04

Chemical Bonding and Molecular Structure

"Chemical bonding is the phenomenon of union of two or more atoms by redistribution of electrons, so that each atom involved in bonding acquires stable configuration to achieve stability or a state of lower energy".

Bond and Valency

A bond is defined as "a kind of net inter-atomic, inter-molecular, or inter-ionic attraction or attractive force which holds two or more constituents, i.e. together." The constituents here can be atoms, molecules or ions.

- The combining capacity of constituents of different element is called their **valency**.
- In case of elements of I A and II A group it is equal to their group number, i.e. 1 and 2 respectively.
- For other elements it varies from group number to (group number −8) Here, group number are taken in accordance with modern periodic table. e.g. Nitrogen, an element of group V A, has valency from + 5 to − 3 [i.e.(5 − 8)].

Bonding Types

Depending upon the nature of combining constituents (atoms, ions) and nature of attractive forces, the bonds can be of following two types

1. Physical Bonds

In this case, various molecules attract each other by physical forces like hydrogen bonding, van der Waals' forces etc. These bonds are weaker than chemical bonds due to less strong attractive forces involved. The energy involved in their formation is less than 40 kJ mol^{-1}.

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2. **Chemical Bonds**

These bonds involve proper redistribution of electrons to achieve the state of lower energy. It is done either by sharing or by transfer of electrons. Here, the energy involved in bond formation exceeds 40 kJ mol^{-1}.

A chemical bond is further classified into following types

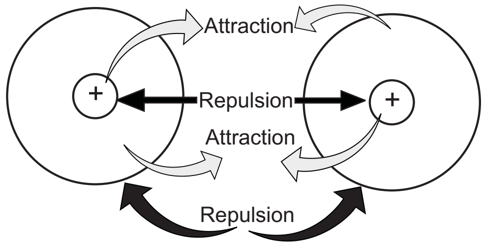
- Electrovalent or ionic bond
- Covalent bond
- Coordinate covalent bond

Before going in detail about these bonds it is better to understand following basics about chemical bonds.

Basis of Chemical Bonding

The cause or basis of attractive forces or chemical bond, can be easily understood if we look at structure of an atom having positive nucleus and negative electrons. When two atoms come closer to combine, their attractive and repulsive forces operate as shown in figure given below

The net result of these forces may be either attraction or repulsion between the atoms. A bond is formed only if the net result of interaction is in the form of attraction. So we can say that the agency, i.e. basis of a chemical bond is similar in all cases. The involvement of charges signify that these forces are **electrostatic** in nature as these operate beween charges.

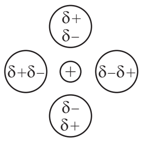
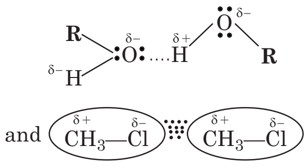


Attractive and repulsive forces between two atoms

Now, the question arises, why these attractive forces are called by different names then?

Answer of this question lies in one sentence and that is "the different names to bonds are assigned due to difference in the intensities of these forces".
These difference are summarised in the following table

Various Attractive Electric Forces

Electric force	Relative strength	Type	Example
Cation-anion (in a crystal) or **ionic bond**	Very strong	⊕ ⊖	Lithium fluoride crystal lattice
Covalent bonds	Strong (140-523 kJ mol^{-1})	Shared electron pairs	H — H (435 kJ mol^{-1}) CH_3 —CH_3 (370 kJ mol^{-1}) I — I (150 kJ mol^{-1})
Ion-dipole	Moderate		Na^+ in water
Dipole-dipole (including hydrogen bonds)	Moderate to weak (4-38 kJ mol^{-1})	$-\overset{\delta-}{Z}\,:\cdots\cdots\overset{\delta+}{H}-$	
van der Waals'	Variable	Transient dipole	Interactions between methane molecules

Basic Theories of Chemical Bonding

Formation of chemical compounds and bonding in them raises many questions like

- Why do atoms combine?
- Why are only certain combinations possible? etc.

In order to answer such questions different theories and concepts have been put forward from time to time, out of which the important one are as follows

Kossel-Lewis Approach (Octet Rule)

In 1961, Kossel and Lewis proposed a concept on the basis of electronic configuration of elements. This concept was called **electronic concept of valency** or octet rule, later on Langmuir, extended it.

The main points of this approach are as follows

- The outer most shell of an atom is called the **valence shell** and the electrons present in it are called **valence electrons**.
- The inertness of noble gases is due to their stable configurations, i.e. due to the presence of eight electrons (except He) in their valence shell.
- On this basis, Kossel and Lewis proposed that elements having eight electrons in their outer shell, i.e. having complete octet, are chemically inert. Hydrogen is the only exception which has 2 electrons in its valence shell. This is called popularly as octet rule.
- Elements that do not have complete octet have a high tendency to attain this configuration either by losing or gaining or sharing electrons to the atoms of same or other elements. All these are used as means in bonding.

Lewis Symbols

These are simplest symbols or notation used to denote bonding patterns between different atoms.

These notations represent the symbol of an element with valence electrons in its one atom as

$$\underset{(2\text{ valence }e^-)}{\cdot\text{Be}\cdot}\ ,\qquad \underset{(3\text{ valence }e^-)}{\cdot\dot{\text{B}}\cdot}\ ,\qquad \underset{(5\text{ valence }e^-)}{\cdot\ddot{\text{N}}:}$$

In Lewis dot structure, the electrons may be represented by a dot or a cross usually. General steps that one can follow to write the Lewis structure are

- Calculate the total number of valence electrons of atom/atoms involved in a molecule.
- If species is charged there substraction or addition of the requisite number of electrons in needed accordingly.
- Here, addition is needed for negative charge and substraction is needed for positive charge.
- Select the central atom which is generally the least electronegative atom and draw the skeletal structure by making an intelligent guess to indicate which atom is linked to which atom.

In Lewis representations, the number of bonds = $\dfrac{n_1 - n_2}{2}$

where, n_1 = number of atoms (other than H) × 8 + no. of H atoms × 2

n_2 = number of valence electrons of all isolated atoms + (negative charge) – (positive charge)

e.g. In N_2, $n_1 = 2 \times 8 + 0 = 16$; $n_2 = 5 \times 2 + 0 - 0 = 10$

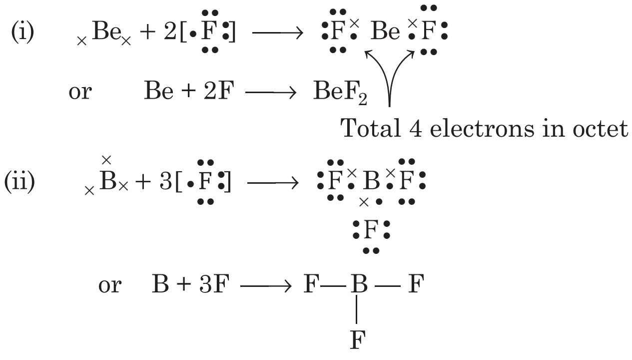
Number of bonds $= \dfrac{n_1 - n_2}{2} = \dfrac{16 - 10}{2} = 3$

So, the Lewis representation of N_2 is $\ddot{\text{N}} \equiv \ddot{\text{N}}$

Violation of Octet Rule

As a general perception this octet rule is acceptable to most of the cases. However, the octet rule is violated also in a significant number of cases. For example

- Be and B have less than 4 valence electrons, hence their octet cannot be completed even if they bind with their full strength. e.g.



(i) Be + 2F ⟶ BeF_2

Total 4 electrons in octet

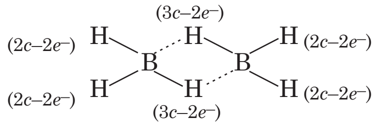
(ii) B + 3F ⟶ F—B—F (with F below B)

Total 6 electrons in octet

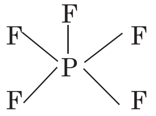
- In molecules with odd number of electrons, the octet rule is not satisfied for all the atoms, e.g. in molecules like NO, NO_2, ClO_2^-, etc., as they have 2 centre three electron bond.

In both above case, there are total 7 electrons in nitrogen octet.

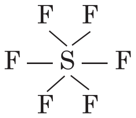
- It also does not explain the formation of 3 centre two electron bonds as found in B_2H_6.



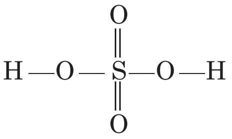
- In a number of compounds there are more than 8 valence electrons present in the central atom. This is termed as **expanded octet.** This tendency is seen in elements beyond the 3rd period of the periodic table as they have vacant *d*-orbitals for bonding.
- Obviously octet rule is not applicable in such cases. Some of the examples of such compounds are PF_5, SF_6, H_2SO_4, etc.



10 electrons in valence shell of P



12 electrons in valence shell of S



12 electrons in valence shell of S

The other limitations of octet rule include

- The shape of the molecule is not clear
- It is totally silent about the energy of the molecule, i.e. relative stability.

Ionic or Electrovalent Bonding and Electrovalency

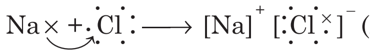
The attractive forces of an ionic bond are developed between an electropositive and an electronegative atom. It is usually said to occur *via* complete transfer of electron from one atom to another. The general condition followed here is, "larger the electronegativity difference between the atoms, stronger is the bond".

e.g. Consider the formation of the compound "NaCl"

$$\underset{(1s^2, 2s^2, 2p^6, 3s^1)}{\text{Na}} \longrightarrow \underset{(1s^2, 2s^2, 2p^6)}{\text{Na}^+} \quad \text{(cation formation)}$$

$$\underset{(1s^2, 2s^2, 2p^6, 3s^2, 3p^5)}{\text{Cl}} + e^- \longrightarrow \underset{(1s^2, 2s^2, 2p^6, 3s^2, 3p^6)}{\text{Cl}^-} \quad \text{(anion formation)}$$

$$\text{Na}^+ + \text{Cl}^- \longrightarrow \overset{+}{\text{Na}}\overset{-}{\text{Cl}} \quad \text{(molecule formation)}$$



(Lewis diagram)

Forces of ionic bond can be seen between any two oppositely charged atoms (or ions) even from different sources, e.g.

$$\text{H}^+\text{Cl}^-(l) + \text{Na}^+\text{OH}^-(l) \longrightarrow \text{Na}^+\text{Cl}^-(s) + \text{H}_2\text{O}\,(l)$$

In the above reaction, Cl^- from H^+Cl^- and Na^+ from $\overset{+}{\text{Na}}\overset{-}{\text{OH}}$ come together to from ionic bonds.

Remember If the difference between electronegativity is around 1.9 or more then the bond is generally ionic.

Electrovalency

The number of electrons lost (or gained) by an atom during the formation of ionic bond is called the electrovalency of that atom.

Variable Electrovalency and its Reasons

For most of the atoms, its value is fixed and depends upon the number of valence electrons. However, certain elements like metals show more than one electrovalency in their electrovalent compounds.

The atoms of these elements lose different number of electrons under different conditions, thereby showing variable electrovalency.

It is due to the following two reasons.

1. Inert Pair Effect

In case of heavier p-block elements, the outer ns^2 electrons attracted strongly towards nucleus. Due to this they don't have tendency to participate in bond formation.

Hence, inert pair effect is defined as, "the reluctance of valence s-electrons to take part in bond formation or tendency of outer s-electrons to remain together".

e.g. Lead and Bismuth

Pb	(IV group)	2,8,18,32,18, $6s^2 6p^2$	
Pb^{2+}		2,8,18,32,18, $6s^2$	Only two $6p$-electrons are lost
Bi	(V group)	2,8,18,32,18, $6s^2 6p^3$	
Bi^{3+}		2,8,18,32,16, $6s^2$	Only three $6p$-electrons are lost

When sufficient energy is available, the s-electrons also enter into bond formation and higher valencies are observed. e.g. Pb^{4+} = 2, 8, 18, 32, 18.

This tendency to show higher valencies is less in the case of Tl, Pb and Bi but more in the case of comparatively lighter elements such as In, Sn, Sb, etc.

2. Instability of the Core

The residue configuration left after the loss of valence electrons is called the **core** or **kernel**. In case of transition elements, ions formed after the loss of valence electrons do not results to a stable core as the configuration of outermost shell is not ns^2np^6, but $ns^2np^6d^{1\text{ to }10}$.

The outer shell generally loses one or more electrons giving rise to metal ions of higher valencies e.g.

Iron

$$\text{Fe}\ (26) = [\text{Ar}] \quad 3s^2 \quad 3p^6 \quad 3d^6 \quad 4s^2$$

$$\text{Fe}^{2+}\ (24) = [\text{Ar}] \quad 3s^2 \quad 3p^6 \quad 3d^6 \quad \text{(Not stable)}$$

$$\text{Fe}^{3+}\ (23) = [\text{Ar}] \quad 3s^2 \quad 3p^6 \quad 3d^5 \quad \text{(Stable)}$$

Thus, iron exhibits $+2$ and $+3$ oxidation state. The compounds of Fe^{3+} (ferric ion) are more stable than the compounds of Fe^{2+} (ferrous ion).

Copper

The only electron present in the outermost shell of copper atom is lost by it to get converted into Cu^+ (cuprous) ion.

$$\text{Cu}(29) = [\text{Ar}] \quad 3s^2 3p^6 3d^{10}, 4s^1$$

$$\text{Cu}^+(28) = [\text{Ar}] \quad 3s^2 3p^6 3d^{10}$$

The $s^2p^6d^{10}$ configuration is not as stable as s^2p^6 configuration and the nuclear charge is not sufficiently strong to hold all the electrons intact in their positions. Thus, Cu^+ ion loses one more electron to form Cu^{2+} (cupric) ion. The Cu^{2+} ion is quite stable as the nuclear charge is sufficient to hold 27 electrons intact.

$$\text{Cu}^{2+} = [\text{Ar}] \quad \text{or} \quad 3s^2 \ 3p^6 \ 3d^9$$

Thus, cupric (Cu^{2+}) compounds are more stable than cuprous (Cu^+) compounds.

However, the above two explanations fail to account why

(i) Co^{2+} ion cannot be easily converted into Co^{3+} ion like Fe^{2+} ion.

(ii) Zn^{2+} ion does not lose one more electron as its configuration $(3s^2\ 3p^6\ 3d^{10})$ is similar to Cu^+ ion.

For the answer to such questions in general, we can say that whenever the core is unstable, it loses one or more electrons to show higher valency. On the other hand, if the core is comparatively stable it always resists the loss of more electrons.

So, the cores of Co^{2+} ion and Zn^{2+} ion are comparatively stable hence, both the ions resist such changes.

Factors Affecting the Formation of Ionic Bonds

The formation of an ionic bond is related to the ease of formation of cations and anions.

All those factors which help in the formation of ions are given below in a summarised way

- The ionisation enthalpies involved should be low so that the metal atom forms a positive ion easily.
- The quantitative values of electron gain enthalpies should be high, (in negative value) so that the non-metal atom forms a negative ion easily.
- Lattice enthalpies involved should be high.

Lattice Enthalpy (U)

The enthalpy involved when gaseous positive and negative ion enthalpy involved come together to form 1 mole of the solid ionic compound is called lattice enthalpy (U). e.g.

$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s); \qquad \Delta H = -U$$

For the reverse process,

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g); \ \Delta H = +U$$

Lattice enthalpy varies in the following manner,

$$\text{Lattice enthalpy} \propto \text{charge of ions and size of anion}$$

$$\propto \frac{1}{\text{size of cations}}$$

It can be calculated using **Born-Haber cycle**.

Born-Haber Cycle

The fundamentals of this cycle is based upon the fact that the formation of an ionic crystal may occur either by direct combination of the elements or by an alternate process in which following steps are involved

- The reactants are vaporised to convert into gaseous state.
- The gaseous atoms are converted into ions.
- The gaseous ions are combined to form ionic lattice of molecules.

So, for the generalised reaction,

$$M(s) + \frac{1}{2}X_2(g) \longrightarrow MX(s), \quad \Delta H_1 = Q$$

Steps involved are

(i) $M(s) \longrightarrow M(g), \qquad \Delta H = S$

(ii) $M(g) \longrightarrow M^+(g) + e^-, \qquad \Delta H = I$

(iii) $\frac{1}{2}X_2(g) \longrightarrow X(g), \qquad \Delta H = \frac{D}{2}$

(iv) $X(g) + e^- \longrightarrow X^-(g), \qquad \Delta H = -E$

(v) $M^+(g) + X^-(g) \longrightarrow MX(s), \qquad \Delta H = -U$

$$\Delta H_2 = S + I + \frac{D}{2} - E - U$$

where, S = heat of sublimation
I = ionisation energy
D = dissociation energy
E = electron gain enthalpy
and U = lattice enthalpy

ΔH_1 and ΔH_2 represent the enthalpy change for the same chemical change. Hence, $\Delta H_1 = \Delta H_2$

$$\therefore \qquad Q = S + I + \frac{D}{2} - E - U$$

$$\therefore \qquad U = S + I + \frac{D}{2} - E - Q$$

Lattice enthalpy (or lattice energy) play an important role in deciding the solubility of ionic solids. It affects the solubility in the following manner

- **If the anion and the cation are of comparable size,** the cationic radius will influence the lattice energy. Since, with increasing ionic size lattice energy decreases much more than the hydration energy so the solubility will increase as we go down the group.
- **If the anion is large as compared to the cation**, the lattice energy will remain almost constant within a particular group.

  Since, the hydration energies decrease down a group, solubility will also decrease as found for alkaline earth metal carbonates and sulphates.

Example 1. If the ionisation energy of Na is 495.8 kJ mol^{-1}, the electron affinity of Cl is 349.4 kJ mol^{-1} and lattice energy is 776 kJ mol^{-1}, the true statement for the formation of ionic bond in NaCl is

(a) total energy released per mole of NaCl formed is 628.6 kJ
(b) the ionic bond formed is unstable
(c) the total energy absorbed per mole of NaCl formed is 1125.4 kJ
(d) net energy released in this process is 629.6 kJ

Sol. *(d)*

$$\mathrm{Na}(g) + 495.8 \longrightarrow \mathrm{Na}^+(g) + e^- \qquad \text{...(i)}$$

$$\mathrm{Cl}(g) + e^- \longrightarrow \mathrm{Cl}^-(g) + 349.4$$

$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s) + 776 \text{ kJ mol}^{-1}$$

Total energy released per mole of NaCl formed

$$= 776 + 349.4 = 1125.4 \text{ kJ}$$

Total energy absorbed in step (i) = 495.8 kJ

Net energy released = 629.6 kJ

Thus, a stable ionic bond is formed between NaCl.

Example 2. *Lattice enthalpy and enthalpy of solution of* NaCl *are* 788 kJ mol^{-1} *and* 4 kJ mol^{-1}, *respectively. The hydration enthalpy of* NaCl *is* ***(JEE Main 2020)***

(a) −780 kJ mol^{-1}
(b) 780 kJ mol^{-1}
(c) −784 kJ mol^{-1}
(d) 784 kJ mol^{-1}

Sol. *(c)* The enthalpy of solution of an ionic solid is numericlly equal to the sum of its hydration and lattice energies, i.e. $\Delta H^\circ_{sol} = \Delta H^\circ_{hydration} + \Delta H^\circ_{lattice}$

$$\begin{tikzcd}
\therefore \ \text{NaCl}(s) \arrow[rr, "\Delta H = 4"] \arrow[dr, "\Delta H^\circ = 788"'] & & \text{NaCl}(aq) \\
& \text{Na}^+(g) + \text{Cl}^-(g) \arrow[ur, "\Delta H^\circ_{hyd}"'] &
\end{tikzcd}$$

$$\Delta_{sol}H^\circ = \Delta_{lattice}H^\circ + \Delta_{hyd}H^\circ$$

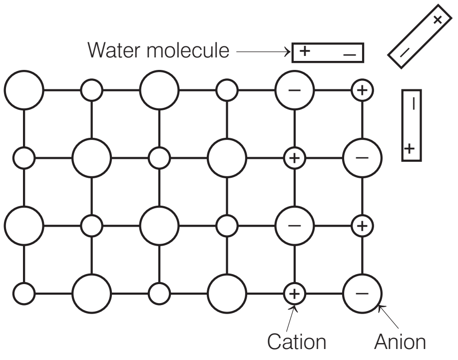
$$4 = 788 + \Delta_{hyd}H^\circ$$

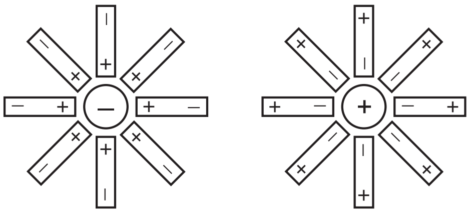
$$\Delta H_{hyd}H^\circ = -784 \text{ kJ/mol}$$

Characteristics of Ionic Compounds

The main characteristics of ionic compounds are as follows

- These are usually crystalline in structure. Thus, at normal temperature and pressure, these are solids with **low volatility, high stability** and **high density.**
- Due to strong forces of attraction, these possess high melting and boiling points.
- These are **very hard** and **brittle** as their crystal planes can be separated very easily.
- Ionic bonds are always **non-rigid** and **non-directional,** and thus, do not exhibit space isomerism.
- Ionic compounds do not conduct electricity in solid state but these are very good conductors when fused or dissolved in a solvent of high dielectric constant. This property is visible due to the presence of mobile ions in them.
- Ionic compounds with same electronic configuration are isomorphous, i.e. structurally same to each other. i.e. ionic compounds undergo very fast reactions in solution which are of simple ion exchange type.
- These are soluble in polar solvents like water because polar solvent molecules interact very strongly with the ions of crystal by **solvation** or **hydration**.
- The high solvation or hydration energy released as the result of interaction is sufficient to break the lattice structure. Ions within the solution acquire greater degree of motion.





Solubility of ionic compounds in polar solvent

Note For dissolution solvation energy > lattice energy and dissolution is also favoured by high dielectric constant of solvent, e.g.

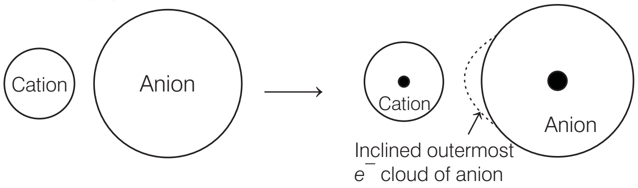
Solvent	H_2O	CH_3OH	C_2H_5OH	CH_3COCH_3	CH_3OCH_3
Dielectric constant	81	35	27	21	4.1

—capacity for dissolving ions decreases ⟶

Polarisation and Polarisability

When two oppositely charged ions of unequal size approach each other closely, the ion with smaller size attracts outermost electrons of the other ion and repel its nuclear charge. The net result of this is distortion or polarisation of the bigger ion which is generally the anion. This distortion is usually done by the cation as its size is smalller than the anion.

In this the electron cloud of anion no longer remains symmetrical but is a bit inclined towards the cation as shown below.



(a) No polarisation (b) Polarised anion by cation

Representation of polarisation

The ability of a cation to polarise the nearby anion is called its **polarising power** and the tendency of an anion to get distorted or deformed or polarised by the cation is called its **polarisability**.

As in the process inclination of electronic character is visible from anion towards cation so some covalent character is visible in such ionic bond.

Variation of Polarising Power/ Polarisability in the Periodic Table

- On moving down the group, the polarising power of the cations decreases.
- Polarising power of the cations increase on moving from left to right in a period.
- The polarisability of the anions by a given cation decreases on moving from left to right in a period.
- The polarisability of the anions by a given cation increases on moving down a group.

Fajan's Rule

Fajan gave the following rules to decide the magnitude of polarisation or covalent character in an ionic bond

(i) **Higher charge on cation or anion** As the charge on the cation increases, its tendency to polarise the anion increases and *vice-versa*. This brings more and more covalent nature in the electrovalent compound, e.g. in case of NaCl, $MgCl_2$ and $AlCl_3$, the polarisation increases from NaCl to $AlCl_3$, thereby covalent character increases as the charge on the cation increases (Na^+, Mg^{2+}, Al^{3+}).

A larger anion, i.e. anion with more charge is polarised more and thus, also result in increased covalent character, e.g. $CaSO_4$ is more covalent than $Ca(NO_3)_2$.

(ii) **Smaller size of cations** Smaller cation usually possess higher charge, thus causing more polarisation of anion. Hence, we can say that ionic compounds having smaller cations show more covalent nature.

(iii) **Larger size of anions** In such anions, the outer electrons will be at a greater distance from the nucleus, hence, more easily influenced by the attractive forces of cation. As the result larger anions will be more easily polarised in comparison to smaller anions.

(iv) **Non-inert gas configuration** The polarising power of those cations which don't have inert gas configuration will be more in comparison to cations having inert gas configuration.

e.g. Polarising power of Cu^+ ion (electronic configuration 2, 8, 18) is more in comparison with polarising power of Na^+ ion (electronic configuration 2, 8).

Effect of Fajan's Rule

Generally, electrovalent compound having high values of polarisation, i.e. more covalent character, are found to be less soluble in water but more soluble in organic solvents. This can be seen in the following examples

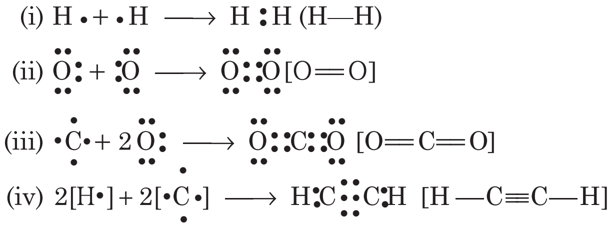
- Sulphides are less soluble in water than oxides of the same metal.
- Lithium salts are soluble in organic solvents.
- Beryllium compounds are less soluble in water than corresponding other alkaline earth metal compounds.
- The solubility of aluminium halides decreases from AlF_3 to AlI_3.

Covalent Bonding

In "covalent bond" the attractive forces are developed due to **the sharing of electron pair**.

Here, usually each member contribute atleast one electron and each element acquires inert gas electronic configuration.

e.g. Consider following Lewis structures



Conditions

Favourable conditions for covalent bond formation are as follows

- Electronegativity difference between the combining atoms should be small.
- Combining atoms should have incomplete valence shell electronic configurations.

Covalency

The number of electron(s) contributed by an atom for the formation of a covalent bond in order to achieve inert gas electronic configuration is known as its covalency.

Generally covalency of an element is equal to sum of unpaired electrons present in its *s* and *p*-orbitals.

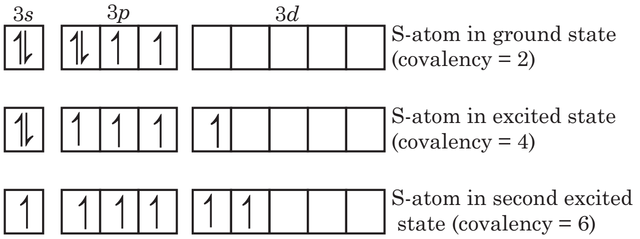
The covalency of hydrogen is 1 and for *p*-blcok non-metals it is calculated by 8 minus group number. Just like electrovalency the elements of *d*-block show variable covalency as well.

Maximum covalency of elements in some periods are

- For second-period-4
- For third-period-6
- For forth-period-8

Such a variation in maximum covalency can be explained on the basis of absence of vacant *d*-orbitals in 2nd period elements and their availability in 3rd and subsequent period elements.

e.g. In case of sulphur,



On this basis, we can explain why compounds like OF_6, NCl_5 or ions like CF_6^{2-}, NF_6^{3-} do not exist and compounds like ICl, ICl_3, IF_5, IF_7 or ion like SiF_6^{3-}, PF_6^{3-} can be formed.

Types of Covalent Bonds

The covalent bonds can be of following two types

(i) **Non-polar covalent bond** If the covalent bond is formed between two **homonuclear** atoms, i.e. between the atoms of exactly equal electronegativity, the electron pair is equally shared between them. Such a bond is called non-polar covalent bond, e.g. H_2, Cl_2, F_2, Br_2, etc.

(ii) **Polar covalent bond** It is seen when the bond forming entities are dissimilar, i.e. **heteronuclear** or have different electronegativity. In such cases the bond formed has partial ionic character as the electron pair is attracted by more electronegative entity. Such a bond is called polar covalent bond. e.g.

$$\overset{\delta+}{H}\cdots\overset{\delta-}{O}\cdots\overset{\delta+}{H} \qquad \overset{\delta+}{H}\cdots\overset{\delta-}{Cl}$$

The greater the difference in electronegativity, higher is the polar nature of bond.

The ionic character in a polar bond can be calculated by the following methods

- **Pauling** gave the following equation to calculate the percentage ionic character of a polar bond by using electronegativity difference $(x_A - x_B)$

  Amount of ionic character in *A* – *B* bond

  $$= [1 - e^{0.25(x_A - x_B)}]\%$$

  or $$[18(x_A - x_B)^{1.4}]\%$$

  With the help of this equation Pauling established the following relation

$(x_A - x_B)$	—	0.6	1.0	1.4	1.7	2.0	2.4	3.0	3.2
% ionic character	—	9	22	39	51	63	76	91	92

At about midway between covalent and ionic character

- **Hannary** and **Smith** also used the electronegativity difference $(x_A - x_B)$ to find the percentage ionic character by the following expression.

  Ionic character in *A*—*B* bond

  $$= [16(x_A - x_B) + 3.5(x_A - x_B)^2]\%$$

- There is an another method also which is based on dipole moment and given on page 127.

Characteristics of Covalent Compounds

The main characteristics of covalent compounds are given below

- Normal covalent compounds are **gases** or **liquids** under ordinary conditions of temperature and pressure. Some of these compounds are soft solids also, e.g. Cl_2 (mol. wt. = 71) is a gas, Br_2 (mol. wt. = 160) is a liquid, I_2 (mol. wt. = 254) is a volatile solid.
- In solid state crystals covalent compounds are of three types mainly
  - (i) **Soft**, **easily fusible**, **volatile crystals** in which molecules are held by weak van der Waals' forces, e.g. crystals of organic compounds, sulphur, iodine etc.
  - (ii) **Very hard crystals** in which every atom is bonded with the other atoms resulting in the formation of a **giant molecule**, e.g. diamond crystal.
  - (iii) The crystals which consists of separate **lattice layer**, e.g. graphite. These crystals are very soft and of lubricating nature.
- With a few exceptions like diamond, carborundum and silica covalent compounds have relatively low values of their melting and boiling points.
- The covalent bond is **rigid** and **directional** hence, different spatial arrangements of atoms are possible. Thus, these compounds exhibit structural as well as space isomerism.
- In general, covalent compounds are bad conductors of electricity in fused as well as in solid state. *However, graphite can conduct electricity as it possess free electrons in its layers.*
- In general, covalent compounds are insoluble in polar solvents like water but have the tendency to dissolve in non-polar solvents like benzene, CCl_4, ether etc. However, some of them like alcohols are miscible with water due to intermolecular H-bonding.
- The reactions of covalent compounds are slow and complex as these involve proper fission of older bonds and formation of new bonds.

Parameters of Covalent Bonds

Covalent bonds are characterised by some parameters which are as follows

1. Bond Length

The average distance between the centre of nuclei of the two bonded atoms in a covalent molecule is known as bond length. It depends upon the size of atoms, hybridisation, steric effect, resonance etc.

Usually bond length of polar bond is smaller as compared to a non-polar bond. Bond length increases as the size of atom or orbital increases.

Bond length of different homonuclear molecules proved very useful in calculations regarding different radii associated with their atoms.

Average bond length of some single, double and triple bonds along with bond lengths of some common molecules is given below.

Average Bond Length for Some Single, Double and Triple Bonds

Bond type	Covalent bond length (pm)
O—H	96
C—H	107
N—O	136
C—O	143
C—N	143
C—C	154
N=O	121
C=C	133
C=N	138

Bond type	Covalent bond length (pm)
C═N	116
C═C	120
H_2 (H—H)	74
F_2 (F—F)	144
Cl_2 (Cl—Cl)	199
Br_2 (Br—Br)	228
I_2 (I—I)	267
N_2 (N≡N)	109
O_2 (O═O)	121
HF (H—F)	92
HCl (H—Cl)	127
HBr (H—Br)	141
HI (H—I)	160

2. Bond Enthalpy

Bond enthalpy is the amount of energy required to break a particular bond in one mole of gaseous molecule.

$$\text{Bond enthalpy} \propto \text{electronegativity}$$
$$\propto \frac{1}{\text{size of atoms}}$$
$$\propto \frac{1}{\text{number of lone pair of electrons}}$$

The units of bond enthalpy are kJ mol^{-1}. Some examples of bond enthalpies are

$$\text{H—H} = 435.8 \text{ kJ/mol}; \text{O} = \text{O} = -498 \text{ kJ/mol};$$
$$\text{N} \equiv \text{N} = -946 \text{ kJ/mol}; \text{H—Cl} = -431 \text{ kJ/mol}$$

Remember, larger the bond (dissociation) enthalpy, stronger will be the bond in the molecule.

In general within the polyatomic molecules the bond enthalpy calculations are more complicated as these enthalpies differ considerably within a single molecule. For example, in case of H_2O the enthalpies of both the bonds differ as

$$\text{Ist OH bond} = -502 \text{ kJ/mol}$$
$$\text{IInd OH bond} = -427 \text{ kJ/mol}$$

This is the reason behind the fact that in polyatomic molecules the term **mean** or average bond enthalpy is used. In simple terms it is obtained by dividing total bond dissociation enthalpy by number of bonds broken.

Example 3. *Arrange the following bonds according to their average bond energies in descending order*

C—Cl, C—Br, C—F, C—I *(JEE Main 2020)*

(a) C—F > C—Cl > C—Br > C—I
(b) C—Br > C—I > C—Cl > C—F
(c) C—I > C—Br > C—Cl > C—F
(d) C—Cl > C—Br > C—I > C—F

Sol. *(a)* The correct descending order of bonds according to their average bond energies is as follows

C—F > C—Cl > C—Br > C—I

Bond length is inversely proportional to bond energy.

So, bond length decreases as bond energy increases.

3. Bond Order

It is the number of covalent bonds present between the two atoms in a molecule.

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

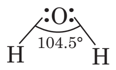
Remember Isoelectronic molecules and ions have identical bond orders. For example F_2 and O_2^{2-} have bond order 1. N_2, CO and NO^+ have bond order 3.

It is described in detail within the molecular orbital theory.

4. Bond Angles

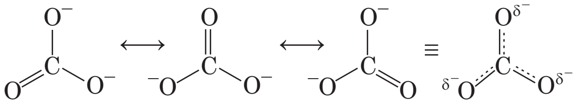
It is the angle between the bonded orbitals. Bond angle is expressed in degrees and is determined by spectroscopic methods. It gives a broad live idea about the distribution of orbitals around the central atom. Thus, it helps is determining the shape of the molecule.

e.g. H—O—H bond angle in water molecule can be represented as



Resonance

It is often seen for some compounds like benzene, CO_3^{--} that a single Lewis structure is indequate for the representation of their molecules especially for explaining all of its properties. Then many structures with similar energy, position of nuclei, bonding and non-bonding pairs of electrons are drawn with the conditions that each of these will explain some properties of the compound. These structures are called **resonating structures** or **canonical forms** and the hybrid of these structures is considered as the real structure of the compound. e.g. Carbonate ion is a resonance hybrid of following canonical forms



⟵ Canonical forms ⟶ Resonance hybrid

Presence of double headed arrow between the resonating forms symbolises resonance.

From the concept of resonance, the bond order (BO) of a molecule (or ion) is calculated as,

$$\text{BO} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of canonical forms}}$$

In general, it may be stated that

- resonance stabilises the molecule as energy of resonance hybrid is always less than the energy of any canonical form involved.
- the difference between the energy of hybrid and that of most stable canonical form is called **resonance energy**.

The stability of a resonating structure can be decided by considering the following points.

- Among all the given canonical forms the form with no charge is the most stable one.
- Among the charged canonical forms
  the form with maximum number of covalent bonds is the most stable one.
  - The structure with least charge separation comes next is stability.
  - The structure with conventionally correct charges comes next in stability.
  - The structure with conventionally incorrect charges is least stable.

Example 4. *Chlorine reacts with hot and concentrated* NaOH *and produces compounds* (*X*) *and* (*Y*). *Compound* (*X*) *gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in* (*Y*) *is* ***(JEE Main 2020)***

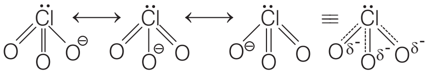
Sol. *(1.67)* The reaction is,

$$\underset{\text{(Hot and conc.)}}{3Cl_2 + 6\,NaOH} \longrightarrow \underset{(X)}{5\,NaCl} + \underset{(Y)}{NaClO_3} + 3H_2O$$

$$5\,NaCl \xrightarrow{+\,AgNO_3} \underset{\text{(White ppt.)}}{AgCl}$$

$Y = NaClO_3\ (Na^+ \text{ and } ClO_3^-)$

The structure of ClO_3^- (chlorate ion) is,



'Cl—O' bond order in the hybrid

$$= \frac{\text{Number of bonds between Cl and O}}{\text{Total number of O (surrounding atoms)}}$$

$$= \frac{5}{3} = 1.66 \text{ or } 1.67$$

Formal Charge (FC)

The atoms of a molecule or ion are usually neutral, i.e. carry no charge. However, for some purposes, such as to find reaction mechanisms, assigning of formal charge of atoms in a molecule or ion is important. Thus, formal charge (FC) is calculated as

$$FC = V - \left[lp + \frac{1}{2} bp \right]$$

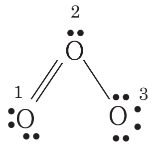
where,

V = total number of valence electrons in the free atom

lp = total number of non-bonding electrons or lone pairs

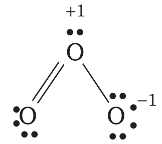
bp = total number of bond pair of electrons

e.g. Formal charge of O atoms in ozone molecule is calculated as,



$$FC \text{ of } O^1 = 6 - \left(4 + \frac{1}{2} \times 4\right)$$
$$= 6 - 6 = 0$$
$$FC \text{ of } O^2 = 6 - \left(2 + \frac{1}{2} \times 6\right)$$
$$= 6 - 5 = +1$$
$$FC \text{ of } O^3 = 6 - \left(6 + \frac{1}{2} \times 2\right)$$
$$= 6 - 7 = -1$$

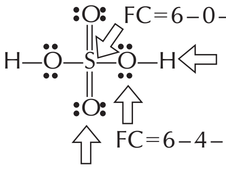
Thus, the correct representation of ozone molecule is



Example 5. *The formal charge of each atom in sulphuric acid is equal to*

(a) 0 (b) 1 (c) 2 (d) 3

Sol. (a)



FC=6−0−1/2(12)=0

FC=1−0−1/2(2)=0

FC=6−4−1/2(4)=0

FC=6−4−1/2(4)=0

Dipole Moment

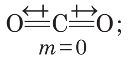
The polarity of covalent bonds results in the formation of electric dipole possessing a permanent dipole moment, μ. This is defined as the product of net charge and the distance between the two charged ends (bond length), i.e.

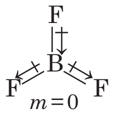
$$\mu = \text{charge}\,(e) \times \text{bond length}\,(d)$$

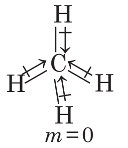
The unit of dipole moment in CGS system is **Debye** (*D*) and in SI system is **Coulomb-metre.**

Features of dipole moment are

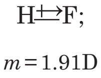
- Dipole moment is a vector quantity, thus indicated by the symbol ($+\!\!\!\longrightarrow$) pointing towards the negative end.
  e.g. $\overset{\delta+}{H} \overset{+\!\!\rightarrow}{—} \overset{\delta-}{Cl}$
- For symmetrical molecules, dipole moment is zero but unsymmetrical molecules have some dipole moment. e.g. CO_2, BF_3, CH_4 etc., being symmetrical therefore all have zero dipole moment.

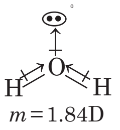


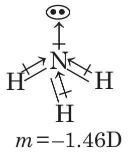




However, unsymmetrical molecules like HF, H_2O, NH_3 have some dipole moment as







Dipole Moment and Percentage Ionic Character

By using dipole moment, the percentage ionic character of a polar bond ($A - B$) can be calculated as,

$$\text{Percentage ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{cal}}} \times 100$$

$$= \frac{\mu_{\text{exp}}}{d_{A-B} \times e} \times 100$$

here, μ_{exp} = experimental (or observed) value of dipole moment of AB molecule,

$(\mu_{\text{cal}})_{\text{ionic}}$ = calculated (theoretical) value of dipole moment of AB molecule when molecule was assumed to be completely ionic. This value can be calculated as $d \times e$, i.e. bond length × charge

Example 6. *The bond length of* HCl *bond is* 2.29×10^{-10} m. *The percentage ionic character of* HCl, *if measured dipole moment is* 6.226×10^{-30} C-m, *is*

(a) 8% (b) 20% (c) 17% (d) 50%

Sol. (c) $\mu_{\text{cal}} = e \times d = 1.6 \times 10^{-19} \times 2.29 \times 10^{-10}$

$$= 3.664 \times 10^{-29} \text{ C - m}$$

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

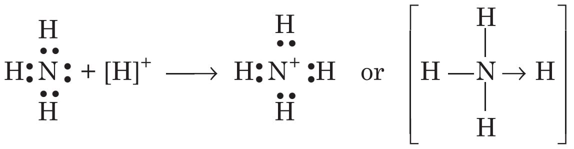
$$= \frac{6.226 \times 10^{-30}}{3.664 \times 10^{-29}} \times 100 = 17\%$$

Coordinate Covalent Bonding

Coordinate covalent bond or **dative bond** is a special type of covalent bond, which involves sharing of a pair of electrons with following speciability

- the shared electron pair is donated by one atom (called donor) and shared by both the atoms
- the other atom being participating in sharing only hence, called acceptor, e.g.

Formation of NH_4^+



Due to its directional nature the coordinate bond is shown as,

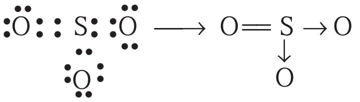
Donor atom ⟶ Acceptor atom (under classical approach)

But under **modern approach**, this bond can also be shown as

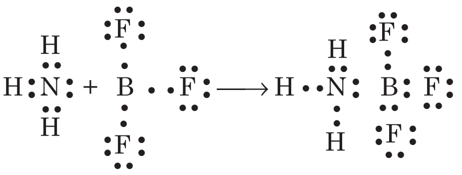
Donor atom + —— – Acceptor atom

Formation of SO_2

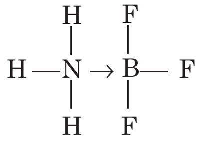
Formation of SO_3



Formation of $NH_3 \rightarrow BF_3$



or



Characteristics of Dative Bond or Coordination Compounds

The important characteristics of dative compounds are as follows

- These compounds exist in all the three states, under ordinary conditions, i.e. solids, liquids and gases.
- The melting and boiling points of these compounds are higher as compared to covalent compounds but lower than those of ionic compounds.
- Like covalent compounds these are also poor conductors of electricity in solid as well as in fused state.
- These compounds are sparingly soluble in polar solvents like water, however, these are readily soluble in organic solvents.
- These compounds are generally as stable as covalent compounds.
- Coordinate linkage is rigid and directional, thus they exhibit space isomerism.
- Dative compounds show molecular reactions just like covalent compounds.
- The dielectric constants for these compounds are higher.

Quantum Mechanical Approach to Covalent Bonding

Electronic theory of covalent bonding was not capable to explain correct shape of molecules, nature of bonds, and formation of bonds. Thus, new theories, collectively called the **quantum mechanical theory** had been proposed. These theories were based upon dual nature of electrons.

Two theories based on quantum mechanical approach are

1. Valence bond theory
2. Molecular orbital theory

Valence Bond Theory (VBT)

It was put forward by **Heitler** and **London** in 1927 and was extended by **Pauling** and **Slater** in 1931.

According to this theory, atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way the unpaired electrons are paired up, and all the atoms involved, attain a stable electronic arrangement, or a noble gas configuration. *Two electrons shared between two atoms constitute a bond*. The number of bonds formed by an atom is usually the same as the number of unpaired electrons in their ground state.

However, in some cases the atoms may form more than one bond. This occurs by excitation of the atom. In excited state electrons, which were paired in the ground state, become unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons and hence, increase the number of bonds which can be formed.

The theory can be summarised as

- A covalent bond is formed when the orbital of one atom overlaps with the orbital of another atom. Each of the orbital contain one unpaired electron.
- The two atomic orbital in such a case, merge to form a single **bonding orbital** or **a localised molecular orbital**, which is occupied by both the electrons.
- The two electrons occupying the bond orbital must have opposite spins. This is called **Pauli principle.**
- Each electron may be considered to belong to both the atomic nuclei.
- As a result of overlapping, there is maximum electron density somewhere between the two atoms. The electrostatic attraction between the nuclei and the accumulated electron clouds provides a large part of the binding force of covalent bond.
- The neutralisation of spin magnetic moments of the two electrons taking part in the bond formation also contributes to the binding force.

The modifications suggested by Pauling and Slater were

- The strength of chemical bond is proportional to the extent of overlapping between the atomic orbital.
- Overlapping will takes place only between those atomic orbitals, electrons of which take part in chemical bonding.
- Between two orbital of the same stability, the one with more directionally concentrated cloud would form a stronger bond, e.g. *p*-orbital will form stronger bonds than *s*-orbital.
- A spherically symmertical orbital, e.g. *s*-orbital, will not show any preference in direction whereas, non-spherical orbital, e.g. *p*-or *d*-orbital will tend to form a bond in their direction of maximum electron density.

For example

(i) In HF, H has a singly occupied *s*-orbital that overlaps with a singly filled 2*p*-orbital of F.

(ii) In H_2O, the O-atom has two singly filled 2*p*-orbitals, each of which overlaps with a single occupied *s*-orbital from two H-atoms.

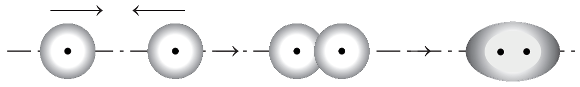
(iii) In NH_3, there are three singly occupied *p*-orbitals on N which overlap with *s*-orbitals from three H-atoms.

Overlapping of Orbitals

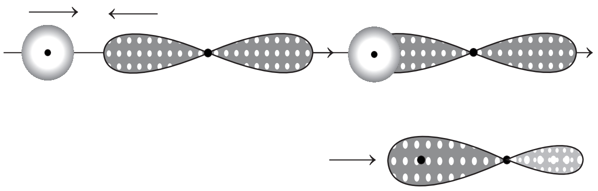
The overlapping of orbitals may be of two types

(i) **End to end overlapping** or **axial overlapping** or **head on overlapping** This overlapping results to σ (sigma) bond formation. Here, the electron density is concentrated in between the two atoms. The main examples of σ-bond include

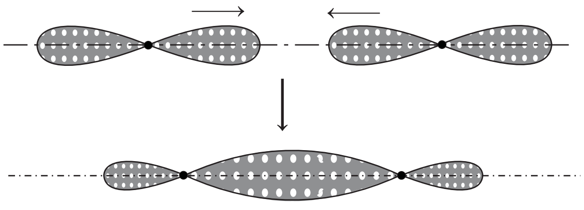
(a) ***s-s* overlapping**



(b) ***s-p* overlapping**



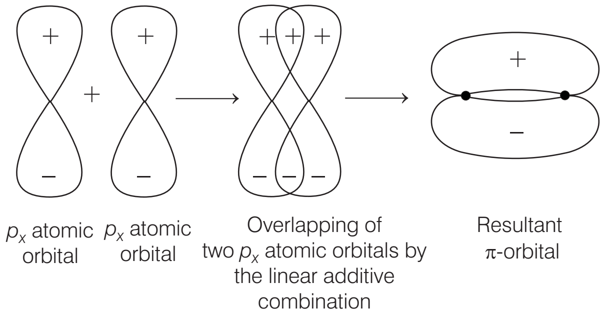
(c) ***p-p* overlapping**



Different cases showing head on axial overlapping

(ii) **Sidewise overlapping** or **parallel overlapping** This overlapping is seen normally after atleast one axial overlapping between orbitals of same atoms and results to a π (pi) bond formation.

Here, also the electron density concentrates between the atoms but on either side of line of joining nuclei as show below.

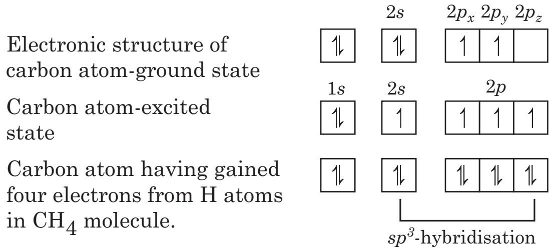


Sidewise overlapping of two p_x atomic orbitals by linear additive combination to give $\pi 2p_x$ bonding orbitals.

From the above, this can be concluded that single bond (—) contains only one σ-bond and no π-bond, double bond (═) contains one σ and one π-bond and triple bond (≡) contains one σ and two π-bonds.

Bonding in CH_4

In CH_4, the C-atom in its ground state has the electronic configuration $1s^2, 2s^2, 2p_x^1, 2p_y^1$ and only has two unpaired electrons and so can form only two bonds. If the C-atom is excited, then the 2*s*-electrons may be unpaired, giving $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ configuration. So, now there are four unpaired electrons which overlap with singly occupied *s*-orbitals of four H-atoms.



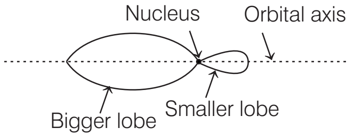
Although in CH_4, 1*s* and 2*p*-orbitals were participating but the resultant bonds formed are all alike. The reason of this similarity can be explained on the basis of the concept of hybridisation.

Hybridisation

This process involves the mixing of orbitals of almost similar energy belonging to same atom, to form the same number of orbitals of exactly equal energy. The new orbitals formed are called **hybrid orbitals.** This phenomenon in actual sense involves redistribution of energy.

Salient Features of Hybridisation or Rules of Hybridisation

- Only the valence shell atomic orbitals of an atom or ion can mix together to give the hybrid orbitals.
- The atomic orbitals of the atom of a given molecule or ion which participate in the formation of π-bonds remain excluded from the hybridisation process. For example in CO_2 molecule (O═C═O), the singly-filled 2*s* and $2p_x$-orbitals of C-atom mix together to form two *sp* hybrid orbitals while the singly-filled $2p_y$ and $2p_z$-orbitals remain excluded from the hybridisation process. These orbitals afterwords process of two (C—O) π-bonds.
- If the central atom of the given molecule or ion also has one or more lone pairs of electrons, then the atomic orbitals having lone pairs of electrons, i.e. completely-filled orbitals are also take part in the process of hybridisation.
- In a few cases, empty atomic orbitals are also involved in hybridisation, e.g. is in B_2H_6.
- A hybrid orbital, like an atomic orbital, can accommodate a maximum of two electrons with opposite spins.
- The number of hybrid orbitals formed is exactly equal to the number of orbitals taking part in the process.
- The electronic charge in hybrid orbitals is concentrated more in one direction as shown below.



A hybrid orbital

- This property make the hybrid orbitals to overlap with the atomic orbitals to a greater extent and hence, give stronger bonds.
- The hybridised orbitals have exactly equal energies with identical size and shape, i.e. **hybrid orbitals are degenerate.** The sum of the energies of all the hybrid orbitals is equal to the sum of the energies of orbitals which participated in the process.
- This simply means, that the process of hybridisation does not involve any loss or gain of energy. Here, only redistribution of energy occurs.
- Atomic orbitals can mix together effectively to give hybrid orbitals only when they are of almost same energy and same symmetry.
- Same atom can assume different hybrid states under different situations.
- The distribution and shapes of hybrid orbitals differ from that of the atomic orbitals which are taking part in the process of hybridisation.
- The energy released in the formation of σ-bonds by the hybrid orbitals is more than that which is released in the formation of bonds by the pure atomic orbitals. π-bonds are formed by the use of pure orbitals. This signifies that σ-bonds are more stronger and stable than π-bonds formed by pure atomic orbitals.

Types of Hybridisation

The hybridisation can be of following types

(1) sp (2) sp^2 (3) sp^3 or dsp^2

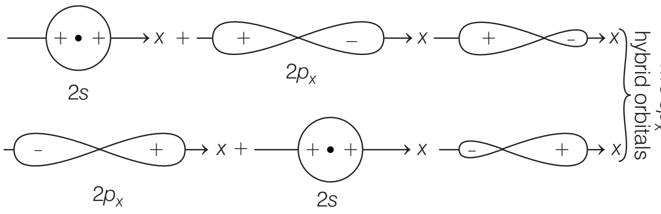
(4) sp^3d (5) sp^3d^2 and (6) sp^3d^3.

Out of these first three are described here in detail.

1. ***sp*-Hybridisation** (Linear Hybridisation)

In this hybridisation, one *s* and one *p*-orbital of the valence shell of atom combine together and give rise to the formation of a set of two equivalent hybrid orbitals, which are called *sp*-hybrid orbitals. Considered above if axis is supposed to be the molecular *x*-axis, then *p*-orbital will be p_x-orbital.

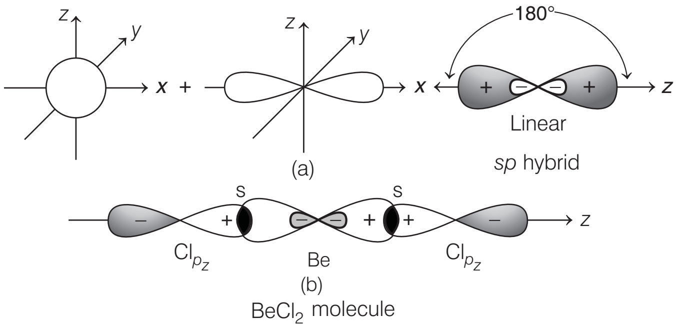
Since, the lobes of this *p*-orbital can combine with an *s*-orbital in two different ways as shown in figure below so, two *sp*-hybrid orbitals are obtained.



Formation of two sp_x hybrid orbitals

Characteristics of *sp*-hybrid Orbitals

- These are collinear, i.e. they lie in one axis in a straight line and hence, the angle between them is 180°. Their spatial arrangement is linear, i.e. they are directed in a straight line in opposite directions.
- *s*-orbital is spherical and *p*-orbital is pear-shaped or cylindical but *sp*-hybrid orbital which results from the mixing of one *s* and one *p*-orbital is oval-shaped due to the presence of 50% *s*-character and 50% *p*-character in it.
- An example of *sp*-hybridised molecule is $BeCl_2$ molecule.



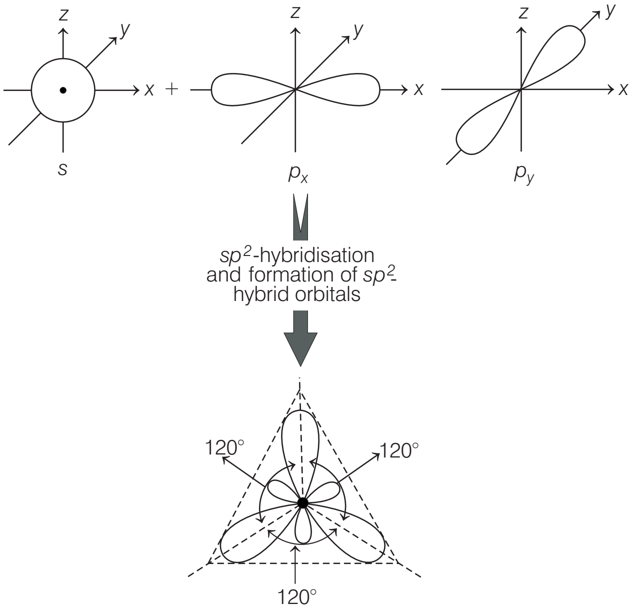
(a) Formation of *sp* hybrids formal *s* and *p* orbits;

(b) Formation of the linear $BeCl_2$ molecule.

2. ***sp*^{2}-Hybridisation** (Trigonal Planar Hybridisation)

In this hybridisation, one *s* and any two *p*-orbitals of the valence shell of the atom combine together and give a set of three equivalent hybrid orbitals.These orbitals are called sp^2 or trigonal hybrid orbitals.

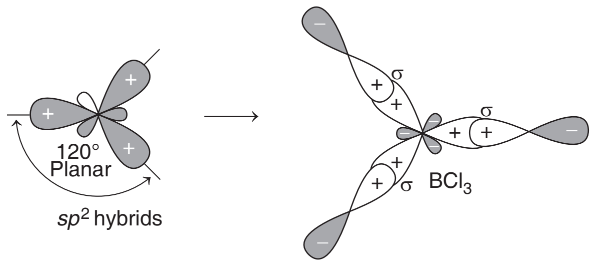
Their formation and resultant distribution is shown below.



Showing sp^2-hybridisation with angle and arrangement of orbitals

Characteristics of *sp*^{2}-hybrid Orbitals

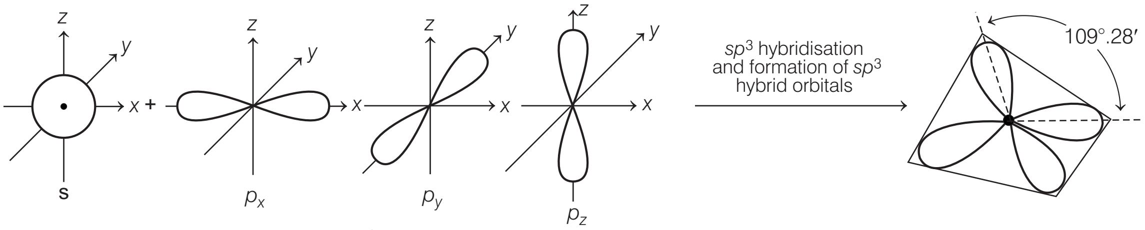
- All these orbitals lie in one plane.
- They are directed towards the corners of an equilateral triangle and hence, the angle between each two of them is 120°. Thus, in other words, we can say that the spatial arrangement of the three sp^2-hybrid orbitals is trigonal.
- These orbitals are less oval than the *sp*-hybrid orbitals because the contribution of the two pear-shaped *p*-orbitals to the formation of sp^2-hybrid orbitals is greater.
- The shape of sp^2-hybrid orbitals, therefore, tends more towards a pear. Here, the *s*-character is 33% and the *p*-character is 67%.
- An example of sp^2-hybridised molecule is BCl_3 molecule



Formation of sp^2 hybrids and the BCl_3 molecule

3. sp^3-Hybridisation (Tetrahedral Hybridisation)

The term sp^3-hybridised means that one *s* and all the three *p*-orbitals (p_x, p_y and p_z orbitals) of the valence shell of the atom combine together and form a set of four hybrid orbitals. These orbitals are called sp^3 or tetrahedral hybrid orbitals. Their formation and resultant distribution is shown below.



Showing sp^3 hybridisation with angle and arrangement of orbitals

Characteristics of sp^3-hybrid Orbitals

- They are directed towards the four corners of a regular tetrahedron and the angle between each two of them is 109°.28° or 109.5°. This angle is called **tetrahedral angle.**
- Each of the four sp^3-hybrid orbitals, has one-fourth *s*-character and three-fourth *p*-character, i.e. 25% *s*-character and 75% *p*-character.
- In case of sp^3-hybrid orbitals, since the contribution of three *p*-orbitals predominates over the contribution of one *s*-orbital, the shape of sp^3-hybrid orbitals is almost the same as that of the parent *p*-orbitals except for the fact that the lobes in sp^3-hybrid orbitals are somewhat more spread and are somewhat shorter in length than the pure *p*-orbitals.

Relationship between Hybridisation, Shape and Bond Angle

No. of atomic orbitals involved in hybridisation	Type of hybridisation	No. of hybrid orbitals formed	Shape of molecules	Bond angles	Examples
2	sp (one s and one p)	2	Linear	180°	$BeCl_2$, BeF_2
3	sp^2 (one s and two p)	3	Planar triangular	120°	BF_3, BCl_3
4	sp^3 (one s and three p)	4	Tetrahedral	109° 28′	CH_4, CCl_4
4	dsp^2 one $(n-1)$ 'd' usually ($d_{x^2-y^2}$), one 's' and two 'p'	4	Square planar	90°	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
5	sp^3d one 's', three 'p' and one d usually d_{z^2}	5	Trigonal bipyramid	120° and 90°	PCl_5
6	sp^3d^2 one 's', three 'p' and two 'd' usually $d_{x^2-y^2}$, $+d_{z^2}$	6	Octahedral	90°	SF_6
7	sp^3d^3 one 's', three 'p' and three 'd' usually $d_{xy}+, d_{yz}+, d_{zx}$	7	Pentagonal bipyramid	72° and 90°	IF_7

Methods for Identification of Hybridisation in Molecules

Following method are used for identification of hybridisation in molecules

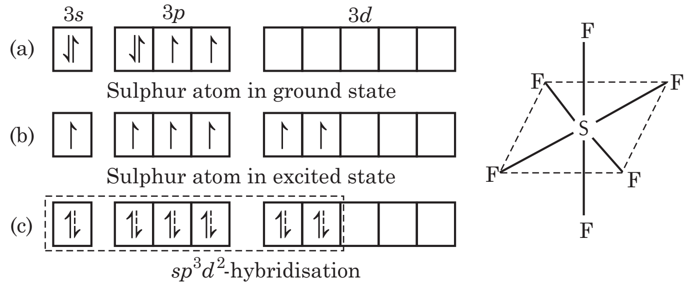
1. First Method

- Write electronic configuration for the outermost orbit or central atom using boxes.
- Find oxidation state of central atom. Excite the electrons from orbits of higher energy in such a way that total no. of upaired electrons = oxidation state of central atom.

Note π-bonds must be excluded from hybridisation calculation.

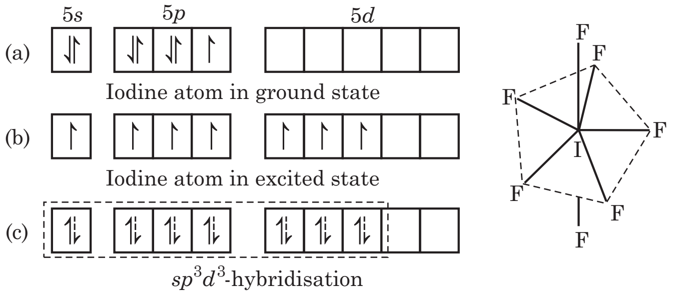
For example, the hybridisation and shape of SF_6 and IF_7 can be described in following molecule

(i) **SF_6 molecule sp^3d^2-hybridisation**



Octahedral geometry of SF_6 molecule resulting from sp^3d^2 hybridisation of the central S-atom. Dotted arrows represent electrons supplied by fluorine atoms.

(ii) **IF_7 molecule sp^3d^3-hybridisation**



Pentagonal bipyramidal geometry of IF_7 molecule resulting from sp^3d^3-hybridisation of the central I atom. Dotted arrows represent electrons supplied by fluorine atoms.

2. Second Method

The type of hybridisation undergone by the atom/ion in a given molecule or ion depends on the sum of σ-bond pairs and lone pairs surrounding the central atom/ion, e.g. if the sum of σ-*bps* and *lps* is 2 then the central atom/ion undergoes *sp*-hybridisation.

Similarly, for the sum equal to 3, 4, 5, 6 and 7, the central atom undergoes $sp^2, sp^3, sp^3d, sp^3d^2$ and sp^3d^3-hybridisation respectively.

Alongwith these, dsp^2-hybridisation is also seen in which $1d, 1s$ and $2p$-orbitals combine to hybridise. The shape of the molecule is **square planar** with a bond angle of 90°.

3. Third Method

An alternative way of finding hybridisation is the use of following formula

$$H = \frac{1}{2}[V + Y - C + A]$$

Here, V = valence shell electrons of the cental metal

Y = number of monovalent atom

C = total positive charge

and A = total negative charge on molecule

For the 2, 3, 4, 5, 6 and 7 value of H, the hybridisation is respectively $sp, sp^2, sp^3, sp^3d, sp^3d^2$ and sp^3d^3. e.g.

PF_5	**$COCl_2$**	**NH_4^+**	**ClO_4^-**
$X = \frac{1}{2}[5+5]$ $= 5$	$X = \frac{1}{2}[2+4]$ $= 3$	$X = \frac{1}{2}[4+5-1]$ $= 4$	$X = \frac{1}{2}[0+7+1]$ $= 4$
Hybrid state of P is sp^3d.	Hybrid state of C is sp^2.	Hybrid state of N is sp^3.	Hybrid state of Cl is sp^3.
NO_3^-	**IF_7**	**CO_2**	**XeF_4**
$X = \frac{1}{2}[0+5+1]$ $= 3$	$X = \frac{1}{2}[7+7]$ $= 7$	$X = \frac{1}{2}[0+4]$ $= 2$	$X = \frac{1}{2}[4+8]$ $= 6$
Hybrid state of N is sp^2	Hybrid state of I is sp^3d^3	Hybrid state of C is sp	Hybrid state of Xe is sp^3d^2

Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

This theory was given by "**Gillespie** and **Nyholm**" and is helpful in predicting the geometric arrangement of atoms in molecules. It includes all molecules which may or may not obey octet rule.

The main postulates of this theory are

- The central atom in a molecule contains 2 types of electron pairs. These are bond pairs and lone pairs. The shape of the molecule is determined by repulsions between all the electrons pairs present in the valence shell.
- A lone pair of electrons takes up more space around the central atom than a bond pair, since the lone pair is attracted by only one nucleus whilst the bond pair is shared by two nuclei.

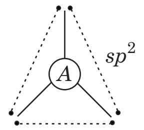
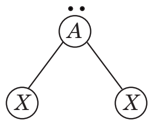
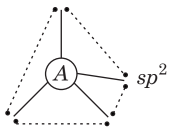
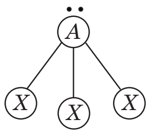
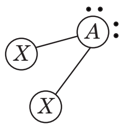
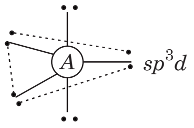
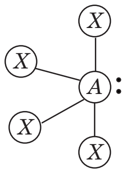
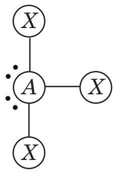
  Thus, the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape calculated from hybridisation.

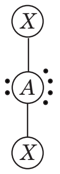
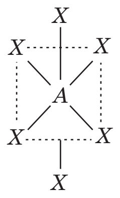
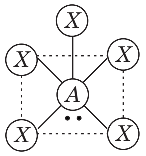
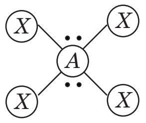
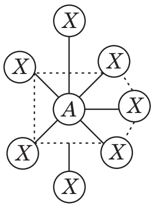
  Thus, repulsion among pairs increases as

  $$bp - bp < bp - lp < lp - lp.$$
- The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
- Double bonds cause more repulsion than single bonds and triple bonds cause more repulsion than double bonds.

A brief summary of molecular shapes resulting from different configurations of electrons pairs is given.

Geometry of Molecules According to VSEPR Theory

Steric number.	Regular geometry of the electron pairs and hybridisation	Bond pairs	Lone pairs	Molecular formula	Actual (modified) shape of the molecule due to electron pair repulsions	Examples
2.	Linear 	2	0	AX_2	Linear	CO_2, BeO_2
3	Triangular planar 	3	0	AX_3	Triangular planar	BF_2, $AlCl_3$, CO_3^{2-}
		2	1	AX_3L	 Bent (V-shape)	$SnCl_2$, NO_2, O_3
4.	Tetrahedral 	4	0	AX_4	Tetrahedral	CH_4, ClO_4^-, SO_4^{2-}, $\overset{+}{N}H_2$
		3	1	AX_3L	 Triangonal pyramidal	NH_3, H_3O^+, PCl_3, PH_3
		2	2	$A\,X_3L_2$	 Bent (V-shape)	H_2O, H_2S, $\overset{-}{N}H_2$, ClO_2^-, SCl_2
5.	Trigonal bipyramidal 	5	0	AX_2	Trigonal bipyrmidal	PCl_3, PF_5, $SbCl_3$, AsF_5
		4	1		 *See-saw* on teeter-totter or irregular saw horse or folded square	SF_4, $TeCl_4$
		3	2	$A\,X_2L_3$	 T-shaped	ClF_3, BrF_3

Steric number.	Regular geometry of the electron pairs and hybridisation	Bond pairs	Lone pairs	Molecular formula	Actual (modified) shape of the molecule due to electron pair repulsions	Examples
		2	3	AX_2L_3		I_3^-, XeF_2, ICl_2^-, Br_3^-
6.	Octahedral sp^3d^2 	6	0	AX_6	Octahedral or square bipyramidal	SF_6, PCl_6^-
		5	1	AX_3L	 Square pyramidal	ClF_5, IF_5, BrF_5
		5	2	AX_3L_2	 Square planar	ICl_4^-, XeF_4
7.	Pentagonal bipyramidal sp^3d^3	7	0	AX_7	 Pentagonal bipyramidal	IF_7

Examples of Electron Pairs Interactions

Some examples of shape modifications due to lone pair and bond pair interaction are given below.

- As the number of lone pairs of electrons increases, bond angle decreases. e.g. The bond angles for CH_4, NH_3 and H_2O are in the order $CH_4 > NH_3 > H_2O$, 109°28′, 106°51′ and 104°31′ respectively.
- Bond angles increases as the electronegativity of the central atom increases, e.g.
  In hydrides of oxygen family, order of bond angle is

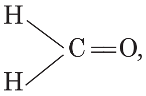
$$\underset{(104.5^\circ)}{H_2O} > \underset{(92^\circ)}{H_2S} > \underset{(91^\circ)}{H_2Se} > \underset{(89^\circ)}{H_2Te}$$

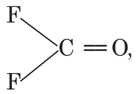
  However, in molecule having same central atom, bond angle increases as the electronegativity of surrounding atoms decreases. e.g. The order of bond angle for PI_3, PBr_3 and PCl_3 is as

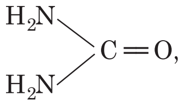
$$\underset{(102^\circ)}{PI_3} > \underset{(101.5^\circ)}{PBr_3} > \underset{(100^\circ)}{PCl_3}$$

  ∵ The order of electronegativity is Cl > Br > I.
- Similarly, NF_3 and NH_3 both have structure based on a tetrahedron with one corner occupied by a lone pair. In NF_3, the high electronegativity of F pushes the bonding electrons further away from N than in NH_3. Hence, the lone pair in NF_3 causes a greater distortion from tetrahedral bond angle. This gives a F — N — F bond angle of 102°30′ as compared with 107°48′ in NH_3. The same effect is found in H_2O (bond angle 104°27′) and F_2O (bond angle 102°).

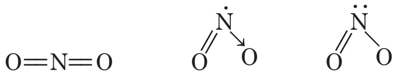
- pi (π) bonds do not affect the stereochemistry of a molecule. However, multiple bond orbitals repel other orbitals more strongly than single bond orbital, thus the bond angle will increase.

(i) 
$\angle \text{H—C—H} \Rightarrow 116^\circ$
and $\angle \text{H—C=O} \Rightarrow 122^\circ$.

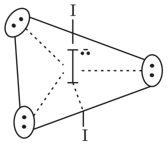
(ii) 
$\angle \text{F—C—F} \Rightarrow 108^\circ$
and $\angle \text{F—C=O} \Rightarrow 126^\circ$

(iii) 
$\angle \text{N—C—N} \Rightarrow 118^\circ$
and $\angle \text{N—C—O} \Rightarrow 121^\circ$

- A lone pair and double bond repulsion is much greater than a lone electron (means single) and double bond repulsion.


Bond angle = 180° (no lone pair) Bond angle = 134° (a lone electron) Bond angle = 115° (a lone pair)

- In an triangle the lone pairs always occupy the equatorial positions rather than the axial positions, i.e. up and down. Thus, in I_3^- ion, the central I atom has five electron pairs in the outer shell, made of two bond pairs and three lone pairs.

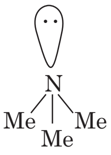


- The lone pairs occupy all the three equatorial positions and the two I atoms occupy the top, and bottom positions in the bipyramid, thus giving a linear arrangement with a bond angle of exactly 180°.

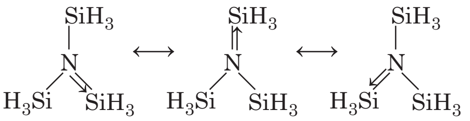
Back Bonding

- The interaction between an empty orbital and lone pair of electrons is known as **back bonding**.

  e.g. The nitrogen in trimethyl amine and trisilyl amine has a lone pair of electrons at nitrogen. This nitrogen in trimethyl amine has pyramidal shape while in trisilyl amine nitrogen has planar shape because in trimethyl amine there is repulsion between lone pair and bond pair that's why the shape becomes pyramidal.



In **trisilyl amine**, there is vacant d-orbital with silicon, which overlaps with lone pair of nitrogen, to form $p\pi$-$d\pi$ back bonding. Hence, the geometry becomes planar.



Finding Shapes of Molecules

To find the shapes of molecules, follow the steps given below.

***Step* I** **Identify the central atom and count the number of valence electrons**. e.g. In PCl_3, P being less electronegative is the central atom.
No. of valence electrons of P = 5

***Step* II** **Find the number of electron pairs shared.** e.g. In PCl_3, there are 3Cl atoms, so total no. of shared electrons = $\underset{\text{(From P)}}{3} + \underset{\text{(From Cl)}}{3} = 6e^-$

$$\text{Use, no. of bond pairs} = \frac{\text{total no. of shared electrons}}{2}$$
$$= \frac{6}{2} = 3$$
$$\text{and no. of lone pairs} = \frac{\text{valence } e^- - \text{bond pair}}{2}$$
$$\frac{5-3}{2} = \frac{2}{2} = 1$$

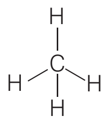
***Step* III** **While counting the number of electron pairs for ion**, value of negative charge is added and positive charge is subtracted with/from the valence e^- of central atom. In PCl_3, no charge is there, so we left this step.

***Step* IV** On the basis of total number of electron pairs bond pairs + lone pairs predict the geometry of the molecule with the help of the table given earlier.

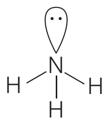
Example 7. *The compound that has the largest* H—M—H *bond angle* (M = N, O, S, C) *is* ***(JEE Main 2020)***

(a) H_2O (b) NH_3 (c) H_2S (d) CH_4

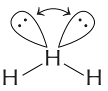
Sol. (*d*)



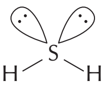
[CH_4 = hybridisation is sp^3, lone pair of electrons is 0, so that bond angle is maximum, i.e. = 109°28'



NH_3 = Hybridisation is sp^3, lone pair of electron is one, so that bond angle is 107°



H_2O = Hybridisation is sp^3 lone pair of electrons are two, so that bond angle is 104°5′



No hybridisation as according to Draga's rule, so that bond angle is 92°

According to VSEPR theory.

Lone pair-Lone pair > Lone pair-Bond pair > Bond pair-Bond pair.

Molecular Orbital Theory (MOT)

Why He_2 molecule does not exist and why O_2 is paramagnetic? Questions like these cannot be explained by valence bond theory.

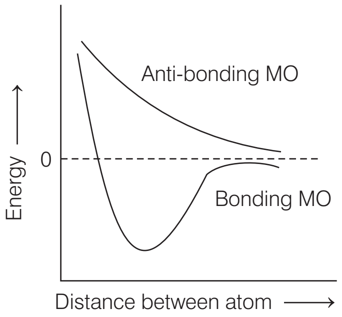
In 1932 F **Hund Huckel** and **R.S. Mulliken** put forward a theory, known as Molecular Orbital Theory. The theory was forwarded to explain above questions and many others on the basis of **Schrodinger** wave equation and its solutions for electrons.

According to this theory,

- A molecule is supposed to have orbitals of varying energy levels in the same way as an isolated atom has. These orbitals of molecule are called **molecular orbitals** (MO).
- Molecular orbitals are formed by the combination of atomic orbitals of comparable energy and proportional symmerty.
- We know that in atomic orbitals, one electron is influenced by one nucleus. On the other hand, in a molecular orbital, it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, orbitals of atoms loose their individual identity. Hence, an atomic orbital is monocentric while a molecular orbital is polycentric.
- Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution in molecule is given by the molecular orbital.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
- Two atomic orbitals combine to give, two types of molecular orbitals. One of these is known as **bonding molecular orbital** (BMO), whereas other is known as **anti-bonding molecular orbital** (ABMO). BMO has lower energy and hence, greater stability than the corresponding ABMO.
- At the time of electron filling in the molecule BMOs are preferred and filled first due to their lower energy or more stability. Hence, BMOs are also called HOMOs, i.e. Highly Occupied Molecular Orbitals.
- ABMOs, on the other hand are less preferred during electron filling due to their higher energy or lower stability. Hence, these are also called **LUMOs**, i.e. **Lowly or Unoccupied Molecular Orbitals**.
- The shapes of molecular orbitals formed depends upon the type of combining atomic orbitals.
- The filling of molecular orbital obey Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Electron density is increased for the bonding MO's in the internuclear region but decreased for anti-bonding MO's. Shielding of the nuclei by increased electron density in bonding MO's reduces internuclear repulsions and thus stabilises the molecule.

On the other hand, lower electron density (even as compared to the individual atom in anti-bonding MO's) increases the repulsions and destabilises the system.



Energy *vs* distance graph of MOT

Linear Combination of Atomic Orbitals (LCAO)

The Schrodinger wave equation is very difficult to apply on the system containing more than one electron because in these system one electron mores in the field of several nuclei so some approximation method is used in the formation of molecular orbitals. This can be explained on the basis of LCAO. It is a very convenient method of approximation.

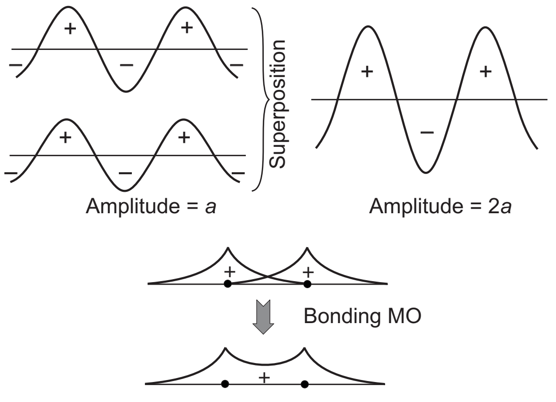
According to LCAO, the wave function (ψ) of individual atomic orbitals linearly combined and form molecular orbitals, i.e. during the formation of AB molecule ψ of A and ψ of B will linearly combine as

$$\psi_{MO} = \psi_A + \psi_B$$

Following two cases may be possible in such a linear combination.

***Case* I** When two waves are in phase the waves adds up and amplitude of new wave becomes

$$\psi_{MO} = \psi_A + \psi_B \qquad \text{(Bonding MO)}$$

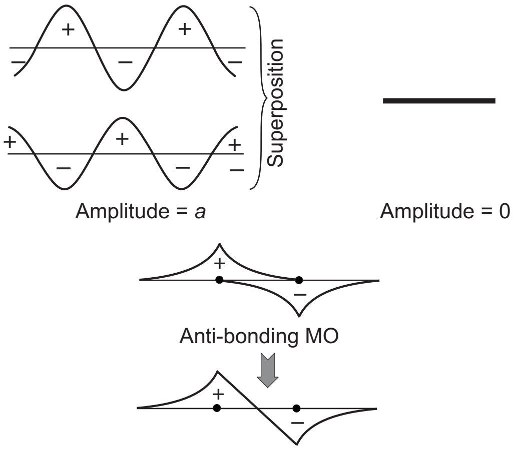


Constructive interaction

These interactions are based upon the fact that when orbitals or lobes of orbitals with same wave function (ψ) combine, the result is **constructive interaction.**

***Case* II** When two waves are out of phase, the waves are subtracted from each other so that the amplitude of new wave becomes,

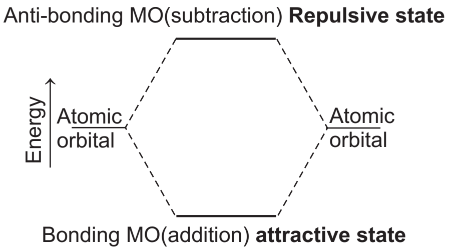
$$\psi^*_{MO} = \psi_A - \psi_B \qquad \text{(Antibonding MO)}$$



Destructive interaction

These interactions are based upon the fact that when orbitals or lobes of orbitals with opposite wave function (ψ) combine, the result is **destructive interaction**.

The condition of lower energy (bonding molecular orbital) is also called **attractive state** for electrons while condition of higher energy (antibonding molecular orbital) is also called **repulsive state for electrons**.



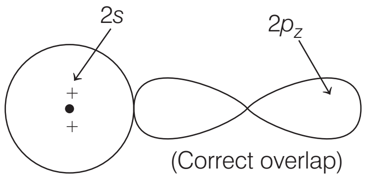
Energy level diagram of molecular orbitals

Conditions for Combination of Atomic Orbitals

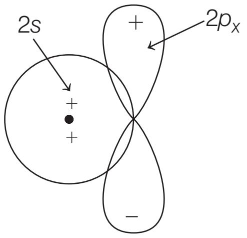
The combination of the atomic orbitals is based on the following conditions.

- The combining atomic orbitals must have comparable energies. It may be noted that in the homonuclear diatomic molecules of the type A_2 (e.g. H_2, O_2, N_2, F_2 etc.), the participating atomic orbitals must have comparable energies. .
- This means that 1*s* atomic orbital of one atom can combine with 1*s* atomic orbital of the other atom and not with its 2*s*-orbital. However, in heteronuclear molecules *AB* (e.g. HF, HCl etc.) such a combination is permissible.
- The extent of overlapping must be large. The overlapping of the atomic orbitals results in decrease in energy and increase in stability. Thus, greater the extent of the overlapping, more will be the stability of the molecular orbital formed.
- The combining atomic orbitals must have same symmetry about internuclear axis. The atomic orbitals taking part in the overlap must have same orientation or same sign of symmetry.

  Correct and wrong overlap between the orbitals is shown below.



(Correct overlap)



(Wrong overlap)

σ (Sigma) and π (Pi) Molecular Orbitals

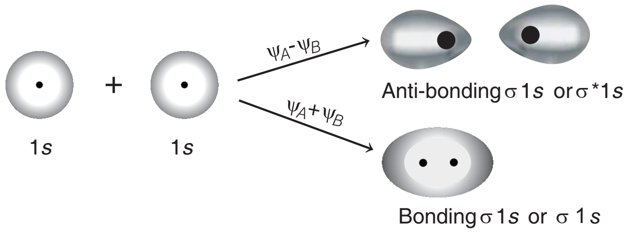
Molecular orbitals of diatomic molecule are designated as σ (sigma) and π (pi) etc. Sigma (σ) molecular orbitals are symmetrical around the bond axis while pi (π) molecular orbitals are not symmetrical.

The bonding molecular orbitals are shown as σ or πns or np while antibonding molecular orbitals are shown as σ^* or $\pi^* ns$ or np^* accordingly.

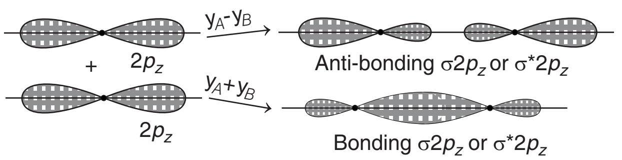
The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

Formation of σ and π HOMOs and LUMOs

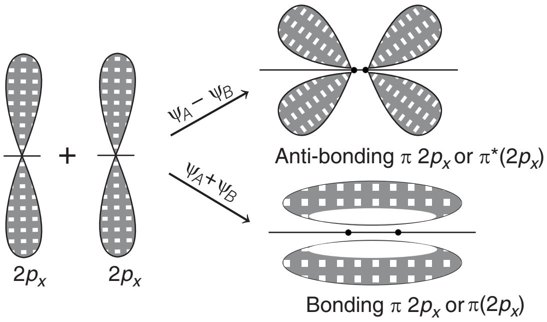
(i) **Combination of *s*-orbitals**



(ii) **Head on combination of two *p*-orbitals**



(iii) **Sidewise combination of two *p*-orbitals**



[Here, *z* axis is considered as internuclear axis]

Electronic Configuration of Molecules

It is the key to get informations like bond order, bond length, bond strength and magnetic nature of a molecule. Just like electronic configuration of atoms this electronic configuration is also aligned with the energy of orbitals.

For homonuclear diatomic molecules of the 2nd period elements of periodic table the energy levels of molecular orbitals have been determined experimentally from spectroscopic data.

The increasing order of energies of molecular orbitals for O_2 and F_2 molecules are given as

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < \pi 2p_x \approx \pi 2p_y < \overset{*}{\pi} 2p_x \approx \overset{*}{\pi} 2p_y < \overset{*}{\sigma} 2p_z$$

However, for remaining molecules, i.e. $Li_2, Be_2, B_2, C_2, N_2$ the order is $\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \pi 2p_x$

$$\approx \pi 2p_y < \sigma 2p_z < \overset{*}{\sigma} 2p_x \approx \overset{*}{\pi} 2p_y < \overset{*}{\sigma} 2p_z$$

i.e. Here the energy of $\pi 2p_x \approx \pi 2p_y$ is less than the energy of $\sigma 2p_z$ molecular orbital.

It is so because except O_2 and F_2 the energy difference between 2*s* and 2*p* atomic energy level is small. As the result both come together and hence, repulsive forces arises which raise the energy $\sigma 2p$ above that of $\pi 2p$ molecular orbitals.

Before moving ahead to explore proper electronic configuration of these molecules, it is better to understand the connectivity of bond order, stability, bond length and magnetic nature of the molecule with their electronic configurations.

Bond Order

The one-half of the difference between the number of electrons present in bonding orbitals and number of electrons present in anti-bonding orbitals is called bond order of that molecule, i.e.

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

Here, N_b = number of electrons in bonding orbitals

N_a = number of electrons in anti-bonding orbitals

The **stability** of a molecule can be determined by its bond order as

- A positive bond order means a stable molecule,
- A negative or zero bond order means an unstable molecule,
- Bond order values 1, 2 and 3 corresponds to single, double and triple bond respectively.

Bond Length

It varies inversely with the bond order, i.e. decreases as the bond order increases.

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

Magnetic Nature

For different molecules, magnetic nature can also be predicted by molecular orbitals as

- If all orbitals are fully occupied, molecules substance is diamagnetic.
- If one or more molecular orbitals are singly occupied, molecules/substance is paramagnetic.

Bonding in Some Homonuclear Diatomic Molecules

(i) **H_2 molecule**

Electronic configuration : $\sigma 1s^2$

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

Conclusion Stable molecule, with single bond between 2H atoms, **diamagnetic**.

(ii) **He_2 molecule**

Electronic configuration : $\sigma 1s^2, \overset{*}{\sigma} 1s^2$

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

Conclusion Unstable molecule, does not exist.

Similarly, Be_2 molecule with possible electronic configuration $\sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2$ does not exist.

(iii) **Li_2 molecule**

Electronic configuration : $\sigma 1s^2, \sigma * 1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

Conclusion Stable (known in vapour phase) with single bond between 2 Li atoms, **diamagnetic.**

(iv) **C_2 molecule**

Electronic configuration

$$\sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$$

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

Conclusion Stable (detected in vapour phase), with **2π-bonds between two C-atoms** instead of 1σ and 1π, **diamagnetic**.

(v) **O_2 molecule**

Electronic configuration

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

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

Conclusion Stable, with double bond between two oxygen atoms, **paramagnetic**.

(vi) **F_2 molecule**

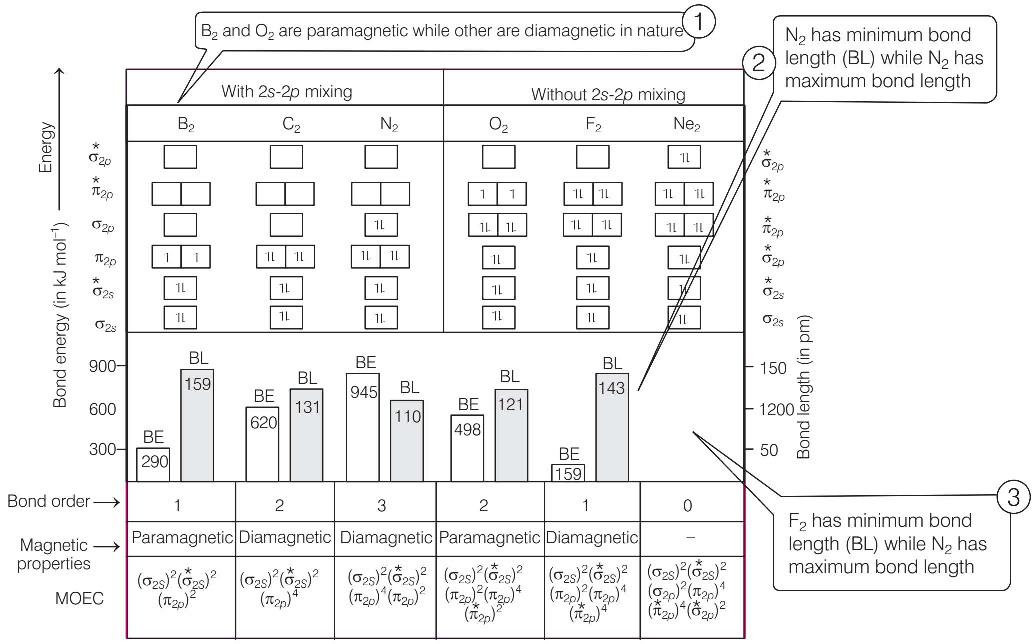
Electronic configuration : $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$

$$\sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$$

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

Conclusion Stable, with one σ bond between two F-atoms, **diamagnetic**.

A brief summary to our discussion can be visualised as following table.



① B_2 and O_2 are paramagnetic while other are diamagnetic in nature

② N_2 has minimum bond length (BL) while N_2 has maximum bond length

③ F_2 has minimum bond length (BL) while N_2 has maximum bond length

MOEC = Molecular Orbital Electronic Configuration

Tabular defriction of homonuclear molecules of IInd period MOEC, magnetic properties, bond order bond length, bond energy all have been depicted.

Example 8. *The bond order and the magnetic characteristics of* CN^- *are* ***(JEE Main 2020)***

(a) 3, diamagnetic
(b) $2\frac{1}{2}$, paramagnetic
(c) 3, paramagnetic
(d) $2\frac{1}{2}$, diamagnetic

Sol. (a) CN^- has 14 electrons (6 from C, 7 from N and 1 for negative charge). Its MO configuration must be similar to

$$N_2 : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$$

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

As there is no unpaired electron in CN^-, thus it is diamagnetic.

Example 9. *Two pi and half sigma bonds are present in*

(a) O_2^+
(b) N_2
(c) N_2^+
(d) O_2

(JEE Main 2019)

Sol. (c) The energy order of MOs of the given species are as follows

$$O_2(16\, e^-{}'\, s) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$
$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 = \pi^* 2p_y^1,$$

$$O_2^+ (15e^-{}'\, s) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$$
$$\pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$$

$$N_2(14e^-{}'s) = \sigma 1s^2\, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$$
$$\pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$$

$$N_2^+ (13e^-{}'s) = \sigma 1s^2 \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2$$
$$\pi 2p_x^2 = \pi 2p_z^2 \sigma 2p_z^1$$

Thus, in case of N_2^+, two π-bonds and half σ-bond are present in the bonding MOs.

Example 10. *During the change of O_2 to O_2^-, the incoming electron goes to the orbital.* ***(JEE Main 2019)***

(a) $\pi 2p_x$ (b) $\pi^* 2p_x$ (c) $\pi 2p_y$ (d) $\sigma^* 2p_z$

Or

Which of the following options represents the correct bond order ? ***(NCERT Exemplar)***

(a) $O_2^- > O_2 > O_2^+$ (b) $O_2^- < O_2 < O_2^+$

(c) $O_2^- > O_2 < O_2^+$ (d) $O_2^- < O_2 > O_2^+$

Sol. (*b*) E.C. of O_2 (16 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

E.C. of O_2^+ (15 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 5) = 2.5$$

E.C. of O_2^- (17 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 7) = 1.5$$

Thus, the order of bond order is $O_2^- < O_2 < O_2^+$ and the incoming electron goes to $\pi^* 2p_x$-orbital

Example 11. *Of the species, NO, NO^+, NO^{2+} and NO^-, the one with minimum bond strength is* ***(JEE Main 2020)***

(a) NO^+ (b) NO (c) NO (d) NO^-

Sol. (*d*) Energy order of MOs $BO = \frac{N_b - N_a}{2}$

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

$$NO(15e^-): 2\ 2\ 2\ 2\ 2 \quad 2 \quad 2 \quad 1 \quad 0 \rightarrow \frac{10-5}{2} = 2.5$$

$$N\overset{+}{O}(14e^-): 2\ 2\ 2\ 2\ 2 \quad 2 \quad 2 \quad 0 \quad 0 \rightarrow \frac{10-4}{2} = 3$$

$$N\overset{2+}{O}(13e^-): 2\ 2\ 2\ 2\ 2 \quad 2 \quad 1 \quad 0 \quad 0 \rightarrow \frac{9-4}{2} = 2.5$$

$$N\overset{-}{O}(16e^-): 2\ 2\ 2\ 2\ 2 \quad 2 \quad 2 \quad 1 \quad 1 \rightarrow \frac{10-6}{2} = 2$$

We know, $\text{Bond length} \propto \frac{1}{\text{BO (Bond order)}} \propto \frac{1}{\text{Bond strength}}$

So, the order of bond strength : $NO^+ > NO = NO^{2+} > NO^-$

So, NO^- has minimum bond strength.

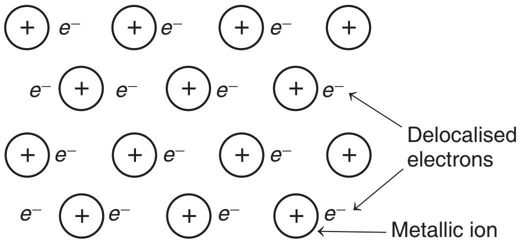
Metallic Bonding

This bonding holds the metal atoms together in a metal crystal. Different models have been proposed to explain the nature of metallic bonding and the two important ones among them are as follows

Electron Sea Model

According to this model, a metal is regarded as a group of positive metal ions packed together as closely as possible in a regular geometric pattern. This set up is immersed in a sea of electrons which move about freely in the vacant valence orbitals.

The positive metal ions, here are called **positive cores** or **kernels** and mobile electrons are **electron pool** or **electron gas.** The attractive force between electrons and kernels is considered as metallic bonding.

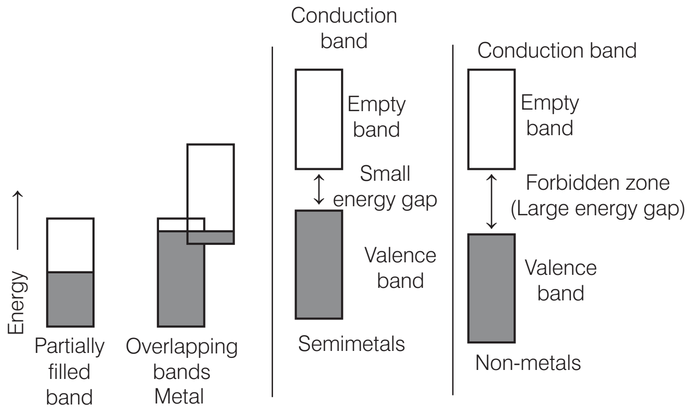


Electron sea model

Band Model

This model is based upon molecular orbital theory. According to this model, a metal lattice has an extremely large number of atoms. The atomic orbitals of these atoms overlap together due to similar symmetry and similar energy resulting to the formation of energy bands. The arrangement of electrons in the different energy bands determines the characteristic of a metal.

The highest occupied energy band is called the **valence band** while the lowest unoccupied energy band is called **conduction band.** The properties of various elemental solids can be explained by the gap present between the top of valence band and the bottom of conduction band. This gap is called the **energy gap** (E_g). In case of metals, semimetals and non-metals this gap is visible as



(In each case, an unshaded area represents a conduction band)
Distinction among metals semiconductor and non-metals.

Hydrogen Bonding

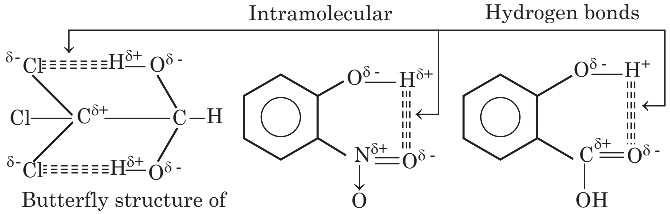
The attractive electrostatic force between a hydrogen atom which is already covalently attached to a strong electronegative atom (i.e. any of F, O and N) and an electronegative atom (any out of F, O and N) is known as hydrogen bond.

Types of H-bonding

Hydrogen bonding is of following two types

1. Intramolecular H-bonding

It is seen in a single molecule and when this type of H-bonding leads to linking of two groups in such a way that a ring like structure is formed, the effect is also called **chelation**. e.g.



Butterfly structure of chloral hydrate ($CCl_3CH(OH_2)$) in which 2–OH groups are show H-bonding with Cl-atom

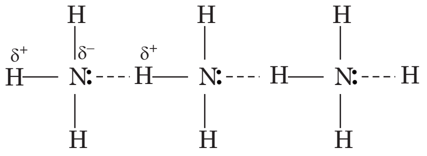
o-nitrophenol

Salicylic acid (*ortho*-hydroxy benzoic acid)

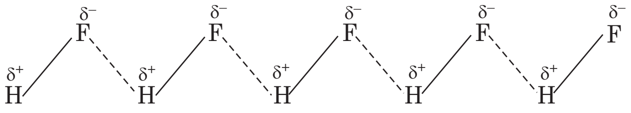
Molecules with intramolecular H-bonding are known to have **lower boiling point and melting point**.

2. Intermolecular H-bonding

It occurs between two or more molecules of similar or different compounds, e.g.



Intermolecular H-bonding in NH_3



Hydrogen fluoride molecule showing intermolecular H-bonding

The intermolecular H-bonding is found to be responsible for **high m.p and b.p of** compounds in which it is seen. Certain organic compounds show miscibility with polar solvents like water. It is also attributed to intermolecular H-bonding, e.g. alcohol and water molecules.

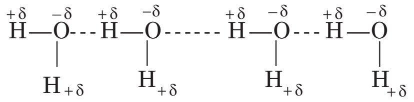
Nature and Importance of H-bonding

- H-bond is simply dipole-dipole attraction within oppositely partially charged ends.
- H-bond never involves more than two atoms.
- Bond energy of H-bond is of the order of 3-10 kcal mol^{-1}, i.e. about 1/10 of covalent bond.
- As the electronegativity difference of H and other atom to which it is covalently bonded increases, the strength of H-bond increases.
  H-bond order : H — F > H — O > H — N > H — Cl
- All the three atoms X—H---X lie in one plane.

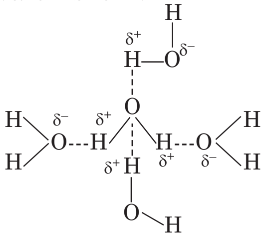
Effects of H-Bonding

Following are the effects of H-bonding

(i) **High boiling point of water** Due to polar nature of H_2O and H-bonding between its molecules there is association of water molecules. This in turn converts H_2O to giving a liquid state of abnormally high boiling point.



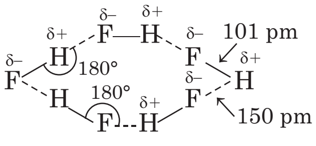
In water, one water molecule is joined to four water molecules (two with H-atom and other two with O-atoms). Thus, coordination number of water molecule in water is four.



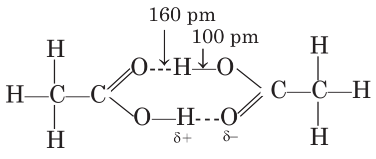
(ii) **Low density of ice as compared to water When ice is formed** from liquid water, some air gap is left in the tetrahedral packing of water molecules. Due to this, volume of ice is greater than liquid water and thus, ice is lighter than water.

In other words, we can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks, hence volume increases and finally, density decreases. Thus, **water has maximum density at 4°C**.

(iii) **Pentagonal arrangement of HF** In the gaseous state, several polymeric forms of HF molecules exist in which the monomers are held together through H-bonding. A pentagonal arrangement of H—F molecules is shown below



(iv) **Dimerisation of carboxylic acids** Carboxylic acid dimerises in gaseous state due to H-bonding.



Practice Exercise

ROUND I Topically Divided Problems

Octet Rule and Ionic Bonding

1. Which of the following compounds does not follow the octet rule for electron distribution?

(a) H_2O (b) PH_3 (c) PCl_3 (d) PCl_5

2. Which of the following has an electrovalent linkage?

(a) CH_4 (b) $SiCl_4$

(c) $MgCl_2$ (d) BF_3

3. As compared to covalent compounds, electrovalent compounds generally have

(a) low melting points and low boiling points

(b) high melting points and high boiling points

(c) low melting points and high boiling points

(d) high melting points and low boiling points

4. Arrange the bonds in order of increasing ionic character in the molecules; LiF, K_2O, N_2, SO_2 and ClF_3. ***(NCERT)***

(a) $N_2 < ClF_3 < SO_2 < LiF < K_2O$

(b) $N_2 < SO_2 < ClF_3 < K_2O < LiF$

(c) $N_2 < ClF_3 < SO_2 < K_2O < LiF$

(d) $N_2 < SO_2 < ClF_3 < Lif < K_2O$

5. Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$, the compounds with the greatest and the least ionic character, respectively are

(a) LiCl and RbCl

(b) RbCl and $MgCl_2$

(c) RbCl and $BeCl_2$

(d) $MgCl_2$ and $BeCl_2$

6. Arrange the following bonds in order of increasing ionic character N—H , F—H, C—H and O—H ***(NCERT)***

(a) F — H < O — H < C — H < N — H

(b) N — H < O — H < C — H < F — H

(c) C — H < N — H < O — H < F — H

(d) F — H < C — H < O — H < N — H

7. A pair of compounds which have odd electrons in the group NO, CO, ClO_2, N_2O_5, SO_2 and O_3 are

(a) NO and ClO_2 (b) CO and SO_2

(c) ClO_2 and CO (d) SO_2 and 0_3

8. X, Y and Z elements have 4, 5 and 7 valence electrons. Among the given the correct formula is ***(NCERT)***

(a) XH_3 (b) YH_4

(c) HZ (d) YH_5

9. Among the following isostructural compounds, identify the compound which has the highest lattice energy.

(a) LiF (b) LiCl

(c) NaCl (d) MgO

10. CaO and NaCl have the same crystal structure and approximately the same ionic radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is

(a) $\frac{U}{2}$ (b) U

(c) $2U$ (d) $4U$

11. An atom X has three valence electrons and atom Y has six valence electrons. The compound formed between them will have the formula

(a) X_2Y_6 (b) XY_2

(c) X_2Y_3 (d) X_3Y_2

12. The isoelectronic set of ions is ***(JEE Main 2019)***

(a) F^-, Li^+, Na^+ and Mg^{2+}

(b) N^{3-}, Li^+, Mg^{2+} and O^{2-}

(c) Li^+, Na^+, O^{2-} and F^-

(d) N^{3-}, O^{2-}, F^- and Na^+

13. The group having isoelectronic species is ***(JEE Main 2017)***

(a) O^{2-}, F^-, Na^+, Mg^{2+} (b) O^-, F^-, Na, Mg^+

(c) O^{2-}, F^-, Na, Mg^{2+} (d) O^-, F^-, Na^+, Mg^{2+}

14. In which of the following pairs, the two species are not isostructural?

(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

15. Which one of the following constitutes a group of the isoelectronic species?

(a) C_2^{2-}, O_2^-, CO, NO (b) NO^+, C_2^{2-}, CN^-, N_2
(c) CN^-, N_2, O_2^{2-}, CO_2^{2-} (d) N_2, O_2^-, NO^+, CO

Covalent Bonding its Parameters, Special Characteristics and Coordinate Covalent Bonding

16. Among the following the maximum covalent character is shown by the compound *(AIEEE 2011)*

(a) $FeCl_2$ (b) $SnCl_2$
(c) $AlCl_3$ (d) $MgCl_2$

17. Which of the following is the most covalent?

(a) C—F (b) C—O
(c) C—S (d) C—Br

18. Which has maximum covalent character?

(a) $SiCl_4$ (b) $MgCl_2$
(c) NaCl (d) $AlCl_3$

19. Which of the following compounds contain(s) no covalent bond(s)?

KCl, , O_2, B_2H_6, H_2SO_4 *(JEE Main 2018)*

(a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6

20. The order of resultant dipole moment in CO_2, NF_3 and $CHCl_3$ is *(NCERT)*

(a) $NF_3 < CO_2 < CHCl_3$ (b) $CHCl_3 < CO_2 < NF_3$
(c) $CO_2 < NF_3 < CHCl_3$ (d) $CO_2 < CHCl_3 < NF_3$

21. Why BeH_2 molecule has a zero dipole moment although the Be—H bonds are polar? *(NCERT)*

(a) Because of its linear geometry
(b) Because of two opposite and equal dipoles
(c) Both (a) and (b)
(d) None of the above

22. N_2 is less reactive than CN^- due to

(a) difference in spin quantum number
(b) presence of more electrons in orbitals
(c) absence of dipole moment
(d) None of the above

23. Which of the following has a bond order of 1.75?

(a) ClO_3^- (b) ClO_4^-
(c) NO_3^- (d) CO_3^{2-}

24. The correct order in which the O—O bond length increases in

(a) $O_2 < O_3 < H_2O_2$ (b) $H_2O_2 < O_3 < O_2$
(c) $O_3 < O_2 < H_2O_2$ (d) $O_2 < H_2O_2 < O_3$

25. The correct order of decreasing polarity is

(a) $HF > SO_2 > H_2O > NH_3$
(b) $HF > H_2O > SO_2 > NH_3$
(c) $HF > NH_3 > SO_2 > H_2O$
(d) $H_2O > NH_3 > SO_2 > HF$

26. Which one of the following compounds has bond angle as nearly 90°?

(a) NH_3 (b) H_2S
(c) H_2O (d) CH_4

27. Which of the following molecule is linear ?

(a) H_2S (b) NO_2
(c) ClO_2 (d) CO_2

28. Which of the following pair has same structure?

(a) PCl_5 and SF_6 (b) SO_2 and NH_3
(c) PH_3 and BCl_3 (d) NH_4^+ and SO_4^{2-}

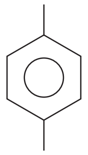
29. In which of the following molecule/ion all the bonds are not equal? *(NCERT Exemplar)*

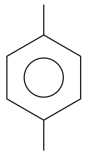
(a) XeF_4 (b) BF_4^- (c) C_2H_4 (d) SiF_4

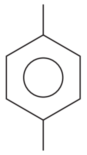
30. The possible number of resonance structures for NO_3^- is *(NCERT)*

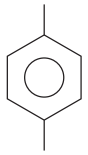
(a) 2 (b) 3 (c) 4 (d) 5

31. For which of the following molecule significant $\mu \neq 0$? *(JEE Main 2014)*









(a) Only (i) (b) (i) and (ii)
(c) Only (iii) (d) (iii) and (iv)

32. Which of the following does not have a coordinate bond?

(a) SO_2 (b) H_2SO_3
(c) HNO_2 (d) HNO_3

33. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only

(a) electrovalent and covalent
(b) electrovalent and coordinate
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent.

VBT, Resonance, Hybridisation

34. In which of the following molecules are all atoms coplanar?

(a) PF_3 (b) NH_3 (c) BF_3 (d) CH_4

35. Which of the following statements is not correct?

(a) Hybridisation is the mixing of atomic orbitals prior to their combining into molecular orbitals
(b) sp^2-hybrid orbitals are formed from two p-atomic orbitals and one s-orbital
(c) d^2sp^3-hybrid orbitals are directed towards the corners of a regular octahedron
(d) dsp^3-hybrid orbitals are all at 90° to one another

36. 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

37. Which orbital is used by oxygen atom to form a sigma bond with other oxygen atom in O_2 molecule?

(a) pure p-orbital (b) sp^2-hybrid orbital
(c) sp^3-hybrid orbital (d) sp-hybrid orbital

38. Two hybrid orbitals have a bond angle of 120°. The percentage of s character in the hybrid orbital is nearly

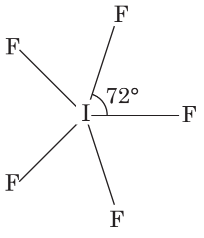
(a) 25% (b) 33% (c) 50% (d) 66%

39. The hybrid state of S in SO_3 is similar to that of

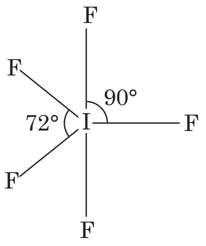
(a) C in C_2H_2 (b) C in C_2H_2
(c) C in CH_4 (d) C in CO_2

40. The structure of IF_5 can be best described as

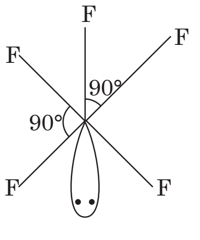
(a)



(b)



(c)



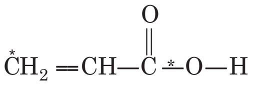
(d) None of these

41. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be ***(NCERT Exemplar, AIEEE 2011)***

(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

42. In which of the following the carbon atoms marked with star is sp hybridised?

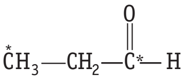
(a)



$\overset{*}{C}H_2=CH-\overset{\overset{O}{\|}}{C}\overset{*}{-}O-H$

(b) $CH_3-\overset{*}{C}H_2-OH$

(c)



$\overset{*}{C}H_3-CH_2-\overset{\overset{O}{\|}}{C}\overset{*}{-}H$

(d) $CH_3-\overset{*}{C}\equiv CH$

43. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. This is due to ***(NCERT)***

(a) lp-lp repulsion in NH_3 and lp bp repulsion in H_2O
(b) lp-lp repulsion in H_2O and lp-bp repulsion in NH_3
(c) bp-bp repulsion in NH_3 and lp-bp repulsion in H_2O
(d) None of the above

44. If AB_4 molecule is a polar molecule, a possible geometry of AB_4 is ***(JEE Main 2020)***

(a) square pyramidal (b) square planar
(c) rectangular planar (d) tetrahedral

45. The molecular geometry of SF_6 is octahedral. What is the geometry of SF_4 (including lone pair(s) of electrons, if any)? ***(JEE Main 2020)***

(a) Tetrahedral
(b) Trigonal bipyramidal
(c) Pyramidal
(d) Square planar

46. The structure of PCl_5 in the solid state is ***(JEE Main 2020)***

(a) tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$
(b) trigonal bipyramidal
(c) square planar $[PCl_4]^+$ and octahedral $[PCl_6]^-$
(d) square pyramidal

47. The ion that has sp^3d^2 hybridisation for the central atom, is ***(JEE Main 2019)***

(a) $^-$ (b) $[BrF_2]^-$
(c) $[ICl_4]^-$ (d) $[IF_6]^-$

48. The correct statements among I to III are :

I. Valence bond theory cannot explain the color exhibited by transition metal complexes.
II. Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.

III. Valence bond theory cannot distinguish ligands as weak and strong field ones.

(JEE Main 2019)

(a) II and III only (b) I, II and III
(c) I and II only (d) I and III only

49. Although both CO_2 and H_2O are triatomic molecules, the shape of the H_2O molecule is bent while that of CO_2 is linear. This is because *(NCERT)*

(a) C is less electronegative than H
(b) C is more electronegative than H
(c) lone pairs are present on O-atom of H_2O but not in O-atom of CO_2
(d) lone pairs carrying O is the central atom in H_2O but not in CO_2

50. Which of the following species has tetrahedral geometry?

(a) BH_4^- (b) NH_2^-
(c) CO_3^{2-} (d) H_3O^+

51. The structure of IF_7 is *(AIEEE 2011)*

(a) square pyramid (b) trigonal bipyramid
(c) octahedral (d) pentagonal bipyramid

Molecular Orbital Theory (MOT)

52. The molecule having smallest bond angle is

(a) (b) $AsCl_3$ *(AIEEE 2012)*
(c) $SbCl_3$ (d) PCl_3

53. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order

(a) $NH_2^- > NH_3 > NH_4^+$ (b) $NH_4^+ > NH_3 > NH_2^-$
(c) $NH_3 > NH_2^- > NH_4^+$ (d) $NH > NH_4^+ > NH_2^-$

54. Which one of the following is paramagnetic and has the bond order half (0.5)?

(a) F_2 (b) N_2 (c) O_2 (d) H_2^+

55. Which of the following molecular orbitals has two nodal planes?

(a) $\sigma 2p_x$ (b) $\pi 2p_y$
(c) $\pi^* 2p_y$ (d) $\sigma^* 2p_x$

56. In which of the following diatomic molecules/ions is the bond order of each molecule/ion = 2.5 ?

(a) O_2^+, NO, CN^- (b) CN^-, N_2^+, N_2
(c) N_2^+, NO, O_2^+ (d) O_2^+, CN^-, N_2^+,

57. The order of bond energies in NO, NO^+ and NO^- are decreases as

(a) $NO^- > NO > NO^+$
(b) $NO^+ > NO^- > NO$
(c) $NO > NO^- > NO^+$
(d) $NO^+ > NO > NO^-$

58. Using MO theory predict which of following species has the shortest bond length?

(a) O_2^+ (b) O_2^{2+}
(c) O_2^- (d) O_2^{2-}

59. The bond length of species O_2, O_2^+ and O_2^- are in the order of

(a) $O_2^+ > O_2 > O_2^-$ (b) $O_2^- > O_2 > O_2^+$
(c) $O_2 > O_2^+ > O_2^-$ (d) $O_2 > O_2^- > O_2^+$

60. In the formation of NO^+ from NO, the electron is removed from

(a) a σ-orbital (b) a π-orbital
(c) a σ^*-orbital (d) a π^*-orbital

61. Which among the following molecules/ions is diamagnetic?

(a) Super oxide ion
(b) Oxygen
(c) Carbon molecule
(d) Unipositive ion of N_2 molecule

62. N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which of the following is wrong?

(a) In N_2^+, N—N bond weakens
(b) In O_2^+, the O—O bond order increases
(c) In O_2^+, paramagnetism decreases
(d) N_2^+ becomes diamagentic

63. Which of the following diatomic molecules would be stabilised by the removal of an electron?

(a) C_2 (b) CN (c) N_2 (d) O_2

64. Among the following species, the diamagnetic molecule is *(JEE Main 2019, 2017)*

(a) CO (b) B_2 (c) NO (d) O_2

65. According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^-?

(a) Both are unstable
(b) Li_2^+ is unstable and Li_2^- is stable
(c) Both are stable
(d) Li_2^+ is stable and Li_2^- is unstable

66. According to molecular orbital theory, which of the following will not be a viable molecule?

(a) He_2^{2+} (b) He_2^+ *(JEE Main 2018)*
(c) H_2^- (d) H_2^{2-}

67. Which of the following species exhibits diamagnetic behaviour?

(a) O_2^{2-} (b) O_2^+ (c) O_2 (d) NO

68. 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+}

69. 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) $Li_2^- < Li_2 < Li_2^+$

70. Among the following, the molecule expected to be stabilised by anion formation is C_2, O_2, NO, F_2. *(JEE Main 2019)*

(a) C_2 (b) F_2
(c) NO (d) O_2

71. 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)*

(a) C_2^{2-} (b) O_2 (c) O_2^{2-} (d) N_2^{2-}

72. In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic? *(JEE Main 2019)*

(a) $O_2 \rightarrow O_2^+$ (b) $N_2 \rightarrow N_2^+$
(c) $O_2 \rightarrow O_2^{2-}$ (d) $NO \rightarrow NO^+$

Metallic and Hydrogen Bonding

73. Which of the following does not apply to metallic bond?

(a) Overlapping valence orbitals
(b) Mobile valence electrons
(c) Delocalised electrons
(d) Highly directed bonds

74. Two ice cubes are pressed over each other until they unite to form one block. Which one of the following forces dominates for holding them together?

(a) Dipole-dipole interaction
(b) van der Waals' forces
(c) Hydrogen bond formation
(d) Covalent attraction

75. The maximum possible number of hydrogen bonds in a H_2O molecule that can participate is

(a) 1 (b) 2
(c) 3 (d) 4

76. 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 *(NCERT Exemplar)*

(a) $HF > H_2O > NH_3$ (b) $H_2O > HF > NH_3$
(c) $NH_3 > HF > H_2O$ (d) $NH_3 > H_2O > HF$

77. Which of the following hydrogen bond is the strongest?

(a) $O—H \cdots N$ (b) $F—H \cdots F$
(c) $O—H \cdots O$ (d) $O—H \cdots F$

ROUND II Mixed Bag

1. The HOMO in CO is

(a) π-bonding (b) π-antibonding
(c) σ-antibonding (d) σ-bonding

2. With which of the given pairs resembles with CO_2?

(a) $HgCl_2, C_2H_2$ (b) C_2H_2, NO_2
(c) $HgCl_2, SnCl_4$ (d) N_2O, NO_2

3. Which of the following has maximum dipole moment?

(a) NCl_3 (b) NBr_3 (c) NH_3 (d) NI_3

4. Carbon suboxide (C_3O_2) has recently been shown as a component of the atmosphere of Venus. Which of the following formulation represents the correct ground state Lewis structure for carbon suboxide?

(a) $:O:C::C:C:O:$
(b) $:O::C::C:C::O:$
(c) $:\ddot{O}::C::C::C::\ddot{O}:$
(d) $:O:C:C:C:O:$

5. Among the species: CO_2, CH_3COO^-, CO, CO_3^{2-}, HCHO which has the weakest C—O bond?

(a) CO (b) CO_2
(c) CO_3^{2-} (d) CH_3COO^-

6. In which one of the following cases breaking of covalent bond takes place?

(a) Boiling of H_2O (b) Melting of KCN
(c) Boiling of CF_4 (d) Melting of SiO_2

7. Which of the following substances has the highest melting point?

(a) BaO (b) MgO
(c) KCl (d) NaCl

8. The species C_2

(a) has one σ-bond and one π-bond
(b) has both π-bonds
(c) has both σ-bonds
(d) does not exist

9. The true statements from the following are

1. PH_5 and $BiCl_5$ do not exist.
2. $p\pi$-$d\pi$ bond is present in SO_2.
3. Electrons travel at the speed of light.
4. SeF_4 and CH_4 have same shape.
5. I_3^+ has bent geometry

(a) 1, 3 (b) 1, 2, 5
(c) 1, 3, 5 (d) 1, 2, 4

10. The electronic configuration of four elements L, P, Q and R are given in brackets $L\ (1s^2, 2s^2, 2p^4)$, $P(1s^2, 2s^2, 2p^6, 3s^1)$, $Q\ (1s^2, 2s^2, 2p^6, 3s^2, 3p^5)$, $R(1s^2, 2s^2, 2p^6, 3s^2)$. The formula of ionic compounds that can be formed between these elements are

(a) L_2P, RL, PQ and R_2Q (b) LP, RL, PQ and RQ

(c) P_2L, RL, PQ and RQ_2 (d) LP, R_2L, P_2Q, and RQ

11. Which of the following hydrogen bonds are strongest in vapour phase?

(a) HF---HF (b) HF---HCl

(c) HCl---HCl (d) HF---HI

12. Which combination is best explained by the coordinate covalent bond?

(a) $H^+ + H_2O$ (b) $Cl + Cl$

(c) $Mg + \frac{1}{2} O_2$ (d) $H_2 + I_2$

13. The species having pyramidal shape is

(a) SO_3 (b) BrF_3

(c) SiO_3^{2-} (d) OSF_2

14. Which of the following compound cannot act as a Lewis base? ***(JEE Main 2021)***

(a) NF_3 (b) PCl_5

(c) SF_4 (d) ClF_3

15. Which of the following conversions involve change in both hybridisation and shape?

(a) $CH_4 \longrightarrow C_2H_6$

(b) $NH_3 \longrightarrow NH_4^+$

(c) $BF_3 \longrightarrow BF_4^-$

(d) $H_2O \longrightarrow H_3O^+$

16. Which of the following has least covalent P—H bond?

(a) PH_3 (b) P_2H_6

(c) P_2H_5 (d) PH_6^+

17. Match the species given in Column I with the geometry/shape given in Column II. ***(NCERT Exemplar)***

Column I		Column II	
A.	H_3O^+	1.	Linear
B.	$HC \equiv CH$	2.	Angular
C.	ClO_2^-	3.	Tetrahedral
D.	NH_4^+	4.	Trigonal bipyramidal
		5.	Pyramidal

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	5	1	2	3
(c)	1	2	5	3
(d)	3	2	4	1

18. Match the species given in Column I with the bond order given in given Column II. ***(NCERT Exemplar)***

Column I		Column II	
A.	NO	1.	1.5
B.	CO	2.	2.0
C.	O_2^-	3.	2.5
D.	O_2	4.	3.0

Codes

	A	B	C	D
(a)	3	4	1	2
(b)	1	2	3	4
(c)	2	4	3	1
(d)	3	1	2	4

Numeric Value Questions

19. The number of Cl = O bonds in perchloric acid is "..........". ***(JEE Main 2020)***

20. The bond angle between two hybrid orbital is 105°. The percentage of *s*-character of hybrid orbital is between x–23%. The value of x will be.......

21. $2H_2^-$, H_2^+, H_2 and He^{2+} are given species. Among them … number of species is/are paramagnetic in nature ?

22. Bond order of N—O bonds in nitrate ion is y. If y is added with 8.67 we get the value as … .

23. Given below are some molecule, H_2O, HF, NH_3 and CH_4. Molecules contains one pair of non-bonding electrons is/are …… .

24. BH_4^-, NH_4^+, CO_3^{2-} and H_3O^+ out of these given ions, …… does not contain coordinate bond.

25. The molecule ML_x is planar with six pairs of electrons around M in the valence shell. The value of x is … .

26. A σ-bonded molecule MX_3 is T-shaped. The number of non-bonding pairs of electron in any MX_3 molecule is … .

27. In a polar molecule, the ionic charge is 4.8×10^{-10} esu. If the interionic distance is 1 Å unit, then the dipole moment is …… debye.

28. Among the following ions, the $p\pi - d\pi$ overlapping could be present in …… ions.

$$PO_4^{3-}, NO_2^-, NO_3^-, CO_3^{2-}$$

29. Consider two elements with atomic no. 37 and 53. Suppose their valencies are x and y. Then the product $x \times y$ is … .

30. Consider the following molecule/ion O_2^{2-}, B_2, N_2^+ and O_2. …… molecule/ion contain unpaired electrons.

31. Number of hybrid orbital of carbon in carbon suboxide is … .

Answers

Round I

1. *(d)*	***2.*** *(c)*	***3.*** *(b)*	***4.*** *(b)*	***5.*** *(c)*	***6.*** *(c)*	***7.*** *(a)*	***8.*** *(d)*	***9.*** *(d)*	***10.*** *(d)*
11. *(c)*	***12.*** *(d)*	***13.*** *(a)*	***14.*** *(c)*	***15.*** *(b)*	***16.*** *(c)*	***17.*** *(c)*	***18.*** *(a)*	***19.*** *(c)*	***20.*** *(c)*
21. *(b)*	***22.*** *(c)*	***23.*** *(b)*	***24.*** *(a)*	***25.*** *(b)*	***26.*** *(b)*	***27.*** *(d)*	***28.*** *(d)*	***29.*** *(c)*	***30.*** *(b)*
31. *(d)*	***32.*** *(c)*	***33.*** *(c)*	***34.*** *(c)*	***35.*** *(d)*	***36.*** *(c)*	***37.*** *(a)*	***38.*** *(b)*	***39.*** *(b)*	***40.*** *(c)*
41. *(b)*	***42.*** *(d)*	***43.*** *(b)*	***44.*** *(a)*	***45.*** *(b)*	***46.*** *(a)*	***47.*** *(c)*	***48.*** *(d)*	***49.*** *(d)*	***50.*** *(a)*
51. *(d)*	***52.*** *(c)*	***53.*** *(b)*	***54.*** *(d)*	***55.*** *(c)*	***56.*** *(c)*	***57.*** *(d)*	***58.*** *(b)*	***59.*** *(b)*	***60.*** *(d)*
61. *(c)*	***62.*** *(d)*	***63.*** *(d)*	***64.*** *(a)*	***65.*** *(d)*	***66.*** *(d)*	***67.*** *(a)*	***68.*** *(c)*	***69.*** *(b)*	***70.*** *(a)*
71. *(a)*	***72.*** *(d)*	***73.*** *(d)*	***74.*** *(c)*	***75.*** *(d)*	***76.*** *(b)*	***77.*** *(b)*			

Round II

1. *(d)*	***2.*** *(a)*	***3.*** *(c)*	***4.*** *(c)*	***5.*** *(c)*	***6.*** *(d)*	***7.*** *(b)*	***8.*** *(b)*	***9.*** *(b)*	***10.*** *(c)*
11. *(a)*	***12.*** *(a)*	***13.*** *(d)*	***14.*** *(b)*	***15.*** *(c)*	***16.*** *(d)*	***17.*** *(b)*	***18.*** *(a)*	***19.*** *(3.00)*	***20.*** *(21)*
21. *(3)*	***22.*** *(10)*	***23.*** *(1)*	***24.*** *(1)*	***25.*** *(4)*	***26.*** *(2)*	***27.*** *(4.8)*	***28.*** *(1)*	***29.*** *(1)*	***30.*** *(3)*
31. *(2)*									

Solutions

Round I

4. $N_2 < SO_2 < ClF_3 < K_2O < LiF$

5. According to Fajan's rule, largest cation and smallest anion form ionic bond.

6. Greater is the electronegativity difference between the two bonded atoms, greater is the ionic character.

$$\text{N — H;}\quad \text{F — H;}\quad \text{C — H and O — H}$$

Electronegativity

$(3.0 - 2.1) = (4.0 - 2.1) = (2.5 - 2.1) = (3.5 - 2.1)$

difference $\quad 0.9 \quad 1.9 \quad 0.4 \quad = 1.4$

Therefore, increasing order of ionic character of the given bonds is as follow

$$\text{C — H} < \text{N — H} < \text{O — H} < \text{F — H}$$

8. In order to complete their octet X requires 4, Y requires 3 and Z requires only one electron.

Thus, valency of X, Y and Z are respectively 4,3,1.

Thus, the formulae of their hydrides are XH_4, YH_3 and YH_5, Z — H.

Thus, among the given option YH_5 is the correct formula.

9. Lattice energy $\propto$ charge of ions $\propto \dfrac{1}{\text{size of ions}}$

10. Lattice energy, $U = \dfrac{q_1 q_2}{r^2}$

Since, interionic distances, i.e. in CaO and NaCl are almost similar, (larger cation has smaller anion and *vice-versa*). Therefore, lattice energy depends only on charge.

Since, the magnitude of charge on Na^+ and Cl^- ions is same, i.e. unity and that on Ca^{2+} and O^{2-} ions is 2 each, therefore, the lattice energy of CaO is four times the lattice energy of NaCl, i.e. 4U.

12. Isoelectronic species contains same number of electrons. The species with their atomic number and number of electrons are as follows

Species (Ions)	**At. no.** (Z)	**No. of electrons**
N^{3-}	7	$7 + 3 = 10$
O^{2-}	8	$8 + 2 = 10$
F^-	9	$9 + 1 = 10$
Na^+	11	$11 - 1 = 10$
Li^+	3	$3 - 1 = 2$
Mg^{2+}	12	$12 - 2 = 10$

Thus, option (d) contains isoelectronic set of ions.

13. Isoelectronic species are those which contains same number of electrons.

Given species with their atomic number and number of electrons are as follow

Species	**Atomic number**	**Number of electrons**
O^{2-}	8	10
F^-	9	10
Na^+	11	10
Mg^{2+}	12	10
O^-	8	9
Na	11	11
Mg^+	12	11

$\therefore$ Option (a) is correct which contains isoelectronic species, i.e. O^{2-}, F^-, Na^+, Mg^{2+}.

14.

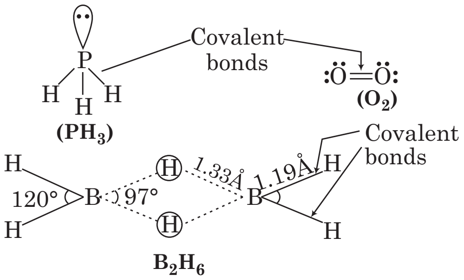
(a)	CO_3^{2-}, NO_3^-	Triangular planar
(b)	$PCl_4^+, SiCl_4$	Tetrahedral
(c)	PF_5	Trigonal bipyramidal
	BrF_5	Square pyramidal
(d)	AlF_6^{3-}, SF_6	Octahedral

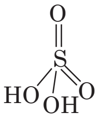
15. Isoelectronic species have same number of electrons, NO^+ C_2^{2-}, CN^- and N_2 all have 14 electrons.

16. In all the given compounds, anion is same (Cl^-), hence polarising power is decided by size and charge of cation. Al^{3+} with maximum charge and smallest size has maximum polarising power hence, $AlCl_3$ has maximum covalent character.

18. $SiCl_4$ because covalent character $\propto$ charge of cation.

19. KCl is the only ionic compound. The structure of PH_3, O_2, B_2H_6 and H_2SO_4 showing covalent bonds are given below

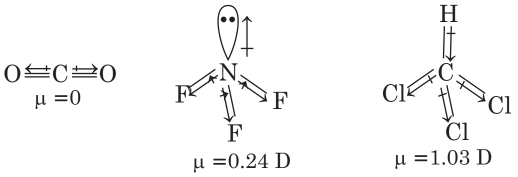




Sulphuric acid
(H_2SO_4)

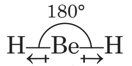
In H_2SO_4 also all bond between S and O-atom are covalent bonds.

20.



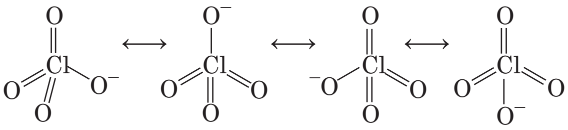
Increasing order of dipole moment is $CO_2 < NF_3 < CHCl_3$

21. BeH_2 molecule is linear. The two equal bond dipoles point in opposite directions and cancel the effect of each other. That's why, its dipole moment is zero.



BeH_2 molecule, m = 0

23. The resonating structures of ClO_4^- are as follows



$$\text{Bond order} = \frac{\text{Total number of bonds between Cl and O}}{\text{Total number of resonating structures}}$$

$$= \frac{7}{4} = 1.75$$

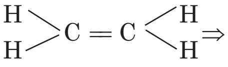
24. H—O—O—H, O ← O═O, O═O

Due to resonance, the O—O bond length in O_3 will be in between *O* ═*O* and O—O.

O—O being a single bond is larger than the O═O

29. $XeF_4 \Rightarrow 4bp + 2\,lp \Rightarrow$ square planar $\Rightarrow$ all bonds are equal

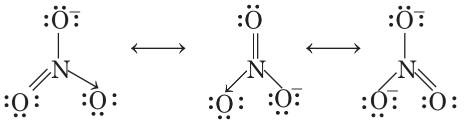
$BF_4^- \Rightarrow 4bp + 0\,lp \Rightarrow$ tetrahedral (all bonds are equal)

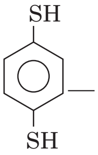
$C_2H_4 \Rightarrow$  $\Rightarrow$ C = C bond is not equal to C — H bond

$SiF_4 \Rightarrow 4\,bp + 0\,lp \Rightarrow$ tetrahedral (all bonds are equal)

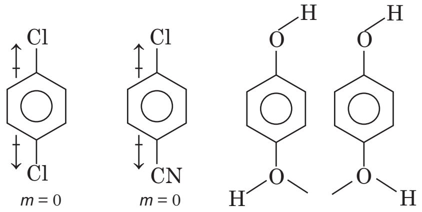
Thus, from the given option only in C_2H_4 all the bonds are not equal.

30. Nitrate ion, NO_3^-



31. In quinol  and thioquinol,  —OH and

—SH groups do not cancel their dipole moments this is due to the existance of different conformations.



2 different conformers [∴ μ ≠ 0]
[same as thioquinol]

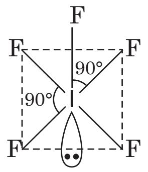
38. Since, bond angle is 120°, orbital is *sp*^{2}-hybridised. In *sp*^{2}-hybridised orbital, % of *s*-character

$$= \frac{1}{1+2} \times 100 = 33\%$$

40. Number of hybrid orbitals = no. of *bp* + no. of *lp*

$$= 5 + 1 = 6$$

Thus, hybridisation is sp^3d^2 but geometry, due to the presence of one lone pair, is square pyramidal, i.e.

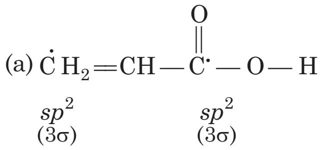


41. $NO_2^+ = 2bp + 0lp$ = linear = sp-hybridised

$NO_3^- = 3\,bp + 0\,lp \Rightarrow sp^2$-hybridised

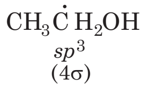
$NH_4^+ \Rightarrow 4\,bp + 0\,lp \Rightarrow sp^3$-hybridised

42. (a)



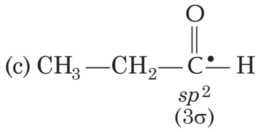
$\dot{C}H_2{=}CH{-}\overset{\overset{O}{\|}}{\dot{C}}{-}O{-}H$; $\underset{(3\sigma)}{sp^2}$, $\underset{(3\sigma)}{sp^2}$

(b)



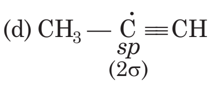
$CH_3\underset{\underset{(4\sigma)}{sp^3}}{\dot{C}}H_2OH$

(c)



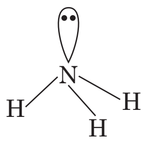
$CH_3{-}CH_2{-}\underset{\underset{(3\sigma)}{sp^2}}{\overset{\overset{O}{\|}}{\dot{C}}}{-}H$

(d)

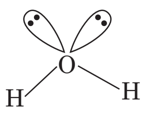


$CH_3{-}\underset{\underset{(2\sigma)}{sp}}{\dot{C}}{\equiv}CH$

43.



NH_3
$bp = 3$
$lp = 1$



H_2O
$bp = 2$
$lp = 2$

In H_2O molecule, there is lone pair-lone pair repulsion due to the presence of two lone pairs of electrons while in NH_3 molecule there found only lone pair-bond pair repulsion.

According to VSEPR theory, the former one is more stronger and hence, the bond angle in water is less than that of ammonia (NH_3).

44. If AB_4 molecule is a polar moelcule, a possible geometry of AB_4 is square pyramidal.

All possible structure of AB_4 molecule are as follows:

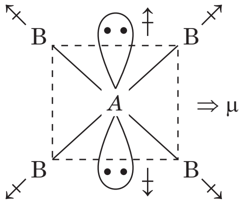
(i) $AB_4 \Rightarrow$ lone pair $= 0 \Rightarrow A$ is sp^3 (tetrahedral) or

A is dsp^2 (square planar)

$\Rightarrow$ Dipole moment, $\mu = 0$ (Non-polar)

(ii) $AB_4L_2 \Rightarrow$ lone pair $= 2 \Rightarrow A$ is sp^3d^2 (octahedral)

$\Rightarrow \mu = 0$ (Non-polar), because

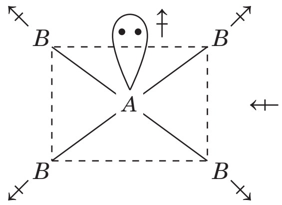


$\Rightarrow \mu_{net} = 0$ (Non-polar)

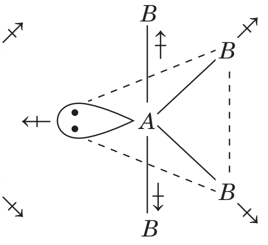
(Assuming, B is more electronegative than A)

(iii) $AB_4L \Rightarrow$ lone pair $= 1 \Rightarrow A$ is sp^3d (square pyramidal or trigonal bipyramidal)

$\Rightarrow \mu \neq 0$ (polar), because



$\mu_{plane} = 0$
$\mu_{axis} \neq 0$
$\mu_{net} \neq 0$ (polar)
[Square pyramidal]

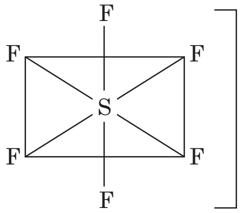


$\mu_{plane} \neq 0$
$\mu_{axis} \neq 0$
$\mu_{net} \neq 0$ (polar)
[Trigonal pyramidal]

So, it can be seen that when AB_4 molecule is a polar molecule then possible geometry of AB_4 is square pyramidal.

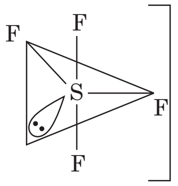
45. The geometry of SF_6 is octahedral and the geometry of SF_4 is trigonal bipyramidal.

SF_6



S: sp^3d^2-hybridised
Geometry = shape
= octahedral

SF_4

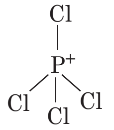


S: sp^3d-hybridised
Geometry = trigonal bipyramidal
Shape = *see-saw*

46. Phosphorus pentachloride (PCl_5) exist

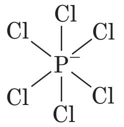
as $[PCl_4]^+$ and $[PCl_6]^-$.

Structure of $[PCl_4]^+$



Tetrahedral
(sp^3-hybridisation)

Structure of $[PCl_6]^-$



Octahedral
(sp^2d^2-hybridisation)

In solid state, PCl_5 prefer to exist as oppositely charged ions like $[PCl_4]^+$ and $[PCl_6]^-$ as the ionic bonding enhances the crystalline nature. These structures providing extra stability to solid.

47. The hybridisation for a central atom in a species can be calculated by using formula

$$H = \frac{1}{2}(V + M - C + A)$$

where,

H = no. of hybridised orbitals used by central atoms.
V = no. of valence electrons of the central atom.
M = no. of mono-valent atoms (bonded).
C = no. of cationic (positive) charge.
A = no. of anionic (negative) charge.

The hybridisation of given species are as follows

For $[ICl_2]^-$ and $[BrF_2]^-$

$$H = \frac{1}{2}(7 + 2 - 0 + 1) = 5\ (sp^3d)$$

For $[ICl_4]^-$,

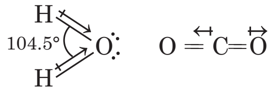
$$H = \frac{1}{2}(7 + 4 - 0 + 1) = 6\ (sp^3d^2)$$

For $[IF_6]^-$,

$$H = \frac{1}{2}(7 + 6 - 0 + 1) = 7\ (sp^3d^3)$$

48. Among the given statements, correct statements are I and III only. Valence bond theory (VBT) cannot explain the colour exhibited by transition metal complexes. This theory cannot distinguish ligands as weak and strong field ones.

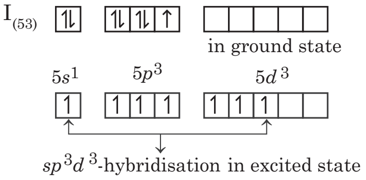
49. The net dipole moment of CO_2 is zero. This is because the two equal bond dipoles ($\overset{\delta^+}{C}—\overset{\delta^-}{O}$) point in opposite directions and cancel the effect of each other. Hence, CO_2 is linear. On the other hand, H_2O molecule is found to have a net dipole moment (1.84 D) which suggests that the two O—H dipoles are not in a straight line opposing each other, i.e. H_2O does not have linear structure, but they (O—H) must be inclined to each other at certain angle. Thus, H_2O molecule has a bent structure in which the two O—H bonds are oriented at an angle of 104.5°.

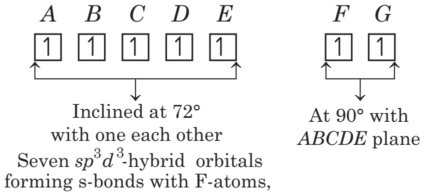


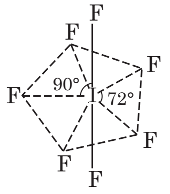
50. $BH_4^- \Rightarrow 4\ bd + 0\ lp \Rightarrow$ B is sp^3-hybridised = tetrahedral geomety

51. IF_7-Outer orbital diagram of I

$I_{(53)}$







Pentagonal-bipyramidal structure

52. N, P, As, Sb — Group = 15; Valence electrons = 5

MCl_3 has sp^3-hybridised M-element with one lone-pair.

Lone-pair and bond-pair repulsion decreases bond angle. However, the bond-pairs of electrons are much farther away from the central atom than they are in NCl_3. Thus, lone-pair causes even greater distortion in PCl_3, $AsCl_3$ and $SbCl_3$. Thus, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

53. As the number of lone pairs of electrons increases, bond angle decreases. Thus, the order of bond angle is

$$\underset{(\text{no}\ lp)}{NH_4^+} > \underset{(1\ lp)}{NH_3} > \underset{(2\ lp)}{NH_2^-}$$

54. $H_2^+\ (1 + 1 - 1 = 1) = \sigma 1s^1$

$$BO = \frac{1-0}{2} = 0.5$$

Since one unpaired electron is peresent, it is a paramagnetic species.

57. $NO^+\ (7 + 8 - 1 = 14)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx 2p_y^2, \sigma 2p_z^2, \overset{*}{\pi} 2p_x^0 \approx \overset{*}{\pi} 2p_y^0$$

$$B.O = \frac{10-4}{2} = 3$$

NO $(7 + 8 = 15)$ $\quad BO = \frac{10-5}{2} = 2.5$

$NO^-\ (7 + 8 + 1 = 16)$

$$B.O = \frac{10-6}{2} = 2$$

Since, bond length $\propto \frac{1}{BO}$

So, the order of bond length is

$$NO^- < NO < NO^+$$

59. Find B.O for each species from M.O configuration (B. O of $O_2^+ = 2.5, O_2 = 2\ O_2^- = 1.5$) and bond length is inversely proportional to bond order. So, the order of bond length is $O_2^- > O_2 > O_2^+$.

60. $NO\ (7+8=15) = \sigma 1\, s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2,\ \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2$
$\approx \pi 2\ p_y^2, \overset{*}{\pi} 2p_x^1$

$NO^+\ (7+\ 8-1=\ 14) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2\ p_z^2, \pi 2p_x^2$
$\approx \pi 2p_y^2$

Thus, electron is removed from $\overset{*}{\pi}$-orbital.

61. $C_2\ (6+6=12)\ \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$

62. $N_2\ (7+\ 7=14) = \sigma 1\ s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2,\ \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$B.O = \frac{10-4}{2} = 3$$

$N_2^+\ (7+\ 7-1=13) = \sigma 1\ s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2,\ \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$

$$B.O = \frac{9-4}{2} = 2.5$$

N_2^+ is paramagnetic.

$O_2\ (8+8=16) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_x^2,$
$\pi 2p_z^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$

$$B.O = \frac{10-6}{2} = 2$$

$O_2^+\ (8+8-1=15)$

$$B.O = \frac{10-5}{2} = 2.5$$

Thus, $N_2 > N_2^+$ and $O_2^+ > O_2$ (stability order)

63. In O_2, there are two electrons in antibonding orbitals. Removal of one electron from the O_2 molecule gives O_2^+ in which the number of antibonding electrons is one less and hence, B.O increases. Thus, removal of one electron from O_2 stabilises the molecule.

64. Magnetic nature can be detected by molecular orbital theory. Presence of unpaired electrons means paramagnetic and absence of unpaired electrons means diamagnetic in nature.

Among the given options, CO is a diamagnetic molecule. It can be proved by molecular orbital (M.O) theory.

The electronic configuration of given diatomic molecules are as follows

(a) CO (Number of electrons = 14)
Electronic configuration
$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2$

Since, there is no unpaired electron in the CO molecule, so it is diamagnetic.

(b) NO (Number of electrons = 15)

Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2,$
$\sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^0$

Since, NO has one unpaired electron in $\pi^* 2p_x^1$ orbital, so it is paramagnetic.

(c) B_2 (Number of electrons = 10)

Electronic configuration
$= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi p_y^1$

Since, two unpaired electrons are present in $\pi 2p_x^1$ and $\pi 2p_y^1$ orbital. So, it is paramagnetic.

(d) O_2 (of electrons = 16)

Electronic configuration $= \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2,$
$\sigma^* 2s^2, \sigma 2pz^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^1$

Since, two unpaired electrons are present in $\pi^* 2p_x^1$ and $\pi^* 2p_y^1$ orbital. So, it is also paramagnetic.

65. Considering molecular orbital theory (M.O.T) :

The electronic configuration of

$$Li_2^+\ (Z=5) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^1$$

$$\text{Bond order (B.O)} = \frac{N_b - N_a}{2} = \frac{3-2}{2} = \frac{1}{2}$$

The electronic configuration of

$Li_2^-(Z=7) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^1$

$$\text{Bond order (BO)} = \frac{N_b - N_a}{2} = \frac{4-3}{2} = \frac{1}{2}$$

For the species having the same value of B.O, the specie having lesser number of antibonding electrons $[N_a]$ will be more stable.

Here, N_a of Li_2^+ (2) < N_a of Li_2^- (3).

So, their order of stability will be $Li_2^+ > Li_2^-$.

66. According to M.O.T, the viability of any molecule can be judged through the calculation of bond order.

Species	Electronic configuration	Bond order
He_2^+	$\sigma_{1s^2}\overset{*}{\sigma}_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^-	$\sigma_{1s^2}\overset{*}{\sigma}_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^{2-}	$\sigma_{1s^2}\overset{*}{\sigma}_{1s^2}$	$\frac{2-2}{2} = 0$
He_2^{2+}	σ_{1s^2}	$\frac{2-0}{2} = 1$

The molecule having zero bond order will not be viable hence, H_2^{2-} (option d) is the correct answer.

67. The correct option is O_2^{2-}.

This species has 18 electrons, which are filled in such a way that all molecular orbitals are fully-filled, so diamagnetic.

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$$

68. Species having zero or negative bond order do not exist.

$$H_2^{2+} (1 + 1 - 2 = 0) = \sigma 1s^0$$

Bond order $= 0$

$$He_2 \, (2 + 2 = 4) = \sigma 1s^2, \overset{*}{\sigma} 1s^2$$

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

So, both H_2^{2+} and He_2 do not exist.

69. $Li_2 \, (3 + 3 = 6) = \sigma 1s^2, \; \overset{*}{\sigma} 1s^2, \sigma 2s^2$

Bond order $= \dfrac{N_b - N_a}{2}$

$= \dfrac{4-2}{2} = 1$

$Li_2^+ \, (3 + 3 - 1 = 5) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^1$

Bond order $= \dfrac{3-2}{2} = \dfrac{1}{2} = 0.5$

$Li_2^- \, (3 + 3 + 1 = 7) \; = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^1$

Bond order $= \dfrac{4-3}{2} = \dfrac{1}{2} = 0.5$

Stability order is $Li_2 > Li_2^+ > Li_2^-$ (because Li_2^- have more number of electrons in antibonding orbitals which destabilises the species).

70. C_2 will be stabilised after forming anion. The electronic configuration of carbon is $1s^2 \, 2s^2 \, 2p^2$. There are twelve electrons in C_2. After forming anion (i.e. C_2^-), the electronic configuration of C_2^- is

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

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

Bond order $= \dfrac{1}{2} (N_b - N_a) = \dfrac{1}{2} (9 - 4) = 2.5$

For other options such as F_2^-, O_2^-, NO^-, the electronic configurations are as follows :

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

Bond order $= 1/2 (N_b - N_a) = 1/2 (10 - 9) = 0.5$

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

Bond order $= \dfrac{1}{2} (N_b - N_a) = \dfrac{1}{2} (10 - 7) = 1.5$

NO^- : $(\sigma 1s)^2 \, (\sigma^* 1s)^2 \, (\sigma 2s)^2 \, (\sigma * 2s)^2 (\sigma 2p_z)^2$
$(\pi 2p_x^2 = \pi 2p_y^2) \, (\pi^* \; 2p_x^1 = \pi^* 2p_y^1)$

Bond order $= \dfrac{1}{2} (N_b - N_a) = \dfrac{1}{2} (10 - 6) = 2$

The value of bond order of C_2^- is highest among the given options. Bond order between two atoms in a molecule may be taken as an approximate measure of the bond length.

The bond length decreases as bond order increases. As a result, stability of a molecule increases.

71.

Species	M.O energy order	Bond order (B.O)	*n*, no. of unpaired e^-	Magnetic character
$C_2^{2-} (14e^-)$	$[8\bar{e}] \pi_{2p_x^2} = \pi_{2p_y^2} \sigma_{2p_z^2}$	$\dfrac{6-0}{2} = 3$	0	Diamagnetic
$O_2 (16e^-)$	$[8\bar{e}] \sigma_{2p_z^2} \pi_{2p_x^2} = \pi_{2p_y^2} \overset{*}{\pi}_{2p_x^1} = \overset{*}{\pi}_{2p_y^1}$	$\dfrac{6-2}{2} = 2$	2	Paramagnetic
$O_2^{2-} (18e^-)$	$[8\bar{e}] \sigma_{2p_z^2} \pi_{2p_x^2} = \pi_{2p_y^2} \overset{*}{\pi}_{2p_x^2} = \overset{*}{\pi}_{2p_y^2}$	$\dfrac{6-4}{2} = 1$	0	Diamagnetic
$N_2^{2-} (16e^-)$	$[8\bar{e}] \pi_{2p_x^2} = \pi_{2p_y^2} \sigma_{2p_z^2} \overset{*}{\pi}_{2p_x^1} = \overset{*}{\pi} 2p_y^1$	$\dfrac{6-2}{2} = 2$	2	Paramagnetic

$$\text{Bond length} \propto \frac{1}{\text{B. O (Bond order)}}$$

So, order of bond length is $\underset{(\text{B.O} = 3)}{C_2^{2-}} < \underset{(\text{B.O} = 2)}{O_2} = N_2^{2-} < \underset{(\text{B.O} = 1)}{O_2^{2-}}$

The diamagnetic species with shortest bond length is C_2^{2-} (option-a).

72.

Species	Valence M.Os	Bond order $\left(\dfrac{N_b - N_a}{2}\right)$	Paramagnetic/Diamagnetic Nature
$NO(15e^-)$	$[8e^-]\ \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^1 = \pi * 2p_y^0 \sigma * 2pz^0$	$\dfrac{6-1}{2} = 2.5$	Paramagnetic
$\xrightarrow{-e^-} NO^+ (14e^-)$	$[8e^-]\ \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^0 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\dfrac{6-0}{2} = 3$	Diamagnetic
$N_2(14e^-)$	$[8e^-]\pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$ $\pi * 2p_x^0 = \pi * 2p_y^0, \sigma 2p_z^0$	$\dfrac{6-0}{2} = 3$	Diamagnetic
$\xrightarrow{-e^-} N_2^+ (13e^-)$	$[8e^-]\pi 2p_x^2 = \pi 2p_y^2 \sigma\ 2p_{z^1}$ $\pi * 2p_x^0 = \pi * 2p_y^0 \sigma * 2pz_0$	$\dfrac{5-0}{2} = 2.5$	Paramagnetic
$O_2(16e^-)$	$[8e^-]\sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^1 = \pi * 2p_y^1 \sigma * 2p_z^0$	$\dfrac{6-2}{2} = 2$	Paramagnetic
$\xrightarrow{-e^-} O_2^+ (15e^-)$	$[8e^-]\sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^1 = \pi * 2p_y^0 \sigma * 2p_z^0$	$\dfrac{6-1}{2} = 2.5$	Paramagnetic
$\xrightarrow{+2e^-} O_2^{2-} (18e^-)$	$[8e^-]\sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ $\pi * 2p_x^2 = \pi * 2p_y^2 \sigma * 2p_z^0$	$\dfrac{6-4}{2} = 1$	Diamagnetic

So, only in the conversion of $NO \rightarrow NO^+$, the bond order has increased $(2.5 \rightarrow 3)$ and paramagnetic character has changed to diamagnetic.

76. Although F forms stronger H-bonding, but H_2O has higher boiling point due to more number of H_2O molecules that bonded together by H-bonds. N is least electronegative than F and O. Thus, hydrogen bonding is less in this case as a result boiling point is also less.

77. Since, H-bond is the electrostatic force of attraction between H-atom and electronegative element.

Thus, fluorine being the most electronegative element forms stronger H-bonds. On the other hand, H—F possesses larger electronegative difference than O—H.

Therefore, H—F molecule is more polarised than O—H, due to which H-atom of H—bears larger amount of partial charge than that of O—H. This suggests H-atom of H—F attracts more strongly F-atom than that of O—H.

Hence, H—F forms more stronger H-bonds with fluorine than that of H—H.

Round II

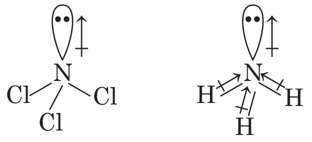
1. HOMO, means highest occupied molecular orbital and in CO (14 electron ion), σ bonding molecular orbital is HOMO.

$CO = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

2. All have linear structure.

$O{=}C{=}O, Cl{-}Hg{-}Cl, H{-}C{\equiv}C{-}H$

3. Electronegativity difference between N (3.0) and Cl (3.0) is zero and hence, N—Cl bonds are non-polar. As a result, the overall dipole moment of NCl_3 molecule and its direction is just the dipole moment of the lone pair of electrons.



On the other hand, N—Br, (3.0 – 2.8), N—I (3.0 – 2.5) and N—H (3.0 – 2.1) bonds are polar and hence, contribute towards the overall dipole moment of the respective molecules. Since, the EN difference is higher in case of N—H bonds, therefore, NH_3 has the higher dipole moment.

4. In structure (c), all the atoms have complete octet. Thus, it is the correct representation of carbon suboxide.

5. 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.

6. During melting of SiO_2, the giant network structure held by covalent bonds breaks to give individual molecules of SiO_2. In contrast, during boiling of H_2O only change of state occurs from liquid to gaseous; during melting of KCN, electrostatic attraction between K^+ and CN^- ions is overcome; during boiling of CF_4, van der Waals' forces of attraction breaks.

7. Melting point depends upon lattice energy. NaCl and KCl have unit charge on their ions while MgO and

BaO have two units of charge, therefore, lattice energies of MgO and BaO are expected to be larger than those of NaCl and KCl. Since, Mg^{2+} is smaller than Ba^{2+}, therefore, MgO has the highest lattice energy and hence, has the highest melting point.

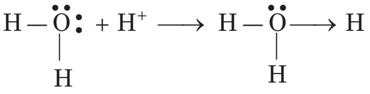
8. In C_2 only 2π-bonds are present.

9. SeF_4 has distorted tetrahedral geometry while, CH_4 has tetrahedral geometry.

Speed of electron ≠ speed of light

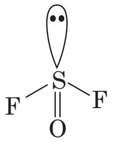
10. Valencies of L, Q, P and R is –2, –1, +1, and +2 respectively. So, they will form P_2L, RL PQ, and RQ_2.

11. A compound having maximum electronegative element will form strong hydrogen bond.

12. 

$$H-\underset{\displaystyle H}{\overset{\bullet\bullet}{\underset{|}{O}}}\!: + H^+ \longrightarrow H-\underset{\displaystyle H}{\overset{\bullet\bullet}{\underset{|}{O}}}\longrightarrow H$$

13. OSF_2 has pyramidal shape.



14. Lewis base : Chemical species which has capability to donate electron pair.

In NF_3, SF_4, ClF_3 central atom (i.e. N, S, Cl) have lone pair therefore act as Lewis base.

In PCl_5, central atom (P) does not have lone pair therefore does not act as Lewis base..

15. (a)

	CH_4	$\longrightarrow$	CH_3-CH_3
	$4bp + 0\,lp$		$4bp$ $4bp$
Hybridisation	sp^3		sp^3 sp^3
Structure	Tetrahedral		Tetrahedral

(b)

	NH_3	$\longrightarrow$	NH_4^+
	$3bp + 1\,lp$		$4bp$
Hybridisation	sp^3		sp^3
Structure	Pyramidal		Tetrahedral

(c)

	BF_3	$\longrightarrow$	BF_4^-
	$3bp$		$4bp$
Hybridisation	sp^2		sp^3
Structure	Trigonal planar		Tetrahedral

(d)

	H_2O	$\longrightarrow$	H_3O^+
	$2bp + 2lp$		$3bp + 1\ lp$
Hybridisation	sp^3		sp^3
Structure angular			Pyramidal

Thus, conversion of BF_3 into BF_4^- involves change in both hybridisation and shape.

16. Due to the presence of positive charge on P, it attracts the electrons of the P—H bond towards itself. Consequently, the bond has some ionic character.

In other words, the P—H bond in PH_6^+ is least covalent.

17. (a) $H_3O^+ = 3bp + 1lp \Rightarrow$ pyramidal

(b) $HC\equiv CH$ = linear as *sp*-hybridised

(c) $ClO_2^- \Rightarrow 2bp + 2lp \Rightarrow$ angular

(d) $NH_4^+ \Rightarrow 4bp + 0lp \Rightarrow$ tetrahedral

18. $NO\ (7 + 8 = 15) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}2p_x^1$$

$$B.O = \frac{10-5}{2} = 2.5$$

CO (6 + 8 = 14)

$$B.O = \frac{10-4}{2} = 3$$

$O_2^-\ (8 + 8 + 1 = 17) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2,$

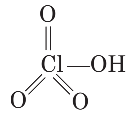
$$\pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}2p_x^2 \approx \overset{*}{\pi}2p_y^1$$

$$B.O = \frac{10-7}{2} = 1.5$$

$O_2\ (8 + 8 = 16)$,

$$B.O = \frac{10-6}{2} = 2$$

19. Perchloric acid is $HClO_4$. Its structure is as follows



Thus, Cl$=$O bond is 3. Hence, the correct answer is 3.

20. *s*-character ∝ bond angle.

For 25% *s*-character (as in sp^3-hybrid orbital), bond angle is 109.5°, for 33.3%, *s*-character (as in sp^2-hybrid orbital), bond angle is 120° and for 50%, *s*-character (as in *sp*-hybrid orbital), bond angle is 180°.

Similarly, when the bond angle decreases below 109.5°, the *s*-character will decrease accordingly.

Decrease in bond angle $= 120° - 109.5° = 10.5°$

$\therefore$ Decrease in *s*-character $= 33.3 - 25 = 8.3$

Actual decrease in bond angle $= 109.5° - 105° = 4.5°$

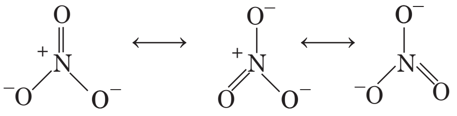
$\therefore$ Expected decrease in *s*-character $= \frac{8.3}{10.5} \times 4.5 = 3.56\%$

Thus, the *s*-character should decrease by about 3.56%, i.e. *s*-character $= 2.5 - 3.56 = 21.44\%$

21. A species is said to be diamagnetic, if it has all paired electrons.

Species	**Electrons**	**M.O electronic configuration**	**Magnetic behaviour**
H_2^-	3	$\sigma 1s^2, \overset{*}{\sigma}1s^1$	Paramagnetic
H_2^+	1	$\sigma 1s^1$	Paramagnetic
H_2	2	$\sigma 1s^2$	Diamagnetic
He_2^+	3	$\sigma 1s^2, \overset{*}{\sigma}1s^1$	Paramagnetic

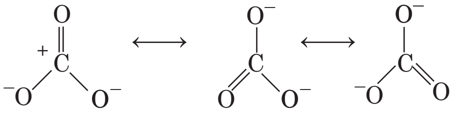
22. Nitrate ion has the following three resonating structure.



As it evident, three O-atoms are attached to the N atom by four bonds, thesefore, bond order of N—O bond is $\frac{4}{3} = 1.33..$ So, the value of y is 1.33. If 1.33 is added with 8.67 we get the value 10.

23. In NH_3, nitrogen has one lone pair of electrons.

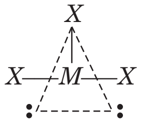
24. CO_3^{2-} has the following structure



Among the given compound CO_3^{2-} is the only one that contains covalent bonds

25. Since, the molecule has six pairs, it should have octahedral geometry. But the structure is planar, therefore, it should have two lone pairs and four bond pairs. Therefore, value of x in ML_x is 4.

26. The formula of MX_3 shows the presence of 3σ-bonds. Since, it has T-shape geometry, it must contain 2 lone pair as



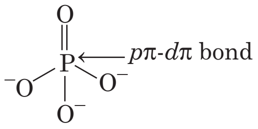
27. Given, ionic charge $= 4.8 \times 10^{-10}$ esu

and ionic distance $= 1\,\text{Å} = 10^{-8}$ cm

We know that,

$$\begin{aligned}\text{Dipole moment} &= \text{ionic charge} \times \text{ionic distance}\\ &= 4.8 \times 10^{-10} \times 10^{-8}\\ &= 4.8 \times 10^{-18}\ \text{esu cm}^{-1} = 4.8\ \text{debye}\end{aligned}$$

28. In PO_4^{3-}, P is sp^3-hybridised, it forms four P—O σ bonds by overlap of sp^3-orbitals of P with p-orbitals of O. The double bond is, however, formed by the overlaping of p-orbitals of O and d-orbitals of P.



N and C, on the other hand, can't form $p\pi$ - $d\pi$ bond, because they do not have d-orbitals.

29. $37 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$

Thus, the element belongs to IA group and has valency +1.

$53 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$

There are 7 electrons in the valence shell of this element, it belong to group VIIA Its valency is – 1.

The magnitude of product of x and y is $= 1$

30. O_2^{2-} (Total numbers of electron = 18)

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2py^2, \overset{*}{\pi} 2px^2 \approx \overset{*}{2}\ py^2$$

Unpaired electron = 0

B_2 (Total number of electron = 10)

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 \approx \pi 2py^1$$

Unpaired electron = 2

N_2^+ (Total number of electron = 13)

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^2 \approx \pi 2py^2, \sigma 2p_z^1$$

Unpaired electron = 1

O_2 (Total number of electron = 16)

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_z^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \pi \overset{*}{2}\ p_y^1$$

Unpaired electron = 2

And hence, there are 3 ion/molecule which contain unpaired electron.

31. The structure of carbon suboxide is

$$:\ddot{O}\ \overset{1\sigma}{\underset{1\pi}{=}}\ C\ \overset{1\sigma}{\underset{1\pi}{=}}\ C\ \overset{1\sigma}{\underset{1\pi}{=}}\ C\ \overset{1\sigma}{\underset{1\pi}{=}}\ \ddot{O}:$$

In C_3O_2, each carbon forms 2 pi bond and 2 sigma bond, so, each carbon is sp-hybridised thus, number of hybrid orbital is 2.z