INTRODUCTION

Section - 1

We have come across the terms *molecules and compounds*. Molecule can be defined as an uncharged entity in which atoms of same kind or of different kinds are held together by some forces. Compound is the collective name of a set of molecules of same kind.

For example : Sulphur dioxide is a compound which contains the molecules of SO_2 , which is made up of atoms of S and O. Cane sugar consists the molecules of $C_{12}H_{22}O_{11}$, which is made up of atoms of C, H and O.

The forces that hold together the atoms in a molecule are known as *Chemical forces* or *Valence forces*. The association between atoms in a molecule by valence forces is called as *Chemical Bond*.

An atom possesses its greatest stability when its valence electron shell (outer shell) is complete. The K shell (n = 1) is complete when it contains two electrons, while the remaining shells are complete when they contain eight electrons. This is referred to as *Lewis Octet Rule*.

Note : The arrangement of electrons in Noble Gases is the criteria of stability, i.e., fully filled sub-shells (ns²np⁶). The atoms of these elements are in a state of great stability and hence do not form compounds and in general are chemically inert.

So it is the valence electrons that determine the chemical behavior of an atom. In a compound, a definite number of valence electrons are involved in the bonding process. The chemical association among atoms can be achieved by many ways depending upon number of valence electrons contained in the atoms. Three major types of chemical bonding are as follows:

| Ionic Bonding | : | Stability through transfer of electrons. |
|--------------------|---|---|
| Covalent Bonding | : | Stability through mutual sharing of electrons. |
| Coordinate Bonding | : | Stability through partial transfer and partial sharing of electrons |
| | | sharing of electrons. |

1. Kossel – Lewis's Electronic Theory of Chemical Bonding :

Lewis pictured the atom in terms of:

- (a) A positively charged 'Kernel' (the nucleus plus the inner electrons) and
- (b) The outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'.

Note:

When all the eight corners of the cube are occupied then an atom is said to have stable electronic configuration. Clearly noble gases which have 8 outer most electrons already have stable configuration while all other atomic achieve stable octet of electrons (set of 8) when they are linked by chemical bonds.

Valence electrons : It refers to the outer shell electrons (of an atom) that take part in chemical combination in the formation of a molecule.

- The inner shell electrons are well protected and are generally not involved in the combination process.
- Common or group valence of an element : It generally refers to no of valence electrons or 8 minus the number of valence electrons.
- Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule.

IONIC OR ELECTROVALENT BONDING

The chemical bond formed due to electrostatic attraction between cations and anions (which are formed by the complete transfer of electron(s) from one atom to the other atom) is called as Electrovalent or Ionic Bond. The Ionic valency or Electrovalence is referred to as the number of electrons that an atom cangive up or gain. In other words it is equal to the number of unit charge(s) on the ion, eg. In NaCl, sodium assigned a positive electrovalence of one, while chlorine a negative electrovalence of one.

Section - 2

The formation of a positive ion involves ionization, i.e., removal electron(s) from the neutral atomand that of the negative ion involves the addition of electron(s) to the neutral atom.

| $M(g) \longrightarrow M^+(g) + e^-;$ | Ionization enthalpy |
|---|------------------------|
| $X(g) + e^- \longrightarrow X^-(g)$; | Electron gain enthalpy |
| $M^+(g) + X^-(g) \longrightarrow MX(s)$; | Lattice energy |

Formation of Lattice :

The compounds which are formed by ionic bonds are mostly solids. These compounds crystallize in different crystal structures determined by factors such as size of the ions, their packing arrangements etc. In the crystalline state, these compounds consist of orderly three-dimensional arrangements of cations and anions (*which is called* lattice) held together by coulombic interaction energies. The energy released when such an arrangement is formed (due to electrostatic attraction) is known as Lattice Energy.

The lattice is a highly stable arrangement and hence all ionic compounds have high melting and boiling points. The higher is the lattice energy, the more stable is the ionic bond.

Factors affecting lattice energy :

Magnitude of charge : More is the magnitude of charge on cation or anion, the more is the lattice energy. For example, the lattice energy of MgCl, is higher than that of NaCl.

Size of ions: For higher lattice energy, the cations should be smaller and anion should be larger. The smaller is the cation, the more effective is the nucleus in pulling the neighbouring anions towards it. As aresult, the lattice formed is highly stable or we can say that the lattice energy is high. Eg : Lattice energy of NaCl is greater than that of CsCl, as Na⁺ cation is smaller than Cs⁺ cation though the ionisation energy of Cs is much lower than that of Na.

Elaboration :

- > There is a formation of negative ion from a halogen atom and and a positive ion from an alkali metal atom due to gain and loss of an electron by the respective atoms.
- The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet), electrons, ns²np⁶.
- > The negative and positive ions are stabilized by electrostatic attraction.

For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as :

Na \longrightarrow Na⁺ + e⁻[Ne] $3s^1$ [Ne]Cl + e⁻ \longrightarrow Cl⁻[Ne] $3s^2 3p^5$ [Ne] $3s^2 3p^5$ \longrightarrow Na⁺ + Cl⁻NaCl or Na⁺ Cl⁻

Similarly the formation of CaF₂ may be shown as :

Ca \longrightarrow Ca²⁺ + 2e⁻ [Ar] 4s² [Ar] F + e⁻ \longrightarrow F⁻ [He] 2s² 2p⁵ [He] 2s² 2p⁶ or [Ne] Ca²⁺ + 2F⁻ \longrightarrow CaF₂ or Ca²⁺ (F⁻)₂

Other examples of molecules involving ionic bonds are MgO, AlCl₃, KI, CaS, MgBr₂, etc.

Ionic Bonding formation depends on the following :

- **1.** Ionisation Enthalpy $(\Delta_i H)$ or ease of formation of positive ions.
- 2. Electron Gain Enthapy $(\Delta_{ee} H)$ / Eectron Affinity (A_e) or ease of formation of negative ions.
- 3. Lattice Enthalpy

lonisation Enthalpy $(\Delta_i H)$: It is the energy required to remove an electron from an isolated gaseous atom in its ground state.



Electron Gain Enthalpy (Δ_{eg} H) : It is the energy required to add an electron to a gas phase atom in its ground state to form a negative gaseous ion.

Note : The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic.

Electron affinity (A_e) : It is the energy released when an electron is added to a neutral gaseous atom in its ground state to form a negative ion. *Electron Affinity of an atom is defined only at absolute zero temperature*.

Lattice Energy : Energy released when gaseous positive and negative ions come together to form 1 mol of solid (crystalline) ionic compound.

Lattice Enthalpy : The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ/mole (and Lattice energy = -788 kJ/mol). This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na⁺(g) and one mole of Cl⁻ to an infinite distance.

Note: Condition for formation of a stable ionic compound is : *Total Ionisation enthalpy* + *Total Electron Gain Enthalpy* – *Total Lattice Enthalpy* < 0

| Metal | Nonmetal | General Formula | lons Present | Example |
|-------|----------|-------------------------------|-------------------------------|--------------------------------|
| IA | VIIA | МХ | $\left(M^{+},X^{-}\right)$ | LiBr |
| HA | VIIA | MX ₂ | $\left(M^{2+}, 2X^{-}\right)$ | MgCl ₂ |
| HIA | VIIA | MX ₃ | $\left(M^{3+}, 3X^{-}\right)$ | GaF ₃ |
| IA | VIA | M ₂ X | $\left(2M^+, X^{2-}\right)$ | Li ₂ O |
| IIA | VIA | МХ | $\left(M^{2+},X^{-}\right)$ | CaO |
| IIIA | VIA | M ₂ X ₃ | $(2M^{3+}, 3X^{2-})$ | Al ₂ O ₃ |
| IA | VA | M ₃ X | $\left(3M^{2+},X^{3-}\right)$ | Li ₃ N |
| IIA | VA | M ₃ X ₂ | $(3M^{2+}, 2X^{3-})$ | Ca ₃ P ₂ |
| IIIA | VA | MX | $\left(M^{3+}, X^{3-}\right)$ | AlP |

Simple Binary Ionic Compounds

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Properties of Ionic Compounds :

- (i) The ionic substances are good conductors of heat and electricity in molten state or aqueous medium. In both these states, the lattice is broken and ions are free to conduct electricity and heat.
- (ii) Due to stability of lattice, ionic compounds have high melting and boiling points.
- (iii) The bond in ionic compounds is non-directional. In these compounds, each ion (cation or anion) has a uniformly distributed electric field, so one can not predict whether a particular ion is bonded to this or that ion.
- (iv) These are soluble in polar solvents like water, which acts as a dielectric (*dielectric is a material which weakens the electric field*). When the electric field is weakened, the ions are relatively free to go in water.

COVALENT BONDING

Certain elements which have high ionisation energies are incapable of transferring electrons and other having low electron affinities, fail to take up electrons. The atoms of such elements share their electrons with the atoms of other elements (and sometimes among themselves) in such a manner that both the atoms form complete outer shell. In this manner they achieve stability. Such an association through sharing of electron pairs among atoms of different or of same kinds is known as Covalent Bond. This was proposed by G.N. Lewis.

The covalent bonding can be achieved in two ways :

- (i) Sharing electrons between atoms of same kinds, formation of F_2 , O_2 , Cl_2 , etc.
- (ii) Sharing of electrons between atoms of different kinds, formation of HCl, CO_2 , H_2O , CH_4 , etc.

Lewis Symbols : To represent <u>valence</u> electrons in an atom, Lewis introduced simple notations called as Lewis symbols. For example, the Lewis symbols for the elements of second period are as under

 $\dot{Li} \quad \dot{Be} \quad \dot{B} \cdot \quad \dot{C} \cdot \quad \ddot{N} \cdot \quad \ddot{O} : : \ddot{F} : : \ddot{N}e :$

The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or group valence of an element.

Formation of F_2 and other like molecules : A Fluorine atom has seven electrons in its outermost shell and thus it needs one more electron to complete an octet of electrons and attain a noble gas configuration. A F_2 molecule is thus formed by combination of two F atoms by sharing one electron each. It is represented by Lewis dot structure as follows:

$$: \stackrel{*}{:} \cdot + \stackrel{*}{*} \stackrel{*}{}_{**} \stackrel{*}{*} \longrightarrow \underbrace{: \stackrel{*}{:} \stackrel{*}{:} \stackrel{*}{:} \stackrel{*}{}_{**} \stackrel{*}{}_{**} \stackrel{*}{*}_{*} \stackrel{*}{}_{*} \stackrel{*}}{}_{*} \stackrel{*}}{}_{*} \stackrel{*}{}_{*} \stackrel{*}{}_{*} \stackrel{*}{}_{}$$

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Note that now both of F atoms now have eight (8) electrons each in their outer shell. In a more simple way, electron (Lewis) dot formula can be expressed by using '-' (a dash) instead of $\bullet x$.

Note :

- Pair of electrons depicted as •• or x x is called as Lone pair (lp) and that by x is called as shared pair or Bond pair (bp). Lone pair is the pair of electrons belonging to one atom only. Thus F₂ has one bp(s) and six lp(s).
- When two atoms share one/two/three electron pair(s) they are said to be joined by a *single/double/triple covalent bond* respectively. Eg in the above example of F_2 molecule there is a single bond between the two fluorine atoms.

| H ₂ | H : H* | H – H |
|-------------------------------|--|---|
| 0 ₂ | :0 :: 0: | : <u>O</u> = O: |
| 0 ₃ | | Ö ⁺ |
| NF ₃ | : <u><u>F</u>:<u>N</u>:<u>F</u>:</u> | $: \overrightarrow{\mathbf{F}} - \overrightarrow{\mathbf{N}} - \overrightarrow{\mathbf{F}}:$ $ $ $: \overrightarrow{\mathbf{F}}:$ |
| CO_{3}^{2-} | $\begin{bmatrix} \vdots \vdots$ | $\begin{bmatrix} :0:\\ \parallel\\ \vdots \\ \vdots \\ -C - \\ \vdots \end{bmatrix}^{2-}$ |
| HNO ₃ | <u>Ö</u> (:: [†] N :: <u>Ö</u> :) H : <u>О</u> : | ö− ⁺ n−ö−н ¦ :о:_ |
| CO ₂ | | ö=c=ö |
| C ₂ H ₄ | H C H H | H C = C H |

The Lewis Representation of some molecules is as follows :

| N ₂ | | :N≡N: |
|----------------|---------------|---------|
| C_2H_2 | H : C : C : H | Н−С≡С−Н |

Explanation for O₂ and N₂ :

 O_2 : Oxygen (O) has six electrons in valence shell, hence requires 2 more to achieve stability. It can accept two electrons to form ionic bond. It can also share two electrons with another atom of O to form covalent bond as shown in the above table. Here, 2 pairs of electrons are shared, thus double covalent bond is formed between the two oxygen atoms. In simpler way it can be represented by sign '='. So O_2 molecule can be shown as O = O.

 N_2 : Nitrogen (N) has five electrons in valence shell and requires 3 electrons to achieve stability. It does so by sharing 3 electrons with another N atom to form covalent bond as shown above. Here, 3 pairs of electrons are shared, so there is a triple covalent bond between two nitrogen atoms. In simpler way it can be represented by sign '='. So N₂ molecule can be written as $N \equiv N$.

Rules for writing Lewis dot structures :

- (i) Add valence electrons of combining atoms of the molecules to get total no. of electrons (T) to be represented in the Lewis structure.
- (ii) In case of ions, number of electrons equal to charge on the ion must also be added (for anions) or subtracted (for cations) from T.
- (iii) Least electronegative atom occupies the central position in the molecule/ion.
- (iv) Draw skeletal structure of the compound/ion using chemical symbols of the combining atom.
- (v) Now use pairs of electrons to represent single bonds between bonding atoms of the molecules/ion and represent the rest of the electrons to as lone pairs of atoms or to show multiple bonds between them (in case each of the bonding atom does not have an octet of electrons).

Note : Lewis dot structure, in general, do not represent the actual shapes of the molecules.

Illustration - 1 Write a Lewis structure for CCl_2F_2 , one of the compounds implicated in the depletion of stratospheric ozone.

SOLUTION :

Step : 1 Place the atoms relative to each other. In CCl_2F_2 carbon has the lowest group number and EN, so it is the central atom. The other atoms surround it but their specific positions are not important.

Step : 2 Determine the total number of valence electrons :

$$\begin{bmatrix} 1 \times C(4e^{-}) \end{bmatrix} + \begin{bmatrix} 2 \times F(7e^{-}) \end{bmatrix}$$
$$+ \begin{bmatrix} 2 \times Cl(7e^{-}) \end{bmatrix} = 32 \text{ valence eff}$$

- Step : 3 Draw single bonds to the central atom and subtract 2e⁻ for each bond : single bonds use 8e⁻,so 32e⁻ - 8e⁻ leaves 24e⁻ remaining.
- Step : 4 Distribute the remaining electrons in pairs, beginning with the surround-atoms, so that each atom has an octet.

Illustration - 2 Writing Lewis Structures for Molecules with More than One central atom. Write the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.

SOLUTION :

- Step : 1 Place the atoms relative to each other. The H atoms can have only 1 bond, so C and H must be adjacent to each other. In nearly all their compounds, C has four bonds and has two, so we arrange the H atoms to shown this.
- **Step : 2** Find sum of valence electrons

$$\begin{bmatrix} 1 \times C(4e^{-}) \end{bmatrix} + \begin{bmatrix} 1 \times O(6e^{-}) \end{bmatrix} + \begin{bmatrix} 4 \times H(1e^{-}) \end{bmatrix} = 14e^{-1}$$

Step : 3 Add single bonds and subtract 2e⁻ for each bond.

Five bonds use $10e^-$, so $14e^- - 10e^-$ leaves $4e^-$ remaining.

Step : 4 Add remaining electrons in pairs.

Carbon already has an octet, so the four remaining valence e^- form two lone pairs on O and give the Lewis structure for methanol.

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Illustration - 3 Write the Lewis dot structure of CO molecule.

SOLUTION :

- Step: 1 The skeletal structure of CO is written as : CO
- Step : 2 Count the total number of outer valence shell electrons of carbon $(2s^2 2p^2)$ and oxygen $(2s^2 2p^4)$ atoms.

Thus the total number of valence electrons available are 4 + 6 = 10.

Step: 3 & 4

Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons will constitute a lone pair on C.

$$:C: O: or :C - O:$$

This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms.

Writing Lewis Structures for Molecules with Multiple Bonds

Illustration - 4 Write the Lewis structure of the nitrite ion NO_2^-

SOLUTION :

Step : 1 The skeletal structure of NO_2^- is written

as :

ΟΝΟ

Step : 2 Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to

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

 \Rightarrow 5 + (2 × 6) + 1 = 18 electrons

Step : 3 & 4

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

[:ö :N: ö:]

Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures.

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Writing Lewis Structures for Molecules with Multiple Bonds

Illustration - 5 Write Lewis structures for the following :

- (a) Ethylene (C_2H_4) , the most important reactant in polymer manufacture
- **(b)** Nitrogen (N_2) , the most abundant atmospheric gas

Plan: We begin the solution after Steps 1 to 4 : placing the atoms, counting the total valence electrons, making single bonds, and distributing the remaining valence electrons in pairs to attain octets. Then are continue with step 5, if needed.

SOLUTION :

(a) For C_2H_4 . After Steps 1 to 4, we have

$$H c - \ddot{c} H$$

- Step : 5 Change a lone pair to a bonding pair. The C on the right has an octet, but the C on the left has only 6e⁻, so we convert the lone pair to another bonding pair between the two C atoms.
- **(b)** For N_2 . After steps 1 to 4 : we have $\ddot{N} \ddot{N}$:
- Step : 6 Neither N has an octet, so we change a lone pair to bonding pair : $\ddot{N} = N$:

In this case, moving one lone pair to make a double bond still does not give each N an octet, so we move another lone pair to make a triple bond : $:N \equiv N$:

H C = C H

Formal Charge

Formal charge is an accounting procedure. If allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons and the number of electrons assigned to that atom in the Lewis structure. It is expressed as :

| Formal charge (F.C.) on | $\left[\begin{matrix} \text{Total number of} \\ \text{valence electrons} \\ \text{in the free atom} \end{matrix} \right] -$ | Total number of | Total number of |
|-------------------------|--|------------------------|------------------|
| an atom in a Lewis = | | non bonding (lone | bonding (shared) |
| structure | | pair) electrons -(1/2) | electrons |

Formal charge = number of valence e^- on neutral atom – $(2 \times LP) - BP$

The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair. Let us consider the ozone molecule (O_3) . The Lewis structure of O_3 may be drawn as :

The atoms have been numbered as 1, 2 and 3. The formal charge on :

- $= 6 2 \frac{1}{2}(6) = +1$ > The centre O atom marked 1 $= 6 - 4 - \frac{1}{2}(4) = 0$ > The end O atom marked 2 $= 6 - 6 - \frac{1}{2}(2) = -1$
- > The end O atom marked 3

Hence, we represent O_3 along with the formal charges as follows : \ddot{O}

If there are more than one possible Lewis structures for a molecule having same number of bonds, the better structure is one which has the least formal charge on each individual atom. If takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure. The non-zero formal charge on any atoms in the molecule are written near the atom.

Formal charge and bond polarity

Formal charge calculations do not indicate how charge is actually distributed in molecules. Remember that most bonds are polar, meaning that the electrons in an bond are skewed toward the more electronegative atom. Formal charges, however, are found by assuming that all bonding electrons are shared equally. As a result, formal charge calculations are extremely useful for assessing whether a valence electron distribution is reasonable, but they do not reliably indicate actual bond polarity or the actual distribution of charge. Some of the following examples illustrate this point.

In chlorine trifluoride, all formal charges are zero. Based on electronegativities, however, each F-Cl bond is significantly polar. The electronegativity of F is 4.0. Indicating that a fluorine atom attracts electrons more strongly than a chlorine atom. In a CIF_2 molecule, each F atom has a small net negative charge (less than one unit), and the Cl atom has a net positive charge of 3 times this amount (also less than one unit). These partial charges are symbolized δ^+ or δ^- .

The ammonium cation illustrates the difference between formal and actual charge even more dramatically. The nitrogen atom of NH_4^+ has a formal charge of 5-4=+1, but electronegativity values indicate that N attracts electrons more strongly than H (\times N = 3.0 = 2.1). Thus the actual electron distribution in an N – H bond is skewed forward nitrogen, leaving each H atom with a partial positive charge and the N atom with a partial negative charge.

The positively charged environment of the hydrogen atoms is reflected in its chemical behaviour. This ion

readily gives up a hydrogen cation to a hydroxide anion : $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

Remember that formal charge are not annual charges. Instead, formal charges are simply a device that helps us determine the most stable distribution of a molecule's valence electron.

CO-ORDINATE COVALENT BONDING

The bonding in which one atom furnishes a pair of electrons to the other atom, in such a manner that both of the atoms achieve stability (*i.e.* 8 *electrons in outer shell*), is called as Co-ordinate Covalent or Dative Bonding.

Compounds such as NH_3 , having one lone pair readily forms coordinate bonds. It combines with H^+ ion (Hydrogen cation) to from Ammonium ion (NH_4^+) as follows :

$$H^{+} + NH_{3} \longrightarrow NH_{4}^{+} \qquad \begin{vmatrix} H \\ | \\ H \\ N - H \\ | \\ H \end{vmatrix}$$

Similarly, H_2O forms Hydronium ion (H_3O^+ ion) by combining with H^+ .

$$H^{+} + H_{2}O \longrightarrow H_{3}O^{+} \qquad \begin{bmatrix} & & & \\ H & O^{-} H \\ & & \\ H \end{bmatrix}$$

Exception to Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. Up to now we have studied the molecules which follow Lewis Octet Rule while forming bonds. It is observed that atoms in some molecules could exist with some other number of electrons in their valence shells, rather than eight electrons without affecting the stability.

There are three types of exceptions to the octet rule :

(i) The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH₂, BCl₃, AlCl₃, BF₃ etc. Li, Be and B have 1.2 and 3 valence electrons only.

 BF_3 : Boron atom has only six electrons in its outer-shell even after making three single F — bonds with three F atoms (i.e., it completes only sixet).

 $BeCl_2$: Beryllium has only four electrons in its outershell even after making two single Cl - Be - Cl bonds with two Cl atoms.

(ii) Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2 , the octet rule is not satisfied for all the atoms (as shown below)

$$\ddot{N} = \ddot{O}$$
 $\ddot{O} = \dot{N} - \ddot{O}$

(iii) The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Eg : PF₅, SF₆, H₂SO₄ and a number of coordination compounds.





Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF₂, KrF₂, XeOF₂ etc.,
- > This theory does not account for the shape of molecules.
- > It does not explain the relative stability and energy of the molecules.

Some Terminologies related to a Chemical Bond :

(i) **Bond Energetics**

The basic rule followed when a chemical bond is formed is that the total energy of the system must be lower in the bonded state than in the non-bonded state (or free atomic state). For both Ionic and Covalent bonding, association can take place only when the combined state achieves the stability, i.e., *a state of minimum energy*.

When two atoms combine to form ionic covalent bond, the total energy of the system must be lowered. Therefore energy must be given off when bonding occurs. This evolved energy is known as Bond Energy. It means, whenever *a bond is to be formed the energy will be released* and to break it, *energy must be supplied*. The covalent bonding is understood in terms of electrostatic interactions. The electrons in atoms are negatively charged and protons are positively charged, so it is electrical columbic interactions between these particles that give rise to covalent bonding.

We know that Ionic bonding is formed through electrostatic attractive force. So in both types of bonding the formation of compounds is the result of electrical interactions by columbic forces in some sense or the other.

(You will study more about electrical forces in Physics).

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(ii) Bond Length

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

 $\mathbf{R} = \mathbf{r}_{A} + \mathbf{r}_{B}$

(R is the bond length and ${\rm r}_{\rm A}$ and ${\rm r}_{\rm B}$ are the covalent radii of atoms A and B respectively





It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods.

It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H - O - H bond angle in water can be represented as under :

Ionic Character in covalent bonds (Polar Covalent Bond) :

Covalent bond when formed between two alike atoms, bonded pair of electrons is equally shared. However when it is formed between two atoms of different kinds (unlike atoms), bonded pair is not equally shared. An atom which has more tendency to attract the shared pair of electrons towards itself (high electronegativity) will pull the bond pair towards itself.

For example: Let us consider a single covalent bond between A and B, i.e., A-B.

Let B be more electronegative than A, then the bond pair will be shifted towards B, i.e., the electron cloud of bond will distort and moves slightly over to B. As a result B acquires a partial negative charge (denoted by – δ). Since the molecule is neutral, A will acquire a partial positive charge (denoted by + δ). Such a state where +ve and –ve charges are separated by a certain distance, is known as *Polarised state* and the process is known as *Polarisation*, and the covalent bond is known as *Polar Covalent Bond*.

A molecule with positive and negative charge centres in *equilibrium* is called as dipole and is characterised by possessing a quantity dipole moment (μ) defined as the product of the magnitude of charge (q) and the distance (d) separating the centres of +ve and –ve charges. $\mu = q \times d$, Its unit in CGS system is debye (D). $1 D = 1 \times 10^{-18}$ esu.cm. The charge q is measured in esu. The distance d is measured in cm and is of order of 1 Å, i.e., 10^{-8} cm. The direction of dipole moment is from +ve end to –ve end. Note : Charge on 1 electron = 1.6×10^{-19} C = 4.8×10^{-10} esu.

Here, $A^{\delta_+} - B^{\delta_-}$ is characterised as dipole and is known as Bond Dipole. The overall dipole moment of a molecule is the vector sum of the dipole moments of all bond dipoles in a molecule.

Now covalent molecules having bond dipoles are classified into two categories :

(a) Polar molecules (b) Non-polar molecules

A molecule is said to be *polar* if the net dipole moment of a molecule is not equal to zero. For example : HF, H₂O, NH₃, CH₃OH, etc, are polar as in all of these, the net dipole moment is not equal to zero ($\mu_{net} \neq 0$).

For a molecule to be polar both of the following conditions must be satisfied :

- (i) There must be at least one polar bond present.
- (ii) The polar bonds, (if there are more than one), and lone pairs must not be so symmetrically arranged that their bond polarities cancel each other.

This means if there are no polar bonds or lone pairs on the central atom, the molecule cannot be polar. And even if these are present, they may be arranged in such a manner that their polarities cancel each other, resulting in a non-polar molecule. So a molecule is non–polar if its net dipole moment is equal to zero. For example : H_2 , Cl_2 , BF_3 , CO_2 , $BeCl_2$, etc, are non-polar as $\mu_{net} = 0$. In such molecules, in spite of bond dipoles, the molecules are non-polar.

| H - H | Cl - Cl |
|--|--|
| (no bond alpole, $\mu_{net} = 0$) | (no bolid dipole, $\mu_{\text{net}} = 0$) $F_{s}^{\delta - s}$ |
| $^{\delta-}$ Cl $-$ Be $-$ Cl $^{\delta-}$ | $\delta_{\overline{F}} = F^{\delta_{-}}$ |
| (2 bond dipoles but $\mu_{net} = 0$) | (3 bond dipoles but $\mu_{net} = 0$) |

The conclusion is that, the dipole moment of a molecule, (zero or non-zero), depends upon the structure or shape (or on geometry) of the molecule. For example H_2O is polar whereas $HgCl_2$ is non-polar. The difference lies in the shapes of two molecules. H_2O is angular ($\mu \neq 0$) and $HgCl_2$ is linear ($\mu = 0$). Both have polar bonds, O–H bond in water while Hg–Cl bond in mercuric chloride, but due to structure of HgCl₂ being linear, the dipole moments of two bond dipoles cancel each other whereas in water, due to angular shape the dipole moments of two bond dipoles do not cancel and give rise to a net dipole moment.

Applications of Dipole Moment

- (i) To decide polarity of the molecule : Molecules having zero dipole moment μ are said to be nonpolar molecules and those having $\mu_R \neq 0$ (resultant dipole moment) are polar in nature.
- (ii) To determine percentage of ionic charcter: The value of dipole moment can be used for determining the amount of ionic character in a bond.

$$\mu = q \times d$$

Consider a diatomic molecules say HCl. Suppose this molecule is completely ionic. Under this condition H⁺ and Cl⁻ ions would bear a unit charge equal to 4.8×10^{-10} esu and the bond distance between H and Cl atoms = 1.27 Å.

Thus, theoretical value of $\mu = 4.8 \times 10^{-10} \times 1.27 \times 10^{-8} = 6.09 \text{ D}$

Dipole moment of HCl is also determined experimentally. Let the experimental value be 1.03 D.

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Percentage of ionic character in H --- Cl bond in HCl molecule

$$=\frac{\text{Experimental value of }\mu}{\text{Theoretical value of }\mu} \times 100 = \frac{1.03}{6.09} \times 100 = 16.9\%$$

Thus, Percentage of ionic character = $\frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$

- (iii) To determine geometry of molecules : The values of dipole moments provide value information about the structure of molecules.
 - (a) CO_2 , CS_2 molecules are linear as value of their dipole moments are zero.
 - (b) H_2O is not a linear molecule as it has dipole moment. Actually, it has V-shaped structure and the bond angle is 105°. Similarly, SO₂ has a bent structure.
 - (c) In ammonia, three hydrogen atoms do not lie symmetrically with respect to nitrogen as it has dipole moment. It has pyramidal structure.

General Formula Molecular Geometry Dipole Moment Example AX HF, HCl Linear May be non-zero AX₂ Linear Zero CO_2, CS_2 Bent or V-shape Non-zero H_2O, NO_2 AX_3 Trigonal planar Zero BF₃ Pyramidal NH₃, PCl₃ Non-zero T-shape Non-zero ClF₃ AX_4 Tetrahedral CH_4 , CCl_4 Zero Zero Square planar XeF_4 Non-zero SF_4 , $TeCl_4$ See saw AX_{5} **Trigonal bipyramidal** Zero PCl₅ Square pyramidal Non-zero BrCl_z AX_6 Octahedral Zero SF_6 Distorted octahedral Non-zero XeF₆ AX_7 Pentagonal bipyramidal IF_7 zero

Molecular Geometry and Dipole Moment

(v) Bond moment : The contribution of individual bond in the dipole moment of a polyatomic molecule is termed bond moment. The measured dipole moment of water molecule is 1.85 D. This dipole moment is the vectorial sum of the individual bond moments of two O—H bonds having bond angle 104.5°.

Thus,
$$\mu_{obs} = 2\mu_{O-H} \cos 52.25$$

1.85 = $2\mu_{O-H} \times 0.6129$
 $\mu_{O-H} = 1.51 \text{ D}$

Illustration - 6 (a) A diatomic molecules has a diple moment of 1.2 D. If the bond distance is 1.0Å, what fraction of an electron charge, e, exists on each atom ?

(b) The diple moment of LiH is 1.964×10^{-29} Cm and the interatomic distance between Li and H in this molecule is 1.596Å. What is the per cent ionic character in LiH ?

SOLUTION :

(a) Partical charge = $\frac{\text{Dipole moment}}{\text{Bond distance}}$

$$=\frac{1.2\times10^{-18}\text{esu cm}}{1.0\times10^{-8}\,\text{cm}}$$

 $= 1.2 \times 10^{-10}$ esu

The fractional of an electronic charge

$$=\frac{1.2\times10^{-10}}{4.8\times10^{-10}}=0.25=25\%$$
 of e.

(b) The diple moment of 100% ionic molecule (Li^+H^-)

= (1 electronic charge) (interatomic distance) = (1.602 × 10⁻¹⁹ C) (1.596 × 10⁻¹⁰ m) = 2.577 × 10⁻²⁹ Cm Fractional ionic character

 $= \frac{\text{Exp. vlaue of dipole moment}}{\text{Theoretical value of dipole moment}}$

$$=\frac{1.964\times10^{-29}}{2.557\times10^{-29}}=0.768$$

The bond in LiH is 76.8% ionic.

Illustration - 7Predict whether each of the following molecules has a dipole moment :(a) IBr(b) BF_3 (c) CH_2Cl_2

SOLUTION :

(a) Since IBr molecules is diatomic, it has a linear geometry. Bromine is more electronegative than iodine, hence, IBr is polar with bromine at the negative end. Thus, the molecules does have a dipole moment.

(b) Since fluorine is more electronegative than boron, each B – F bond in BF₃ is polar and three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another.

F B F (c) CH₂Cl₂ is similar to CH₄ (tetrahedral), but it has three different bond angles : HCH, HCCl, and ClCCl, which are close to but not equal to 109.5°. Since Cl is more electronative than C and which is more electronagetive than H, the bond moments do not cancel and the molecule possesses a dipole moment. CH₂Cl is thus a polar molecule.



Resultant diple moment is indicated by

Section 4

Covalent Character in Ionic bonds :

When a cation is placed near an anion, it distorts the spherical shape of the anionic electron cloud due to its attractive force. Such a distorted anion is said to be polarized.

Since the electrons now have a better tendency to stay between the two nuclei rather than entirely on the anion, the ionic compound is said to have acquired a certain covalent character. The tendency of cation to polarize the anion is called its polarizing power.

The tendency of the anion to undergo polarisation is called its polarisability.

Greater the polarizing power of cation or polarisability of anion, greater is the covalent character of the molecule.



No polarization Idealized ionic bond Anion is polarized. Cation may be slightly polarized Some covalent character. Anion and cation are both polarized. Covalent bond.

The covalent character of an ionic compound is favoured by :

- (a) A small cation : In a small cation the positive charge is concentrated over a small surface area and as a result its effect in polarizing the anion would be large. e.g, the covalent character of the chorides of the Be group decreases in the order, Be > Mg > Ca > Sr > Ba.
- (b) A large anion : Large anions have a high polarisability since their outermost orbitals are shielded from the positive nuclear field by a number of completely occupied orbitals and are thus readily polarized by a suitable cation. E.g, the halides of Ca; the covalent character increases in order

 $CaF_2 < CaCl_2 < CaBr_2 < CaI_2. \quad ; \qquad polarisability is F^- < Cl^- < Br^- < I^-$

- (c) There should be a high charge on either the cation or the anion or both. It is obvious that the electrostatic forces which cause polarization will be considerably enhanced, if the ions are highly charged. e.g., polarizing power of cations increases in the order $Na^+ < Mg^{2+} < Al^{3+}$ (all the three are isoelectronic).
- (d) The cation should possess an electronic configuration which is not that of an "inert" gas. It follows that the noble gas electronic configuration must be the most effective in shielding the nuclear charge of a cation from its surface. Cations without this configuration will have high positive field at their surface and consequently will have high polarizing powers.

The combined influence, of ionic size and charge on the polarizing power of a cation is sometimes

expressed in terms of ionic potential. $\phi = \frac{\text{cationic charge}}{\text{cation radius}}$

Fazan rule is used to decide relative ionic and covalent character in molecules. According to this rule a molecule is predominant covalent if :

- > smaller the size of cation
- larger the size of anion
- > greater the charge on cation and anion.
- > ion does not have inert gas configuration.

We can also say that these factors favour polarisation.

Note : Greater the covalent nature

- lower the mp/bp
- smaller conducting nature
- lower solubility in polar solvent
- > higher solubility in non polar solvent.
- (a) LiCl, NaCl, KCl, RbCl, CsCl

Size of cation is the deciding factor (charge of each ion and size of Cl is same)

 $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ size of cation

_____ polarisation

LiCl > NaCl > KCl > RbCl > CsCl covalent

 \longrightarrow mp/bp

 \longrightarrow solubility in H₂O (polar solvents)

composition of the solution of the solution

(b) NaF, NaCl, NaBr, NaI

Deciding factor is the size of the anion. Larger size of the anion, greater the polarization hence greater the covalent nature.

 $F^- < Cl^- < Br^- < I^-$ size of cation

 $F^- < Cl^- < Br^- < I^-$ polarisation

NaF < NaCl < NaBr < NaI, covalent nature

(c) NaCl, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5

 $\underbrace{Na^+ > Mg^{2+} > Al^{3+} > Si^{4+} > P^{5+}}_{\text{size of cation}} \text{ size of cation}$

 \longrightarrow charge on cation

Section 4

| Note: | Grea | Greater the charge, smaller the size then greater the polarisation | | |
|-------|---|--|--|--|
| | $\underbrace{\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Si}^{4+} < \text{P}^{5+}}_{\text{polarisation}} \text{ polarisation}$ | | | |
| | $\underbrace{\text{NaCl} < \text{MgCl}_2 < \text{AlCl}_3 < \text{SiCl}_4 < \text{PCl}_5}_{\text{covalent nature}} \xrightarrow{\text{covalent nature}}$ | | | |
| L | (d) | NaF, Na ₂ O, Na ₃ N | | |
| | | $\xrightarrow{F^- < O^{2-} < N^3} \text{ size of anion}$ | | |
| | | $\xrightarrow{F^- < O^{2-} < N^{3-}} \rightarrow \text{charge on anion}$ | | |
| | | $\xrightarrow{F^- < O^{2-} < N^{3-}} \text{polarisation}$ | | |
| | | $MaF < Na_2O < Na_3N$ covalent nature | | |
| | (e) | CuCl and NaCl | | |
| | | $[Cu^+]$ [Ar] 3d ¹⁰ | | |

[Na⁺] [Ne]

Cations with 18– electron shells have greater polarising power than the 8-electron shell ions with the same charge and size. This is due to the increased electronegativity of the 18-electron shell ions as the inner electrons have poor shielding effect on the nucleus. Thus CuCl is covalent and NaCl is ionic.

SHAPES OF MOLECULES (VSEPR THEORY)

Section - 5

The shapes or geometry of a molecule is quite accurately predicted by VSEPR (Valence Shell Electron Pair Repulsion) theory. According to this theory *all valence shell electron pairs surrounding the central atom arrange themselves in such a manner as to be as far away from each other as possible*. By separating the electrons from each other, the electrostatic repulsion, (that is the cause of higher energy), is minimised. As a result each molecule tends to acquire a state of lowest energy.

The basic ideas can be summarized as follows :

Valence shell pairs of electrons are arranged about the central atoms so that repulsion among them is minimised, or so that there is maximum separation among the regions of high electron density (bond pairs) about the atom. For instance, two regions of high electron density would be most stable on opposite side of the central atom (*Linear arrangement*), while three regions would be most stable when they are arranged at the corners of an equilateral triangle *Trigonal planar arrangement*). The resulting arrangement of these regions is referred to as the electronic geometry of the the central atom.

| Number of Bond Pairs | Electronic Geometry | Bond Angles |
|----------------------|-----------------------|-----------------|
| 2 | Linear | 180° |
| 3 | Trigonal planar | 120° |
| 4 | Tetrahedral | 109° 28′ |
| 5 | Trigonal Bi-pyramidal | 90°, 120°, 180° |
| 6 | Octahedral | 90°, 180° |

As mentioned earlier, there are two distinct types of electron pairs around the central atom : Bonding electron pairs (bp) and Nonbonding electron pairs or lone pairs (-lp). The strength of repulsion between the electron pairs varies as :

-lp--lp > -lp-bp > bp-bp

This is very significant while deciding the final geometry of a molecule. We will divide our study of shapes in two categories :

- > The molecules containing only bond-pairs of electrons and
- > The molecules containing both bond-pairs and lone (non-bonding) pairs.

Note: Before we go into the details of shapes, first let us discuss the *Theory of Covalent Bonding*.

THEORIES OF COVALENT BONDING

Section - 6

Orbital theory of Covalent Bonding :

As discussed earlier that covalent bonding is the result of sharing of electrons between atoms. The main requirement for sharing of electrons is: *only a single electron must be present in an orbital of the outer shell.* Such an orbital (i.e. containing an odd electron) will combine with another orbital (containing an odd electron *but of opposite spin*) of same kind or of another kind of atom to form covalent bond. This combination of orbitals is known as *overlapping of orbitals.* So according to atomic orbital theory, *the covalent bond is formed by the overlapping of atomic orbitals having electrons with opposite spins, belonging to the external shells of two atoms of same or of different kinds.* After overlapping the electron–pair now belongs to both the orbitals of two atoms.

Depending upon the types of orbitals which take part in overlapping, we can classify overlapping as follows: (a) s-s overlapping (b) s-p overlapping (c) p-p overlapping From above, we observe that overlapping can further be analysed as lateral and end to end. s-s, s-p and one of p-p type overlapping is of end-to-end type and one of the p-p overlapping is of lateral type.



Sigma (σ) **bond**: The bond formed as a result of end to end type of overlapping is called as σ **bond**. Here overlapping of orbitals takes place along the same axis. The bond formed by this type of overlapping is very strong as the extent of overlapping is sufficiently high. *The extent of overlapping determines the strength of covalent bond*. In sigma bond, the electron density accumulates between the centres of the atoms being bonded and lies on the imaginary line joining the nuclei of bonded atoms.

Pi (π) **bond** : The bond formed between two atoms by the sideways overlapping (also called lateral overlapping) of the two half-filled orbitals is called a pi (π) bond. The extent of overlapping in case of a pi bond is much less than in sigma bond, so strength of pi bond is low. In this bond, the electron density lies above and below the imaginary line joining the centres of nuclei of bonded atoms. Whenever there is multiple bonding, i.e., double and triple bonds, pi bond is formed.

Hybridisation and Hybrid Orbital :

The electronic configuration of carbon (C), 1s² 2s²2p², is rather misleading if we talk about the tetravalency of carbon (which is its most common valency in its compounds). Its configuration predicts the carbon to divalent due to two unpaired p electrons. This is actually not the case. In bond formation, the atomic orbitals of carbon atom are mixed in such a manner as to produce *four equivalent orbitals*, which are confined to the corners of a regular tetrahedron, in order to maximise the separation among them (VSEPR theory). The mixing of atomic orbitals in order to produce new orbitals is called as Hybridisation. This concept was given by Linus Pauling in 1937. This concept not only predicts the correct shapes but also explains the actual microscopic observations of the geometry of molecules. The different cases of hybridisation arise by mixing of s, p and d orbitals are discussed below.

sp³ Hybridisation :

This type of hybridisation results from mixing of one *s*, three *p* orbitals of outer (valence) shell of an atom. To understand the concept clearly, let us consider the formation of CH_4 molecule. The outer-shell configuration of C atom in ground state is $2s^22p_x^{-1}2p_y^{-1}$. Note that $2p_z$ orbital is empty. One of the electrons in the $2s^2$ orbital is excited (or promoted) to this vacant $2p_z$ orbital. This results in the following picture.

Ground state

Excited state

After the electron is promoted, all the four orbitals are mixed to give four equivalent hybrid orbitals (in sense that all of them are of equal energy) called as sp^3 hybrid orbitals.

 $2s^{1} 2p_{X}^{1} 2p_{Y}^{1} 2p_{Z}^{1} \longrightarrow mixed \text{ or hybridised} \longrightarrow \text{ four sp}^{3} \text{ hybrid orbitals}$

These four hybrid orbitals are of same energy and equivalent in every other way. They are directed at the corners of a regular tetrahedron. This is best geometry for four bonded pairs to be at the maximum distance apart and thus minimise the repulsion and hence the energy of the system is minimised. Each of four sp³ orbitals in carbon can now combine with a 1*s* orbital of a hydrogen atom, forming four equivalent CH bonds involving sp³–s overlapping and forming four sigma bonds. The extent of overlapping by hybrid orbitals is very high due to their strong orientation in space or one can now imagine a bond formed by hybrid orbital to be highly stable. This additional stability accounts for the energy required in the promotion step before mixing.



*sp*² hybridisation :

To account for the shapes of molecules like BF_3 , BCl_3 etc., let us consider the valence-shell configuration of Boron: $2s^2 2p_X^{-1}$. Note that p_y and p_z orbitals are vacant, so promotion of one 2s electron takes place to $2p_y$ orbital to account for three B-F bonds in BF_3 .

Ground stateExcited state $2s^2 2p_X^1 \longrightarrow one \ electron \ excited \ \longrightarrow 2s^1 2p_X^1 2p_y^1$ $to \ a \ 2p_y^1 \ orbital$ from a 2s orbital

The three orbitals in excited state are mixed to give three sp^2 hybrid orbitals of equivalent energy. These are all in a same plane with central atom (Boron) at the centre of an equilateral triangle with three sp^2 orbitals at its corners. This is the best possible geometry for three bond–pairs to be at maximum distance (VSEPR theory). Each of these orbitals now form three sigma bonds with three 2p orbitals of F atoms to form B–F bonds and hence forms a BF₃ molecule.



sp hybridization :

A sp hybrid orbital is formed when in an atom *one s* and *one p* orbital mix with each other to form two equivalent orbitals. Two such orbitals, i.e., sp hybrid orbitals are most stable when they adopt an angle of 180° between them so that they are at the maximum distance apart. It means that the molecule involving sp hybrid orbitals will be *linear in shape*. The geometry of BeF₂ is linear and is explained by sp hybridisation of Be atom. The valence shell configuration of Be is $2s^2$ which means one electron from 2s orbital can be promoted to vacant 2p orbital and form the excited state.

Ground state

Excited state

 $2s^2 \longrightarrow promotion of one s electron \longrightarrow 2s^1 2p_X^1$ to a p_X orbital

The $2s^1$ and $2p_X^{-1}$ electron can now mix or hybridised to give two sp hybrid orbitals, which form two sigma bonds with F atoms (as in BF₃) to form BeF₂ molecule.



BeF₂ molecule sp-p overlapping linear shape Bond angle 180°

2 sp hybrid orbitals

*sp*³*d* hybridisation (PF₅ molecule) :

Since phosphorus is the central element in PF_5 molecules, it must have five half–filled orbitals to form bonds with five Fluorine atoms. Hybridisation is again the answer. This time using one d orbital from the vacant set of 3d orbitals in addition of the 3s and 3p orbitals of the phosphorus atom.

Ground state

Excited state

 $3s^2 3p^3 3d^0 \longrightarrow promotion of one \ s \ electron \longrightarrow 3s^1 3p_x^{-1} 3p_y^{-1} 3p_z^{-1} 3d^1$ to a vacant d orbital

:F:

The Chemical Bond - I

:F:

sp^3d^2 hybridisation (SF₆) :

forms a total of five covalent bonds.

The sulphur atoms can form six hybrid orbitals to accommodate six electron pairs, and in Valence Bond theory terminology, we have :

Ground state $3s^2 3p^4 3d^0 \longrightarrow promotion of one s electron \longrightarrow 3s^1 3p_x^{-1} 3p_y^{-1} 3p_z^{-1} 3d^1 3d^1$ and p electron to a vacant d orbitals

The six sp^3d^2 hybrid orbitals are directed toward the corners of a regular octahedron. Each sp^3d^2 hybrid orbital is overlapped by a half–filled 2p orbital from Fluorine to form a total of six covalent bonds.

The five sp³d hybrid orbitals are directed toward the corners of a trigonal

bipyramid. Each is overlapped by the (only) 2p orbital of a Fluorine atom that contains a single electron. The resulting pairing of P and F electrons

We should note the sp³d hybridisation involves utilisation of an available d orbital in the outermost shell of the central atom, P. The heavier Group 15 elements P, As, and Sb, can form five co-ordinate compounds utilising this hybridisation. But it is not possible for Nitrogen (also in Group 15) to form such five–coordinate compounds. Why ?

- (i) Nitrogen is too small to accommodate five (even very small) substituents without excessive crowding which causes instability.
- (ii) It has no low-energy d orbitals.

In fact, we can generalise; no element of the second period can be central element in five-coordinate molecules (or higher-coordinate ones) because they have no low energy d orbitals available for hybridisation and because they are too small.

It is important to realise that the set of s and p orbitals in a given energy level, and therefore any set of hybrids composed only of them, can accommodate a maximum of eight electrons and participate in a maximum of four covalent bonds.

In the following section, we will discuss the hybridisation of molecules in which the central atom has lone pair(s). The actual geometry of the molecule containing one or more lone pairs of electrons is different from the geometry (distorted Geometry) which is expected from the type of hybridisation involved in the molecule.





sp² hybridisation in SnCl₂:

The outer electronic configuration of Sn is $5s^2 5p_x^{-1} 5p_y^{-1}$. To explain the shape of SnCl₂, the concept of hybridisation is applied. Here one 5*s*, two 5*p* orbitals hybridise to give three sp^2 hybridised orbitals of equivalent energy.

In this case one of the hybrid orbitals contains a lone pair, whereas other two contain an electron each. These two orbitals containing one electron overlap with two 3p orbitals of two chlorine atoms to form two Sn–Cl bonds. The geometry of SnCl₂ molecule should have been Trigonal planer, but due to presence of lone pair over the central atom (Sn), there is some distortion in the shape of the molecule. The bond angle is slightly less than 120° and the molecule is *bent or V–shaped*. The reason is the *greater repulsion between a bp and a –!p* than normal bp–bp repulsion.

sp³ hybridisation in NH₃ and H₂O molecule :

In Ammonia, NH_3 : N is the central atom and its outer–shell configuration is $2s^2 2p_X^{-1} 2p_y^{-1} 2p_Z^{-1}$. One s orbital (containing a lone pair) hybridises with three p orbitals (containing one electron each) to give four sp³ hybrid orbitals. Of these four hybrid orbitals, the three orbitals containing one electron each overlap with three 1s orbitals of three H–atoms to form N–H bonds.

Due to lone pair over N, the geometry of the molecule gets distorted from regular tetrahedron (which is the exact geometry for sp^3 hybrid orbitals) and the bond angle changes from 109.5° to 107° The final shape is *pyramidal* where N is at the centre with three H–atoms forming the base and the lone pair forming the apex of the pyramid.

In Water, H_2O : O is the central atom with $2s^2 2p_x^2 2p_y^1 2p_z^{-1}$ as its outer-shell configuration. Here, one s orbital (containing a ℓp), one p orbital (containing a ℓp) and two p orbitals (containing one electron each) hybridises to give four sp³ hybrid orbitals of equivalent energy. Of these two orbitals (containing one electron each) overlap with two 1s orbitals of H atoms to form two O–H bonds.

2-Lone pairs H Water (V-shaped)

Due to two lps over O atom, the actual geometry of molecule is distorted. Apart from lp-bp repulsion, lp-lp repulsion also exists in this molecule, so the distortion is much greater than the ammonia molecule. The bond angle changes form 109.5° to 104.5° in water and the final is *bent or V-shaped*.

Note: The actual geometry of the molecule containing one or more lp of electrons is different form the geometry which is expected from the type of hybridisation involved in the molecule.

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Н

Η

Hybridisation and Multiple Bonding : (Shapes of C_2H_4 and C_2H_2) Geometry of C_2H_4 molecule :

In ethylene (C_2H_4), two carbon atoms in the excited state undergo hybridisation in a different manner than the carbon atom in C_2H_4 molecule. After the promotion of one 2s electron to the vacant 2p orbital, one s orbital and two p orbitals of two carbon atoms hybridises to form three sp² hybrid orbitals (leaving one p orbital in unhybridised state).

Now one of the sp² hybrid orbitals of each carbon atom overlaps with each other to form one C–C bond (sigma bond) and other two hybrid orbital of two carbons overlaps with 1*s* orbitals of H atoms to form *four* C–H bond (sigma bonds) in total. It is important to note that two unhybridised *p* orbitals are perpendicular to the plane of three sp² orbitals. These two *p* orbitals form a *pi* (π) bond with each other (Recall the formation of pi bond).

H

(H)

σ

We, now observe that two covalent bonds that make up the double bond between the carbon atoms are not equivalent, they are different. One of them is a sigma (σ) bond and other is the pi (π) bond.

Geometry of C₂H₂ molecule :

In acetylene (C_2H_2), after achieving the excited states, both the carbon atoms undergo sp hybridisation. One *s* orbital and one *p* orbital hybridise to form two *sp* hybrid orbitals (leaving two *p* orbitals in unhybridised state perpendicular to the plane of *sp* hybrid orbitals). Now one sp hybrid orbital belonging to each carbon atom form a C–H sigma bond and other *sp* hybrid orbital form sigma bond with 1*s* orbital of H atom (in all two C–H bonds).



 $sp^2 - sp^2$

р

Two unhybridised *p* orbitals of each carbon atom form two *pi* bonds with each other. This means that a carbon-carbon triple bond comprises of one sigma bond and two *pi* bonds.

TYPES OF BONDING IN A COMPOUND & INTERMOLECULAR FORCES Section - 7

From the *difference in electronegativities* of the atoms forming a bond, it can be predicted *what type of bond is formed* by the atoms. When the difference is zero or very small, the bond is essentially *covalent*, and the electron density is more or less equally share d by two atoms. When the difference is large, one atom more-or-less completely withdraws the electron pair to it (one having higher electronegativity) and the bond is ionic. A bond *AB* (between two atoms *A* and *B*) is Ionic if difference in electronegativities of *A* and *B* is greater than 1.7 and it is Covalent, if it is less than 1.7.

- Metals form Ionic bonds by losing electrons. However some metals form covalent bonds also and some don't form covalent bonds at all. The tendency of normal metals increases to form covalent bond as we proceed from left to right across a period in the *Periodic Table*, e.g., Ce and Ba form only Ionic bonds, Pb and Bi form both Ionic as well as Covalent bonds. Also metals rarely form bonds with other metals.
- Non-metals form Ionic bonds by gaining electrons. All non-metals can also form Covalent bonds as well. The tendency to form Ionic bond increases in going from left to right across a period and in going down the group, e.g., C forms only Covalent bond, F forms both Covalent as well as Ionic bonds. O forms O²⁻ in few compounds whereas S forms S²⁻ in many compounds.
- *Note*: Most compounds of metals with non-metals are ionic and most compounds of non-metals with non-metals are covalent.
 - Some non-metals such as C, Si, Ge, N, P, O are very reluctant to form negative ions. C, Si, Ge form only. Covalent bonds whereas N, P, O can form both Ionic and Covalent bonds.
- *Note*: If these atoms form Ionic bonds, they also form Covalent bond with some other atom in the same compound. For example: In KOH, O forms Ionic bond with K but forms Covalent bond with H.

Metallic Bond :

Metals have low ionisation energies and hence valence electrons in them are weakly bounded to the positive charged nucleus or *kernel* (*kernel* means nucleus and the electrons other than the valence electrons). In metals the number of valence electrons is less than the number of orbitals to hold them. This makes possible for an electron to pass from one another through overlapping orbitals. Consider the case of Li, which has one s valence electron. In the solid crystal, each Li atom is close to eight other atoms, so that its orbitals will overlap with all of them at the same time and this picture is continued throughout the crystal. The electrons are shared by all the atoms, i.e., they are *delocalised* throughout the crystal.



So metal is network of ions (kernels) in a sea of electrons, with the electron sea acting as the binding force which holds the metal ions (kernels) together.

The valence electrons are not associated with any particular atom and can therefore move here and there. If the two ends of piece of a metal are connected to the poles of a battery, electrons will move towards the positive pole of the battery where they will flow out of the metal into the battery, being replaced by fresh electrons from the negative pole of the battery. In this manner an electric current can be conducted by the metals.

Intermolecular Forces

Intermolecular forces are the sum of the forces of attraction and repulsion between interacting particles (atoms and molecules). Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837-1923), who explained the deviation of real gases from the ideal behaviour through these forces (You will study about this in 'States of Matter'). These forces are other than due to covalent bonds, the hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules or charged molecules. The term includes:

- > force between two instantaneously induced dipoles (London disperison force)
- force between two permanent dipoles
- > force between a permanent dipole and a corresponding induced dipole

Note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces.

Dispersion Forces or London Forces

Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other [Figure (a)]. It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.*, the charge cloud is more on one side than the other [Figure (b and c)]. This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.

The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as London forces. Another name for this forces is dispersion force.



Dispersion forces of London forces between atoms

These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where *r* is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess "particle charges" and these charges are shown by Greek letter *delta* (δ). Partial charges are always less than the unit electronic charge (1.6×10^{-19} C). The polar molecules interact with neighbouring molecules. Figure (a) shows electron cloud distribution in the dipole of hydrogen chloride and Figure (b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.

The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules.



(a) Distribution of electron cloud in HCl a polar molecule, (b) Dipole-dipole interaction between two molecules

Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $/r^6$, where *r* is the distance between polar molecules. Besides dipoledipole interaction, polar molecules can interact by London forces also. This cumulative effect is that the total of intermolecular forces in polar molecules increase.

Dipole-Induced Dipole Forces

This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to $1/r^6$ where *r* is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. We have already learnt in Unit 4 that molecules of large size can be easily polarized. High polarisability increases the strength of attractive interactions.



In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

Hydrogen Bonding :

Molecules that contain F–H, O–H, N–H bonds (e.g., Water, Alcohols, Organic acids, Amines, Aromatic alcohols, etc.) show a strong tendency to associate, i.e., to link up to form larger molecules. This feature exists in solid form and as well as in solutions in certain solvents. In all of such compounds, OH, or N–H or F–H, bond is highly polar due to large difference in electronegativity. The electrostatic attraction between such molecules should be quite strong. The *positive end* of one molecule attracts and is strongly attracted by the *negative end* of the neighbouring molecule. In this manner a large number of molecules are associated to form a cluster of molecules. Since in each case the hydrogen atom is responsible for the formation of linkages, this is known as *Hydrogen bond* or H-bond. It is impossible for hydrogen to form a second covalent bond so the additional linkage is shown by a *dotted line*. Hydrogen bonds are always of type : -A-H....B-, where A and B may be atoms of O, F, N. Hydrogen bonds are comparatively weak, with bond energies of 10–100 kJ/mol, but they are widespread and have important effect on many physical properties of many Organic and Inorganic compounds.



Hydrogen Bonding is of two types :

(i) Intermolecular H-bonding (ii) Intramolecular H-bonding

You will learn about Hydrogen Bonding in the Chapter Chemical Bonding-II

| RESONANCE | Section - 8 |
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|-----------|-------------|

There are certain molecules whose properties can not be explained by a single structure.

For example : The molecules of CO_3^{2-} ion, three Lewis dot structures are possible. Similarly Lewis structure for ozone (O_3) shows that one of O atom is bounded to a O atom by a double bond and by a coordinate covalent bond to the other O atom and there are two possible structures for it.



The length of three bonds in CO_3^{2-} ions and two bonds in O_3 is expected to be different. However from spectroscopic analysis, it is observed that the lengths of bonds are equal and lie somewhere between that of a single and double bond. Hence a particular structure is not sufficient to account for the observed facts.

The actual structure of CO_3^{2-} ion and O_3 molecule has neither of these Lewis structures. The real structure is an average (midway between) of these structures. This phenomenon of representing the actual structure in such a manner is called as Resonance. The individual structures are known as *Canonical forms* or *Resonance structures*. The actual structure is called as Resonance hybrid.



Thus resonance hybrid may be defined as the actual structure of all the canonical forms that are possible for a given molecule without changing the relative positions of its atoms. The resonance hybrid is more stable than any of the other canonical forms. The difference in the energy between the resonance hybrid and the most stable canonical form is called as Resonance energy. *The more the number of possible resonating forms, the higher is the resonance energy and hence more is the stability of the compound.*

The resonating structure of a few more molecules and ions are shown below :



Effects of Resonance :

- It imparts stability to the molecule and hence decreases its reactivity. The reactivity of the molecule is decreased due to delocalisation of electrons over the entire surface of the molecule.
- Since the electrons are not localised between any particular atoms, and are uniformly distributed in the resonance hybrid, all the bond are similar and are of equal bond lengths. *The bond length of a single covalent is decreased as a result of resonance*.

Illustration - 8 The bond length of normal C = O double bond is 121 pm. However each carbon to oxygen bond length in CO, is found to be 115 pm. Explain the structure of CO, molecule.

SOLUTION :

If we consider only structure I for CO_2 molecules there should be two carbon to oxygen double bonds. As per question the bond length of normal C = O double bond is 121 pm. However, each carbon to oxygen bond length in CO_2 is found to be 115 pm which is in between that of C = O DOUBLE BOND (121 pm) and C = O triple bond (110 pm). Hence, CO_2 is considered a resonance hybrid of the follow ing three Lewis structures.

$$\mathbf{O} = \underset{[\mathbf{I}]}{\mathbf{C}} = \mathbf{O} \leftrightarrow \overset{+}{\mathbf{O}} = \underset{[\mathbf{II}]}{\mathbf{C}} - \overset{-}{\mathbf{O}} \overset{-}{\mathbf{O}} - \underset{[\mathbf{III}]}{\mathbf{C}} = \overset{+}{\mathbf{O}}$$

Section 8