+ and CH_3^- which has sp^2 and sp^3 hybridisation respectively.

(9) **(A).** This is clear from its structure as shown :



(10) **(C).** Out of 15 e^- in N_2^-, 10 are in bonding MO's and $5e^-$ are in the anti bonding MO's.

$$\text{Hence bond order} = \frac{1}{2}(10 - 5) = 2.5$$

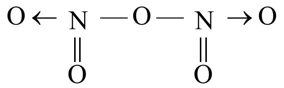
(11) **(B).** Bond order of O_2^+ is 2.5 which is maximum among all the species hence its bond strength will also be the maximum.

(12) **(D).** Sn[Z = 50], [Kr] $\overset{5s}{\boxed{\uparrow\downarrow}}\ \ \overset{5p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}$

sp^2 – hybridisation : $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

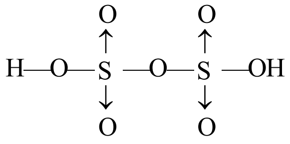
(13) **(A).** Though all compounds have covalent bond but there is coordination bond also between N and C in C_2H_5NC

(14) **(D).** The structure of N_2O_5 clears about it

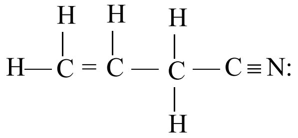


$$O \leftarrow \underset{\underset{\textstyle O}{\|}}{N} - O - \underset{\underset{\textstyle O}{\|}}{N} \rightarrow O$$

(15) **(A).** Structure of $H_2S_2O_7$ is as follows



(16) **(B).** This is clear from structure of allylcyanide



(17) **(D).** Bond strength $\propto$ difference in electronegativity of atoms.

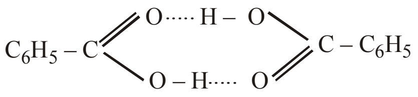
(18) **(A).** NaCl is an ionic compound solubility of an ionic compound depends on the value of dielectric constant of the solvent. Higher the value of dielectric constant of the solvent more is the solubility of the ionic compound..

Solvent	H_2O	C_2H_5OH	CH_3COCH_3	$C_2H_5OC_2H_5$
Dielectric constant	80	27	21	4.1

(19) **(B).** Symmetrical with linear structure will have zero dipole moment.

(20) **(B).** AgI has maximum covalent character. [I^- is a large anion], while AgF has minimum covalent character, Therefore, it has more solubility.

(21) **(C).** Dimerisation of benzoic acid involves intermolecular H-bonding.



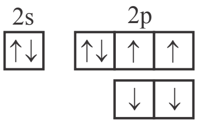
(22) **(C).** Because in other compounds there is more than 8 e^- in outermost shell of central atom.

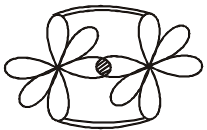
(23) **(D).** As the size of anion increases covalent character increases.

(24) **(C).** The covalent character increases according to charge on cation.

(25) **(C).** Compound is carbontetrachloride because CCl_4 has sp^3–hybridisation 4 orbitals giving regular tetrahedron geometry. In others the geometry is little distorted inspite of sp^3 hybridisation due to different atoms on the vertices of tetrahedron.

(26) **(D).** Configuration of O atom





Configuration of O molecule

σ bond of O = O is formed by axial overlapping of p – p orbital while π bond is formed by sidewise overlapping of p – p orbital.

(27) **(D).** Valency of metal is + 2 by formula MO so its phosphate would be $M_3(PO_4)_2$ because valency of $[PO_4]$ is –3.

(28) **(A).** Melting point and boiling point of electrovalent compounds are high due to strong electrostatic force of attraction between the ions.

(29) **(B).** Molecule X is nitrogen because nitrogen molecule has triple bond. It's configuration will be $1s^2$, $2s^2$ $2p^3$.

(30) **(D).** Among the given species. The bond dissociation energy of C – O bond is minimum in case of CO_3^{2-} by which C–O bond become more weaker in CO_3^{2-} or the bond order of CO_3^{2-} (1.33) is minimum so the bond become weaker.

(31) **(B).** Electronic configuration of

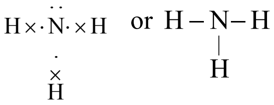
$${}_{16}S^{32} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$$

In the last orbit it has only 6 electron. So it require 2 electron to complete its octet, therefore it share 2 electron with two hydrogen atom and forms 2 covalent bond with it.

(32) **(B).** The electronic configuration of nitrogen is

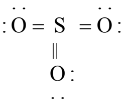
$${}_7N = 1s^2, 2s^2, 2p^3$$

It has 5 electrons in valency shell, hence in ammonia molecule it complete its octet by sharing of three electron with three H atom, therefore it has 8 electrons in its valence shell in ammonia molecule



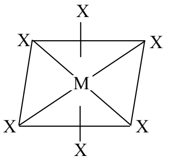
(33) **(D).** Co-ordinate bond is a special type of covalent bond which is formed by sharing of electrons between two atoms, where both the electrons of the shared pair are contributed by one atom. Since this type of sharing of electrons exists in O_3, SO_3 and H_2SO_4. Therefore all these contains coordinate bond.

(34) **(D).**



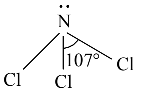
5 atoms has 12 electrons in its outermost shell. One $(S-O)\pi$ bond will be (p-p) π bond while two $(S-O)\pi$ bond will be (p-d) π bond.

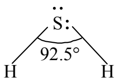
(35) **(C).** In octahedral molecule six hybrid orbitals directed towards the corner of a regular octahedron with a bond angle of 90°.



According to this geometry, the number of X – M – X bond at 180° must be three.

(36) **(D).** In NCl_3 and H_2S the central atom of both (N and S) are in sp^3 hybridisation state





while in BF_3 and NCl_3 central atoms are in sp^2 and sp^3 hybridisation respectively. In H_2S and $BeCl_2$ central atom are in sp^3 and sp^2 hybridisation In BF_3, NCl_3 & H_2S central atom are in sp^2, sp^3 & sp^3 hybridisation and in the central atom are in $sp^3$and sp hybridisation.

(37) **(A).** Except CO_3 other choice CO_2, $CS_2$and $BeCl_2$ have sp-hybridisation and shows the linear structure while CO_3 have sp^3 hybridisation and show the non linear structure because sp^3 generate tetrahedral structure.

(38) **(C).** In resonance structure there should be the same number of electron pairs.

(39) **(B).** Because CsF is electrovalent compound.

(40) **(B).** CH_4 have regular tetrahedron so its dipole moment is zero.

(41) **(A).** Carbon tetrachloride has a zero dipole moment because of its regular tetrahedral structure.

(42) **(D).** As the size of anion increases, polarity character increases.

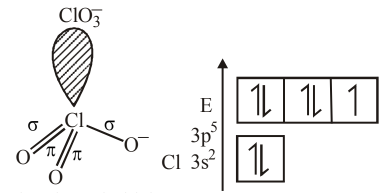
(43) **(C).** In fluorine molecule formation p-p orbitals take part in bond formation.

(44) **(B).** π-bond is formed by lateral overlapping of unhybridised p-p orbitals.

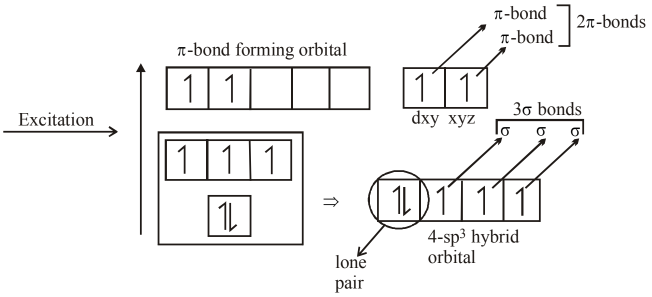
(45) **(B).** In ethylene both Carbon atoms are sp^2- hybridised so 120°.

EXERCISE-3

(1) **2.**



Triangle pyrimidal



There are two (d – p) (π) bond

dπ – pπ bond.

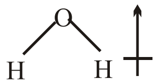
(2) **2.** Cl – Be – Cl

No. of 2C - $2e^-$ bonds = 2ü
ý
No. of 3C - $4e^-$ bonds = 0þ

⇒ Total no. of 2C – $2e^-$ and 3C – $2e^-$ bonds = 2

(3) **3.** Resultant dipole moment

$$\mu_R = \sqrt{\mu^2 + \mu^2 + 2\mu^2 \cos 105°} = \mu\sqrt{2\,(1 + \cos 105°)}$$



Let the fraction of electronic charge be $\delta \times 1e^-$ charge.

Since $1e^-$ charge $= 1.6 \times 10^{-19}\,C = 4.8 \times 10^{-10}$ esu

$\therefore\ \mu = \delta \times 4.8 \times 10^{-10}$ esu $\times 0.94 \times 10^{-8}$ cm

Also, 1.85×10^{-18} esu. cm

$= \delta \times 4.8 \times 10^{-10}$ esu $\times 0.94 \times 10^{-8}$ cm $\sqrt{2\,(1 + \cos 105°)}$

$\therefore\ \delta = 0.33$

Hence, fraction of e^- charge = 1/3

(4) **2.** To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs orbitals. The valence electrons of He are in the 1s orbital. Hence, the 1s orbitals combine to give anMO diagram like that for H_2. He_2^+ ion has a total of three electrons. Two are placed in the bonding orbital, the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \frac{1}{2}\,(2-1) = \frac{1}{2}$$

(5) **1416.**

We are asked to estimate the enthalpy change for a chemical process by using averaged values for chemical bonds that are broken in the reactants and formed in the products.

Among the reactants, we must break six C – H bonds and a C – C bond in C_2H_6; we also break $\frac{7}{2}O_2$ bonds.

Among the products, we form four C = O bonds (two in each CO_2) and six O – H bonds (two in each H_2O).

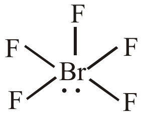
$$\Delta H = 6\,\Delta(C-H) + \Delta(C-C) + \frac{7}{2}\Delta(O_2)$$
$$-4\,\Delta(C=O) - 6\,\Delta(O-H)$$

$= 6\,(413\text{ kJ}) + 348\text{ kJ} + \frac{7}{2}\,(495\text{ kJ}) - 4\,(799\text{ kJ}) - 6\,(463\text{ kJ})$

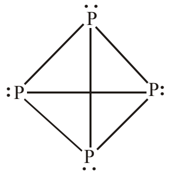
$= 4558\text{ kJ} - 5974\text{ kJ} = -1416\text{ kJ}$

(6) **5.** The electron-pair arrangement of IF_5 is octahedral. The iodine atom uses sp^3d^2 hybrid orbitals. The F – I – F bond angles are about 90°, and each bond is formed from overlap of an sp^3d^2 hybrid orbital on iodine with a p orbital on a fluorine atom. The remaining hybrid orbital holds a lone pair.

(7) **8.**



(8) **75.** P is sp^3 hybridised in P_4.



(9) **100.** $E_{C-C} \cong 100$ Kcal/mole

(10) **1.** For molecules lighter that O_2, the increasing order of energies of molecular orbitals is :

$$\sigma 1s \sigma^* 1s \sigma 2s \sigma^* 2s \begin{bmatrix} \pi\, 2p_y \\ \pi\, 2p_z \end{bmatrix} \sigma 2p_x \sigma^* 2p_x \begin{bmatrix} \pi^* 2p_y ... \\ \pi^* 2p_z \end{bmatrix}$$

where, $\pi 2p_y$ and $\pi 2p_z$ are degenerate molecular orbitals, first singly occupied and then pairing starts if Hund's rule is obeyed. If Hund's rule is violated in B_2, electronic arrangement would be :

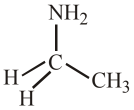
$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \begin{bmatrix} \pi\, 2p_y^2 ... \\ \pi\, 2p_z^2 ... \end{bmatrix}$$

No unpaired electron-diamagnetic.
Bond order

$$= \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{6-4}{2} = 1$$

EXERCISE-4

(1) **(B).**



$CH_3\underline{C}H_2NH_2$
sp^3 hybridised carbon

(2) **(C).** Chemical bond formation takes place when forces of attraction overcome the forces of repulsion

(3) **(B).** Square plane → dsp^2 hybridisation
$\rightarrow d, s, p_x, p_y$

(4) **(B).** The reason for double helical structure of DNA is operation of hydrogen bonding.

(5) **(B).** Both NO_2 and O_3 have dipole moment zero ($\mu = 0$) due to their bent structure.

(6) **(A).** In XeF_2, there are three lone pair e^- present around Xe atom but lone pair and bond pair form trigonal bipyramidal structure in which lone pair present in equatorial position and bond pair (Xe – F) present in axial position. CO_2 also have linear shape.

(7) **(A).** The bond angle around the central atom is having following sequence :

H_2S <	NH_3 <	SiH_4 <	BF_3
(92°)	(107°)	(109°28')	(120°)

(8) **(B).** We know that, bond length $\propto \dfrac{1}{\text{bond order}}$

therefore bond length of $NO > NO^+$

(9) **(B).** In H_3BO_3, the hybrid state of B is sp^2 where as that of O is sp^3.

(10) **(A).** From the option only BF_4^- having regular tetrahedral structure.

(11) **(D).** In d^2sp^3 hybridization (octahedral shape) has maximum no. of 90° angle (eight)

(12) **(C).** Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in exhibiting maximum covalency in compound.

(13) **(B).** $H_2 \rightarrow 1s^2 \rightarrow$ do not having unpaired e^- therefore it is diamagnetic in nature.

(14) **(D).** Lattice energy depends upon
(a) size of the ion
(b) magnitude of charge of ion
size of the ion ↑
Lattice energy ↑

(15) **(D).**

XeF_4	SF_4	CF_4
two lone pair e^-	$1 - \ell p\ e^-$	ℓp absent

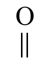
(16) **(C).** SO_3^{2-}, CO_3^{2-}, NO_3^-

(17) **(B).** In calcium carbide, the no. of bonds are one sigma and two pi.

(18) **(C).** $O_2^{2-} = \sigma_{1s^2} \sigma^*_{1s^2} \sigma_{2s^2} \sigma^*_{2s^2} \sigma_{2p_z^2} \pi_{2p_x^2} \pi_{2p_y^2} \pi^*_{2p_x^2} \pi^*_{2p_y^2}$

All paired $e^- \Rightarrow$ Diamagnetic

(19) **(D).** $CH_3 - C \equiv N$



$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$

Acetonitrile Acetone

Major Dipole-dipole interaction occurs in permanent dipolar molecule.

(20) **(A).** MCl_2 is more ionic than MCl_4

(21) **(C).** In SF_4 two lone pair and four F at oms around the sulphur atom adopt trigonal bipyramidal arrangement, hence the axial S – F bonds are relatively longer than equatorial S – F bonds.

(22) **(D).** Bond angle ∝ E.N.
E.N. ↓
Bond angle ↓

(23) **(A).**

	NO	⟶ NO^+
Bond order	2.5	3
Magnetic behaviour	paramagnetic	diamagnetic

(24) **(A).** Hydrogen bonded with more electronegative atom form strongest hydrogen bond.

(25) **(D).** $O_2^{-2} \rightarrow$ all es^- are paired
→ form diamagnetic character

(26) **(B).** $K^+ < Ca^{+2} < Mg^{+2} < Be^{+2}$

(27) **(B).** NO^+, C_2^{2-}, CN^- and N_2 all have fourteen electrons.

(28) **(A).** Both are isoelectronic and have same bond order.

(29) **(D).** Boron in BF_3 has a vacant p¡Vorbital, allowing $p\pi - p\pi$ back bonding while carbon in CF_4 has no vacant orbital, so no back bonding is feasible.
Thus, B – F bond is stronger than CF_4.

(30) The bond order of $O_2^{2-}, O_2^{2+}, O_2^{+}$ & O_2^{-} is 1, 3, 2.5 and 1.5 respectively. Since, O_2^{2+} has highest bond order, so it has shortest bond length.

(31) **(D).** Energy required for 1 Cl_2 molecule $= \dfrac{242 \times 10^3}{N_A}$ Joules.

This energy is contained in photon of wavelength 'λ'.

$$\frac{hc}{\lambda} = E \Rightarrow \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{\lambda} = \frac{242 \times 10^3}{6.022 \times 10^{23}}$$

$\lambda = 4947\ \text{Å} \approx 494\ \text{nm}$

(32) **(C).** Covalent character in ionic compounds is governed by Fazan's Rule. $AlCl_3$ will show Maximum covalent character on account of higher polarising power of Al^{3+} because of its having higher positive charge and smaller size.

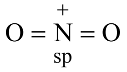
(33) **(B).** **NO_2^+ :**

Number of electron pairs = 2

Number of bond pairs = 2

Number of lone pair = 0

So, the species is linear with sp hybridisation.

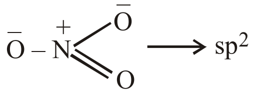


$$O = \overset{+}{\underset{sp}{N}} = O$$

NO_3^- : Number of electron pairs = 3

Number of bond pairs = 3, Number of lone pair = 0

So, the species is trigonal planar with sp^2 hybridisation.



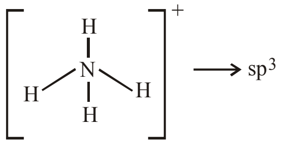
NH_4^+

Number of electron pairs = 4

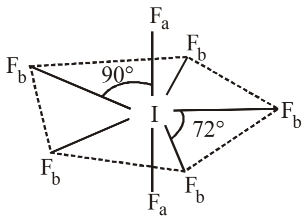
Number of bond pairs = 4

Number of lone pair = 0

So, the species is tetrahedral with sp^3 hybridisation.



(34) **(D).** The structure is pentagonal bipyramid having sp^3d^3 hybridisation as given below :



$F_b - I - F_b = 72°$ (5 number)

$F_b - I - F_a = 90°$ (10 number)

$F_b - I$ bond length $= 1.858 \pm 0.004$ Å

$Fa - I$ bond length $= 1.786 \pm 0.007$ Å.

(35) **(C).** PF_5 trigonal bipyramidal

BrF_5 square pyramidal (distorted)

(36) **(C).** H_2^{2+} Bond order = 0

He_2 : Bond order $\dfrac{2-2}{2} = 0$

So, both H_2^{2+} & He_2 do not exist.

(37) **(B).** $Li_2 : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2$ Bond order = 1

$Li_2^+ : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^1$ Bond order = 0.5

$Li_2^- : \sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^1$ Bond order = 0.5

Stability order $Li_2 > Li_2^+ > Li_2^-$

(38) **(B).** N_2 and C_2 both are diamagnetic.

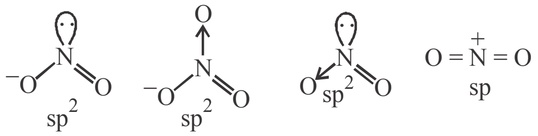
(39) **(D).** $CsI_3 \longrightarrow Cs^+ + I_3^-$

⇒ Cs cannot show +3 oxidation state.

⇒ I_2 molecules are too large to be accommodated in lattice.

(40) **(C).** H-bond is one of the dipole-dipole interaction and dependent on inverse cube of distance between the molecules.

(41) **(D).**



(42) **(C).** (A) $B_2 : \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_x}^1\ \pi_{2p_y}^1$

B_2 contains two unpaired electrons hence paramagnetic.

(B) NO : odd electron species hence paramagnetic

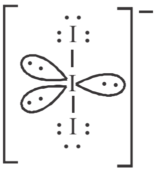
(C) $CO : \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_x}^2\ \pi_{2p_y}^2, \sigma_{2p_z}^2$

CO contains no unpaired electron hence diamagnetic.

(D) $O_2 : \sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_z}^2, \pi_{2p_x}^2\ \pi_{2p_y}^2, \pi_{2p_x}^{*1}\ \pi_{2p_y}^{*1}$

O_2 contains two unpaired electron hence paramagnetic.

(43) **(A).** I_3^- is - sp^3d hybridised - linear shape



Total number of lone pair of electron = 9

(44) **(A).** KCl exist as K^+ and Cl^-.

(45) **(B).** H_2^{2-} does not exist as Bond order is zero.

Electronic configuration of $H_2^{2-} : \sigma^2_{1s}\ \sigma^{*2}_{1s}$

(46) **(D).** Both Li_2^+ and Li_2^- has 0.5 bond order and hence both are stable.

(47) **(C).**

Chemical species	**Hybridisation of central atom**
ICl_2^-	sp^3d
IF_6^-	sp^3d^3
ICl_4^-	sp^3d^2
BrF_2^-	sp^3d

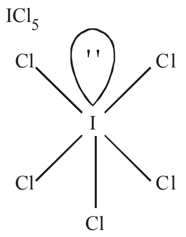
(48) **(A).**

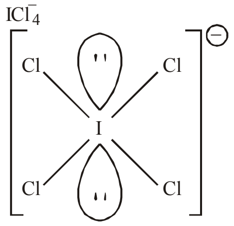
Chemical Species	Bond Order	Magnetic behaviour
C_2^{2-}	3	Diamagnetic
N_2^{2-}	2	Paramagnetic
O_2	2	Paramagnetic
O_2^{2-}	1	Diamagnetic

$$\text{B.O.} \propto \frac{1}{\text{Bond length}}$$

(49) **(C).**

Chemical species	Hybridisation	Shape
ICl_5	sp^3d^2	Square pyramidal
ICl_4^-	sp^3d^2	Square planar

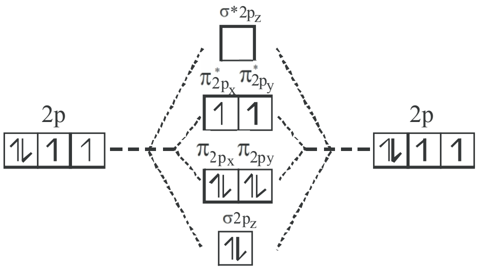


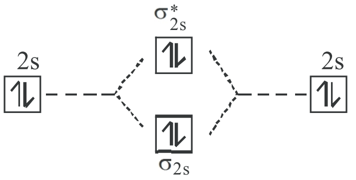


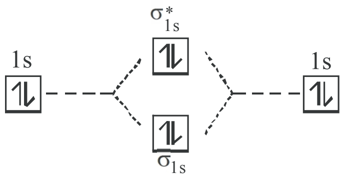
(50) **(B).** In case of only C_2, incoming electron will enter in the bonding molecular orbital which increases the bond order and stability too. Whereas rest of all takes electron in their antibonding molecular orbital which decreases bond order and stability.

(51) **(D).** O_2, NO, B_2 are paramagnetic according to M.O.T. where as CO is diamagnetic.

(52) **(C).** Molecular orbital diagram of O_2 is



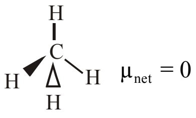


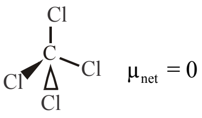


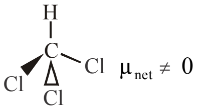
An incoming electron will go in $\pi^*_{2p_x}$ orbital.

(53) **(D).** In complex $[Ni(CO)_4]$ decrease in Ni–C bond length and increase in C–O bond length as well as it's magnetic property is explained by MOT.

(54) **(A).**







(55) **(A).** According to MOT (If z is internuclear axis)
The configuration of

$$CN^- : \sigma^2_{1s}, \sigma^{*2}_{1s}, \sigma^2_{2s}, \sigma^{*2}_{2s}, \pi^2_{2p_x} = \pi^2_{2p_y}, \sigma^2_{2p_z}$$

$$\text{Bond order} = \frac{1}{2}(10-4) = 3$$

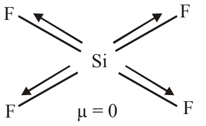
CN^- is diamagnetic due to absence of unpaired electron.

(56) **(C).** Bond energy $\propto \frac{1}{\text{Bond length}}$

EXERCISE-5

(1) **(C).** As difference of electronegativity increases % ionic character increases and covalent character decreases.
Further greater the charge on the cation more will be its covalent character. Be has maximum (+2) charge.

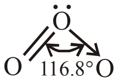
(2) **(B).** SF_4 has permanent dipole moment.
SF_4 has sp^3d hybridisation and see saw shape (irregular geometry).



XeF_4 shows square planar geometry.
SiF_4 has tetrahedral shape
BF_3 has trigonal planar shape.
All these are symmetric molecules. Hence $\mu = 0$.

(3) **(A).** BF_3 is sp^2 hybridized. So, it is trigonal planar. NH_3, PCl_3 has sp^3 hybridisation hence has trigonal bipyramidal shape, IF_3, has sp^3d hybridisation and has linear shape.

(4) **(B).** NO_2^- **:** Due to sp^2 hybridisation of N-atom and the presence of one lone pair on it, NO_2^- has angular shape:

O_3 :  V-shaped

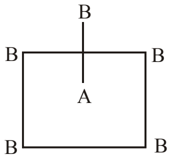
SO_2 : Due to the presence of one lone pair of electrons in one of the three sp^2-hybrid orbitals and sp^2 hybridisation of S or S^+ atom, SO_2 molecule has angular (V-shaped) structure : 

NO_2^+ : Due to sp hybridisation of N^+, NO_2^+ ion has linear shape : $:\ddot{O}=\overset{+}{N}=\ddot{O}:$

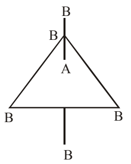
(5) **(D).** SCl_4, NH_4^+, SO_4^{2-} and PO_4^{3-} ions are the examples of molecules/ions which are of AB_4 type and have tetrahedral structure. SCl_4 is AB_4 (lone pair) types species. Although the arrangement of five sp^3d hybrid orbitals in space is trigonal bipyramidal, due to the presence of one lone pair of electron in the basal hybrid orbital, the shape of AB_4 (lone pair) species gets distorted and becomes distorted tetrahedral or see-saw.

(6) **(B).** Statement (A), (C), (D) are correct. Statement (B) is incorrect statement.

AB_5 may have two structures as follows :



square pyramidal



Trigonal Bipyramidal

(7) **(C).**

(a) SO_3^{2-} = pyramidal (sp^3, one lone pair)
NO_3^- = trigonal planar (sp^2)

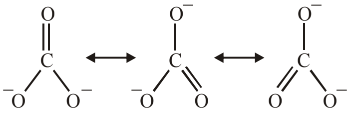
(b) BF_3 = trigonal planar (sp^2)
NF_3 = pyramidal (sp^3)

(c) BrO_3^- = pyramidal (sp^3, one lone pair)
XeO_3 = pyramidal (sp^3, one lone pair)

(d) SF_4 = irregular tetrahedron (sp^3d, one lone pair)
XeF_4 = square planar (sp^3d^2, two lone pair)

(8) **(C).** All these structures exhibits resonance and can be represented by the following resonating structures.

(i) $:\overset{-}{C}\equiv\overset{+}{O}: \longrightarrow :C=\ddot{O}:$

(ii) 

(iii) $:\underset{\cdot\cdot}{O}=C=\underset{\cdot\cdot}{O}: \longrightarrow :\overset{+}{O}-C\equiv\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}: \longrightarrow \overset{-}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\equiv C-\overset{+}{O}:$

More is the single bond character in resonance hybrid more is the bond length. Hence, the correct order is : $CO < CO_2 < CO_3^{2-}$

(9) **(A).** C_2^{2-} : B.O. = 3
NO : B.O. =2.5
O_2^- : B.O. = 1.5
He_2^+ : B.O. = 0.5

(10) **(C).** $NO_2^+ \rightarrow 180°$; $NO_2 \rightarrow 132°$
$NO_2^- \rightarrow 118°$

(11) **(D).** In between CH_3OH molecules intermolecular H-bonding exist.

(12) **(A).** Bond order $N_2 = 3$; $N_2^- = 2.5$
$N_2^{2-} = 2.0$

(13) **(B).** For sp^2 hybridisation, there must be 3σ-bonds or 2σ-bonds along with a long pair of electrons.

(i) $NO_2^- \Rightarrow 2\sigma + 1\ \ell p = 3$, i.e., sp^2 hybridisation
(ii) $NH_3 \Rightarrow 3\sigma + 1\ \ell p = 4$, i.e., sp^3 hybridisation
(iii) $BF_3 \Rightarrow 3\sigma + 0\ \ell p = 3$, i.e., sp^2 hybridisation
(iv) $NH_2^- \Rightarrow 2\sigma + 2\ \ell p = 4$, i.e., sp^3 hybridisation
(v) $H_2O \Rightarrow 2\sigma + 2\ \ell p = 4$, i.e., sp^3 hybridisation

Thus, among the given pairs, only BF_3 and NO_2^- have sp^2 hybridisation.

(14) **(B).** Molecules with zero bond order, do not exist.

(a) $Be_2^+ (4+4-1=7) = \sigma 1s^2, \sigma 1s^2, \sigma 2s^2, \sigma 2s^1$

$$BO = \frac{4-3}{2} = 0.5$$

(b) $Be_2\ (4+4=8) = \sigma 1s^2, \sigma 1s^2, \sigma 2s^2, \sigma 2s^2$;

$$BO = \frac{4-4}{2} = 0$$

(c) $B_2\ (5+5=10) = \sigma 1s^2, \sigma 1s^2, \sigma 2s^2, \sigma 2s^2,$
$\pi 2p_x^1 \approx \pi 2p_y^1$

$$BO = \frac{6-4}{2} = 1$$

(d) $Li_2\ (3+3=6) = \sigma 1s^2, \sigma 1s^2, \sigma 2s^2$ $BO = \frac{4-2}{2} = 1$

Thus, Be_2 does not exist under normal conditions.

(15) **(C).** Molecules having the same number of hybrid orbitals, have same hybridisation and number of hybrid orbitals, $H = \frac{1}{2}[V + X - C + A]$

where, V = number of valence electrons of central atom, X = no. monovalent atoms,
C = charge on cation, A = Charge on anion.

(1) In SF_4, $H = \frac{1}{2}(6+4-0+0) = 5$

(2) In I_3^-, $H = \frac{1}{2}(7+2+1) = 5$

(3) $SbCl_5^{2-}$, $H = \frac{1}{2}(5+5+2) = 6$

(4) In PCl_5, $H = \frac{1}{2}(5+5+0-0) = 5$

Since, only $SbCl_5^{2-}$ has different number of hybrid orbitals (i.e., 6) from the other given species, its hybrisation is different from the others, ie, sp^3d^2. (The hybridsation of other species is sp^3d).

(16) **(B).** For neutral molecules,
No. of electron pairs = No. of atoms bonded to it

$\frac{1}{2}$ [Group number of central atom
– Valency of central atom]

∴ For CH_4,

Number of e^- pairs $= 4 + \frac{1}{2}[4-4] = 4$

(sp^3 hybridisation)

For SF_4,

Number of e^- pairs $= 4 + \frac{1}{2}[6-4] = 5$

(sp^3d hybridisation)

For ions,

Number of electron pairs = Number of atoms bonded to it $+ \frac{1}{2}$ [Group number of central atom – Valency of central atom ± No. of electrons]

∴ For BF_4^- number e^- pairs

$= 4 + \frac{1}{2}[3-4+1] = 4$ (sp^3 hybridisation)

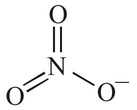
For NH_4^+, Number of e^- pairs $= 4 + \frac{1}{2}[5-4-1]$

$= 4$ (sp^3 hybridisation)

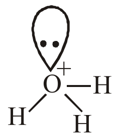
(17) **(A).** NO_3^-, $H = \frac{1}{2}[5+0-0+1]^3$

Thus, in NO_3^-, the central atom is sp^2 hybridised and it has trigonal planar geometry.

In H_3O^+, $H = \frac{1}{2}[6+3-1+0] = 4$



Thus, O is sp^3 hybridised in H_3O^+ and H_3O^+ has pyramidal geometry due to the presence of one lone pair of electrons.



(18) **(B).** $O_2^{(+)}$ has B.O 2.5

and B.O ∝ (1/ Bond length)

(19) **(B).** $NO_2^{(-)}$ and $NO_3^{(-)}$ both have same hybridisation

(20) **(B).** C – H : 0.109 nm ; C = C : 0.134 nm

C – O : 0.143 nm; C – C : 0.154 nm

(21) **(D).** Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally the lowest energy structure is the one with the smallest formal charges on the atoms.

(22) **(C).** MOT configurations of O_2 and O_2^+

$$O_2 : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x^2 = \pi 2p_y^2)\ (\pi^* 2p_x^1 = \pi^* 2p_y^1)$$

Number of unpaired electrons = 2,
so paramagnetic.

$$O_2 : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x^2 = \pi 2p_y^2)\ (\pi^* 2p_x^1 = \pi^* 2p_y^0)$$

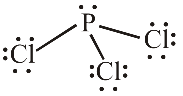
Number of unpaired electrons = 1,
so paramagnetic.

(23) **(D).** NF_3 (pyramidal) and BF_3 (trigonal planar)
BF_4^- (tetrahedral) and NH_4^+ (tetrahedral)
BCl_3 (trigonal planar) and $BrCl_3$ (trigonal bipyramidal)
NH_3 (pyramidal) & NO_3^- (trigonal planar)
Thus, BF_4^- & NH_4^+ are isostructural species.

(24) **(B).**

Species	**Bond order**
O_2^+	2.5
O_2^-	1.5
O_2^{2-}	1
O_2	2

(25) **(D).** PCl_3 :



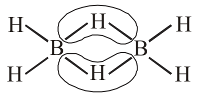
(26) **(A).** Both O_2^{2-} and B_2 had bond order = 1

(27) **(A).**

$$\underbrace{\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \begin{matrix} \pi 2p_x^2 \\ \pi 2p_y^2 \end{matrix} \begin{matrix} \pi^* 2p_x^2 \\ \pi^* 2p_y^1 \end{matrix} \sigma 2p_z^0}_{\text{For } O_2^-}$$

(28) **(D).** He_2^+ : B.O. = 0.5 ; O_2^- : B.O. = 1.5
NO : B.O. = 2.5 ; C_2^{2-} : B.O. = 3.0

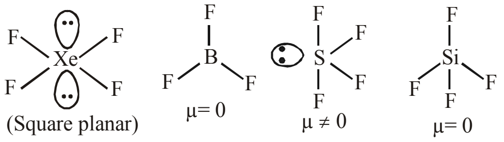
(29) **(D).** $(BH_3)_2 \rightarrow B_2H_6$



(3 centre- 2e⁻ bond electron deficient)

(30) **(C).** XeF_2 is isostructural with ICl_2^-.

(31) **(C).** Unsymmetrical distribution of e⁻ cloud leads to the formation of polar molecule

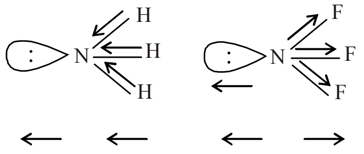


(32) **(C).** $O_2^-\ (2 \times 8 + 1 = 17)$ has odd number of electrons and hence it is paramagnetic. All the remaining molecules/ions, i.e., $CN^-(6+7+1=14)$ diamagnetic NO (7 + 8) = 15 has odd number of electrons and hence it is paramagnetic.

(33) **(D).** Dipole - induced dipole occurs b/w polar & Non-polar molecule HCl : Polar - $\mu \neq 0$ He : Non-polar - $\mu = 0$

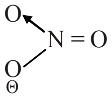
(34) **(C).** $\mu = \frac{:NH_3 >: NF_3}{\mu \neq 0} > \frac{CH_4 = CO_2}{\mu = 0}$

$$\mu = \ddot{N}H_3 :: NF_3$$



Atomic dipole & bond dipole are in same direction

Atomic dipole & bond dipole are in opposite direction

(35) **(B).** NO_3^-


Hybridisation : sp^2 ; Shape : plane triangular

(36) **(C).** ClO_3^- (sp^3 Hybridisation)

SO_3^{2-} (sp^3 Hybridisation) both have pyrimidal shape

Both contains same no of $e^- = 42\ e^-$

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

$O_2^+ \Rightarrow$ Bonding electrons = 10

antibonding electrons = 5;

$$B.O. = \frac{1}{2}[10-5] = 2.5$$

$O_2^- \Rightarrow$ Bonding $e^- = 10$; AB $e^- = 7$

$$B.O. = \frac{1}{2}[10-7] = \frac{3}{2} = 1.5$$

$O_2^{2+} \Rightarrow$ Bonding electrons = 10

Antibonding electrons = 4

$$B.O. = \frac{1}{2}[10-4] = \frac{6}{2} = 3$$

Bond order is : $O_2^- < O_2^+ < O_2^{2+}$

(38) **(B).** NO_2^+ sp-hybridisation so it is linear with bond angle 180°. $O = \overset{+}{N} = O$

(39) **(C).** Given species : $O_2, O_2^-, O_2^+, O_2^{2-}$

Total number of electrons

$O_2 \rightarrow 16e^-$

$O_2^{-1} \rightarrow 17e^-$

$O_2^{+1} \rightarrow 15e^-$

$O_2^{2-} \rightarrow 18e^-$

	O_2^{+1} >	O_2 >	O_2^- >	O_2^{2-}
Bond order	2.5	2	1.5	1

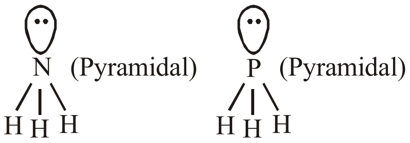
Stability × B.O.

* Stability order $[O_2^{+1} > O_2 > O_2^{-1} > O_2^{2-}]$

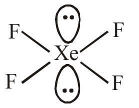
(40) **(B).**

(i) Hybridisation of NH_3 [σ = 3, lp = 1]

sp^3 geometry : tetrahedral



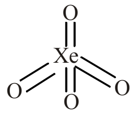
(ii) Structures of XeF_4 is square planar.



sp^3d^2 hybridisation

(Square planar)

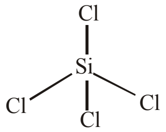
Structure of XeO_4 is tetrahedral



sp^3 hybridisation

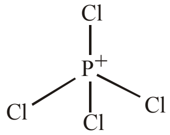
so XeF_4 and XeO_4 are not isostructural

(iii) Structure of $SiCl_4$ is tetrahedral



sp^3 hybridisation

Structure of PCl_4^+ is tetrahedral



sp^3 hybridisation

(iv) Diamond & SiC both are isostructural because both have tetrahedral arrangement and central atom is sp^3 hybridised.

(41) **(B).** Molecules Bond angle

$CH_4 \rightarrow 109.5°$; $NH_3 \rightarrow 107.5°$

$H_2O \rightarrow 104.45°$

(42) **(A).** The order of repulsion force according to VSEPR theory : lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

(43) **(C).** In acetic acid, H_2O_2 and HCN inter molecular hydrogen bond present but in cellulose intramolecular hydrogen bond present.

(44) **(C).** NO_2^+ : Number of electron pairs = 2

Number of bond pairs = 2

Number of lone pair = 0

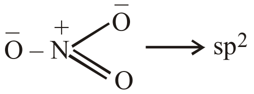
The species is linear with sp hybridisation.

$$O = \underset{sp}{\overset{+}{N}} = O$$

NO_3^- : Number of electron pairs = 3

Number of bond pairs = 3, Number of lone pair = 0

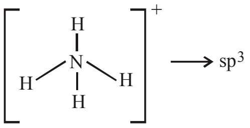
So, the species is trigonal planar with sp^2 hybridisation.

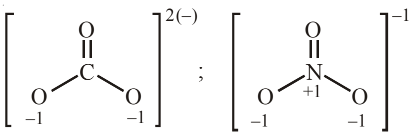


NH_4^+ : Number of electron pairs = 4

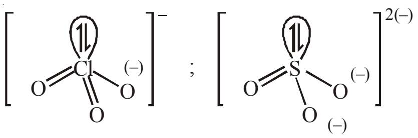
Number of bond pairs = 4, Number of lone pair = 0

So, the species is tetrahedral with sp^3 hybridisation.



(45) **(D).**


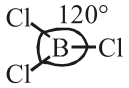
Both have 32 electrons with trigonal planar structure.



Both have 42 electrons with pyramidal structure.

(46) **(B).** Both IBr_2^- and XeF_2 are linear and sum of all the valence electrons in both the species is same so they are iso-electronic also.

(47) **(C).** BCl_3 :



Regular geometry

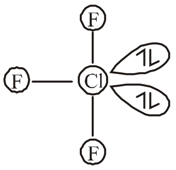
$\Rightarrow$ Hybridysation sp^2

(48) **(B).** Total no. of electrons in CN^- is 14.

Total no. of electrons in CO is also 14.

Hence, B.O. of both CN^- & CO is 3.

(49) **(B).** The structure of ClF_3 is



The number of lone pair of electrons on central Cl is 2.

(50) **(B).** NO : $(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^*2p_x)^1 = (\pi^*2p_y)^0$

$$BO = \frac{10-5}{2} = 2.5$$

CN^- : $(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^*2p_z)^2$

$$BO = \frac{10-4}{2} = 3$$

CN : $(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma\, 2p_z)^1$

$$BO = \frac{9-4}{2} = 2.5$$

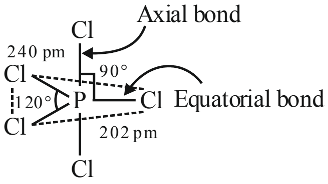
CN^+ : $(\sigma 1s)^2, (\sigma^*1s)^2, (\sigma 2s)^2, (\sigma^*2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2$

$$BO = \frac{8-4}{2} = 2$$

(51) **(C).** MO configuration C_2 is:

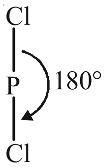
$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \pi 2p_x^{\,2} = \pi 2p_y^{\,2}$

(52) **(D).**



(A) True

(B) True



(C) True. Axial bond : 240 pm ; Equatorial bond : 202 pm

(D) False. Due to longer and hence weaker axial bonds, PCl_5 is a reactive molecule.