

Chapter - 4



CHEMICAL BONDING

1 ELECTRONIC THEORY OF VALENCY

The theory of valency explains chemical combination in terms of electrons. The theory was developed independently by W. Kossel and G.N. Lewis (1916) and extended by Irving Langmuir (in 1919).

The chemical behaviour of an atom is determined to a large extent by the number and arrangement of electrons in the outer orbitals of the atom. Only these electrons are involved in chemical combination and so these are called the valence electrons.

COMPLETED ELECTRON OCTET OR DUPLET

Group 0 of the periodic table contains the noble gases. With the exception of helium which has a $1s^2$ electron arrangement others have $ns^2 np^6$ configuration in the outer orbitals.

He $1s^2$

Ne $1s^2 2s^2 2p^6$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

Kr $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Xe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Since the atoms of the noble gases were not known to form chemical bonds, it was argued that the presence of 8 electrons (an electron octet) in the valence shell makes the atom stable. Therefore **all other atoms must undergo bonding by gaining or losing or sharing electrons so as to acquire the electronic configuration of the nearest inert gas**. The presence of 8 electrons gives the name **octet rule** to this concept. In the case of the first few elements such as hydrogen, lithium and beryllium the atoms combine in such a way as to attain the stable structure of helium with 2 electrons (**duplet**) in its only one valence shell. There are, however, many exceptions to the octet rule. Also compounds of noble gases, especially xenon, have been synthesized. The various types of chemical bonds are discussed below.

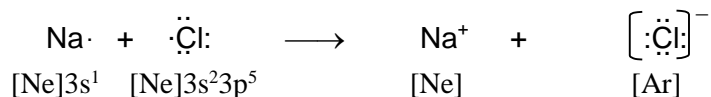
2 IONIC BOND (OR ELECTROVALENT LINKAGE)

An ionic bond is formed **by the complete transfer of electron(s) from one atom to another**. Atoms of metals generally lose electrons and those of non-metals gain electrons.

(i) Formation of sodium chloride, NaCl

A sodium atom ($Z = 11$) transfers its valence electron to a chlorine atom ($Z = 17$). The sodium atom by losing an electron acquires the electronic configuration of neon ($1s^2 2s^2 2p^6$) and becomes sodium ion Na^+ carrying a unit positive charge. The chlorine atom by gaining an electron acquires the stable configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$) and becomes a chloride ion, Cl^- , with a unit negative charge.

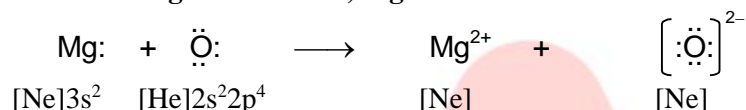
The transfer of electron results in the formation of the ionic bond.



- Here we have used **Lewis dot symbols** in which the symbol of an element is surrounded by dots (or crosses) to represent electrons in the outermost (valence) shell. Formulae of compounds using Lewis symbols are called **Lewis formulae**.
- When atoms form a bond by electron transfer, the **number of electrons lost and gained must be equal**, because the resulting ionic compound is neutral.

- The number of electrons lost or gained by an atom in the formation of an ionic bond is its valence. Thus Na and Cl have a valence of 1.
- Loss of electron** is called **oxidation**; thus Na is oxidised to Na^+ . The **gain of electron is reduction**; thus Cl is reduced to Cl^- . Formation of an ionic bond from elements is an oxidation - reduction or **redox reaction**. Generally the metal is oxidised and the non-metal is reduced.
- Na^+ and Ne are **isoelectronic**: since they contain the **same number of electrons**. Similarly Cl^- and Ar are isoelectronic.
- Because Na^+ and Cl^- carry opposite charges, electrostatic forces of attraction hold them together. Sodium chloride may be represented as Na^+Cl^- .

(ii) **Formation of magnesium oxide, MgO**



2.1 CONDITIONS FOR THE FORMATION OF IONIC BOND

- (i) The difference between the electronegativity of two combining atoms must be greater than two.
- (ii) **Low ionization energy of the metal:** Low ionization energy means that the metal atom requires only a small amount of energy to release its valence electron. For example, sodium, which has a low I.E. readily gives up its loosely held electron and forms Na^+ ion. Metals of s-block have low ionization energies and so readily form the corresponding cations.

Ionization energy of an element with a single electron in its valence shell is less than that with two electrons. In going across a period of the periodic table from left to right, I.E. increases and the formation of the cation is less likely. On going down a group, the outermost electron gets further away from the nucleus, and hence is more easily removed i.e., I.E. decreases; the formation of the cation becomes more likely.

- (iii) **High electron affinity of the non-metal:** An atom with a high electron affinity releases a lot of energy when it takes up an electron and forms an anion. For example, chlorine which has a high electron affinity, readily takes up an electron from the Na atom and forms Cl^- ion. Non-metals of groups VI A and VII A have high electron affinity and can form ionic bonds.

In going across a period from left to right, electron affinity (energy released) increases and so the formation of the negative ion becomes more likely. On going down a group, electron affinity decreases and so the formation of anion becomes less likely.

- (iv) **High lattice energy of the crystal:** In the formation of sodium chloride crystal, the Na^+ ion attracts the Cl^- ion to form an ion-pair Na^+Cl^- . Since the electrostatic force of attraction is present in all directions, this ion-pair will attract other ion-pairs and build up into a crystal lattice. A crystal lattice is three dimensional basic pattern of points, in which each point corresponds to a unit of the crystal, say an ion (atom or molecule). As the lattice builds up, energy is released. The energy released when sufficient number of cations and anions come together to form 1 mole of the compound is called the lattice energy of the compound.

Therefore, an ionic compound is formed when the energy released in (iii) and (iv) exceeds the energy absorbed in (ii).

2.2 GENERAL CHARACTERISTICS OF IONIC COMPOUNDS

- (i) Generally ionic compounds are hard solids. As single ions of a metal are not associated in the solid with single ions of a non-metal, separate units of ionic compounds do not exist.

It is, therefore, wrong to talk of a molecule of an ionic compound. The formula only indicates the ratio of number of ions and the crystal consists of a very large number of oppositely charged ions. Thus in NaCl crystal each Na^+ ion is surrounded by 6 Cl^- ions and vice versa (in an octahedral arrangement). The attraction between Na^+ and Cl^- ions is quite large.

- (2) As a good deal of thermal energy is required to overcome the large electrostatic forces of attraction in an ionic crystal, ionic compounds have high melting and boiling points.

- (3) Ionic compounds are commonly soluble in water and other polar solvents (which separate the ions). They are practically insoluble in organic solvents such as benzene, carbon tetrachloride, etc., as there is no attraction between ions and the molecules of the non-polar liquids.
- (4) Ionic compounds are electrolytes. In the presence of an ionizing solvent such as water, the electrostatic forces between the ions are so greatly reduced that the ions get separated. (This is due to the electrostatic attraction between the ions and the polar molecules of the solvent.) The free ions in solution conduct electricity and on passing a current, the ionic compound undergoes chemical decomposition (called electrolysis). When an ionic compound is melted, the crystal lattice structure is broken and free ions are produced. It is the free movement of ions, which makes an ionic compound a conductor and to undergo electrolysis in the molten condition.
- (5) When an ionic compound dissolves in water, the ions get solvated (in this case hydrated). The energy released is called solvation energy. This energy counters wholly or in part the high lattice energy of the ionic compound. Insoluble ionic compounds (eg., sulphates, phosphates and fluorides of Ca, Sr and Ba) have very high lattice energies and the solvation energy of the constituent ions is insufficient to counteract the high lattice energies and make them soluble.
- (6) The chemical properties of an ionic compound are the properties of its constituent ions. Thus all chlorides give the characteristic reactions of the chloride ion (reactions with conc. H_2SO_4 , AgNO_3 solution, etc). All acids, which contain H^+ ions give the same reactions (change blue litmus to red, effervesce with a carbonate, etc).
- (7) Reactions between solutions of ionic compounds are almost instantaneous, because they are reactions between ions (and do not involve the breaking up of bonds as in covalent compounds, q.v.). For example, when silver nitrate solution is added to sodium chloride solution, silver chloride is immediately precipitated. The reaction may be represented thus:



3 COVALENT BOND

A covalent bond is formed by *the sharing of a pair of electrons between two atoms, each atom contributing one electron to the shared pair*. The shared pair of electrons should have opposite spins and they are localized between the two nuclei concerned. A covalent bond is usually represented by a short line (i.e., a dash) between the two atoms. Note that the covalent bond consists of a pair of electrons shared between two atoms, and occupying a combination of two stable orbitals, one of each atom; the shared electrons of each covalent bond are counted for each of the two atoms connected by the covalent bond.

The difference between the electronegativities of the combining atoms is less than two.

(1) Formation of the hydrogen molecule

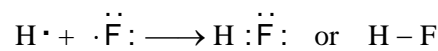
Each hydrogen atom requires 1 electron to become isoelectronic with helium, the nearest inert gas. The hydrogen atoms share their electrons thus:



Once the covalent bond is formed, the two bonding electrons are attracted by the two nuclei (instead of one) and the bonded state is more stable than the non-bonded state. The resultant attraction is responsible for the strength of the covalent bond.

(2) Formation of hydrogen fluoride

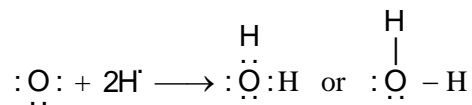
The hydrogen atom has in its orbital 1 electron. It can achieve the helium configuration by forming a single covalent bond with another atom. Fluorine has 7 electrons in its outer, i.e., L shell. F can acquire the Neon configuration by forming a single covalent bond using its unpaired electron. This may be represented as follows.



The single covalent bond holds the H and F atoms firmly together. Similarly we can explain the formation of HCl, HBr and HI.

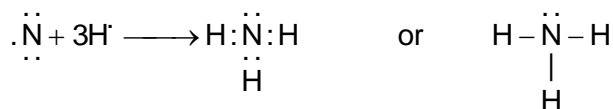


(3) Formation of water, H₂O



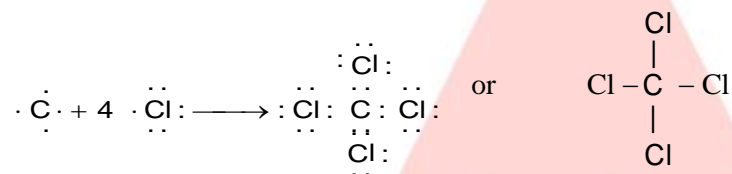
Similarly we can explain the formation of H₂S (hydrogen sulphide), H₂Se (hydrogen selenide) and H₂Te (hydrogen telluride).

(4) Formation of ammonia, NH₃

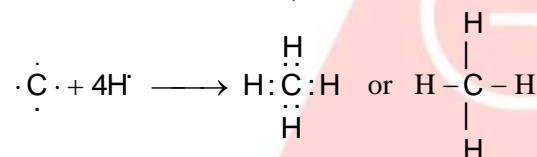


The structures of phosphine (PH₃), arsine (AsH₃) and stibine (SbH₃) are similar to that of ammonia.

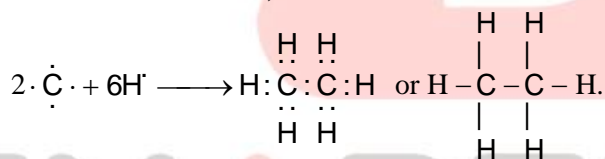
(5) Formation of carbon tetrachloride, CCl₄



(6) Formation of methane, CH₄



(7) Formation of ethane, C₂H₆



(i) The number of electrons needed by an atom to acquire its octet (C-4, N-3, O-2, Cl-1) is equal to the number of covalent bonds commonly formed.

(ii) When two pairs of electrons are shared between two atoms, there is a double bond as in ethylene, C₂H₄.

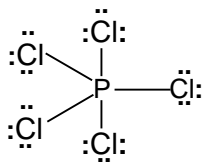


(iii) When three pairs of electrons are shared between two atoms, there is a triple bond as in acetylene, C₂H₂.

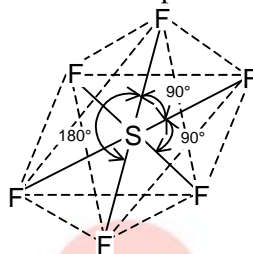


(iv) Generally all atoms involved in covalent bonding have completed octets (except hydrogen, which has a duplet of electrons). Sometimes an atom forms more than 4 covalent bonds.

An example is phosphorus pentachloride PCI₅. In this molecule phosphorus atom is surrounded by 5 chlorine atoms, with each of which it forms a covalent bond (with some ionic character, about which we shall learn later). In this compound the phosphorus atom seems to use 5 of the nine orbitals of the M shell (rather than only 4 of the most stable orbitals). It seems likely that of the nine or more orbitals in the M, N and O shells, four are especially stable, but one or more others may be occasionally utilized.



Another example is SF₆



3.1 GENERAL CHARACTERISTICS OF COVALENT COMPOUNDS

- (i) In a purely covalent compound the electrons in the bond are shared equally between the atoms linked by the bond; the resultant particles formed are not electrically charged. So, separate molecules of the covalent compounds exist. Covalent compounds may therefore be expected to be gases or low boiling liquids or soft, low melting solids at ordinary temperature. In the solid state they may be amorphous or present as molecular crystals, the molecules being held together by what are called weak van der Waals' forces of attraction.
- (2) Since the molecules are held together by weak van der Waals' forces, covalent compounds (except those consisting of giant molecules) have low melting and boiling points; very little thermal energy is needed to overcome these weak intermolecular forces.
- (3) They are non-electrolytes, i.e., they do not contain ions. Even in giant molecules such as diamond there are no free electrons. So they are very poor conductors of electricity.
- (4) They are generally soluble in organic (non-polar) solvents such as benzene or carbon tetrachloride but are insoluble in water or other ionizing solvents. (The solubility of covalent compounds is very much dependent on the size of the molecules; giant molecules are practically insoluble in nearly all solvents.)
- (5) Reactions between covalent compounds are slow and often incomplete and reversible. This is so because the reaction involves breaking and making of bonds i.e., energy considerations are involved for reactants, activated complexes and products.
- (6) A covalent bond is a space-directed bond and it may exhibit isomerism.

3.2 POLAR COVALENT BONDS – ELECTRONEGATIVITY

The shared pair of electrons may be shared equally between two atoms; then the covalent bond is said to be non-polar. Equal sharing occurs between identical atoms, as in H – H or Cl – Cl (i.e., in homonuclear molecules) or between identical atoms with identical neighbours as in H₃C–CH₃. When the two bonded atoms are dissimilar (i.e., in heteronuclear molecules) the sharing is unequal. For example a chlorine atom has a greater electron attracting power than a hydrogen atom; so in H – Cl, the shared pair of electrons are drawn more towards chlorine and away from hydrogen. The result is separation of charges within the molecule, the chlorine end acquiring a slight negative charge and the hydrogen end a slight but

equal positive charge: $\overset{\delta+}{\text{H}} - \overset{\delta-}{\text{Cl}}$. Such covalent bonds are said to be polar (i.e., bonds formed by sharing a pair of electrons between two atoms but displaced towards the nucleus of one of the bonded atoms).

The net tendency of a bonded atom in a covalent molecule to attract the shared pair of electrons towards itself is known as electronegativity. (This word does not mean the actual content of the electric charge, but just the tendency to acquire it in a molecule). Thus F is highly electronegative, but F⁻, which has already an extra electron, is not.

Table 3.2a: Table of Electronegativities (Pauling)

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca			As	Se	Br
0.8	1.0			2.0	2.4	2.8
Rb	Sr			Sb	Te	I
0.8	1.0			1.9	2.1	2.5

To assess the tendency of an atom of a given element to attract electrons towards itself in a covalent bond, relative electronegativity values are used. Table 3.2a. gives the relative electronegativity values of atoms calculated by Pauling (adopting arbitrarily the value of 4 units for the electronegativity of fluorine).

- ☛ (i) Electronegativity values increase across a period and decrease down a group.
- (ii) Smaller atoms have greater electronegativity than larger ones and so they attract electrons more towards them than larger ones. Alkali metals have low electronegativities and halogens high electronegativities.
- (iii) Atoms with nearly filled shells of electrons (e.g., halogens) have greater electronegativity than those with sparsely occupied shells.
- (iv) Elements with low electronegativity values such as Cs (0.8) and Rb (0.8) tend to form positive ions, i.e., these are metals. Elements with high electronegativity values such as F(4.0) and O(3.5) tend to form negative ions, i.e., these are non-metals.
- (v) Electronegativity value may be used to make rough predictions of the type of bonding to be found in a compound. The larger the difference between electronegativity values of two combining atoms, the more polar the covalent bond. If the difference is greater than 2, the greater the chance for ionic bonding (i.e., the chance of covalent bond assuming 100% ionic character). From this point of view ionic bond may be considered to be an extreme case of a polar bond (with total separation of charges).

If the difference between the electronegativities of the combining atoms is zero or small, the bond is essentially non-polar.

Let X_A and X_B represent the electronegativities of two atoms A and B.

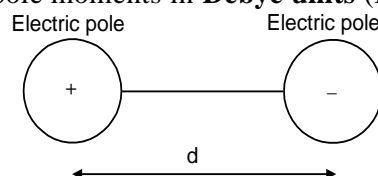
If $X_B - X_A = 1.7$, the covalent bond A – B is said to have 50% ionic character. On this basis, the % ionic character in some typical bonds is calculated (Table 3.2b). These calculations are very qualitative.

Table 3.2b: % Ionic Character of Bonds

C – H	N – H	O – H	F – H
4%	19%	39%	60%
C – F	C – Cl	C – Br	C – I
43%	11%	3%	0%

3.3 DIPOLE MOMENTS

A dipole consists of a positive and an equal negative charge separated by a distance within a molecule. The degree of polarity of a bond is given by the dipole moment (μ), which is the product of either charge (e) and the distance (d) between them. $\mu = d \times e$. 'e' is of the order of magnitude of the electronic charge, i.e., about 10^{-10} esu and d is the distance between the atomic centres, i.e., about 10^{-8} cm. Hence dipole moments may be expected to have values around $10^{-10} \times 10^{-8} = 10^{-18}$ esu-cm. It is however, general practice to express dipole moments in **Debye units (D)**, $1 D = 10^{-18}$ esu-cm.



If the charge is in SI units (Coulombs) and d in metre, μ will be coulomb-metre ($C \cdot m$) units. $1 D = 3.336 \times 10^{-30} C \cdot m$.

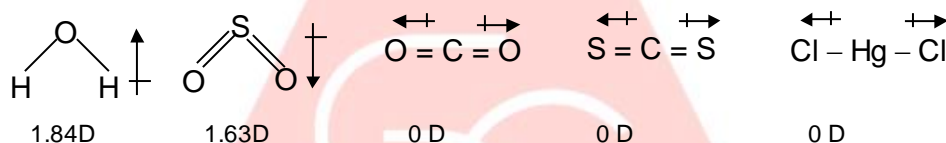
Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compounds containing such bonds will have dipole moments, for the **polarity of the molecule as a whole is the vector sum of the individual bond moments**. For example, CO_2 has zero dipole moment, although the $\text{C}=\text{O}$ bond is a polar bond. This shows that CO_2 is a linear molecule, $\text{O}=\text{C}=\text{O}$, so that the dipole moments of the two $\text{C}=\text{O}$ bonds cancel out. The $\text{C} \rightarrow \text{Cl}$ bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4 $\text{C}-\text{Cl}$ bond moments is zero. On the contrary CH_3Cl , CH_2Cl_2 and CHCl_3 have definite dipole moments.

3.4 APPLICATIONS OF DIPOLE MOMENT MEASUREMENTS

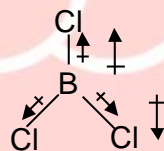
Dipole moment is a measure of the electrical dissymmetry (polarity) in the molecule and so its measurement provides valuable information concerning the shapes of molecules. Conversely, when the symmetry of the molecules is known, dipole moment could be estimated fairly.

(A) Inorganic substances:

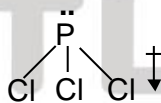
- (i) **Monatomic molecules** such as He, Ne, etc., have zero dipole moment because they are symmetrical.
- (ii) **Diatomic molecules** such as H_2 , Cl_2 and N_2 have no dipole moment; so these molecules are symmetrical.
- (iii) **Triatomic molecules:** Some of these molecules possess zero dipole moment; so they have a symmetrical linear structure, e.g., CO_2 , CS_2 , HgCl_2 . Others like water and sulphur dioxide have definite dipole moments. They are said to have angular or bent structure or V-shaped structure.



- (iv) **Tetrahedral molecules:** Some molecules like BCl_3 have zero dipole moment. They are said to possess a flat and symmetrical (triangular) structure; other examples are BF_3 , BBr_3 , CO_3^{2-} and NO_3^- .

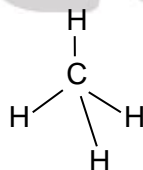


PCl_3 , AsCl_3 , NH_3 , PH_3 , AsH_3 , H_3O^+ have appreciable dipole moments. They possess trigonal pyramidal structures.



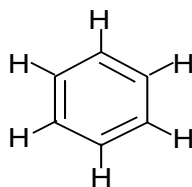
(B) Organic substances

- (i) **Methane and CCl_4** have zero dipole moment. So they possess symmetrical tetrahedral structures with C atom at the centre of the tetrahedron.



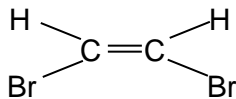
Methane

- (ii) **Benzene** has zero dipole moment. All the 6 C and 6 H atoms are assumed to be in the same plane (symmetrical hexagonal structure).

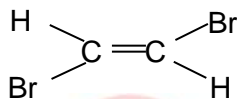


- (iii) **Measurement of dipole moments will enable** us to detect cis- and trans-isomers of organic compounds (you will learn about cis-trans or geometrical isomerism later in the organic chemistry).

The trans-isomer, which is symmetrical, has zero dipole moment while the cis-isomer has a definite dipole moment.



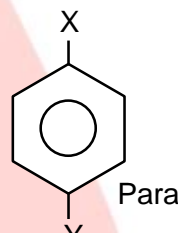
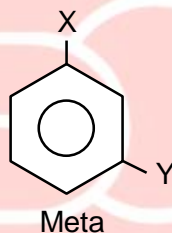
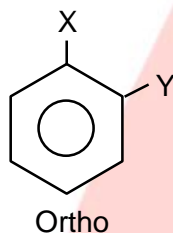
cis-dibromoethylene ($\mu = 1.4 \text{ D}$)



trans-dibromoethylene ($\mu = 0$)

- (iv) **Dipole moment in aromatic ring system**

The dipole moments of the aromatic compounds present a very good illustration of dipole moment. We know that when substituted benzene is treated with reagent different products (namely ortho, meta and para products) are formed. The dipole moments of these products are different since the orientation of the groups is different. Let us take an example to clarify it. Let us take three isomers, o-nitrophenol, m-nitrophenol and p-nitrophenol. We have also have three other isomers, o-aminophenol, m-aminophenol and p-aminophenol. We want to arrange these isomers in the order of their dipole moments.



In those cases where $X = Y$, the para isomer becomes symmetrical and have zero dipole moment. In order to find their dipole moment, we need to know about the nature of the groups linked to the benzene ring. In nitro phenols, one group (OH) is electron pushing and the other (NO_2) is electron withdrawing while in aminophenols, both the groups (OH and NH_2) attached are electron pushing. So, depending on the nature of the groups attached, the isomers have different dipole moment. Then calculation of dipole moment follows as:

Case (i): When X and Y both are electron pushing or electron withdrawing.

Let the bond dipole of C-X bond is represented by μ_1 and that of C-Y bond by μ_2 . Now let us assume that the electron pushing groups have +ve bond moment and the electron withdrawing groups have -ve bond moment. The net dipole moment is the resultant of two bond dipoles at different orientations.

$$\mu_{\text{ortho}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 60^\circ} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cdot \frac{1}{2}}$$

$$\therefore \mu_o = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2}$$

$$\mu_{\text{meta}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 120^\circ}$$

$$\therefore \mu_m = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2}$$

$$\mu_{\text{para}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos 180^\circ} = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2}$$

$$\therefore \mu_p = \mu_1 - \mu_2$$

From the above expressions of μ_o , μ_m and μ_p , it is clear that when both X and Y are of the same nature i.e., both are electron withdrawing or both are electron pushing the para product has the least dipole moment and ortho product has the highest dipole moment. When $X = Y$, $\mu_1 = \mu_2$, thus μ_p would be zero.

Case (ii): When X is electron pushing and Y is electron withdrawing or vice versa.

Let the bond moment of C–X dipole is μ_1 and that of C–Y dipole is μ_2 .

$$\begin{aligned}\mu_o &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 60^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 - \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - 3\mu_1\mu_2} \\ \mu_{\text{meta}} &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 120^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 + \mu_1\mu_2} \\ &= \sqrt{(\mu_1 + \mu_2)^2 - \mu_1\mu_2} \\ \mu_{\text{para}} &= \sqrt{\mu_1^2 + (-\mu_2)^2 + 2\mu_1(-\mu_2)\cos 180^\circ} \\ &= \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2} = \mu_1 + \mu_2\end{aligned}$$

Looking at the expressions of μ_o , μ_m and μ_p , it is clear that the para isomer has the highest dipole moment and ortho has the least.

3.5 DIPOLE MOMENT AND PERCENTAGE IONIC CHARACTER

The measured dipole moment of a substance may be used to calculate the percentage ionic character of a covalent bond in simple molecules.

1 unit charge = Magnitude of electronic charge = 4.8×10^{-10} e.s.u.

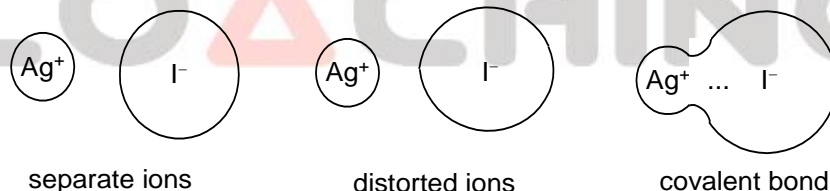
1 D = 1×10^{-18} e.s.u.–cm.

$$\therefore \% \text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Theoretical dipole moment is confined to when we assume that the bond is 100 % ionic and it is broken into ions while observed dipole moment is with respect to fractional charges on the atoms of the bond.

3.6 TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

Just as a covalent bond may have partial ionic character, an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character. The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



FACTORS INFLUENCING ION – DEFORMATION OR INCREASING COVALENT CHARACTER

(i) Large charge on the ions:

The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl, AlF_3 , AgF are ionic.

(2) Small cation and large anion:

For a small cation, the electrostatic force with which its nucleus will attract the anion will be large.

Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalence with a small cation and a large anion, as in AgI.

(3) Cation with a non-inert gas type of electronic configuration:

A cation with a 18 electron outermost shell such as Ag^+ ($[\text{Kr}] 4d^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+ . The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+ . Thus AgI is more covalent than KI, although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

The above statements regarding the factors, which influence covalent character, are called Fajans' rules. It can thus be seen easily that there is nothing like a purely ionic compound or a purely covalent compound.

4 LEWIS STRUCTURES OF MOLECULES

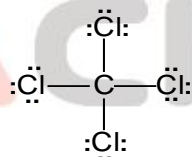
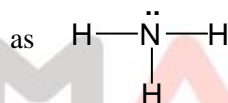
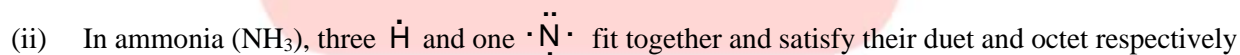
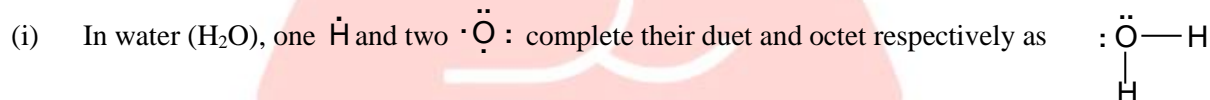
The formula of a molecule shows the number of atoms of each element but does not show the bonding arrangement of the atoms. To represent the bonding pattern in a molecule, the electron dot symbols of the elements are arranged such that the shared pairs and unshared pairs (called lone pairs) are shown and the octet rule (or duet for hydrogen) is satisfied. For example,

a molecule of fluorine is shown as $:\ddot{\text{F}}:\ddot{\text{F}}:$ or $:\ddot{\text{F}}-\ddot{\text{F}}:$ and a molecule of hydrogen fluoride is shown as



Arrangement of dot symbols used to represent molecules are called *Lewis structures*. Lewis structures do not convey any information regarding the shape of the molecule. Usually, the shared pairs of electrons are represented by lines between atoms and any unshared pairs are shown as dot pairs.

Lewis structures are written by fitting the element dot symbols together to show shared electron pairs and to satisfy the octet rule. For example,



For the given molecules, we have adopted hit & trial method to fit the dot symbols together and satisfy the octet rule. But remember that hydrogen form one bond, oxygen forms two bonds, nitrogen three bonds and carbon forms four bonds. For simpler molecules, the hit & trial method works perfectly but for slightly complicated polyatomic species, this may give us more than one possible structure. Thus, a systematic approach is needed to design the Lewis structures of such polyatomic species. But before proceeding further, let us understand the limitation of this approach.

4.1 LIMITATIONS OF LEWIS THEORY OF DRAWING STRUCTURE

This method would be applicable to only those molecules/species, which follow octet rule except hydrogen.

There are three kinds of molecules/species, which do not follow octet rule.

(a) Molecules, which have contraction of octet. Such molecules are electron deficient. For example,

- BH₃, BF₃, BCl₃, AlCl₃, GaCl₃ etc.
- (b) Molecules, which have expansion of octet. Such species have more than eight electrons in their outermost shell. This is possible in those molecules, which have vacant d-orbitals, thus they can expand their octet. For example, PCl₅, SF₆ etc.
- (c) Molecules containing odd number of electrons (in total) cannot satisfy octet rule. Such species are called odd electron species and are paramagnetic in nature due to presence of unpaired electron. For example, NO, NO₂ and ClO₂.

4.2 METHOD OF DRAWING LEWIS STRUCTURES

To draw the Lewis structures of polyatomic species, follow the given sequence.

- (i) First calculate n_1 .
 $n_1 =$ Sum of valence electron of all the atoms of the species \pm net charge on the species.
 For a negatively charged species, electrons are added while for positively charged species, the electrons are subtracted. For an uninegatively charged species, add 1 to the sum of valence electrons and for a dinegatively charged species, add 2 and so on.
- (ii) Then calculate n_2 .
 $n_2 = (8 \times \text{number of atoms other than H}) + (2 \times \text{number of H atoms})$
- (iii) Subtract n_1 from n_2 , which gives n_3 .
 $n_3 = n_2 - n_1 =$ number of electrons shared between atoms = number of bonding electrons.

$$\frac{n_3}{2} = \frac{n_2 - n_1}{2} = \text{number of shared (bonding) electron pairs} = \text{number of bonds.}$$
- (iv) Subtracting n_3 from n_1 gives n_4 .
 $n_4 = n_1 - n_3 =$ number of unshared electrons or non-bonding electrons.

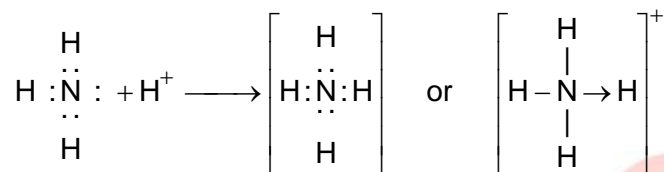
$$\frac{n_4}{2} = \frac{n_1 - n_3}{2} = \text{number of unshared electron pairs} = \text{number of lone pairs.}$$
- (v) Identify the central atom. Generally, the central atom is the one, which is least electronegative of all the atoms, when the other atoms do not contain hydrogen. When the other atoms are hydrogen only, then the central atom would be the more electronegative atom. However some exceptions are possible, for example Cl₂O.
- (vi) Now around the central atom, place the other atoms and distribute the required number of bonds (as calculated in step (iii)) & required number of lone pairs (as calculated in step (iv)), keeping in mind that every atom gets an octet of electrons except hydrogen.
- (vii) Then calculate the formal charge on each atom of the species.
 Formal charge on an atom = number of valence electrons of the atom – number of bonds formed by that atom – number of unshared electrons ($2 \times$ lone pairs) of that atom.
- (viii) When two adjacent atoms get opposite formal charges, then charges can be removed by replacing the covalent bond between the atoms by a dative (co-ordinate) bond. This bond will have the arrowhead pointing towards the atom with negative formal charge. It is not mandatory to show the dative bonds unless required to do so.
- (ix) The given Lewis structure should account for the factual aspects of the molecule like resonance (delocalization), bond length, $p\pi-d\pi$ back bonding etc.
 Sometimes, there are more than one acceptable Lewis structure for a given species. In such cases, we select the most plausible Lewis structure by using formal charges and the following guidelines:
- For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
 - Lewis structures with large formal charges (+2, +3 and/ or -2, -3 and so on) are less plausible than those with small formal charges.
 - Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

5 CO-ORDINATE COVALENT BOND OR DATIVE BOND

We have seen that in the formation of a covalent bond between two atoms, each atom contributes one electron to the shared pair. Sometimes *both the electrons of the shared pair may come from one of the atoms*. The covalent bond thus formed is a co-ordinate bond or dative bond.

(i) Formation of ammonium ion

The ammonia molecule has a lone pair of electrons i.e., an unshared pair. The hydrogen ion H^+ , has an empty s orbital. The lone pair comes to be shared between the nitrogen and hydrogen atoms:

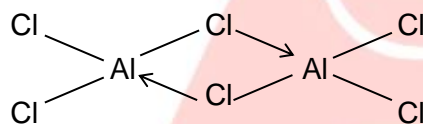


Nitrogen atom is called the donor and H^+ , the acceptor. The arrow-head in $\text{N} \longrightarrow \text{H}$ shows that N-atom is electron donor and H-atom is electron acceptor. NH_3 is a neutral molecule. H^+ carries a unit positive charge; so NH_4^+ ion carries a unit positive charge. Once the NH_4^+ ion is formed, all the N-H bonds become identical.

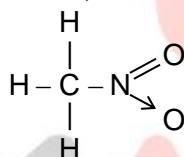
(2) Hydronium ion, H_3O^+



(iii) Aluminium chloride, Al_2Cl_6



Nitromethane, CH_3NO_2



GENERAL CHARACTERISTICS OF COORDINATE COVALENT COMPOUNDS

As is to be expected the properties of coordinate covalent compounds are mostly similar to the properties of covalent compounds.

- (1) The nuclei in coordinate covalent compounds (such as in NH_4^+) are held firmly by shared electrons and so do not form ions in water.
- (2) Their covalent nature makes them sparingly soluble in water and more soluble in organic solvents.
- (3) The coordinate bond is also rigid and directional, just like covalent bonds.

6 RESONANCE

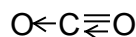
Carbon dioxide may be represented by Lewis dot formula as



The bond length of $\text{C} \equiv \text{O}$ is 1.22 \AA , but the actual measured value is 1.15 \AA . Further CO_2 is quite stable and does not show the characteristic reactions of the carbonyl group, as shown by aldehydes and ketones. Without shifting, the relative positions of atoms of CO_2 can be represented by two more Lewis formulae:

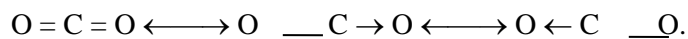


(ii)



(iii)

In (ii) and (iii), the two bonds between C and O are different, one being a triple bond and the other a single bond. Both the C–O bonds in CO₂ are identical. It is now obvious that none of these structures actually represents CO₂. To explain this difficulty the concept of resonance was introduced, according to which CO₂ cannot be accurately depicted by any Lewis formula. The actual structure of CO₂ is a resonance hybrid of the three structures:



These different structures are called the *canonical or contributing structures*. *The actual structure of CO₂ is different from the canonical structures and although it is closely related to them, the actual structure cannot be represented on paper using the accepted symbols. All the molecules of CO₂ have the same structure.* Usually, a double-headed arrow \longleftrightarrow is used between the canonical structures.

6.1 CONDITIONS FOR RESONANCE

Resonance can occur when the canonical structures

- (i) have the constituent atoms in the same relative positions;
- (2) have nearly the same energy;
- (3) have the same number of unpaired electrons (to allow for continuous change from one type of bond to another);
- (4) differ in the distribution of electrons around the constituent atoms;
- (5) (molecules or ions) are planar.

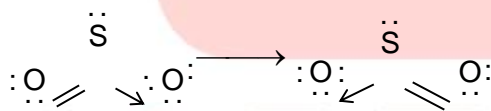
6.2 RESONANCE ENERGY

The resonance hybrid is a more stable structure than any of the contributing structures. This means that resonance hybrid has less energy than any of the contributing structures. *The difference in energy between the actual observed energy of the resonance hybrid and the most stable of the contributing structures is called resonance energy.*

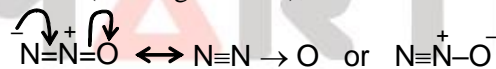
For CO₂, structure (i) has less energy than structure (ii).

6.3 OTHER EXAMPLES OF RESONANCE

(i) Sulphur dioxide SO₂



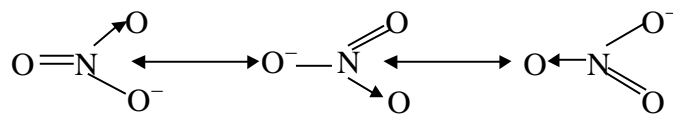
(ii) Nitrous oxide (dinitrogen oxide), N₂O



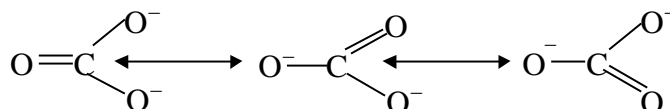
(3) Nitric oxide, NO



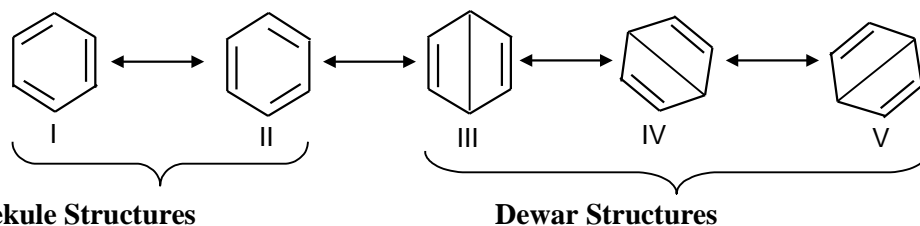
(iv) Nitrate ion, NO₃⁻ (planar, triangular)



(v) Carbonate ion, CO₃²⁻ (planar, triangular)



(6) **Benzene, C_6H_6 .** It is a resonance hybrid of the following structures (hexagonal, planar).



C–C bond length is 1.54 Å; C=C bond length is 1.34 Å. In benzene, all the C–C bonds are identical in length, 1.39 Å, i.e., intermediate between those of single and double bonds. Note that shortening of bond length and therefore increased stability is an indication of the existence of resonance [Decrease in dipole moment also indicates resonance]. Resonance energy of benzene is –152 kJ/mol.

6 MOLECULAR GEOMETRY AND VSEPR THEORY

Molecular geometry is the three-dimensional arrangement of atoms in a molecule.

A molecule's geometry affects its physical and chemical properties such as melting point, boiling point and the types of reactions it undergoes. In general, bond length and bond angles are determined by experiments. However, there is a simple procedure to predict the overall geometry of a molecule or ion with considerable accuracy, if we know the number of electrons surrounding a central atom in its Lewis structure. The basis of this approach is the assumption that electron pairs in the valence shell (outermost electron-occupied shell of an atom) of an atom repel one another. In a polyatomic species, the repulsion between electrons in different bonding pairs causes them to remain as far as possible. Thus, the geometry assumed by the species ultimately minimizes the repulsion. This approach is called valence-shell electron-pair repulsion (VSEPR) theory because it accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs.

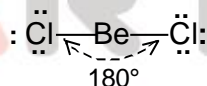
Molecules in this theory are divided into two categories, depending on whether the central atom has lone pair of electrons or not.

7.1 Molecules in which the central atom has no lone pairs.

For simplicity, we will consider molecules that contain only two types of atoms, A and B, of which A is the central atom. These molecules have the general formula AB_x , where x is an integer 2, 3, (if $x = 1$, the molecule will be diatomic, which is linear by definition).

(a) Molecules having general formula AB_2

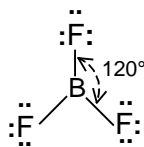
$BeCl_2$ is representing the general formula AB_2 . The Lewis structure of beryllium chloride in the gaseous state is



Since the bonding pairs repel each other, they must be at opposite ends of a straight line in order for them to be as far apart as possible. Thus, ClBeCl bond angle is predicted to be 180° and the molecule is *linear*.

(b) Molecules having general formula AB_3

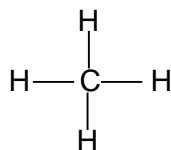
The general formula AB_3 is represented by the molecule BF_3 . BF_3 has three bonding pairs, which points to the corners of an equilateral triangle with boron at the center of the triangle.



This geometry of BF_3 is referred as *trigonal planar* with FBF bond angle to be 120°. In this structure, all four atoms lie in the same plane,

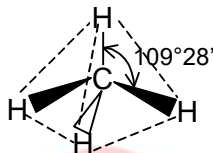
(c) Molecules having general formula AB_4

Methane (CH_4) represents the best example of this class of molecules. The Lewis structure of CH_4 is



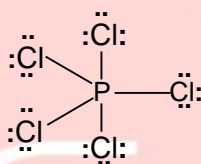
The four bonding pairs in CH_4 can be arranged to form a tetrahedron, so as to minimize the repulsion between them. A tetrahedron has four faces, all of which are equilateral triangles.

In a **tetrahedral** molecule, the central atom (carbon) is located at the center of the tetrahedron and the other four atoms (H) are at the corners. The HCH bond angles are all $109^\circ 28'$.



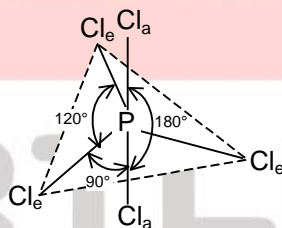
(d) Molecules with general formula AB_5

The general formula AB_5 is represented by the molecule PCl_5 . The Lewis structure of PCl_5 (in gas phase) is



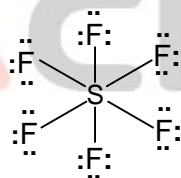
The only way to minimize the repulsive forces among the five bonding pairs is to arrange the P-Cl bonds in the form of a **trigonal bipyramid**. Joining two tetrahedrons along a common triangular base can generate a trigonal bipyramid.

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

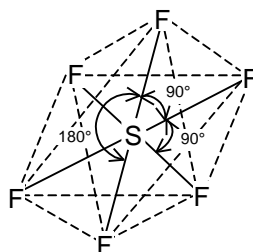


(e) Molecules having general formula AB_6

The molecule SF_6 exhibits the general formula AB_6 . The Lewis structure of SF_6 is



The most stable arrangement of the six S-F bonding pairs is in the shape of an **octahedron**. An octahedron has eight faces and can be generated by joining two square pyramids on a common base. The central atom (S) is at the center of the square base and the surrounding atoms (F) are at the six corners. All bond angles are 90° except the one made by the bonds between the central atom and the pairs of atoms that are diametrically opposite to each other, which is 180° . Since, all the bonds are equivalent in an octahedral molecule, the terms axial and equatorial are not used here.



7.2 MOLECULES IN WHICH THE CENTRAL ATOM HAS ONE OR MORE LONE PAIRS

In such molecules, there are three types of repulsive interactions—between bonding pairs, between lone pairs and between a bonding pair and a lone pair. In general, according to VSEPR theory, the repulsive forces decrease in the following order: lone pair–lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion.

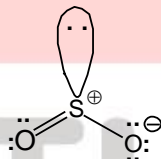
Bond pair electrons are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less “spatial distribution” than lone pairs i.e., they take up less space than lone pair electrons, which are associated with only one nuclei (or one atom). Because lone–pair electrons in a molecule occupy more space, they experience greater repulsion from neighbouring lone pairs and bonding pairs.

To keep track of total number of bonding pairs and lone pairs, we designate molecules with lone pairs as AB_xE_y , where A is the central atom, B is the surrounding atoms and E is a lone pair on A. Both x and y are integers, $x = 2, 3, \dots$ and $y = 1, 2, \dots$. Thus, x and y denote the number of surrounding atoms and number of lone pairs on the central atom, respectively.

(a) Molecules with general formula AB_2E

Example of this type is SO_2 . The Lewis structure of SO_2 is $:\ddot{O}=\overset{\oplus}{S}-\ddot{O}^-:$

VSEPR theory treats double bond and triple bonds as though they were single bonds. Thus, SO_2 molecule can be viewed as having three electron pairs on the central atoms, of which, two are bonding pairs and one is a lone pair. The overall arrangement of three electron pairs is trigonal planar. But since one of the electron pair is a lone pair, the SO_2 molecule looks like

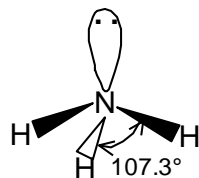


This shape is referred as **bent or angular**. The shape is determined only by the bonding pairs and not by lone pairs. Since lone pair repels the bonding pairs more strongly, the SO bonds are pushed together slightly and the OSO angle is less than 120° .

(b) Molecules having general formula AB_3E

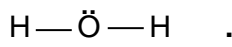
The general formula AB_3E is exhibited by the molecule NH_3 . Ammonia has overall four electron pairs, of which three are bonding pairs and one is lone pair. The overall arrangement of four electron pairs is tetrahedral but since one of the electron pairs is a lone pair, so the shape of NH_3 is **trigonal pyramidal**.

Because the lone pairs repels the bonding pairs more strongly, the three N–H bonds are pushed closer together. Thus the HNH bond angle is smaller than the ideal tetrahedral angle of $109^\circ 28'$.

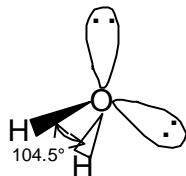


(c) Molecules with general formula AB_2E_2

Example of such a molecule is H_2O . A water molecule has 2 bonding pairs and two lone pairs

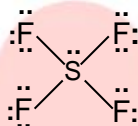


The overall arrangement of the four electron pairs in water is tetrahedral. However, unlike NH_3 , H_2O has 2 lone pairs on the central O atom. These lone pairs tend to be as far from each other as possible. Consequently, the two OH bonding pairs are pushed toward each other and H_2O shows even greater deviation from tetrahedral angle than in NH_3 . The shape of H_2O is referred as ***bent or angular*** with HOH bond angle of 104.5° .



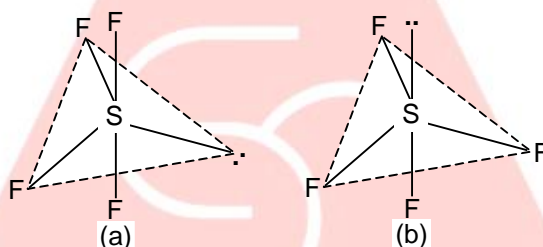
(d) Molecules having general formula AB_4E

Example to this class of molecule is SF_4 . The Lewis structure of SF_4 is



The S atom in SF_4 has 5 electron pairs, which can be arranged as trigonal bipyramidal.

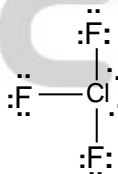
In SF_4 , since one of the electron pair is a lone pair, so the molecule can have any one of the following geometries:



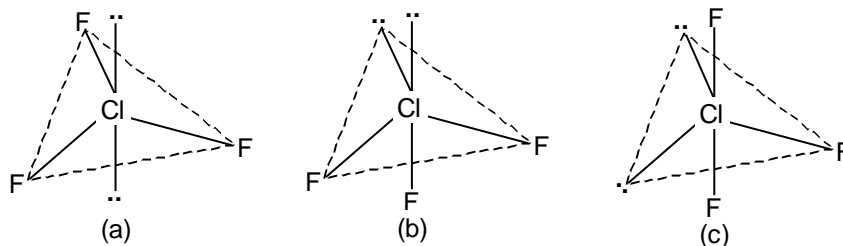
In (a), the lone pair occupies an equatorial position and in (b), it occupies an axial position. Repulsion between the electrons pairs in bonds only 90° apart are greater than repulsion between electron pairs in bonds 120° apart. Each axial bond has three electron pairs 90° away while each equatorial bond has only two electron pairs 90° away. Thus axial bonds (electron pairs) experience greater repulsion than the equatorial bonds. Thus, atoms at the equatorial positions are closer to the central atom than atoms at the axial positions i.e. equatorial bond lengths are smaller than axial bond lengths. Thus, when the central atom also has lone pairs along with the bonding pairs, it will occupy a position where the repulsions are less, so lone pairs in trigonal bipyramidal are more comfortable at equatorial positions. Thus, (a) is the appropriate structure of SF_4 . It is referred as ***see-saw shaped or irregular tetrahedron***.

(e) Molecules with general formula AB_3E_2

Example of this type is ClF_3 . The Lewis structure of ClF_3 is



The Cl atom in ClF_3 has 5 electron pairs, of which 2 are lone pairs and 3 are bonding pairs. The molecule can have any of the following three geometries:



In structure (a), there are 6 lone pair–bond pair repulsions at 90° and one lone pair – lone pair repulsion at 180° . In structure (b), 1 lone pair – lone pair repulsion is at 90° and there are 3 lone pair–bond pair repulsions at 90° , 2 at 120° and 1 at 180° . While in structure (c), there are 4 lone pair–bond pair repulsions at 90° , 2 at 120° and one lone pair–lone pair repulsion at 120° . The structure (b) is out rightly ruled out since the lone pair–lone pair repulsion is of highest magnitude. Among structures (a) and (c), each structure has 4 lone pair–bond pair repulsions at 90° . Apart from these repulsions, (a) has 1 lone pair–lone pair repulsion at 180° and 2 lone pair–bond pair repulsions at 90° while (c) has 1 lone pair–lone pair repulsion at 120° & 2 lone pair–bond pair repulsions also at 120° . So, the structure (c) has overall lesser repulsions than (a). Thus, (c) is the appropriate structure of ClF_3 . It is called *T-shaped* structure.

7.3 PREDICTING GEOMETRY OF SPECIES USING VSEPR THEORY

With the help of VSEPR theory, we can predict the geometry of various species in a systematic way. The scheme makes use of the following steps:

- Identify the central atom and count the number of valence electrons on the central atom.
- Add to this, the number of other atoms (which form single bonds only). Here, oxygen atoms are not added as they form two bonds.
- If the species is an anion, add negative charges and if it is a cation, subtract positive charges.
- This gives us a number, which we refer as N.
- Divide N by 2 and we get the sum of bonding and non–bonding electron pairs.

$$\frac{N}{2} = \text{Number of other atoms} + \text{number of lone pairs.}$$

- Compare the result $\left(\frac{N}{2} \text{ value}\right)$ with the value given in table, corresponding to the given number of lone pairs.

N/2 value	No. of lone pairs	Shape of the species	Example
2	0	Linear	$\text{HgCl}_2, \text{BeCl}_2$
3	0	Triangular planar	$\text{BF}_3, \text{AlCl}_3, \text{BH}_3, \text{NO}_3^-, \text{SO}_3$
	1	Angular or bent	$\text{SnCl}_2, \text{SO}_2, \text{NO}_2^-$
4	0	Tetrahedral	$\text{CCl}_4, \text{BeF}_4^{2-}, \text{BF}_4^-, \text{PCl}_4^+, \text{ClO}_4^-$
	1	Trigonal pyramidal	$\text{NH}_3, \text{PCl}_3, \text{PF}_3, \text{ClO}_3^-$
	2	Angular or bent	$\text{H}_2\text{O}, \text{H}_2\text{S}, \text{OF}_2, \text{ClO}_2^-$
	3	Linear	ClO^-
5	0	Trigonal bipyramidal	$\text{PCl}_5, \text{PF}_5$
	1	See–saw or irregular tetrahedron	$\text{SF}_4, \text{IF}_4^+$
	2	T–shaped	$\text{ClF}_3, \text{BrF}_3$
	3	Linear	$\text{I}_3^-, \text{Br}_3^-, \text{XeF}_2$
6	0	Octahedral or square bipyramidal	$\text{SF}_6, \text{PCl}_6^-$
	1	Square pyramidal	$\text{BrF}_5, \text{IF}_5$
	2	Square planar	$\text{ICl}_4^-, \text{XeF}_4, \text{IF}_4$
7	0	Pentagonal bipyramidal	IF_7

Note: XeF_6 does not have octahedral structure. It's structure is *capped octahedron*.

Let us see the usefulness of the VSEPR theory to predict the geometry of few molecules/ ions.

(i) BeCl_2 molecule:

The central atom is Be and it has two other Cl atoms.



$$\therefore \frac{N}{2} = \frac{2+2}{2} = 2$$

Since, the number of other atoms are 2, so the number of lone pairs are zero. Thus, shape of BeCl_2 is **linear**.

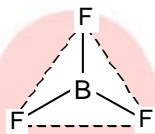


(ii) **BF_3 molecule:**

In BF_3 , central atom is boron and it has three other atoms.

$$\therefore \frac{N}{2} = \frac{3+3}{2} = 3$$

Since, the number of other atoms are three, so the number of lone pairs are zero. Therefore, shape is **triangular planar**.

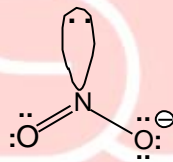


(iii) **NO_2^- ion:**

The central atom in NO_2^- is N and it has two other atoms.

$$\therefore \frac{N}{2} = \frac{5+1}{2} = 3$$

Since, the number of other atoms are 2, so the number of lone pairs would be 1. Thus, shape of NO_2^- ion is **angular or bent**.

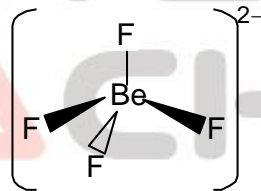


(iv) **BeF_4^{2-} ion:**

In BeF_4^{2-} , the central atom is Be and it has four other F atoms.

$$\therefore \frac{N}{2} = \frac{2+4+2}{2} = 4$$

The number of lone pairs are zero, as the number of other atoms are 4. Therefore, shape of BeF_4^{2-} is **tetrahedral**.

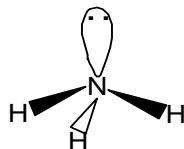


(v) **NH_3 molecule:**

In NH_3 , the central atom is N and it has 3 other H atoms.

$$\therefore \frac{N}{2} = \frac{5+3}{2} = 4$$

Since, the number of other atoms is 3, so the number of lone pairs would be 1. Therefore, shape of NH_3 molecule is **trigonal pyramidal**.

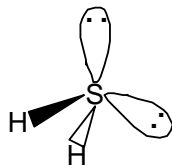


(vi) H₂S molecule:

The central atom is S and there are 2 other H atoms in H₂S molecule.

$$\therefore \frac{N}{2} = \frac{6+2}{2} = 4$$

Since, the number of other atoms is 2, so the number of lone pairs would be 2. Thus, the shape of H₂S is *angular or bent*.

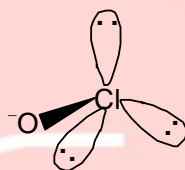


(vii) ClO⁻ ion:

The central atom is Cl and it has one other atom.

$$\therefore \frac{N}{2} = \frac{7+1}{2} = 4$$

The number of lone pairs would be 3 as the other atom is only one. Thus, the shape of ClO⁻ is *linear*.

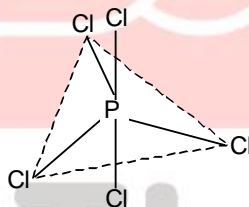


(viii) PCl₅ molecule:

The central atom in PCl₅ is P and it has 5 other Cl atoms.

$$\therefore \frac{N}{2} = \frac{5+5}{2} = 5$$

The number of lone pairs would be zero, as the number of other atoms is 5. Thus, the shape of PCl₅ is *trigonal bipyramidal*.

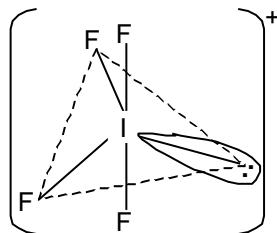


(ix) IF₄⁺ ion:

The central atom in IF₄⁺ ion is I and it has 4 other F atoms.

$$\therefore \frac{N}{2} = \frac{7+4-1}{2} = 5$$

Since, the number of other atoms is 4, so the number of lone pairs would be 1. Thus, the shape of IF₄⁺ ion is *see-saw or irregular tetrahedron*.

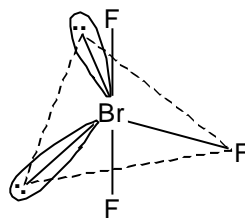


(x) BrF₃ molecule:

In BrF₃ molecule, the central atom is Br and it has 3 other F atoms.

$$\therefore \frac{N}{2} = \frac{7+3}{2} = 5$$

Since, the number of other atoms is 3, so the number of lone pairs is 2. Therefore, the shape of BrF_3 is *T-shaped*.

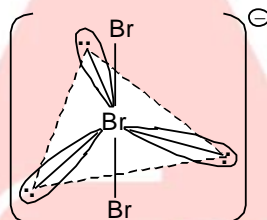


(xi) Br_3^- ion:

The central atom is a Br atom and it has 2 other Br atoms as surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+2+1}{2} = 5$$

Since, the number of other atoms is 2, so the number of lone pairs is 3. Thus, the shape of Br_3^- ion is *linear*.

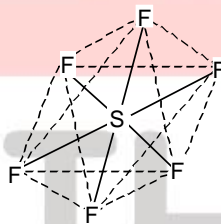


(xii) SF_6 molecule:

The central atom in SF_6 is S and it has 6 other F atoms as surrounding atoms.

$$\therefore \frac{N}{2} = \frac{6+6}{2} = 6$$

Since, the number of other atoms is 6, so the number of lone pairs are zero. Thus, the shape of SF_6 molecule is *octahedron or square bipyramidal*.

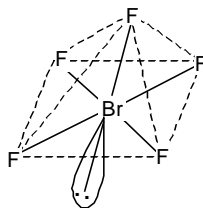


(xiii) BrF_5 molecule:

In BrF_5 , the central atom is Br and 5 F atoms are the surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+5}{2} = 6$$

Since, the number of other atoms is 5, so the number of lone pairs would be 1. Therefore, the shape of BrF_5 is *square pyramidal*.

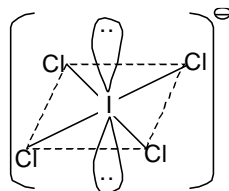


(xiv) ICl_4^- ion:

In ICl_4^- ion, the central atom is I and 4 Cl atoms are the surrounding atoms.

$$\therefore \frac{N}{2} = \frac{7+4+1}{2} = 6$$

The number of lone pairs would be 2 as the number of other atoms is 4. So, the shape of ICl_4^- ion is *square planar*.

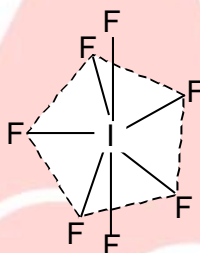


(xv) IF_7 molecule:

In IF_7 molecule, the central atom is I and 7 F atoms are the surrounding atoms.

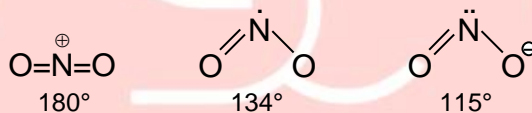
$$\therefore \frac{N}{2} = \frac{7+7}{2} = 7$$

Since, the number of other atoms is 7, so the number of lone pairs would be zero. Thus, the shape of IF_7 molecule is *pentagonal bipyramidal*.

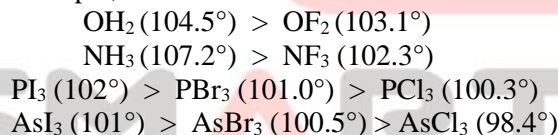


In addition to all this, VSEPR theory can also be used to determine the geometry of other covalently bonded molecules and their bond angles. In order to predict these, following generalizations would be helpful.

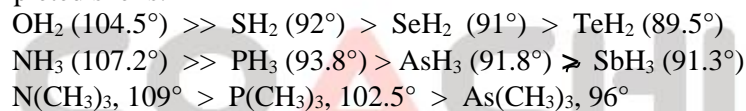
1. Lone pair causes greater repulsions than a lone electron. For example,



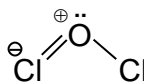
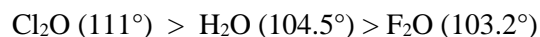
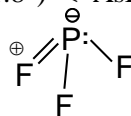
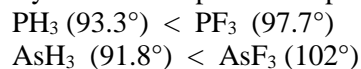
2. Repulsions exerted by bond pair's decrease as the electronegativity of the bonded atom increases. For example,



3. Repulsion between bonded electron pairs in filled shells is greater than those between electron pairs in incompleting shells.



4. When an atom with a filled valence shell & one or more lone pairs is bonded to an atom with an incomplete valence shell, or a valence shell that can become complete by electron shifts, there is a tendency for the lone pairs to be partially transferred from the filled to the unfilled shell.



5. The size of a bonding electron pair decreases with increasing electronegativity of the ligand. Also, the

two electron pairs of a double bond (or the three electron pairs of a triple bond) take up more room than does the one electron pair of a single bond.

Using above facts one can rationalize size the trends which are given below:

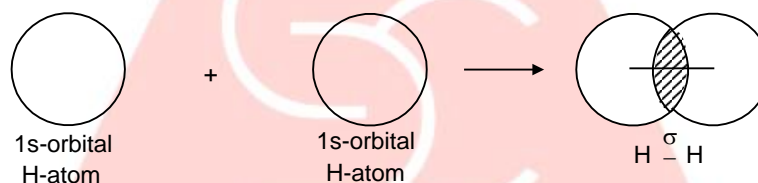
Molecule	Angles		
	XCX	XCO	XCC
F ₂ CO	108°	126°	–
Cl ₂ CO	111°	124°	–
(NH ₂) ₂ CO	118°	121°	–
F ₂ SO	93°	107°	–
H ₂ C=CF ₂	110°	–	125°
OPF ₃	103°	–	–
OPCl ₃	104°	–	–
H ₂ C=CCl ₂	114°	–	123°

7 SIGMA AND PIE BOND

Valence bond theory explains that a covalent bond is formed by the overlapping of the electron clouds of the atomic orbitals of the constituent atoms. The greater the overlap, the stronger the bond.

1. Formation of hydrogen molecule:

Hydrogen (1s¹) has only one electron in its 1s-orbital. When two hydrogen atoms come together, overlap of their s-orbitals takes place (s-s overlap), energy is released (bond energy) and a covalent bond called the σ bond is formed.

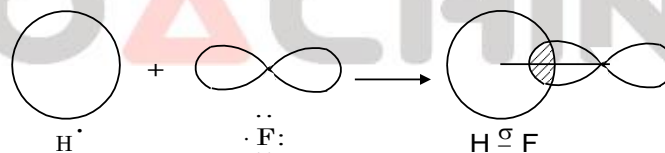


The electrons shared between the two atoms are to a large extent located in the region of space between the two nuclei. So the region of overlap is the region of high electron density. The electron density (or electron cloud) is distributed symmetrically about the bond axis, i.e., the line joining the nuclei. *Such a bond formed by the axial overlapping of the orbitals is called a sigma (σ) bond.*

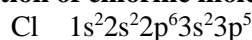
2. Formation of hydrogen fluoride molecule:



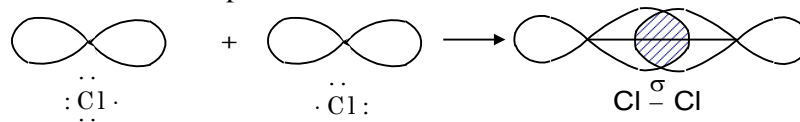
The 1s-orbital of the hydrogen atom and one of the 2p-orbitals of the fluorine atom contain only one electron each. The 1s-orbital of the hydrogen atom and the partly filled p-orbital of the fluorine atom overlap axially and form a σ bond (s-p overlap).



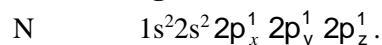
3. Formation of chlorine molecule:



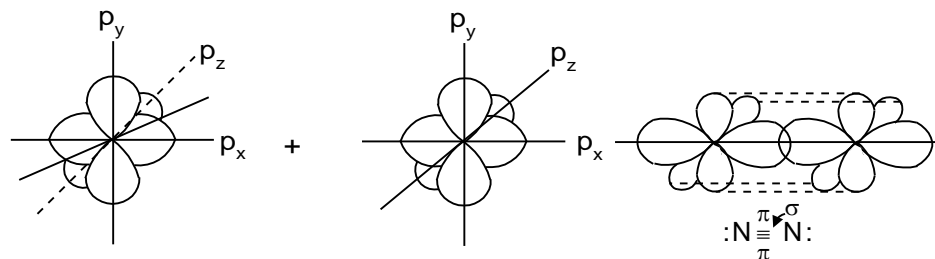
One of the 3p-orbitals of the chlorine atom contains only one electron. The half-filled p-orbital of a chlorine atom overlaps axially with the half-filled p-orbital of the other chlorine atom and forms a σ bond (p-p overlap).



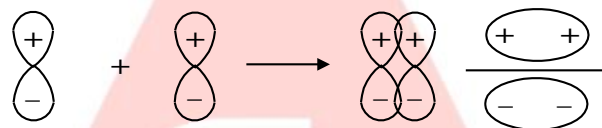
4. Formation of nitrogen molecule:



There are three unpaired electrons in the 2p-orbitals of a nitrogen atom. When two nitrogen atoms combine the three 2p-orbitals of one atom mutually overlap with those of the other atom and form three bonds.



Suppose the orbitals approach along the x -axis the p_x -orbitals overlap axially and form a σ bond ($p-p$ overlap). The p_y and p_z -orbitals of the N atoms cannot overlap axially and so make a lateral (side to side) overlap forming two Pi (π) bonds.



Generally in any multiple bond between two atoms one bond is a σ bond and the others π bonds. A double bond will consist of a σ bond and a π bond and a triple bond will consist of a σ bond and two π bonds. In a π bond formed between two p -orbitals, the upper lobe overlaps the upper lobe and the lower lobe overlaps the lower lobe. Together they constitute π bond.

The π electron cloud will lie above and below the plane of the bond.

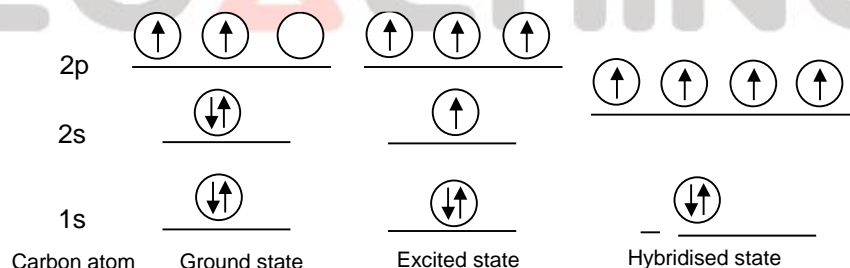
9 HYBRIDISATION

9.1 sp^3 HYBRIDISATION

Carbon atom has the electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$. It has two half-filled orbitals.

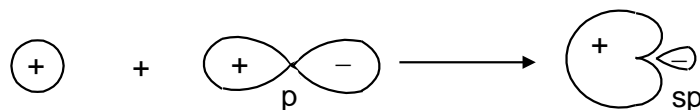
It should be expected to show a covalency of 2. In its millions of compounds carbon shows tetravalency. To explain this the concept of hybridisation is introduced. Consider the formation of methane, CH_4 .

It may be supposed just for the sake of a picture that one of the electrons in the 2s-orbital is promoted to the vacant p_x orbital (excited state). This is possible because energy released during bond formation will compensate for this. Then the four orbitals, one s and three p -orbitals, get mixed up and form four new 'hybrid' orbitals, of equal energy which are called sp^3 hybrid orbitals, as they are formed by the mixing up (or blending) of one s and three p -orbitals.



sp^3 hybridisation of carbon atom

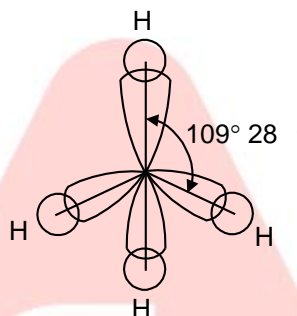
So hybridisation is nothing but **combination of a certain number of atomic orbitals of slightly different energies to form the same number of new (hybrid) orbitals of equal energy.**



sp^3 hybrid orbital

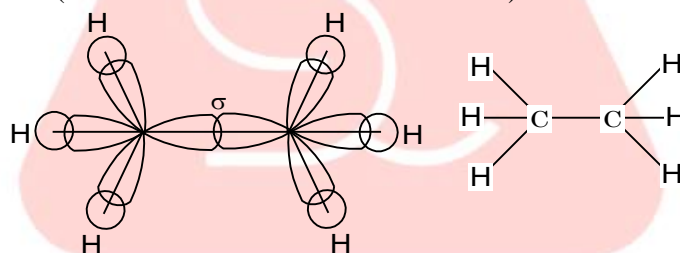
Each sp^3 hybrid orbital is like a p-orbital, but with 2 lobes of unequal size (In figures, the small lobe is usually omitted).

Since the hybrid orbitals repel one another, they orient themselves with an angle of $109^\circ 28'$ between them and point to the four corners of a regular tetrahedron. Each hybridised orbital overlaps the 1s-orbital of a hydrogen atom and forms a σ bond. Each sp^3 hybridised orbital has one fourth s character and three-fourths p character. Note that a hybrid atomic orbital from s and p-orbitals can form only σ bonds. (4 C – H σ bonds.)



CH₄ molecule

Formation of Ethane: In this case there is sp^3-sp^3 overlap resulting in the formation of the C – C bond and sp^3-s overlap forming C – H bonds. (1 C – C σ bond and 6 C – H σ bonds.)

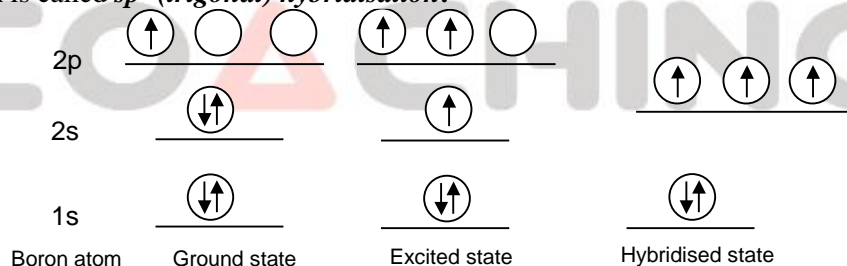


Formation of Ethane

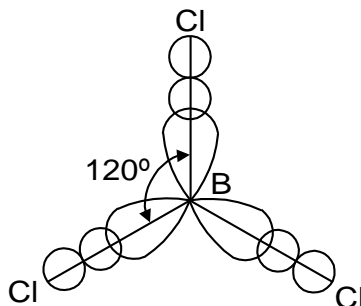
9.2 SP² HYBRIDISATION

Formation of boron trifluoride/trichloride, BF₃/BCl₃

Boron has the electronic configuration $1s^2 2s^2 2p^1$. One of the s electrons is promoted to a vacant p_y -orbital (excited state). Then *one s-orbital and two p-orbitals* hybridise to form three sp^2 hybrid orbitals of equivalent energy. This kind of hybridisation is called sp^2 (*trigonal*) hybridisation.



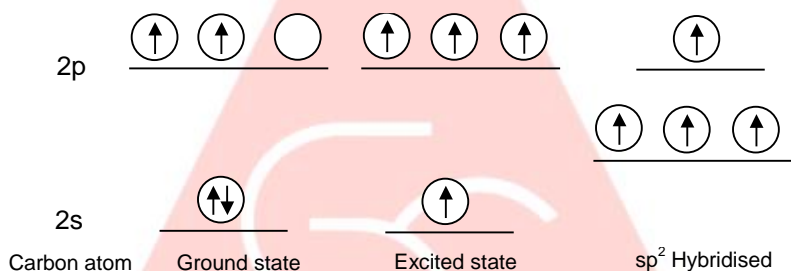
sp^2 hybridisation of Boron



Formation of BCl₃

The three sp² hybrid orbitals are *co-planar* and are at angles of 120° to each other. Each hybrid orbital overlaps with the vacant p-orbital of the chlorine atom and forms a σ bond. The other halides or Boron have similar structures. An sp² hybrid orbital has one-third s character and two-thirds p character. (3 σ bonds.)

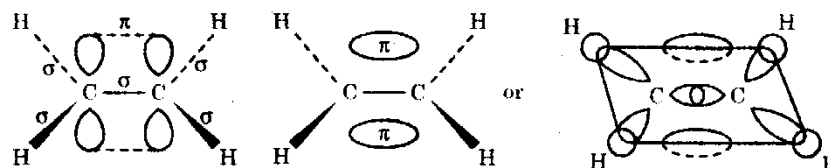
Formation of Ethylene molecule



sp² hybridisation of carbon

In the formation of ethylene, carbon atom undergoes sp² hybridisation. Two of the sp² orbitals of each atom form σ bonds with 1s-orbitals of hydrogen atoms by axial overlapping.

The sp²-sp² overlap results in the formation of a C – C σ bond. The two carbon atoms and the four hydrogen atoms are all in the same plane and the bond angles are 120°.



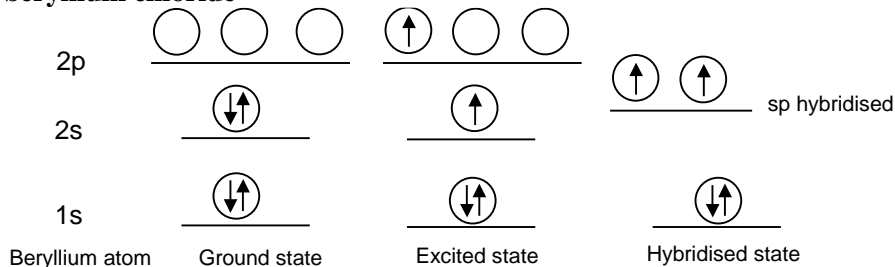
Ethylene molecule

At right angles to this plane there remains the 2p_z orbital of each carbon atom which overlap laterally to form a π bond between the two carbon atoms. The double bond between the two carbon atoms consists of a σ bond and a π bond. (4 C – H σ bonds, 1 C – C σ bond and 1 π bond)

9.3 SP HYBRIDISATION

One s and one p-orbital combine to form two hybrid orbitals known as sp (or linear or diagonal) orbitals. They are of equal energy and are collinear. Each sp-orbital has one-half s character and one-half p character.

(i) Formation of beryllium chloride

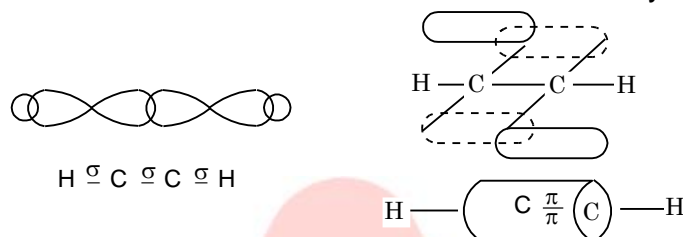


sp hybridization of Beryllium

The sp hybrid orbitals of beryllium atom overlap with the vacant p_x -orbitals of two chlorine atoms and form two σ bonds. $Cl \sigma Be \sigma Cl$ since sp hybrid orbitals protrude along the axis farther than the corresponding s or p -orbitals they are able to overlap better and form stronger bonds than s or p -orbitals alone.

(ii) Formation of acetylene

Hybridization of the one $2s$ and $2p$ carbon orbitals leads to the formation of two sp hybrid orbitals. $sp-sp$ overlap between two carbon atoms form a σ bond between them. The other sp orbital on each carbon atom forms a σ bond with the $1s$ orbital of a hydrogen atom.



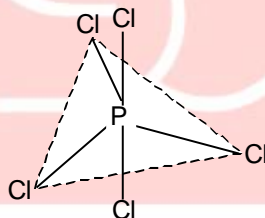
Acetylene molecule

Each of the carbon atom has two remaining p -orbitals which are mutually at right angles to each other. They laterally overlap and form two π bonds, sometimes pictured as a cylindrical sheath about the line joining the nuclei. One triple bond between 2 carbon atoms contains one $C-C \sigma$ bond and 2π bonds. (1 $C-C \sigma$ bond, 2 $C-H \sigma$ bonds and 2π bonds)

The carbon-carbon triple bond is made up of one strong σ bond and two weaker π bonds; it has a total strength of 198 kcal/mole. It is stronger than a carbon-carbon double bond (163 kcal) or $C-C$ single bond in ethane (88 kcal) and therefore is shorter than either.

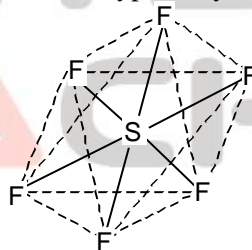
9.4 sp^3d HYBRIDIZATION

In this type of hybridization, one 's', three 'p' and one 'd' orbitals of the same shell mix to give five sp^3d hybrid orbitals. These five sp^3d hybrid orbitals orient themselves towards the corners of a trigonal bipyramidal.



9.5 sp^3d^2 HYBRIDIZATION

In this type of hybridization, one 's', three 'p' and two 'd' orbitals of the same/different shell mix to give six sp^3d^2 hybrid orbitals. These six sp^3d^2 hybrid orbitals orient themselves towards the corners of an octahedron. This type of hybridization is exhibited by SF_6 , SCl_6 etc.



9.6 SCHEME FOR DETERMINING HYBRIDIZATION OF THE CENTRAL ATOM OF A SPECIES

- Identify the central atom of the species.
- Write outermost electronic configuration of the central atom.
- Determine oxidation state of the central atom.
- Excite the electrons (if necessary) to the orbitals of higher energy in order to make the number of unpaired electrons equal to the oxidation state of the central atom.
- Now start putting orbitals into your pocket, beginning from 's' orbitals. The number of orbitals added to the pocket must have orbitals with unpaired electrons equal to number of other atoms of the species.
- All the orbitals added to the pocket (including s orbital, whether it has paired or unpaired electrons) are

now summed. If there are one 's' and one 'p' orbital in the pocket, then the hybridization is sp. If there are one 's' and '2p' orbitals in the pocket, it is sp² hybridization, and so on.

- (vii) Each unpaired electron left (outside the pocket) will form a pi-bond.
- (viii) Each orbital with paired electrons in the pocket will exist as lone pair on the central atom.

The working of this scheme can be seen in the following illustrations.

10 HYDROGEN BOND

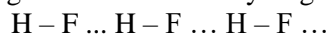
A hydrogen atom normally forms a single bond. In some compounds, however, the hydrogen atom may be located between two atoms acting as a bridge between them. Hydrogen atom is now involved in two bonds, one a normal covalent bond, the other a hydrogen bond.

A hydrogen bond is always formed between two small, strongly electronegative atoms such as fluorine, oxygen and nitrogen.

10.1 INTERMOLECULAR HYDROGEN BONDING – MOLECULAR ASSOCIATION

(i) Hydrogen fluoride:

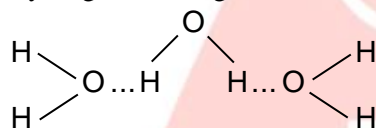
From molecular measurements, it is known that hydrogen fluoride is associated (i.e., many molecules are joined together). HF is a polar molecule, with the fluorine atom acquiring a slight negative charge and the hydrogen atom acquiring an equal positive charge. The electrostatic attraction between the oppositely charged ends results in hydrogen bonding as shown below.



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

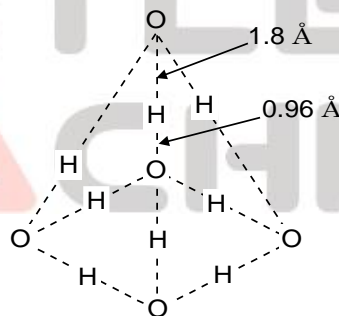
(ii) Water:

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



The crystal structure of ice shows a tetrahedral arrangement of water molecules.

Each oxygen atom is surrounded tetrahedrally by 4 others. Hydrogen bonds link pairs of oxygen atoms together as shown in Figure 6.19. The arrangement of water molecules in ice is a very open structure and this explains the low density of ice. When ice melts, the structure breaks down and the molecules pack more closely together so that water has a higher density; this packing goes to a maximum upto a temperature of 4°C.



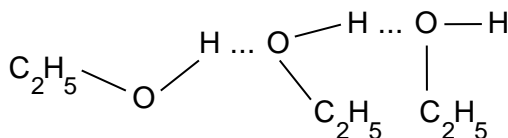
(iii) Ammonia

is also associated through hydrogen bonding; hence it has higher boiling point than PH₃ or AsH₃.

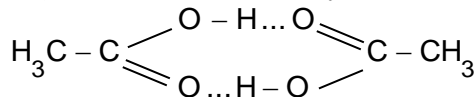
Note: Methane has normal values for its melting and boiling points. It is not associated as carbon has no lone pairs and is not sufficiently electronegative to be linked by hydrogen bonds.

(iv) Alcohols and phenols:

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



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

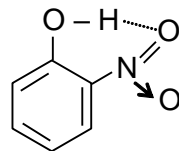


In aqueous solution molecules of a carboxylic acid link up with water molecules through hydrogen bonding rather than form dimers.

10.2 INTRAMOLECULAR HYDROGEN BONDING

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

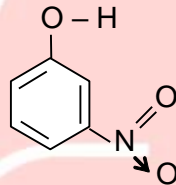
(i) **Nitrophenols**



o-nitrophenol

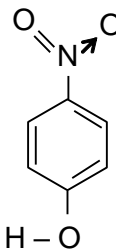
B.P. 214°C

less soluble in water



m-nitrophenol

B.P. 290°C



p-nitrophenol

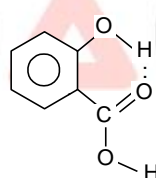
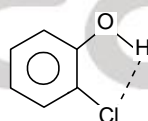
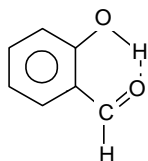
B.P. 279°C

comparatively more soluble

Because of the proximity of -OH and -NO₂ groups in o-nitrophenol there is intramolecular hydrogen bonding which prevents intermolecular hydrogen bonding between two or more molecules. Since molecular association cannot take place, the boiling point of o-nitrophenol is lower than that of the other two. Because of the distance between -OH and -NO₂ groups in m- and p-nitrophenols there is no possibility of intramolecular hydrogen bonding. Intermolecular hydrogen bonding may take place to a certain extent which causes some degree of molecular association; this is responsible for the higher boiling points of the two nitrophenols.

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

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



11 MOLECULAR ORBITAL THEORY AND BOND ORDER

The Valance Bond Theory (V.B. Theory) with the concepts of hybridisation and resonance is used to explain the structure and properties of several molecules, but there are limitations. For example, the V.B. theory in its original form, is not able to explain the paramagnetic behaviour of O₂ molecule. Hence the Molecular Orbital Theory (or M.O. Theory) due to Hund and Mulliken. The following are the essential features of the M.O. Theory.

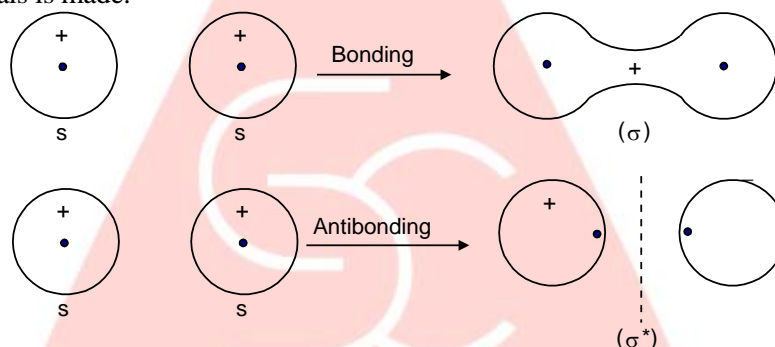
- In the M.O. model, all the electrons are taken together and considered as moving in the field of all the nuclei. (In the V.B. model, only the bonding electrons are considered and they are taken to move in the field of the nuclei involved in bonding.)
- The atomic orbitals are combined to form, what are called molecular orbitals and electrons are fed into these orbitals. (In the V.B. model, electrons are fed into the atomic orbitals, which are then supposed to overlap.)
- The number of combining atomic orbitals is equal to the number of molecular orbitals formed.
- When two atomic orbitals combine, two M.O.'s are formed, of which one has a lower energy, while the other has a higher energy. The former is known as the bonding orbital and the latter antibonding.

Mathematically, if ψ_1 represents the wave function corresponding to orbital

1 and ψ_2 for orbital 2, the total function is a linear combination of ψ_1 and ψ_2 i.e., $\psi = \psi_1 \pm \psi_2$ (omitting the constants). This is known as linear combination of atomic orbitals (L.C.A.O.). Of these,

$\psi_1 + \psi_2$ corresponds to the bonding M.O., while $\psi_1 - \psi_2$ corresponds to antibonding M.O. i.e., $\psi_b = \psi_1 + \psi_2$ and $\psi_a = \psi_1 - \psi_2$. The electron density or probability of finding an electron is directly proportional to ψ^2 .

For the bonding orbital, $\psi_b^2 = (\psi_1 + \psi_2)^2 = \psi_1^2 + \psi_2^2 + 2\psi_1\psi_2$, which is greater than $\psi_1^2 + \psi_2^2$ i.e., the electron density between the two nuclei is concentrated when the bonding M.O. is formed, than when no such combination of orbitals is made.



For the antibonding orbital, $\psi_a^2 = (\psi_1 - \psi_2)^2 = \psi_1^2 + \psi_2^2 - 2\psi_1\psi_2$, which is less than $\psi_1^2 + \psi_2^2$ i.e. the electron density between the nuclei is withdrawn in an antibonding M.O. In the bonding M.O., since the electron density between the two nuclei is large, it holds the two nuclei together; hence the name bonding orbital; in the antibonding M.O. the bonding of the nuclei is poor.

- There are different notations for representing bonding and anti-bonding M.O.'s obtained from A.O.'s. We give a simple notation below.

Atomic orbitals that are mixed	s and s	p_z and p_z	p_x and p_x	p_y and p_y
Bonding M.O.	σs	$\sigma(p_z)$	$\pi(p_x)$	$\pi(p_y)$
Antibonding M.O.	$\sigma^* s$	$\sigma^*(p_z)$	$\pi^*(p_x)$	$\pi^*(p_y)$

We have assumed the two p_z orbitals to overlap end to end, so that the M.O. formed is of the ' σ ' type (similar to the ' σ ' bond in V.B. theory); then the two p_x atomic orbitals, as also the two p_y orbitals will overlap laterally to give M.O.'s of the π type. Some authors follow the convention of choosing two p_x orbitals for end to end (i.e., axial) overlap, so that the M.O.'s formed are $\sigma(p_x)$ and $\sigma^*(p_x)$.

- When electrons are successively placed in the M.O.'s, Aufbau principle, Hund's rule and Pauli's principle are followed, as in the case of the atomic orbitals.

Aufbau Principle: M.O.'s are occupied in the order of increasing energy. The following is the general arrangement of M.O.'s in the order of increasing energy.

$$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z) \dots \text{etc.}$$

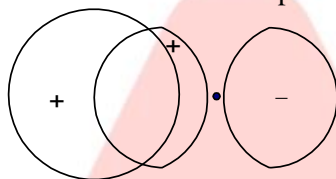
The above is only a general order and slight variations often occur due to interaction between s and p orbitals. For example, sometimes, $\pi(2p_x) = \pi(2p_y) < \sigma(2p_z)$.

7. Hund's rule of maximum multiplicity:

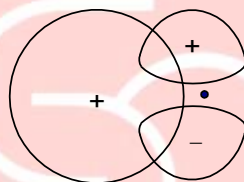
The degenerate M.O's are occupied singly, before any pairing could occur. The maximum capacity for each M.O. is 2 electrons.

8. Only atomic orbitals of equal or nearly equal energies combine to give the M.O's. In the case of homonuclear diatomic molecules, energies of corresponding A.O's of the two atoms are equal. So the above condition of combination of A.O's assumes special significance in the case of heteronuclear diatomic molecules and it has to be used with caution.

Further, for effective combination or overlap, the A.O's should have the same symmetry. Thus we have the $s-s$, p_z-p_z , p_y-p_y and p_x-p_x overlaps to give bonding and antibonding orbitals as pointed out earlier (see point 5). Regarding the $s-p$ overlap, a $2s$ orbital may overlap with a $2p_z$ orbital as shown in Figure (a) below, since both have axial symmetry around the internuclear axis. However, the $2s-2p_x$ or $2s-2p_y$ overlap makes no contribution to bonding, as shown in Figure (b) below, where the constructive overlap in one region is exactly cancelled by the effect of the destructive overlap in the other.



(a) Enhanced amplitude



(b) Decreased amplitude

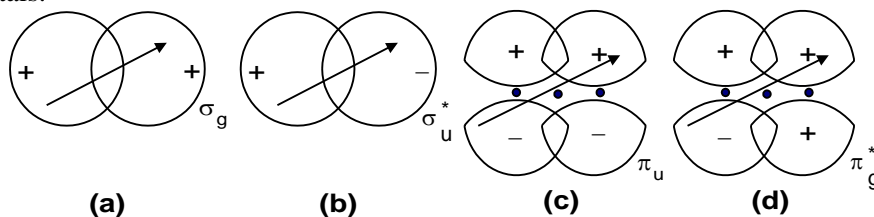
9. It has been already pointed out that electrons in the bonding M.O's tend to pull the nuclei together and that the electrons in the antibonding M.O's tend to separate them. Hence the combined influence of bonding and antibonding electrons may either stabilize or destabilize the molecule, depending on the relative number of these two types of electrons. The stabilizing power is expressed in terms of what is called the "bond order".

$$\text{Bond order} = \frac{1}{2} \left[\left(\text{number of electrons in the bonding M.O.} \right) - \left(\text{number of electrons in the antibonding M.O.} \right) \right]$$

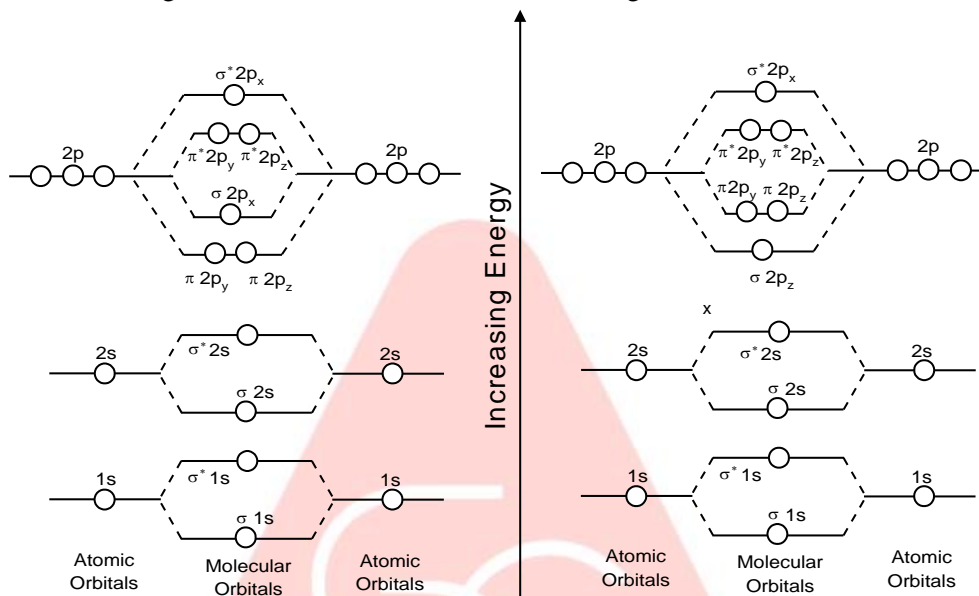
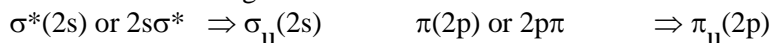
The greater the bond order, the greater the bond stability and the shorter the bond distance.

10. The M.O's are also named on symmetry grounds. For **homonuclear diatomic molecules**, the symbols 'g' ('gerade' meaning 'even') and 'u' ('ungerade' meaning 'uneven' or 'odd') are used. The symbol 'g' is used, if the orbital has a centre of symmetry. i.e., if along any straight line passing through the centre (This is called the centre of inversion), at equal distances from it, the electron densities are equal and the orbital signs are the same (i.e., the wave function has the same amplitude and sign at the two points which are opposite and equidistant from the centre). If the electron densities are equal, but the orbital signs are opposite at the two points mentioned above, the symbol 'u' is used.

In the ' σ ' type of orbitals, the bonding orbitals are 'g' and the antibonding 'u'; in the ' π ' type of orbitals, the bonding orbitals are 'u' and the antibonding 'g'. Figure (a) and (b) below correspond to overlap of 's' orbitals to form ' σ ' type of M.O's; Figure (c) and (d) correspond to the formation of ' π ' type of M.O's from 'p'-orbitals.



The equivalence of the different notations used to represent the M.O's is shown for a few cases (the x, y, z subscripts in the case of p-orbitals are dropped).



For elements with $Z \leq 7$

Molecular orbital energy level diagram

For elements with $Z > 7$

Molecular orbital energy level diagram

11.1 HOMONUCLEAR DIATOMIC MOLECULES

We shall now consider the electronic configuration of a few homonuclear diatomic molecules.

1. H_2 : Electronic configuration of H atom: $1s^1$.

\therefore in H_2 molecule there are 2 electrons. M.O. configuration of H_2 is $\sigma 1s^2$. There is no electron in antibonding M.O. \therefore Bond order (B.O.) = $\frac{2-0}{2} = 1$

2. He_2 : Electronic configuration of He atom: $1s^2$

\therefore in He_2 molecule there are 4 electrons. The M.O. configuration for He is $\sigma 1s^2, \sigma^* 1s^2$.
 \therefore Bond order = $\frac{2-2}{2} = 0$.

\therefore He_2 molecule is not stable.

Taking He_2^+ , the structure is $\sigma 1s^2, \sigma^* 1s^1$.

\therefore B.O. = $\frac{2-1}{2} = \frac{1}{2}$.

\therefore He_2^+ is stabler than He_2 .

3. Li_2 : (Li atom: $1s^2 2s^1$). Total number of electrons in $Li_2 = 6$. Molecular orbital configuration of Li_2 is $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^0$ or [KK] $\sigma 2s^2, \sigma^* 2s^0$.

where KK corresponds to filled $\sigma(1s)$ and $\sigma^*(1s)$ levels. The contribution of [KK] to bond order is zero. Therefore, we can ignore it and consider only the valence electrons.

B.O. = $\frac{2-0}{2} = 1$

\therefore Li_2 is stable and it is found to exist to some extent in lithium vapour.

4. Be_2 : (Be: $1s^2 2s^2$)

Molecular orbital structure of Be_2 is:

[KK] $\sigma 2s^2, \sigma^* 2s^2$. Ignoring [KK], B.O. = $\frac{2-2}{2} = 0$. \therefore Be₂ is not stable.

5. B₂: (B: 1s² 2s² 2p¹)

M.O. structure of B₂ is [KK] $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^1, \pi 2p_z^1$.

Note that though $\pi(2p)$ orbital is usually more energetic than $\sigma(2p)$, there is an inversion of the order here due to mixing (hybridization) of $\sigma(2s)$ and $\sigma(2p)$ orbitals. Also note that the degenerate M.O.'s $\pi(2p_y)$ and $\pi(2p_z)$ have one electron in each according to Hund's principle.

$$\text{B.O.} = \frac{4-2}{2} = 1$$

\therefore B₂ is stable.

Since there are two unpaired electrons in the molecule, B₂ is paramagnetic.

6. C₂: (C: 1s² 2s² 2p²).

M.O. picture of C₂ is:

[KK] $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi 2p_z^2$

Here again $\pi(2p)$ orbital is less energetic than $\sigma(2p)$.

$$\text{B.O.} = \frac{6-2}{2} = 2 \text{ and the molecule is stable.}$$

Since there is no unpaired electron, C₂ is diamagnetic. [If $\pi(p)$ orbital had been more energetic than $\sigma(p)$, C₂ would have been paramagnetic, which is contrary to experimental observation.]

7. N₂: (N: 1s² 2s² 2p³).

M.O. picture of N₂ is:

[KK] $\sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi 2p_z^2, \sigma 2p_x^2$

Ignoring the subscripts x, y and z for the p-orbital and considering, only valence electrons, the representation is $\{\sigma(2s)\}^2 \{\sigma^*(2s)\}^2 \{\pi(2p)\}^4 \{\sigma(2p)\}^2$.

$$\text{B.O.} = \frac{8-2}{2} = 3; \quad \text{The molecule is diamagnetic. For } \text{N}_2^+, \text{ B.O.} = \frac{7-2}{2} = 2.5.$$

8. O₂: [O: 1s² 2s² 2p⁴]

M.O. structure of O₂ is:

[KK] $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_y^1, \pi^* 2p_z^1$; B.O. = $\frac{8-4}{2} = 2$

Due to the presence of unpaired electrons in the two antibonding orbitals (Hund's rule), O₂ is paramagnetic. The M.O. theory here is superior to the V.B. theory, which does not explain the paramagnetic behaviour of O₂.

Let us now compare the bond strengths of O₂, O₂⁺, O₂⁻, O₂²⁻. For O₂, B.O. = 2.

For O₂⁺: one electron from the antibonding M.O. has been removed.

$$\therefore \text{B.O.} = \frac{8-3}{2} = 2.5$$

For O₂⁻: one electron is added to the antibonding M.O.

$$\therefore \text{B.O.} = \frac{8-5}{2} = 1.5$$

$$\text{For } \text{O}_2^{2-}: \text{B.O.} = \frac{8-6}{2} = 1$$

\therefore the bond is strongest in O₂⁺ and the bond length the least.

MIND MAP

