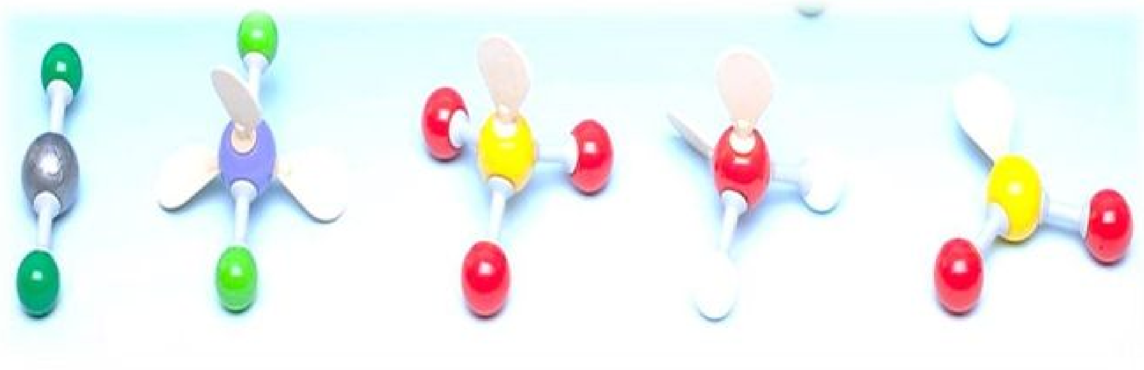


2. Structure and Bonding

Content

Introduction

Chemical bonds and structure of molecules are conceptual models based on the modern atomic model, in order to explain the physical and chemical properties of matter.

Many atoms do not have stable outermost valance shell configurations, therefore chemical bonds occur between atoms in order to achieve stability. The following table (Figure 2.1) explains how valence electrons participate in different types of chemical bonding using several acceptable models.

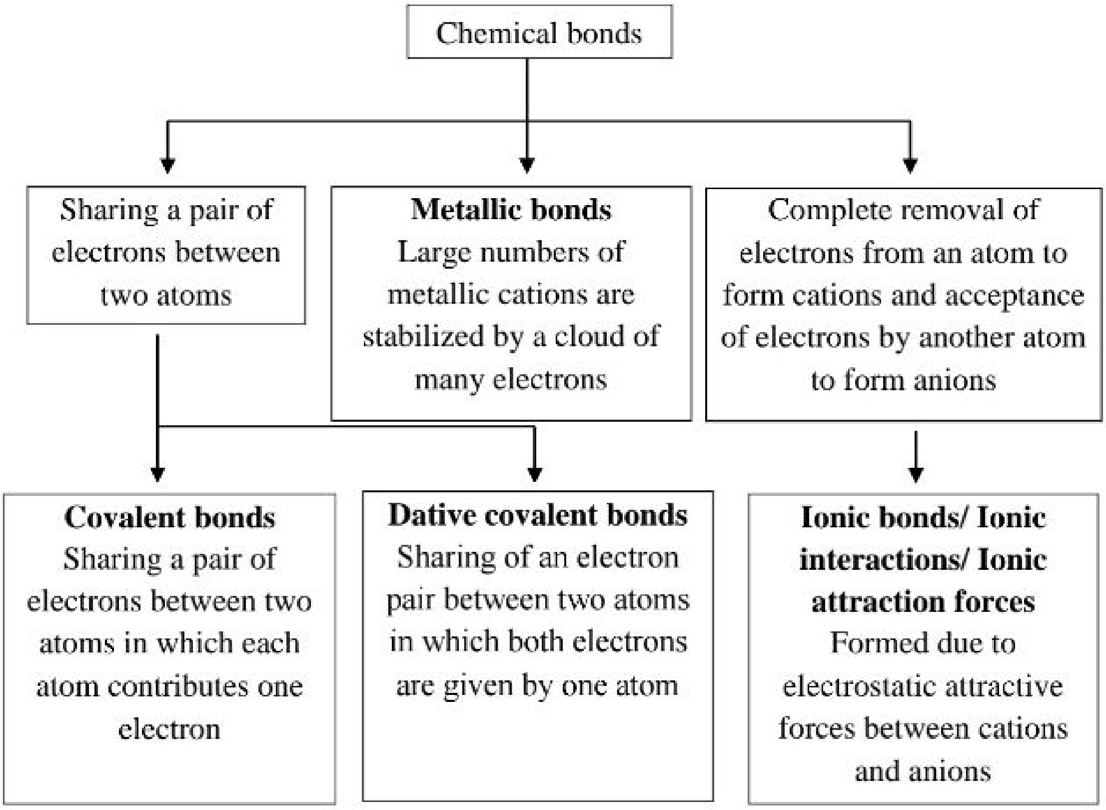


Figure 2.1 Types of chemical bonds

2.1 Covalent bonds

Covalent bonds are formed when a pair of electrons is shared between two atoms of the same element or different elements. The sharing pair of electrons contribute one electron from each atom to form the electron pair. Consequently, stable electron configurations are often achieved by both atoms in respect to the total number of electrons in the valence shells.

Kossel, Langmuir and Lewis stated that the filling of electrons into a valance shell up to the maximum value of 8 results a stable electron configuration, hence called 'octet' rule.

According to the current knowledge of electron configurations, the maximum number of valance electrons in 2*s* and 2*p* orbitals of elements in the second period (n=2) is 8.

Therefore, elements in the second period complete the octet when forming chemical bonds thereby achieving a greater stability. This is more likely for elements such as C, N, O and F which form chemical bonds to complete the octet.

The valance shell of elements in the third period (n=3) and subsequent periods consist of *d* sub energy level in addition to *s* and *p* sub energy levels. Therefore, when forming chemical bonds, there could be instances where the number of electrons in the valance shell may exceed eight. Examples of such molecules are SO_2 and SO_3. In such molecules the number of electrons in the valance shell of sulphur is greater than eight. The presence of *d* orbitals in the valence shell of the sulphur atom permits 18 electrons. Since, the *d* orbitals in the valance shell also participate in bonding, the number of valance electrons in the sulphur atom can exceed the octet. However, for such atoms, it is not always necessary for the *d* orbitals to participate in bonding. For example, in the H_2S molecule, the sulphur atom complete the octet without involving *d* orbitals.

There are other situations where atoms of some elements do not necessarily complete the octet. Elements like Be, B and Al form some electron deficient compounds such as $BeCl_2$, BH_3, BCl_3 and $AlCl_3$ are examples of such compounds with an incomplete valance shell. In the case of hydrogen atom where only 1*s* orbital is present, the stable electron configuration is achieved when the valance shell consists of two electrons. In all instances described above, the number of electrons in the valance shell after forming chemical bonds is an even number. However, this is not always true, as there are compounds such as NO and NO_2 each having an odd number of electrons even without completing the octet.

In order to understand the arrangement of bond pairs and lone pairs in molecules and ions, a "model" was introduced by Gilbert Lewis known as "Lewis dot structure".

2.1.1 Lewis dot diagrams and Lewis dot-dash structures

The Lewis dot diagram is used to illustrate the atomic skeleton, nature of the bonding present (single, double and triple bond) and the distribution of the valance shell electrons around each atom of the given chemical formula. In Lewis dot-dash structure, a bonding electron pair is denoted by a short line drawn between the two atoms.

Chemical formula → Lewis dot diagram →Lewis dot-dash structure

Cl_2

$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$

The following factors need to be considered when drawing Lewis dot diagrams:

- Elements H and F are generally not considered as the central atom since these can form only single bonds. Atoms which are capable of forming multiple bonds are placed as the central atom.
- The element with the lower electronegativity is generally the central atom.

It is important to consider the following facts for molecules and ions with one central atom.

(i) Identification of the central atom and surrounding atoms.

(ii) Calculating the total number of electrons for a given chemical formula considering all electrons in the valence shell of each atom.
e.g.: In H_2O, oxygen atom contributes 6 electrons and one electron from each hydrogen atom (two electrons from two hydrogen atoms), which sum up to 8 when considering the total electron count $(6 + 2 = 8)$ of the valence shells.

If it is a negatively charged ion, then negative charges should be counted as well.
e.g.: In the OH^- ion, contribution of electrons from oxygen atom is six and hydrogen atom one together with one electron due to negative charge of the ion adding up to eight as the total number of electrons $(6 + 1 + 1 = 8)$.

If the ion is positively charged, then an equivalent number is deducted from the total valance electron count.
e.g.: In NH_4^+ ion, N atom contributes 5 valance electrons and four hydrogen atoms contribute 4 electrons. However, since it is a cation, then one electron (equivalent to number of positive charges) is deducted resulting 8 electrons in the valance shell of nitrogen atom $(5 + 4 - 1 = 8)$.

(iii) A bond is denoted by a pair of dots between the central atom and a surrounding atom. Each surrounding atom is connected to the central atom with at least one bond.

(iv) Bonding electron pairs are denoted first as a pair of dots (Lewis dot diagram) or a short line (Lewis dot-dash diagram) drawn between central atom and each of surrounding atoms. Next, the remaining electrons are distributed, starting from the most electronegative atom, to complete the octet. Each electron pair is marked by pair of dots (lone pair electrons). If the electronegative atoms are surrounding atom, then lone pairs are marked on these surrounding atoms in order to complete the octet of each atom. CCl_4 is an example for this.

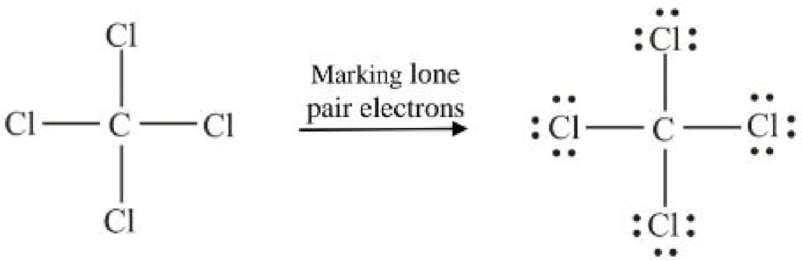


Figure 2.2 Lewis dot-dash structure of CCl_4

In the case of ammonia, surrounding atoms are hydrogen, remaining pair of electrons is marked on the nitrogen atom.

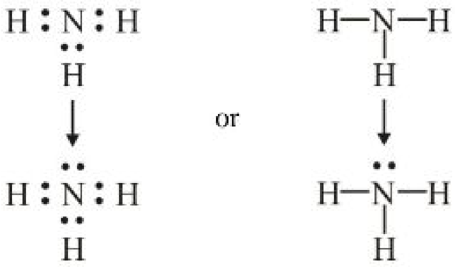


Figure 2.3 Lewis dot-dash structure of NH_3

In the Lewis dot diagrams bond electrons between two atoms can be represented as follows.

Single bond	⟶	M••L or M : L
Double bond	⟶	M :: L
Triple bond	⟶	M ⋮⋮ L
Dative bond from L to M	⟶	L : M

(v) If electron pairs are remaining after distributing electron pairs on the surrounding atoms (satisfying the octet rule), then left over pairs of electrons are marked on the central atom.

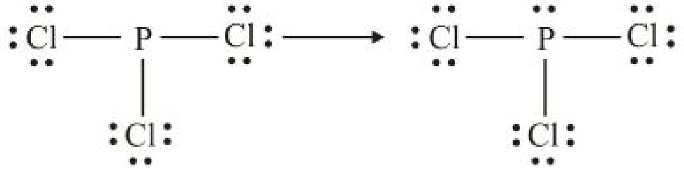


Figure 2.4 Lewis dot-dash structure of PCl_3

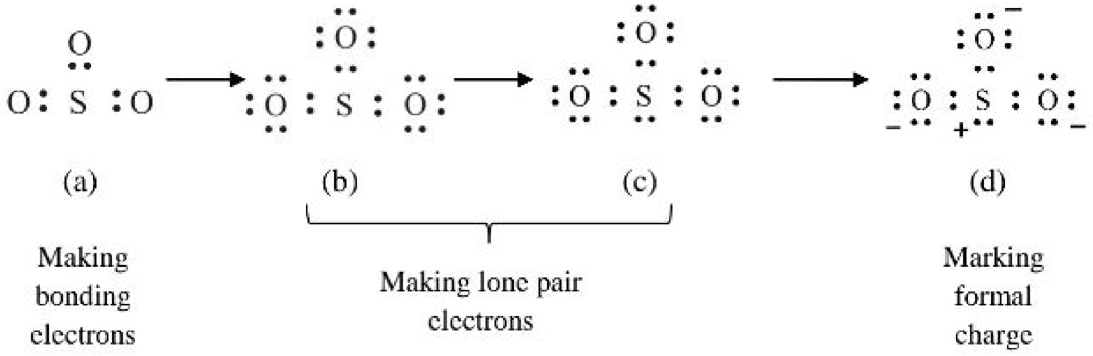
(vi) After distributing all the electron pairs, the number of electrons on each atom should be compared with the number of electrons in the non-bonded state of the atom (free atom) to assign the formal charge and then check completion of the octet. In the case of a bond, one electron is counted for each atom and if lone pairs are present, both electrons are counted to the particular atom. Priority is given for completion of the octet.

As an example, NH_2^- ion:

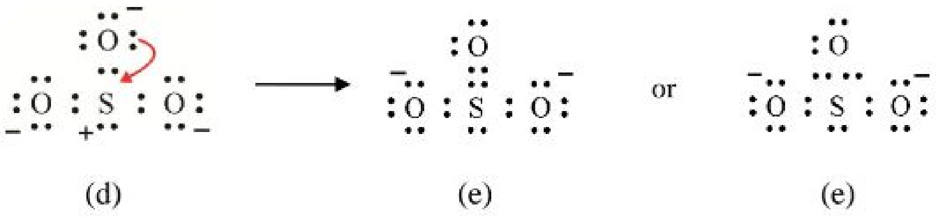
Here the total electron count on the nitrogen atom is 8. Though the nitrogen atom has contributed only 5 electrons, from the Lewis dot diagram, it appears as if the nitrogen has contributed 6 electrons. Since it has one extra electron, (-1) the charge is marked on the nitrogen atom as the formal charge.

(vii) Electron distribution shall be rearranged in order to minimize the formal charge on atoms and completion of octet by converting lone pair of electrons to bonding pairs of electrons.

If SO_3^{2-} ion is taken as an example, sulphur atom will contribute 6 electrons and each oxygen will contribute 6 electrons. Hence 18 electrons come from three oxygen atoms. Addition of two more electrons due to (-2) charge add up to 26 electrons (6 + 3(6) + 2 = 26) for the Lewis dot structure.



All atoms of Lewis dot structure (d) have satisfied the octet, but it is not stable, since it has maximum formal charge distribution. Hence the lone pair electrons are rearranged in order to obtain the stable Lewis structure having minimum formal charge distribution. The following sketch shows the way of rearrangement.



Finally, the Lewis dot dash structure for SO_3^{2-} is given as below.

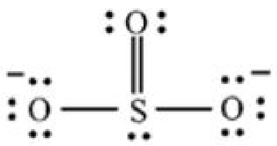
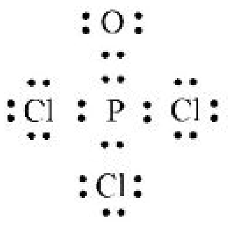
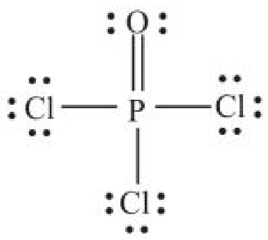
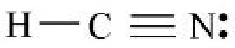
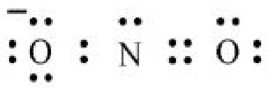
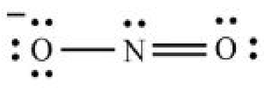
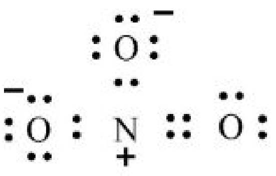
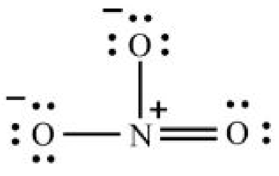
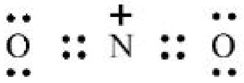
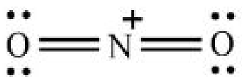


Figure 2.5 Lewis dot dash structure of SO_3^{2-}

Here, all oxygen atoms have completed octets. There are total of 10 electrons in the valance shell of sulphur atom which exceeds the octet. However, this is allowed due to the presence of empty *d* orbitals in addition to the *p* orbitals in the valance shell of the sulphur atom.

It is important to know the skeleton of atoms of a given chemical formula when multiple central atoms (e.g.: C_3H_6O) are present. Table 2.1 shows Lewis dot diagrams and Lewis dot-dash structures of selected molecules and ions.

Table 2.1 Lewis dot diagrams and Lewis dot dash structures of some selected molecules and ions

Formula	Number of valance shell electrons	Lewis dot diagram	Lewis dot dash structure
CO_2	16		
$POCl_3$	32		
HCN	10		
NO_2^-	18		
NO_3^-	24		
NO_2^+	16		

Example 2.1

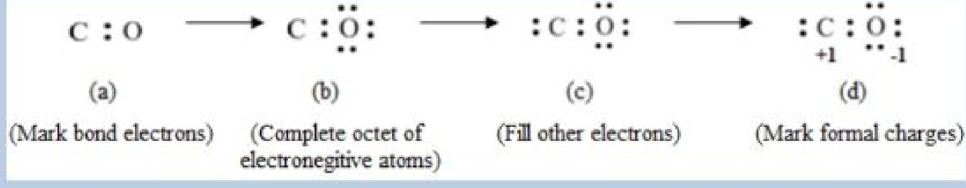
Draw the Lewis dot diagram and the Lewis structure of carbon monoxide (CO)

Answer

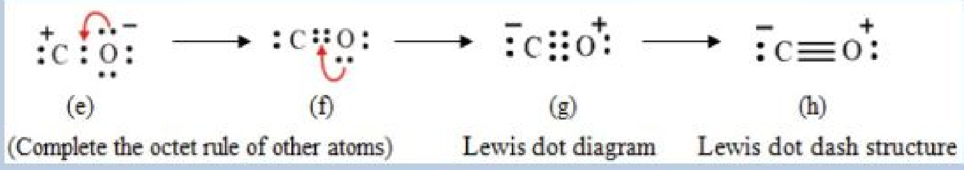
Valance electrons from C atom = 4*e*
Valance electrons from O atom = 6*e*
Total number of valance electrons = 4*e* + 6*e* = 10*e*

After marking the bonding electron pair, the number of remaining electrons is eight. After distributing the electron pairs around the more electronegative oxygen atom completing octet, another pair is left. This lone pair of electrons is marked on the carbon atom.

The initial electron distribution is illustrated below. However, the octet is not completed for the carbon atom. Therefore, rearrangement of a lone pair of electrons on the oxygen atom as shown by curved arrows in *(e)* and *(f)* is done in order to complete the octet on the C atom whilst attempting to minimize the formal charge result in structure *(g)*. Therefore, the structure *(g)* is considered to be the Lewis dot diagram and *(h)* illustrates the Lewis structure of CO. Notice that there is a positive charge marked on the more electronegative oxygen atom. Although positive charge is on the more electronegative oxygen atom, it is very unlikely and in this case it is accepted since higher priority is given to completion of octet where possible. This is the fundamental principal of the octet rule. This example shows that octet rule is more powerful than the charge criteria.



(a) (Mark bond electrons)
(b) (Complete octet of electronegitive atoms)
(c) (Fill other electrons)
(d) (Mark formal charges)



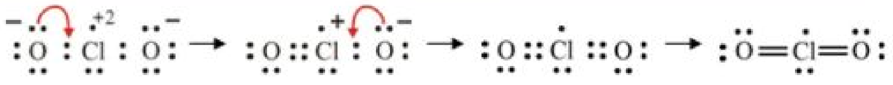
(e) (f) (Complete the octet rule of other atoms)
(g) Lewis dot diagram
(h) Lewis dot dash structure

Example 2.2

Draw the Lewis dot diagram and the Lewis dot dash structure for ClO_2.

Answer

This is an example for a species with an odd number of electrons. The total number of the valance electrons is 19 in ClO_2 ($7e + 2(6e) = 19e$). The following illustrates the initial distribution of the electrons and the final Lewis dot diagram and Lewis dot-dash structure of ClO_2.



(a) Maximum charge distribution (unstable)

(b)

(c) Lewis dot diagram

(d) Lewis dot-dash diagram

2.2 Dative covalent bonds

In a molecule or ion, dative bonds are formed when atoms with empty orbitals interact with atoms with a lone pair of electrons. In certain cases when the free atom of the element has less than four valance electrons (as in Be, B), the number of covalent bonds that the particular atom can form is less than four. This results in incomplete octet with lower stability. Therefore, such electron deficient central atoms preferably react with the atom having lone pairs which can donate an electron pair to the central atom to complete the octet. The reaction of BH_3 with CO to produce borane carbonyl and the reaction with CN^- to produce cyanoborohydride are example with such dative bonds. Furthermore, reaction of NH_3 with BF_3 to form a dative covalent bond between B and N is another example. The dative bond is formed when the empty orbitals in B overlaps with the orbital having the lone pair in the nitrogen atom. In this case a central atom cannot be chosen precisely. Since the lone pair on the nitrogen atom is donating the electron pair to B, the bond can be denoted by an arrow. The arrow head is pointed to the electron deficient atom. This can be illustrated using formal charges as well as shown below.

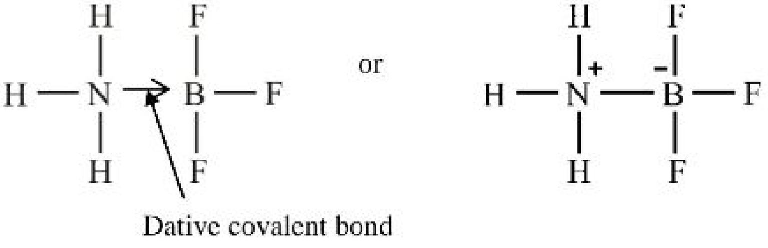


Figure 2.6 Dative covalent bond (H_3N-BF_3)

Dative covalent bonds are also formed when metal ions or some metal atoms react with molecules or ions having lone pairs (H_2O, NH_3, CO molecules and CN^- ions) in order to form complexes. The following illustrates the formation of a complex ion when Cu^{2+} is reacted with four NH_3 molecules to form dative covalent bonds.

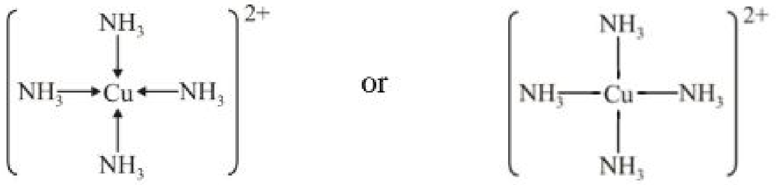


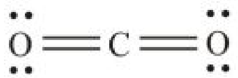
Figure 2.7 Dative covalent bond in $[Cu(NH_3)_4]^{2+}$ complex

2.3 Valance Shell Electron Pair Repulsion theory (VSEPR theory)

Ronald Gillespie and **Ronald Sydney Nyholm** suggested that electron pairs surrounding the central atoms of a given molecule or ion are arranged in a way to keep maximum spatial distance apart from each other. Gillespie has explained the shapes of molecules when the central atom is a main group element while Nyholm discussed the shapes of molecules with transition elements as the central atom. By 1963, Gillespie introduced VSEPR theory for finding shape of molecules or ions.

There are mainly two kinds of electron pairs surrounding the central atom. The first type is the bonding electron pair which is held between two nuclei, by attractive forces. The second type is electron pairs not participating in the bonding known as lone pairs. Since lone pair of electrons are under the influence of a single nucleus, the electron cloud occupies a relatively larger spatial volume. Both bonding and lone pairs of electrons of an atom act as repulsive unit to keep further away from each other. If multiple bonds (double or triple bonds) are present between atoms, each multiple bond is considered as a single repulsive unit.

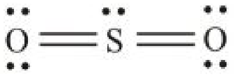
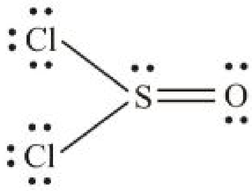
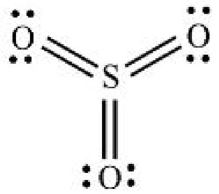
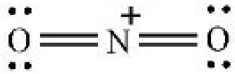
There are three different types of bonding when the number of covalent bonds formed between the central atom and a surrounding atom is considered. These are single bonds, double bonds and triple bonds where double and triple bonds represent multiple bonds. For example, in the CO_2 molecule, double bonds are present between the central carbon atom and the surrounding oxygen atoms. In the HCN molecule a triple bond is present between the central C atom and N atom as shown below. Each single, double, triple bond or lone pair is considered as one repulsive unit or a VSEPR unit.



The three pairs of electrons in the triple bond of HCN molecule is considered as a single repulsive unit. This is because the three electron pairs are located between C and N atoms preventing independent movement of three electron pairs from each other, thus the triple bond can be considered as a single repulsive unit or single VSEPR unit.

The number of repulsive units surrounding the central atom can be clearly identified using the Lewis structure. Table 2.2 gives few examples on how to identify the number of electron pairs surrounding the central atom and the VSEPR units around the central atom.

Table 2.2 Lewis dot dash structure, electron pairs and VSEPR units around the central atom of selected molecules and ions

Lewis dot dash structure	Electron pairs around the central atom	Repulsion (VSEPR) units around the central atom
 $O=S=O$	5	3
	5	4
	6	3
$H-C\equiv N:$	4	2
 $O=\overset{+}{N}=O$	4	2

According to the VSEPR theory, molecules/ ions achieve stability by maintaining a maximum distance between repulsion units, to get the minimum repulsion force between them.

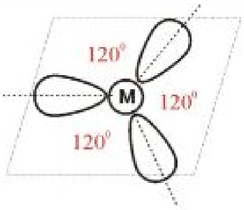
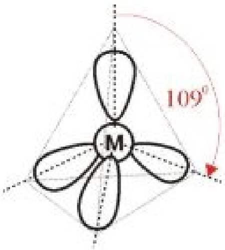
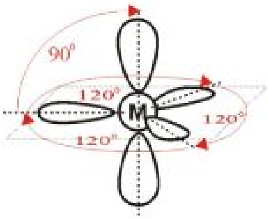
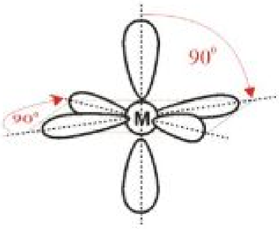
A lone pair of electrons occupies greater spatial distribution (spatial volume) compared to a bonding electron pair. Hence, it is considered that the repulsion between two lone pairs of electrons (lone pair ↔ lone pair) is higher than the repulsion between two pairs of bonding electrons (bonding pair ↔ bonding pair). This results in intermediate repulsive force for interaction between lone pair and bonding pair (lone pair ↔ bonding pair) of electrons.

Repulsion between two bonding electron pairs < Repulsion between bonding electron pair and lone pair of electrons < Repulsion between two lone pairs of electrons

Figure 2.8 Comparison of repulsive forces between bonding and lone pairs of electrons

The distribution of repulsive units (bonding or lone pairs) in space around the central atom is called "electron pair geometry". When stating the geometry of a particular molecule or ion it is necessary to report bonding angles. Table 2.3 summarizes the different electron pair geometries depending on how the repulsive units are distributed in 3D space. When reporting the shape of a molecule/ ion, it is not mandatory to report the bond angles. However, when stating the geometry of a molecule/ ion it is necessary to mention the bond angles. Therefore, electron pair geometry, shape and geometry of a molecule/ ion are considered as three independent parameters. Geometry of a molecule carries the shape and the angle. Geometry of molecule associated with the bond angle in Lewis structure representing the shape. Shape of the molecule represents the Lewis structure in order to illustrate the shape without the bond angles. Electron pair geometry represents geometry of repulsive units.

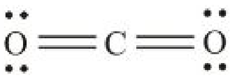
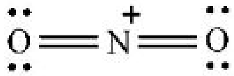
Table 2.3 Electron pair geometry of repulsion units

Repulsion units	Electron pair geometry	
2		Linear
3		Trigonal planar
4		Tetrahedral
5		Trigonal bipyramidal Three repulsive units are on the same plane with 120° angle. The other two repulsive units lie perpendicular to this plane.
6		Octahedral Four repulsive units are in one plane with 90° angle between them. The other two repulsive units lie perpendicular to this plane.

Linear electron pair geometry

Here two VSEPR units are present around the central atom. Consider the situation where the central atom is bonded to two other atoms. The shape of such a species is linear. Table 2.4 provides more examples for linear molecules.

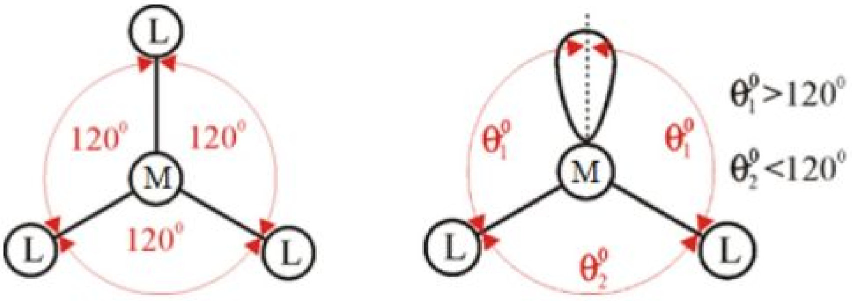
Table 2.4 Molecules/ ions with two repulsion units

Chemical Formula	Lewis dot dash structure	Shape
CO_2	 $\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$	Linear
HCN	$H-C\equiv N:$	Linear
NO_2^+	 $\ddot{\underset{\cdot\cdot}{O}}=\overset{+}{N}=\ddot{\underset{\cdot\cdot}{O}}$	Linear

Trigonal planar electron pair geometry

Two types of electron pair geometries can be identified when electron pairs are divided as bonding and lone pairs.

- All three repulsive (VSEPR) units are bonding
- Two repulsive (VSEPR) units are bonding and the other is a lone pair



(a)

All three repulsive units are bonding

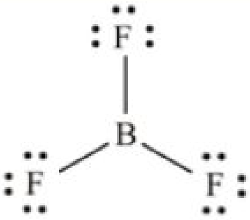
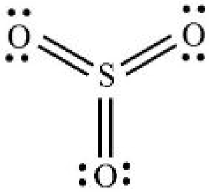
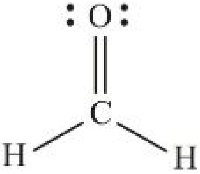
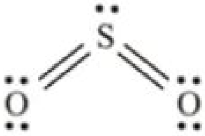
(b)

Two repulsive units are bonding while the other is a lone pair

Figure 2.9 Trigonal planar electron pair geometry

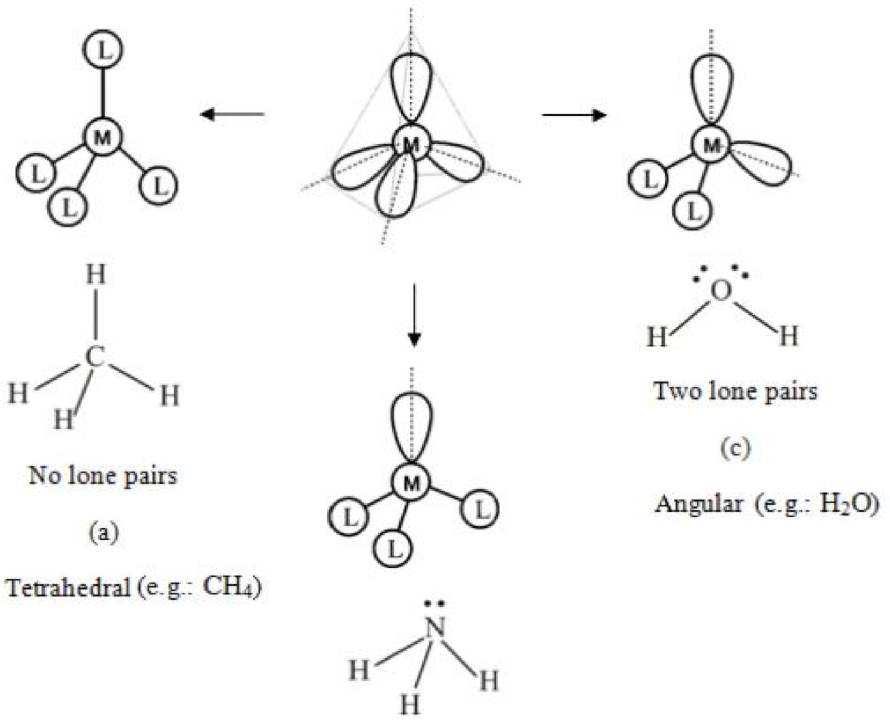
In Table 2.5 the central atoms in BF_3, SO_3 and HCHO do not contain lone pairs of electrons resulting in trigonal planar shape. However, in SO_2 the presence of a lone pair of electron on 'S' atom results in an angular shape.

Table 2.5 Molecules/ ions with three repulsive units

Chemical formula	Lewis dot dash structure showing the shape	Shape
BF_3		Trigonal planar
SO_3		Trigonal planar
HCHO		Trigonal planar
SO_2		Angular

Tetrahedral electron pair geometry

There are three possibilities when four repulsive units (VSEPR pairs) are considered separately as bonding and lone pairs of electrons. Figure 2.10 illustrates these briefly.



No lone pairs

(a)

Tetrahedral (e.g.: CH_4)

One lone pair

(b)

Trigonal pyramidal (e.g.: NH_3)

Two lone pairs

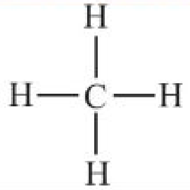
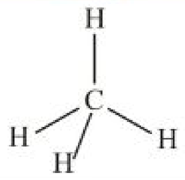
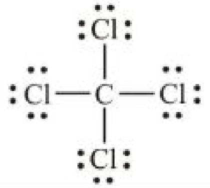
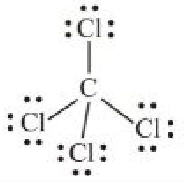
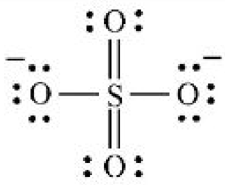
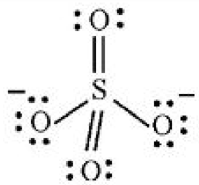
(c)

Angular (e.g.: H_2O)

Figure 2.10 Tetrahedral electron pair geometry

Table 2.6 provides more examples for molecules with tetrahedral geometry.

Table 2.6 Examples for tetrahedral molecules/ ions

Molecule	Lewis dot dash structure	Shape
CH_4		
CCl_4		
SO_4^{2-}		

Trigonal bipyramidal electron pair geometry

Here there are five VSEPR units/ repulsive units around the central atom. These are arranged in four different types when bonding and lone pairs are considered.

- All five repulsive units around the central atom are bonding electron pairs. e.g.: PCl_5. The shape of PCl_5 is given below.

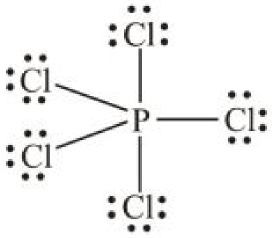
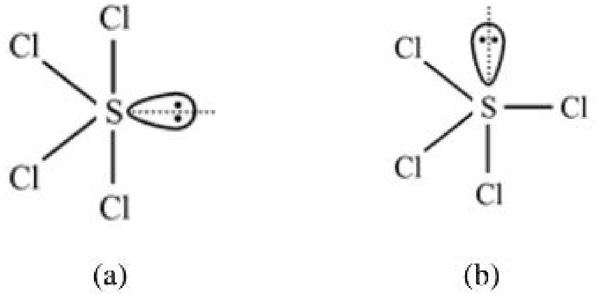


Figure 2.11 Electron pair geometry of PCl_5

- Four repulsive units are bonding while the remaining electron pair is a lone pair of electrons. e.g.: SCl_4. There are two possible positions for the lone pair at the S atom of the SCl_4 molecule as shown below.



The structure (a) has less repulsion than structure (b). Therefore structure (a) is more stable than structure (b) as per the VESPER model.

The theoretical shapes of molecules with four bonding pairs and a lone pair of electrons is called '*see-saw*'(distorted see-saw/ irregular see-saw) shape. The imaginary axis for lone pair of electrons and the two S-Cl bonds are in one plane while the remaining two S – Cl bonds are placed perpendicular to this plane.

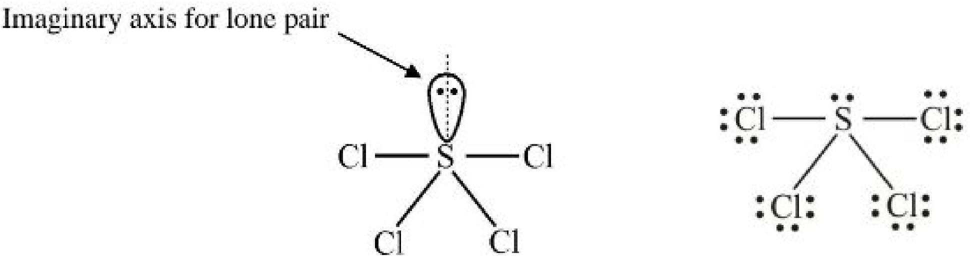


Figure 2.12 Electron pair geometry of SCl_4

However, the repulsion of the lone pair on S-Cl bonding electrons slightly distorts the regular see-saw shape. Hence the shape of SCl_4 is called distorted tetrahedral/ distorted see-saw/ irregular see-saw.

- Three repulsive units are bonding while the other two repulsive units are lone pair of electrons. e.g.: ICl_3

  In the case of ICl_3, the most stable shape with minimum repulsive forces between VSEPR units is given below. The sketch of ICl_3 results in 'T' shape (distorted T' shape/ irregular T' shape) when the surrounding Cl atoms are considered. Therefore, it is called a 'T' shape molecule. Here, two lone pairs and one I–Cl bond are in one plane while the remaining two I – Cl bonds lie perpendicular to this plane.

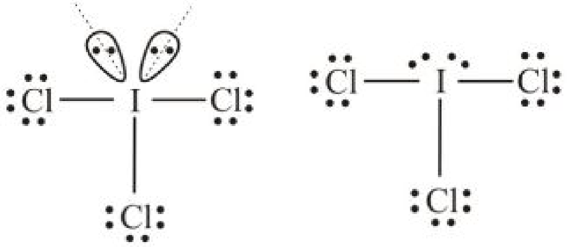


Figure 2.13 Electron pair geometry of ICl_3

- Two repulsive units are bonding while the remaining three units are lone pairs of electrons. e.g.: XeF_2

  In this type, all atoms are in line thus the molecule has 'linear' shape. The following Lewis structure illustrates the linear shape of the XeF_2 molecule. Note that all three lone pairs are in one plane which is perpendicular to the F-Xe-F axis.

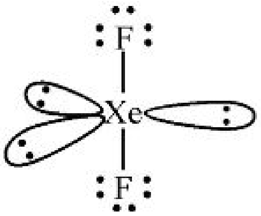
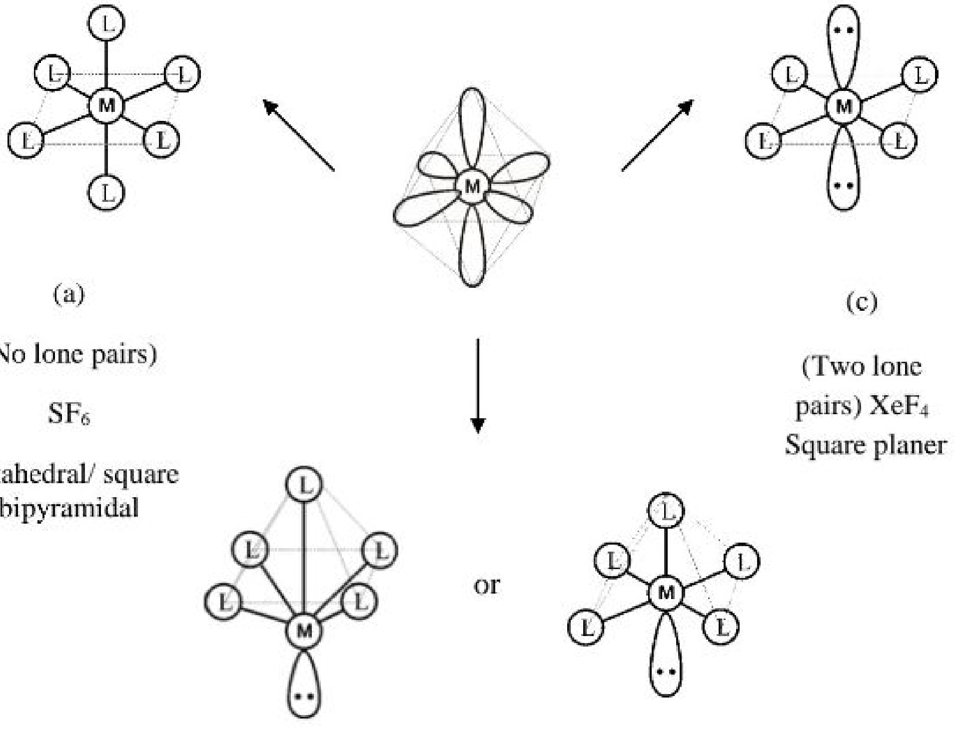


Figure 2.14 Electron pair geometry of XeF_2

Octahedral electron pair geometry

In this geometry, the angle between each two adjacent repulsion units is 90°. The following Figure 2.15 illustrates the octahedral electron pair geometry of such molecules having three possible shapes. Four repulsive units are in one plane while remaining two units lie perpendicular to this plane.



(a)

(No lone pairs)

SF_6

Octahedral/ square bipyramidal

(c)

(Two lone pairs) XeF_4

Square planer

(b)

(One lone pair)

$XeOF_4$

Square pyramidal/ distorted square pyramidal

Figure 2.15 Octahedral electron pair geometry

First consider the situation where all the repulsive units are bonding (e.g.: SF_6). When the substituted atoms surrounding the center are connected with imaginary dotted lines, an octahedron with eight planes is created. Therefore, shape of such molecules are called 'octahedral'.

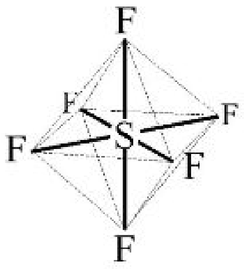


Figure 2.16 Electron pair geometry of SF_6

Next, consider the molecules with five repulsive units in the form of bonding pairs and one repulsive unit in the form of lone pair of electrons ($XeOF_4$). The electron pair geometry of $XeOF_4$ is octahedral. When the surrounding atoms of $XeOF_4$ are connected with imaginary lines pyramid, with a square shaped base is created. Therefore the theoretical shape is 'square pyramidal'. The repulsion between the lone pair on the Xe atom and Xe - F bond has changed the regular shape of the molecule. Therefore the shape of $XeOF_4$ is called distorted square pyramidal.

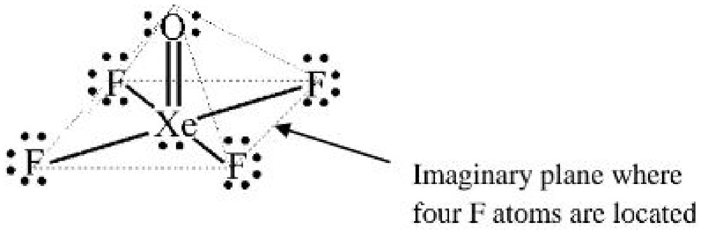


Figure 2.17 Electron pair geometry of $XeOF_4$

When a molecule consists of four repulsive units in the form of bonding electron pairs and two repulsive units in the form of lone pairs, then the shape is called 'square planar' as illustrated by the XeF_4 molecule.

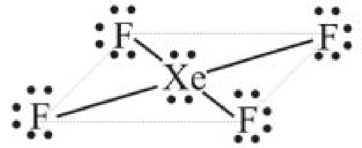


Figure 2.18 Electron pair geometry of XeF_4

Example 2.3

Draw the Lewis dot-dash structures of the following molecules and predict their shapes

(i) SO_3 (ii) CH_2Cl_2

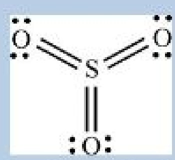
Answer

(i) SO_3

Electrons from S atom = 6

Electrons from 3 O atoms = 3(6e) =18

Total electrons =24



Lewis dot-dash structure

Distribute 24 electrons in order to represent the Lewis dot-dash structure

Repulsive units around the central atom = 3

Lone pairs on "S" atom = 0

Shape = trigonal planar

(ii) CH_2Cl_2

Electrons from C atom = 4

Electrons from 2H atoms = 2(1e) = 2

Electrons from 2 Cl atoms = 2(7e) =14

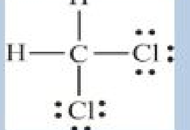
Distribute 14 electrons in order to represent the Lewis dot-dash structure

Total electrons =20

Repulsive units around the central atom = 4

Lone pairs on "C" atom = 0

Shape = tetrahedral



Lewis dot-dash structure

2.3.1 Hybridization of atomic orbitals

The conceptual model of hybridization can be explained qualitatively using a carbon atom. The valance shell of carbon atom in the ground state consists of one electron pair and two unpaired electrons ($2s^2$ $2p^2$). However, in order to form four covalent bonds, the presence of four orbitals with an unpaired electron in each is necessary. Therefore, electrons in the ground state rearrange to form an excited state with four unpaired electrons.

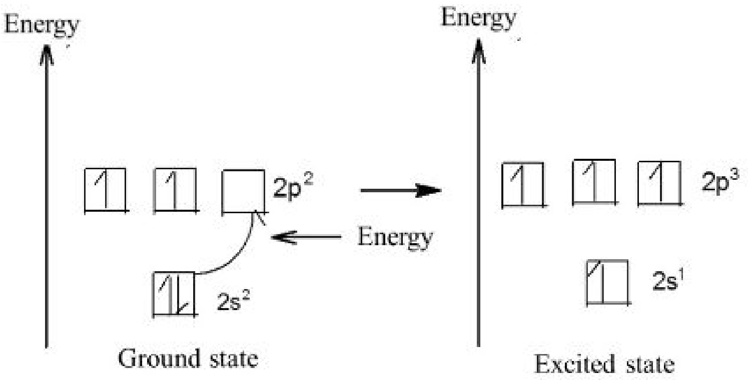


Figure 2.19 Energy level diagram of carbon atom in ground and excited states

Here, one of the 2*s* electrons in the valance shell of carbon atom absorbs energy and gets promoted to an empty 2*p* orbital as shown in Figure 2.19. This transition is feasible as the energy gap between 2*s* and 2*p* orbitals is relatively low. Now the atom is in the excited state with unpaired electrons in 2*s* and 2*p* energy levels as illustrated above. Though there are four unpaired electrons available for bonding, these electrons are in two different energy levels and in two different shapes of atomic orbitals (spherical *s* orbital and dumbbell shaped *p* orbitals). At this state, if C atom forms 4 bonds with 4 H atoms to form CH_4, the type of bonding consists of one C-H bond formed between 2s orbital of carbon with the *s* orbital of the hydrogen and three C-H bonds formed with overlap of 2*p* orbitals from carbon and *s* orbitals from hydrogen. Then the CH_4 molecule is expected to have two different types of bonds with different bond angles.

However, all four C-H bonds and bond angle in CH_4 are identical. Therefore, a valid assumption is mixing of these 2*s and* 2*p* orbitals to form four atomic orbitals with same energy and same shape when forming the C-H bonds. This concept is called '**hybridization**'. It is not possible to depict a valid structure for the CH_4 molecule without the concept of hybridization, for the formation of identical four C-H bonds by 2*s* and 2*p* orbitals of the C atom, if considered separately. It is also not possible to explain the bond angle of HCH as 109.5°.

The following facts are important for understanding the model of hybridization of atomic orbitals.

(i) The concept of hybridization cannot be used for an atom alone, but it is used to describe the bonding formed by a particular atom in a molecule.

(ii) There should be a minimum of two atomic orbitals with different shapes and energy mixed to form hybrid orbitals.

e.g.: A *s* orbital can hybridize with one or more of *p* orbitals (up to 3) of the same atom. These hybrid orbitals do not have clear identity; hence, has a shape different from original orbitals.

(iii) The number of hybrid orbitals formed is equal to the number of atomic orbitals that participate in the hybridization. Though atomic orbitals at different energy levels are mixed, the resulting hybrid orbitals will be at the same energy level. These hybrid orbitals differ only in the orientation in 3D space but are identical in shape and energy when the atomic orbitals are *s* and *p*.

(iv) A hybrid orbital in a particular atom can overlap (linear overlap) with a hybrid orbital or un-hybridized atomic orbital of another atom to form bonds.

Note that hybridization is not a true physical process and is an imaginary process presented as a concept. According to this imaginary process, there are three different kinds of hybridizations possible with a carbon atom in the excited state. A summary is given below.

(i) Mixing of the *s* orbital with three *p* orbitals to form four ***sp*^{3} hybridized** orbitals. (**tetrahedral** geometry)

(ii) Mixing of the *s* orbital with two *p* orbitals to form three ***sp*^{2} hybridized** orbitals. (**trigonal planar** geometry)

(iii) Mixing of the *s* orbital with one *p* orbital to form two ***sp* hybridized** orbitals. (**linear** geometry)

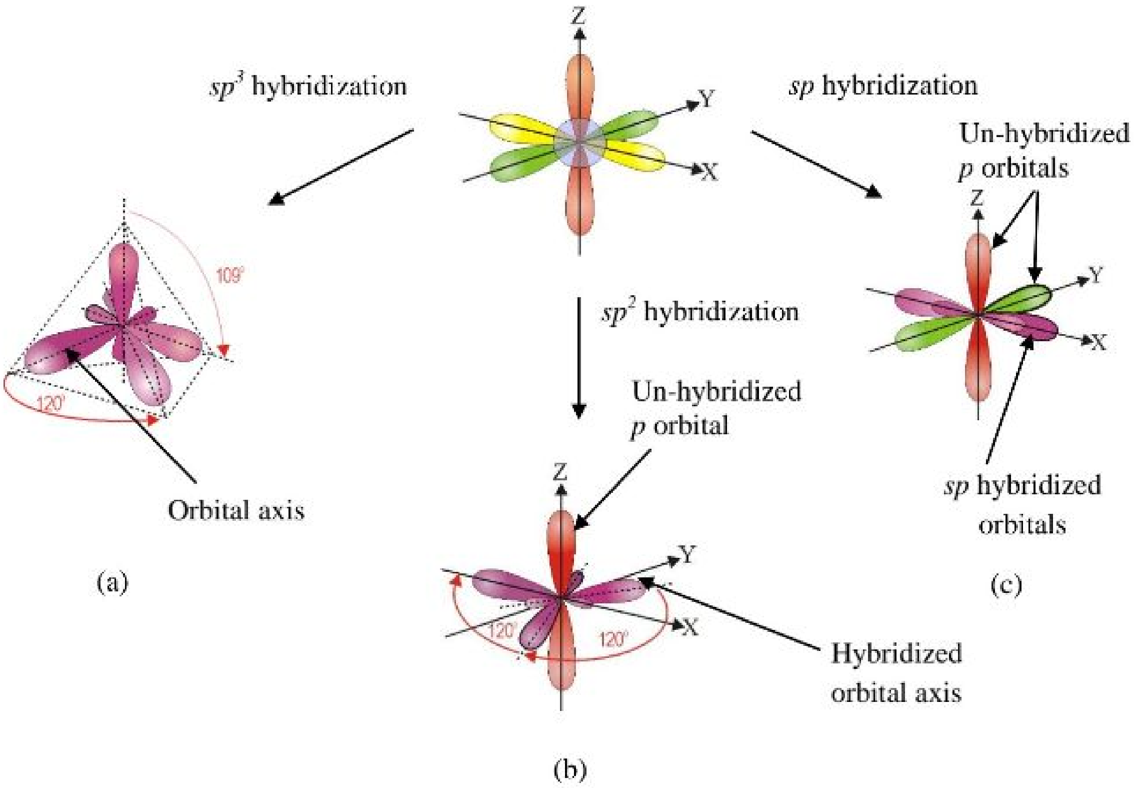
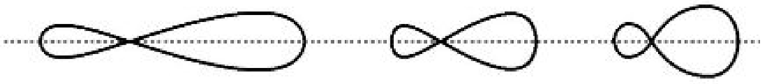


Figure 2.20 sp^3, sp^2 and sp hybridization

The following diagrams compare the sp^3, sp^2 and sp hybridized orbitals in terms of shape and percentage of s and p character.



	sp^3 hybridized orbital	**sp^2 hybridized orbital**	**sp hybridized orbital**
s character	25%	33.3%	50%
p character	75%	66.3%	50%

Figure 2.21 Comparison of sp^3, sp^2 and sp hybridized orbitals comparison

(a) **Orientation of sp^3 hybrid orbitals**: The orbitals are located inside a tetrahedron with 109°28′ angle among orbitals.

(b) **Orientation of sp^2 hybrid orbitals**: The axis of all three hybrid orbitals is in one plane with 120° angle among hybrid orbitals. One of the p orbitals does not participate in hybridization and lies perpendicular to this plane.

(c) **Orientation of sp hybrid orbitals**: There is a180° angle between axes of hybrid orbitals, so both axes are in a straight line. The axes of two p orbitals which do not participate in hybridization lie perpendicular to each other as well perpendicular to the axis of sp hybrid orbital.

2.3.2 Formation of double and triple bonds

If there are two bonds between two atoms, one bond is called a 'σ bond' while the other bond is called a'π bond'. Consider the formation of a double bond between two carbon atoms in the ethene molecule (CH_2CH_2). Linear overlap of two hybridized orbitals form a σ bond and the π bond is formed with lateral overlap of the unhybridized *p* orbitals in each carbon atom.

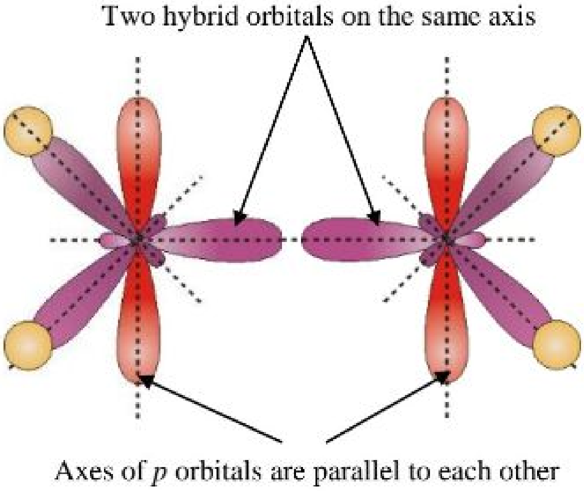
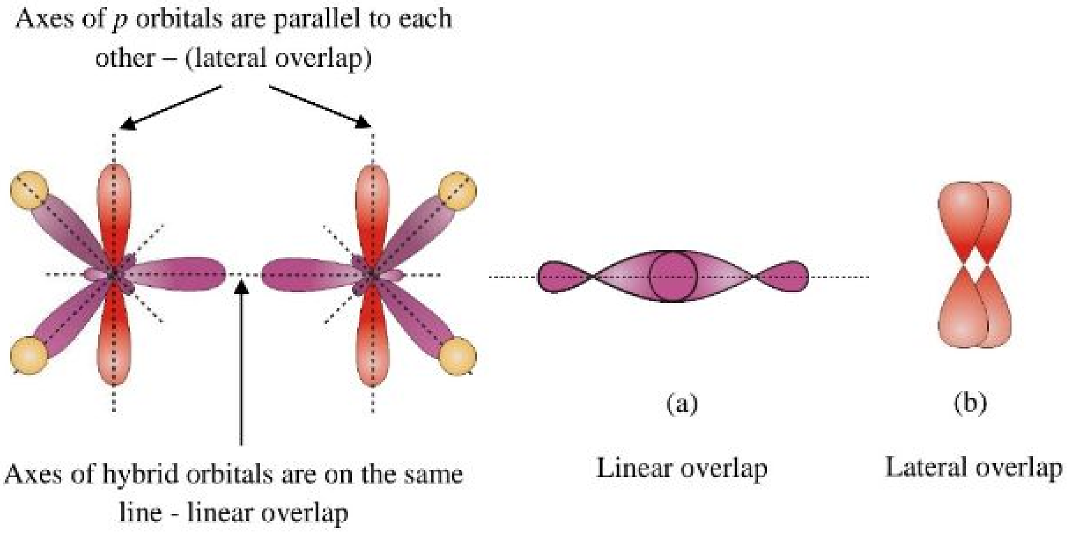


Figure 2.22 sp^2 hybridized orbitals and *p* orbital orientation in C_2H_4

Since the axes of two *p* orbitals are parallel to each other, *lateral overlap* is observed between these dumbbell shaped *p* orbitals. If the axes of *p* orbitals are not parallel to each other, there is less chance for these orbitals to overlap. In the above diagram, the axes of two hybrid orbitals are aligned on a straight line, thus the overlap between these orbitals is considered a *linear overlap*.

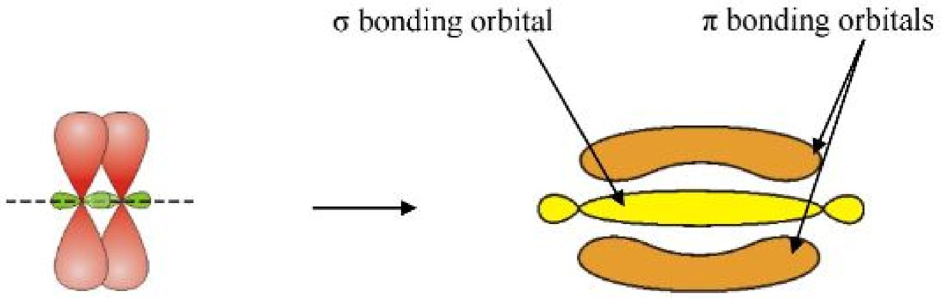


Linear overlap

Lateral overlap

Figure 2.23 Linear and lateral overlap of orbitals in C_2H_4

The Figure 2.24 shows the general idea of the proposed model for the arrangement of bonding orbitals in double bond.



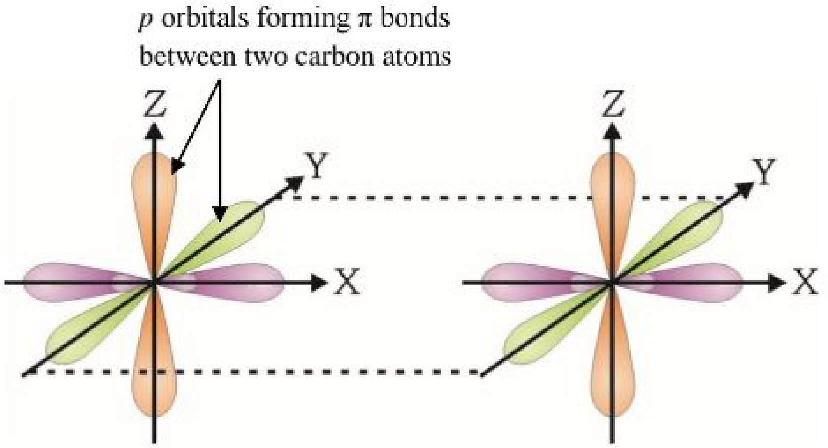
Lateral overlap between *p* orbitals and linear overlap of sp^2 orbitals

Figure 2.24 σ bond and π bond

The triple bond between two carbon atoms in ethyne (C_2H_2) can be used to study how triple bonds are formed. This triple bond consists of one σ bond and two π bonds between two carbon atoms. The Lewis structure of ethyne is shown below.

$$H-C\equiv C-H$$

Each carbon atom in ethyne forms two σ bonds (C-H and C-C). Therefore, these carbon atoms have *sp* hybridization and the axes of the remaining two *p* orbitals of two carbon atoms lie parallel to each other. It is clearly illustrated in the Figure 2.25.



- Axes of p_y orbitals are parallel to each other
- Axes of p_z orbitals are parallel to each other
- Two *sp* hybridized orbitals facing each other in the x axis from a σ bond between the two carbon atoms

Figure 2.25 *sp* hybridized orbitals and *p* orbitals interaction between the two carbon atoms in ethyne

The axes of *p* orbitals forming a particular π bond are parallel to each other. However the axes of the remaining *p* orbitals forming the other π bond are perpendicular to the orbitals forming the first π bond. In a triple bond, imaginary axes of π electron distribution are perpendicular to each other.

2.3.3 Resonance structures

It is possible to draw a number of Lewis structures for a certain molecule or ion. These Lewis structures with the same skeleton or atom positions are called '**Resonance structures**'. The reason is when there are multiple bondings present (double or triple bonds), the position of the π bond and lone pair of electrons could be changed without changing the atomic arrangement (skeleton of the molecule). The following Figure 2.26 are the two resonance structures for NO_2^- ion, in which the position of π bond has been changed without changing the atomic arrangement.

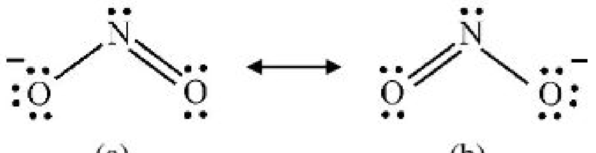

(a) (b)

Figure 2.26 Resonance structures of the NO_2^- ion

In NO_2^- ion, two resonance structures can be drawn changing the position of the negative charge and the π bond. In this case, both structures (a) and (b) are identical and cannot be distinguished from each other. Figure 2.27 clearly explains how one resonance structure can be converted to the other using curved arrows. In general, to mark the movement of a lone pair of electrons or π bonding electrons, a curved arrow is used. The arrow head is pointed to the place where electrons have moved. The diagram given below shows the formation of resonance structure in NO_2^- ion.

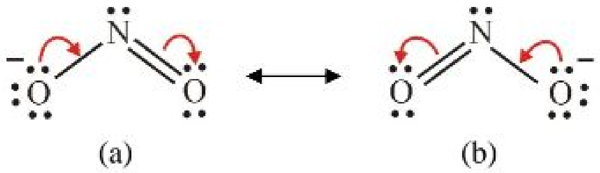

(a) (b)

Figure 2.27 Conversion of the resonance structures of the NO_2^- ion into one another

Characteristics of resonance

(i) Resonance structures (contributing structures) do not have real existence. They are imaginary structures drawn for convenience of understanding the nature of molecules or ions. It is assumed that the concept/ model of resonance hybrid represents real existence of molecule or ion.

(ii) Resonance for equal resonance structures, the bond lengths in the resonating unit becomes equal (e.g.: NO_2^-, where both N – O bond lengths are equal).

(iii) The resonance hybrid has comparatively lower energy and thus a greater stability than any of the contributing structures.

(iv) Equivalent resonance structures make equal contribution to the resonance hybrid.

(v) Non–equivalent resonance structures make unequal contribution to the resonance hybrid, whereas most stable resonance structures make major contribution.

Formal Charges

Formal charge is the hypothetical charge on an atom in a molecule or polyatomic ion. This concept is used to identify the energetically most stable Lewis structure. In general, it is considered that the formal charge on each of the atom is zero or close to zero, when the Lewis structure is stable.

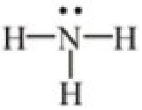
The following steps help to evaluate the formal charge (FC).

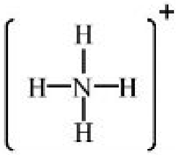
(i) $$\text{FC} = \begin{bmatrix}\text{Number of valence}\\ \text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\ \text{in lone pairs}\end{bmatrix}\right]$$

(ii) In a Lewis formula, an atom that has the same number of bonds as its number of valence electrons in the atom, its formal charge is zero.

(iii) Add formal charges of all the atoms to find the total value.
  (a) In a molecule, the sum of the formal charges is zero.
  (b) In a polyatomic ion, the sum of the formal charges is equal to the net charge of the ion.

e.g.:





In NH_3 the N atom has three bonds and two unshared electrons (which are not involved in bond formation).

For N atom of NH_3

$$\text{FC} = \begin{bmatrix}\text{Number of valence}\\ \text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\ \text{in lone pairs}\end{bmatrix}\right]$$

$$= 5 - (3+2) = 0$$

Formal charge of N atom in ammonia is zero.

For H atom of NH_3

$$FC = \begin{bmatrix}\text{Number of valence}\\ \text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\ \text{in lone pairs}\end{bmatrix}\right]$$

$$= 1 - (1+0) = 0$$

Formal charge of H atom of ammonia is zero.

The formal charges of N and H are both zero in NH_3, so the sum of the formal charges of the molecules is zero.

In NH_4^+ the N atom has 4 bonds and no unshared electrons is on the N atom. Hence, formal charge on the N atom of NH_4^+ ion is +1 and formal charge on each H atom is zero. Total of formal charges of NH_4^+ ion is equal to +1 and it is the charge of ammonium ion.

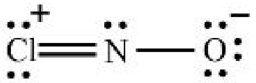
(i) The most likely Lewis structure for a molecule or ion is the one in which the formal charge on each atom is zero or closer to zero as possible.

(ii) Negative formal charges are more likely to occur on more electronegative elements.

(iii) Lewis structure in which adjacent atoms have formal charges of the same sign are not stable, hence not an accurate representations.

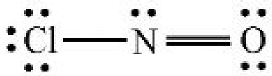
Following examples assign formal charges to the atoms in nitrosyl chloride, NOCl. The Cl atom and the O atom are both bonded to the N atom. Two Lewis formulae that satisfy the octet rule whereas formal charges are not same.

(a)



$\overset{+}{Cl}=N-\overset{-}{O}$

(b)



$Cl-N=O$

For Cl, FC = 7 – (2 + 4) = +1

For N, FC = 5 – (3 + 2) = 0

For O, FC = 6 – (1 + 6) = -1

For Cl, FC = 7 – (1 + 6) = 0

For N, FC = 5 – (3 + 2) = 0

For O, FC = 6 – (2 + 4) = 0

These two structures have satisfied the octet rule. But the Lewis structure (b) is energetically more stable since the formal charge on each atom is zero.

Rules to estimate relative stability of resonance structures

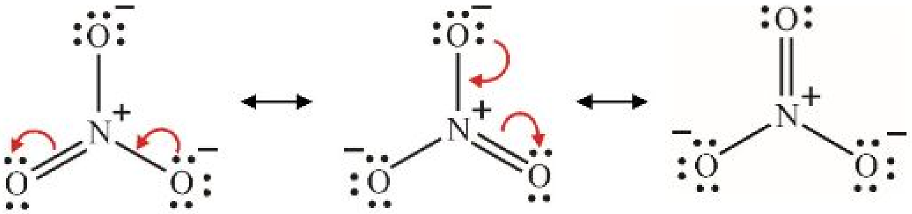
(i) The most stable resonance structure has the least formal charge separation. Thus it contains the greater number of covalent bonds and it contributes mostly to the resonance hybrid. Both maximizing the number of bonds and satisfying the octet rule should be achieved.

(ii) Structures in which adjacent atoms have formal charges of the same sign tend to be unstable.

(iii) When opposite formal charges are placed on adjacent atoms, positive charge should fall on electropositive atom and negative charge on electronegative atom.

(iv) When positive formal charges placed on highly electronegative atoms such as F and O, the structures are unstable.

Formation of resonance structures of nitrate ion (NO_3^-) is given in Figure 2.28.

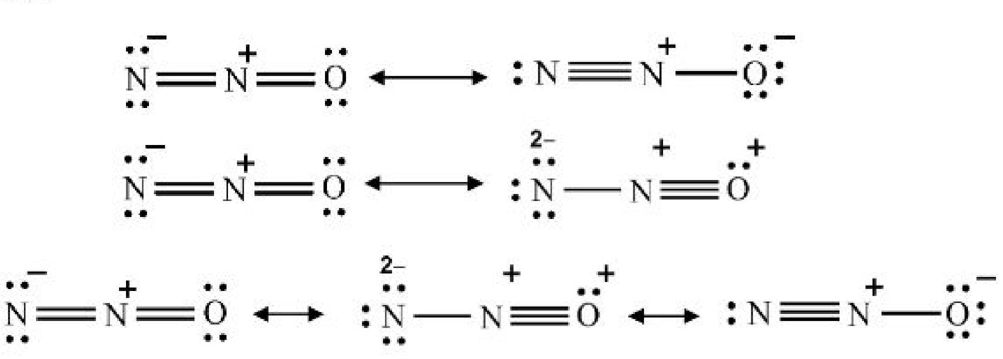


(a) (b) (c)

Figure 2.28 Conversion of resonance structures of NO_3^- ion to one another

All the resonance structures are equivalent. Hence their stabilities are equal. Hence, they contribute equally for the resonance hybrid.

The resonance structures of N_2O are as follows. These resonance structures have satisfied the octet rule.



(a) (b) (c)

Figure 2.29 Resonance structures of N_2O

However based on the formal charge concept, the stability of these resonance structures are not equivalent. According to the rule (iii) given, structure (b) makes the least contribution to the resonance hybrid. (a) and (c) are the stable structures compared to (b) and hence (a) and (b) are the main contributors for the resonance hybrid.

Formation of resonance structures of the carbonate ion (CO_3^{2-}) is given in Figure 2.30 below.

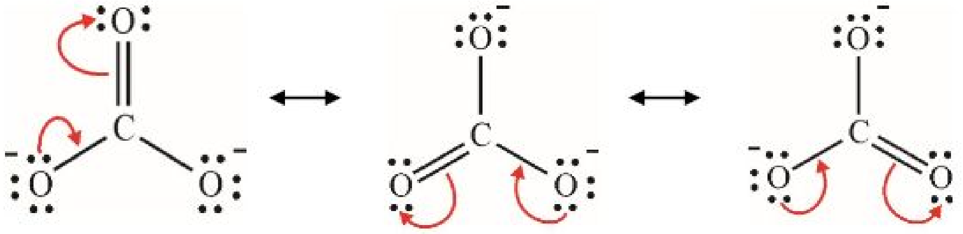


Figure 2.30 Formulation of resonance structures of CO_3^{2-} ion into one another

The corresponding resonance structures of carbonate ion are as follows.

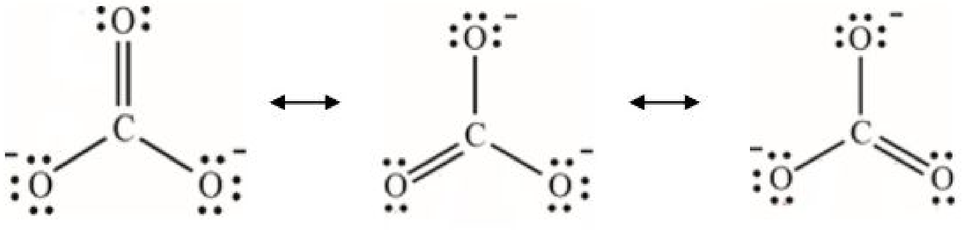


Figure 2.31 Resonance structures of the CO_3^{2-} ion

Resonance structures of the carbonate ion can be used to describe the structure of the resonance hybrid. When resonance structures of the carbonate ion are considered, there are at least two lone pairs of electrons present on each oxygen atom. However the third lone pair may or may not be present on oxygen atoms as position of π bond is changed when forming the resonance structures. Since the position of the π electron cloud is changed, then the electron cloud is delocalized among all three C-O bonds. The resonance hybrid can be represented by Figure 2.32. Note that delocalized electron cloud on C-O bonds is denoted by dotted lines. Bond lengths of CO_3^{2-} are the same since actual structure is the combination of all features of the three resonance structures (resonance hybrid).

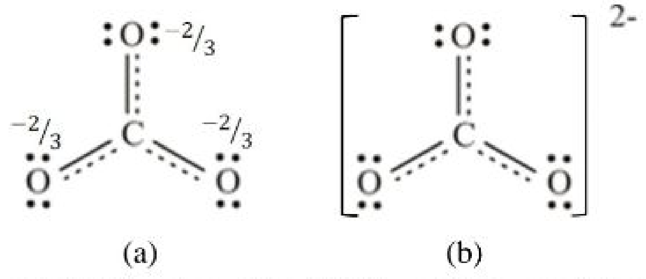


Figure 2.32 (a) Resonance hybrid structure of the CO_3^{2-} ion with charges (b) resonance hybrid structure of the CO_3^{2-} ion without charges on terminal atoms

The hybrid shown above with the charges on individual atoms is valid only when equivalent resonance structures are used to draw the hybrid (e.g.: O_3, NO_3^-, CO_3^{2-}, NO_2^-). However, this is not valid for unsymmetrical molecules/ ions (e.g.: N_2O, $S_2O_3^{2-}$).

The ozone molecule can be represented by two resonance structures as shown below.

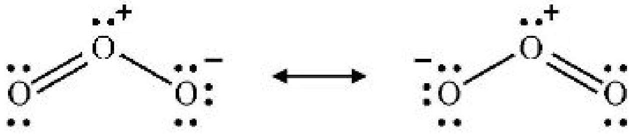


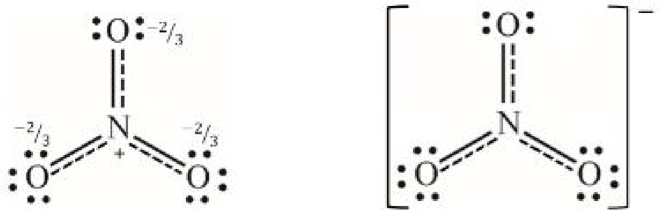
Figure 2.33 Resonance structures of O_3

The bond lengths of the two bonds formed by central atom of O_3 molecule with the other two oxygen atoms in O_3 molecule are same and hence the real structure of O_3 is considered a combination of these two. The combination of the two resonance structures (resonance hybrid) of O_3 is illustrated as follows.

(a) (b)

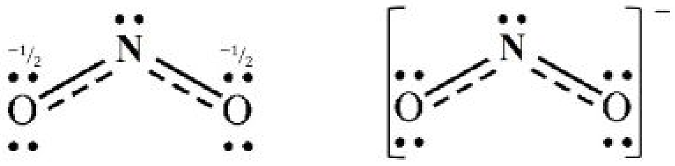
Figure 2.34 (a) Resonance hybrid structure of the O_3 with charges (b) Resonance hybrid structure of the O_3 without charges on terminal/ central atom(s)

Similarly the resonance hybrid structure of NO_3^- and NO_2^- is given in Figure 2.35 and Figure 2.36 respectively.



(a) (b)

Figure 2.35 (a) Resonance hybrid structure of the NO_3^- with charges (b) Resonance hybrid structure of the NO_3^- without charges on terminal/ central atom(s)



(a) (b)

Figure 2.36 (a) Resonance hybrid structure of the NO_2^- with charges (b) Resonance hybrid structure of the NO_2^- without charges on terminal atoms

2.3.4 Effect of electronegativity and geometry on the polarity of molecules

If the electronegativity difference between the atoms forming a chemical bond is large, then electron cloud can be considered to be polarized. The electrons in this polarized covalent bond have higher probability of being found closer to the more electronegative atom. Electronegativity difference plays a vital role in determining the polarity of a bond. Therefore, the higher the electronegativity difference, the higher is the polarity. However, when considering polarity of the entire molecule, then the geometry of the molecule is also important; for example, though C=O bond is polar, CO_2 molecule is non-polar. The reason is the total symmetric linear geometry of the CO_2 molecule. Similarly, C-Cl bond is polar but, CCl_4 molecule is non-polar due to the total symmetric tetrahedral shape of the molecule. Diatomic molecules of same element (e.g.: Cl_2, O_2, N_2 etc.) are examples for nonpolar simple molecules. Bonds of those molecules are examples for the totally nonpolar covalent bonds.

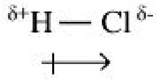
Figure 2.37 CO_2 and CCl_4 molecules

2.3.5 Dipole moment

This concept can be clearly understood by taking a molecule with one single bond such as HCl. In a polar molecule, negative pole is created on one end of the molecule, and the positive pole is created on the opposite end of the molecule. Accordingly, in HCl molecule, negative pole is on the Cl atom and the positive pole is created on the H atom. Following is the way of representing such polar bonds.

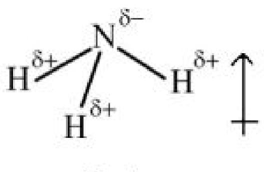
$$^{\delta+}H - Cl^{\delta-}$$

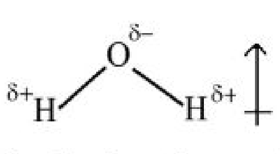
Dipole is notated as ' $\mapsto$ ' and the arrow head is pointed towards the negative pole of the molecule.



$$\underset{\mapsto}{^{\delta+}H - Cl^{\delta-}}$$

e.g.:





If there is a permanent dipole present in a molecule, then the magnitude of polarization on each pole of dipole is equal, resulting in an electrically neutral molecule. Dipole moment is calculated by multiplying the magnitude of a polarity by the distance between the two atoms. When considering HCl molecule, due to asymmetric distribution of the electron cloud, one of the poles is located on the H atom and the other pole is on the Cl atom. The dipole moment of the HCl molecule can be calculated as follows:

Magnitude of dipole moment (μ) = charge of the pole (δ) × bond length (r)

In the above equation units of δ is Coulombs (C) and r is meters (m). Therefore the unit of dipole moment is Cm.

Dipole moments (vector quantity- it has a magnitude and direction) of molecules are usually expressed in Debye (D), a unit equal to 3.34×10^{-30} Cm.
Since the electronegativity of an atom describes the ability to pull electrons towards itself, models are available to estimate the percentage of ionic nature in a chemical bond using the electronegativity difference. Information on dipole moment and bond length can also be used to calculate percentage ionic character. However, it should be supported by experimental details. Hence the bond between atoms of two different elements is not purely covalent. It has certain percentage of ionic characteristics.

2.3.6 Factors affecting the magnitude of electronegativity

The electronegativity of an element varies slightly depending on the environment of the element, although it is invariably assumed to be a constant. Given below are four important factors that influence the electronegativity.

- **Hybridization**
  Higher the *s* character, greater the electronegativity.
  Electronegativity of C: $C(sp^3) < C(sp^2) < C(sp)$
  Hence, the electronegativity of carbon atoms in CH_4, C_2H_4 and C_2H_2 increases in the given order $CH_4 < C_2H_4 < C_2H_2$.
- **Charge**
  e.g.: electronegativity of N: $NH_2^- < NH_3 < NH_4^+$
  All nitrogen atoms are sp^3 hybridized, electronegativity $N^- < N < N^+$; Higher the positive charge on the atom, greater the electronegativity when compared to the neutral atom which in turn has a higher electronegativity than an atom with a negative charge.
- **Oxidation number**
  The hybridization of sulphur atom in H_2S, SO_3^{2-} and SO_4^{2-} species is sp^3 and the charge on sulphur atom is zero. The hybridization and the charge of the given three molecules are same. Therefore electronegativity of sulphur in the given species are determined by oxidation number of the sulphur atom in each species. The oxidation numbers on the sulphur atom of H_2S, SO_3^{2-} and SO_4^{2-} are -2, +4 and +6 respectively. The higher the positive charge, greater the electronegativity when compared to the neutral atom. Therefore the electronegativity of sulphur in $H_2S < SO_3^{2-} < SO_4^{2-}$

- **Nature of the other atoms to which the atom of interest is attached in the molecule**
  e.g.: Electronegativity of C in CF_4 is greater than that of CCl_4. Higher electronegativity of fluorine makes the carbon atom is attached to four fluorine atoms highly positive compared to the carbon atom attached to four chlorine atoms. This makes the carbon attached to fluorine to have a higher electronegativity.

In applying the above rules, when an atom of same element in different molecules, priority is always given for hybridization over the charge of the atom. If the hybridization is same, then the priority is given based on the charge of the atom. For an example, hybridization of nitrogen in NH_3 and NH_4^+ are the same. Hence, electronegativity of nitrogen atoms in these two forms is determined by the charge. Nitrogen atom of NH_3 is neutral and nitrogen atom of NH_4^+ is positive and hence nitrogen atom of NH_4^+ is more electronegative.

Likewise, if the hybridization and the charge are same, then the oxidation number can be considered. For an example, hybridization and charge in CH_3F and CH_4 are the same. The oxidation number of carbon in CH_3F is -2 and in CH_4 is -4. Therefore, the electronegativity can be determined based on the oxidation number of carbon atoms. The electronegativity of carbon in CH_3F which has higher oxidation number is higher than that of CH_4.

The effect of the other atoms to be considered when the hybridization, charge and oxidation number are same. For an example, electronegativity of carbon atom in $CHCl_3$ and CHF_3 can be compared with respect to the electronegativity of the atoms attached to the carbon atom. Hence, carbon atom of CHF_3, is more negative than that of $CHCl_3$.

2.4 Ionic bonds/ ionic interactions

Ionic bonds are created due to electrostatic attractive forces between positive and negative ions. These positive and negative ions are packed in a certain pattern called **'lattice structure'** in solid (crystalline) state. Here, each positive ion is surrounded by negatively charged ions and vice versa. In NaCl lattice, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions.

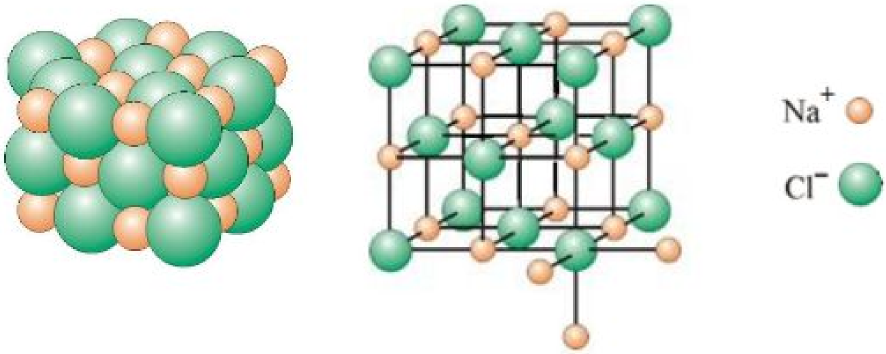
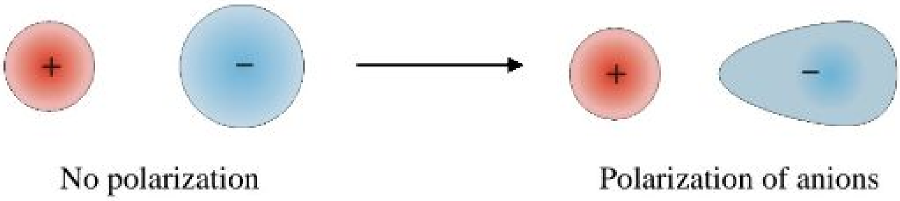
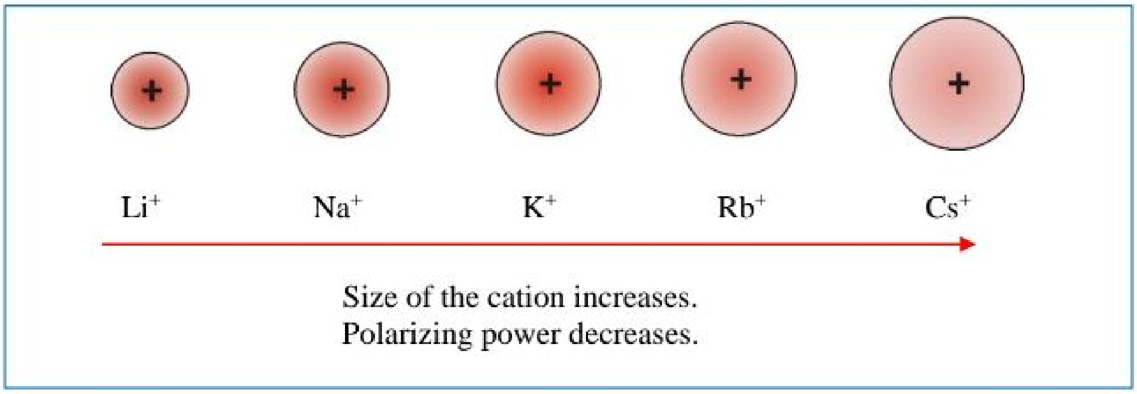


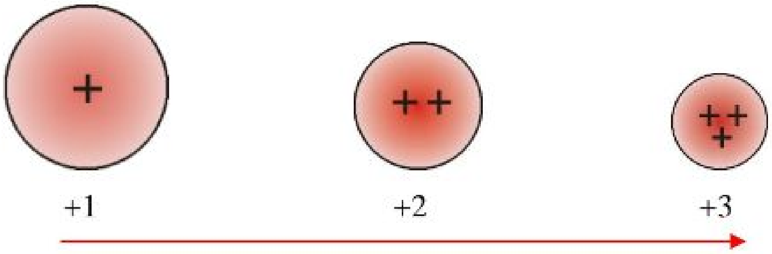
Figure 2.38 Lattice structure of NaCl

The cation is the smaller ion in an ionic lattice and its electron cloud is strongly bound to the nucleus. The anion is the large ion in an ionic lattice and hence has more loosely held outermost electrons compared to the cation. The shape of the electron cloud of an anion can easily be changed as a result of an external electric field. Large anions are more susceptible to a change in the shape of the electron cloud under the influence of an electrostatic attraction of cation. The field strength of a cation can pull the electron cloud of an anion. The ability of a cation to pull the electron cloud of an anion is called **polarizing power**. When a cation moves towards an anion, the tendency of the electron cloud of an anion to change its spherical shape, as a result of the positive field strength of the cation, is called **polarizability**.



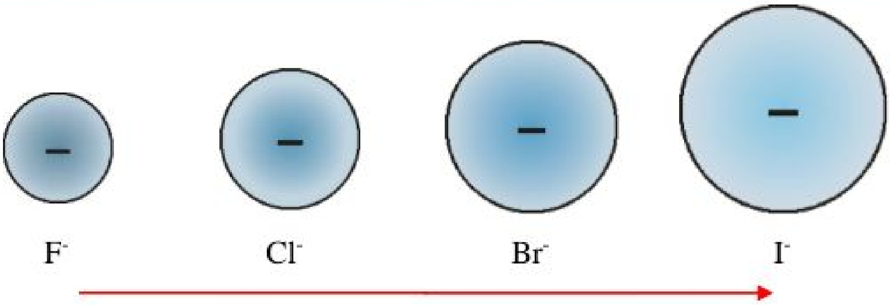
Cation has a strong polarizing power, if it is small and highly charged.



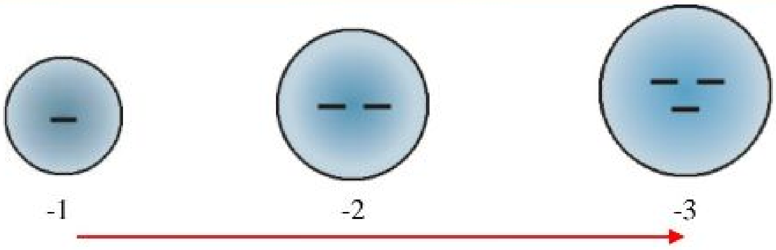


In isoelectronic species:

Charge of the cation increases.
Size of the cation decreases.
Charge density increases.
Polarizing power increases.



Size of the anion increases.
Polarizability increases.



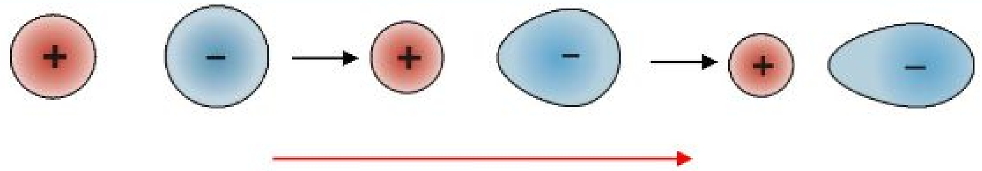
In isoelectronic species:

Charge of the anion increases.
Size of the anion increases.
Polorizability increases.

The degree of ionic character and covalent character of a bond depend on the polarization (polarizing power of the cation and polarizability of the anion).

Polarization is increased by:

- High charge and small size of the cation
- High charge and large size of the anion



Ionic characters decreases as polarization increases.
Covalent character increases.

2.5 Metallic bonds

In general, small molecules with simple covalent bonding exhibit relatively low melting points compared to ionic compounds. Ionic solids do not conduct electricity in the solid state but are capable of conducting electricity in the liquid (molten) state due to the mobility of ions. The melting point of different metals can be observed in a wide range and metals are excellent conductors of electricity and heat regardless of liquid or solid state. For example, melting point of mercury (Hg) is as low as -39 °C while tungsten (W) melts at 3410 ºC. Also, in nuclear reactions, liquid sodium is used as a coolant due to its heat transfer capacity. These differences in metals compared to ionic and covalent compounds cannot be explained using models of covalent or ionic bonding.

The model for metallic bonding was proposed by Paul Karl Ludwig Drude and Hendrik Lorentz based on the kinetic model on the behaviour of gases. According to this model, metal atoms are converted to positive ions donating electrons in the valance shell to form the metallic bond. Therefore, a massive electron cloud is created by valance electrons released by large number of atoms. This electron cloud is capable of overcoming repulsive forces among positively charged metal ions keeping them in a lattice. The entire arrangement of lattice structure in massive electron cloud including the electrostatic force between the electron cloud and positively charged metal ions (cations) is considered as metallic bond. In order to stabilize this lattice of positively charged metal ions and electrons are constantly moving in the lattice structure. The strength of a metallic bond is primarily dependent on three main factors.

- **Number of electrons donated by atoms to create the metallic bond**
  For example, sodium atom can donate one electron as it has one electron in the valance shell while, magnesium atom donates two electrons to the metallic bond. When the number of electrons donated by an atoms increases, the strength of the metallic bond is enhanced as well.

- **Ionic radius**
  When the radii of the cations increase, the density of the electron clouds decrease resulting in poor metallic bonds.
- **Ionic nature**
  This means the extent to which valance shell electrons are contributing towards the metallic bond. For example, sodium completely releases the electron on the valance shell to form the metallic bond. However, with increasing ionization energy, there is a less probability to release these electrons to form the metallic bond. This factor has almost no influence on alkaline metals and alkaline earth metals, but it is important when transition metal elements are considered.

2.6 Secondary interactions

All types of intermolecular interactions exist among molecules are known as secondary interactions. They are commonly referred as van der Waals interactions. Those interactions can be categorized into five types.

- Ion - dipole interactions
- Dipole - dipole interactions and hydrogen bonding
- Ion - induced dipole interactions
- Dipole - induced dipole interactions
- Dispersion interactions (London forces)

Van der Waals forces are the attractive or repulsive forces between molecular entities or between groups within the same molecular entity. It includes dipole – dipole interaction, dipole – induced dipole interactions and London forces.

Ion – dipole interactions

Ionic salts such as NaCl are soluble in water due to secondary interactions between positive ions and negative ions with water molecules. The cation in an ionic compound (e.g.: Na^+ in NaCl) interacts with a negatively polarized atom (δ-) in a molecule (O in water) and vice versa to establish ion-dipole interactions. Therefore, in an aqueous solution of NaCl, cations (Na^+) and anions (Cl^-) are surrounded by water molecules to achieve stability in an aqueous medium through these ion-dipole interactions.

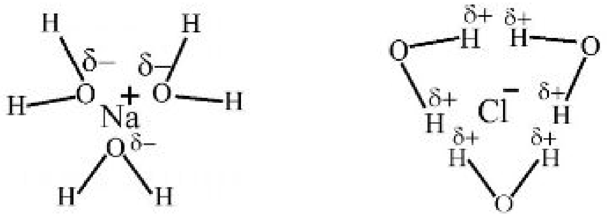


Figure 2.39 Ion dipole interactions formed between H_2O and ions of NaCl

Dipole – dipole interactions

Interactions among molecules with a permanent dipole moment are called **dipole – dipole interactions**. It is clearly illustrated as a model by Figure 2.40. The strength of these attractive forces are generally ranged between 0.5 – 15 kJ mol^{-1}.

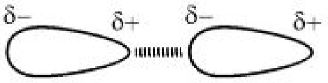


Figure 2.40 Dipole – dipole interactions

Attractive forces between two opposite poles (δ$^+$ and δ$^-$) of polar molecule can be more specifically called dipole–dipole interactions. Interactions between two formaldehyde molecules can be taken as an example for dipole – dipole interactions.

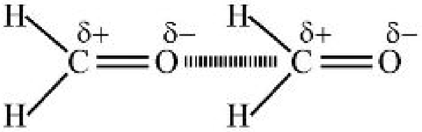


Figure 2.41 Dipole – dipole interactions in formaldehyde

Hydrogen bonding

This is a type of dipole-dipole interactions, some of hydrogen bonds are stronger than the other kinds of dipole–dipole interactions (0.5 – 15 kJ mol^{-1}). In general, the strength of hydrogen bonds range between 4 - 40 kJ mol^{-1}.

When a hydrogen atom is bonded to a N, O or F atom, the partial positive charge on hydrogen atom (*δ*+) is much higher compared to the bonding with other atoms. The reason is the relatively higher electronegativity difference between hydrogen and these electronegative atoms (N, O, F). Since hydrogen is a smaller atom, a strong electrostatic field is available. When it has an electrostatic interaction between a hydrogen atom with a partial positive charge (δ+) and an electronegative atom (N, O, F) with a partial negative charge (δ-) is called a **hydrogen bond**. It is not necessary that the electronegative atom with (*δ*-) is bonded to a hydrogen atom (H-O, H-N, H-F), but could be any other atom. (e.g.: Hydrogen bonding between H atom of $CHCl_3$ and O atom of acetone).

In the Figure 2.42, one water molecule is bonded to another water molecule forming hydrogen bonds. Examples for hydrogen bonds formed between same molecules are H_2O and NH_3.

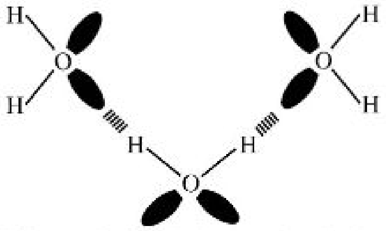


Figure 2.42 Hydrogen bonds in water

The model of polarity could be matched with the behaviour and the properties of molecular substance, e.g.: water. Ice floats on water since it is about 9% less dense than liquid water. As the thermal energy of water is removed by cooling, kinetic energy of molecules decreases freezing water to ice at 0 ^{0}C. Lowering of kinetic energy of water molecules leads to increase the number of hydrogen bonds around each water molecule. Water molecules become compact in a regular order since each of the water molecule forms maximum number of hydrogen bonds with the nearby water molecules when the kinetic energy is lowered by cooling it to 0 ^{0}C.

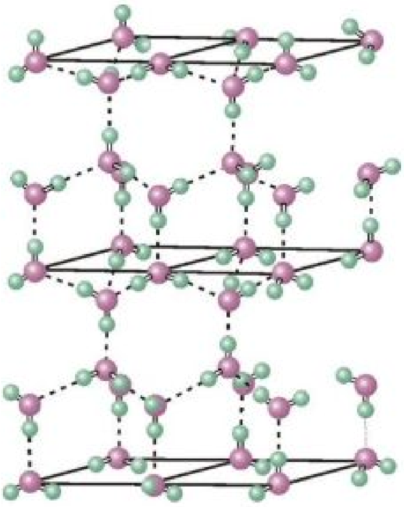


Figure 2.43 Arrangement of H_2O molecules in ice

Each water molecule can form two hydrogen bonds using the two hydrogen atoms and it can form another two hydrogen bonds by attracting two hydrogen atoms of adjacent water molecules using two lone pairs of electrons on the oxygen atom. These four hydrogen bonds at 0 ^{0}C lead to a compact tetrahedral arrangement around each water molecule. The arrangement of water molecules in a regular ordered state of ice occupies 9% more space than the free space of liquid water. There are number of crystal structures of ice and the nature of the crystal structures depends on the condition of cooling.

However, hydrogen bonds can also be formed as intermolecular interactions among different molecules. Hydrogen bonding present in a mixture of acetone and water clearly illustrates this.

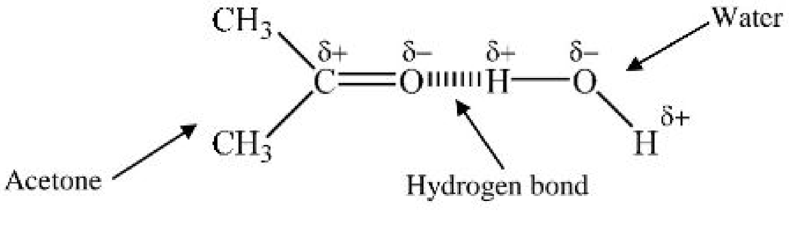


Figure 2.44 Hydrogen bonds in acetone/ water mixture

Hydrogen bonding in acetic acid is possible between the hydrogen atom in the carboxylic group and the oxygen atom in the carbonyl group (C=O) of the carboxylic acid group as indicated below. The electronegative atom with (δ-) charge is not necessarily bonded to hydrogen. It shows that the presence of required degree of polarity at H atom and the other electronegative atoms (O, N, F) is important, in order to form hydrogen bonding.

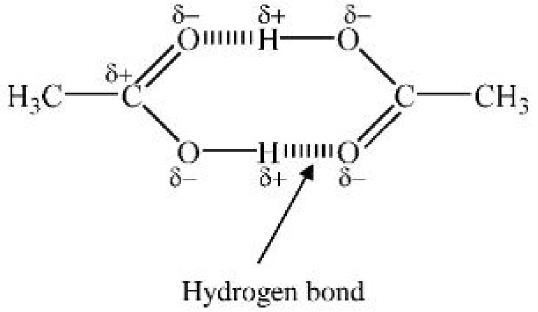
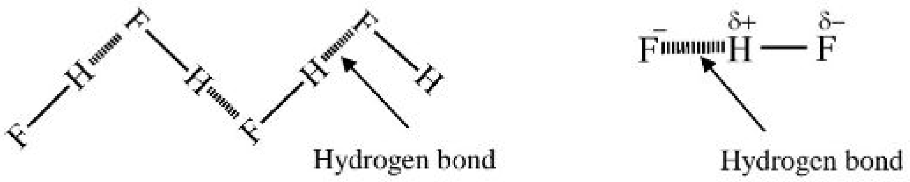


Figure 2.45 Hydrogen bonds in acetic acid

Hydrogen bonds, are present in pure HF. The Figure 2.46 (a) below shows the arrangement of HF molecules in pure HF. In the case of a solution of a mixture of HF and F^-, hydrogen bonds can form between F^- ions and $\delta+$ charged hydrogen atoms in HF molecules (b).



(a) (b)

Figure 2.46 (a) Hydrogen bonds in HF, (b) H bonds in NaF and HF mixture

When hydrogen bonding is present between two molecules then it is called **inter-molecular hydrogen bond** while hydrogen bonding is present between a hydrogen atom and an electronegative atom of the same molecule it is called **intra-molecular hydrogen bond.** The hydrogen bonding present in *ortho*-nitrophenol and *para*-nitrophenol are given below in Figure 2.47 to illustrate the difference between inter-molecular and intra-molecular hydrogen bonding.

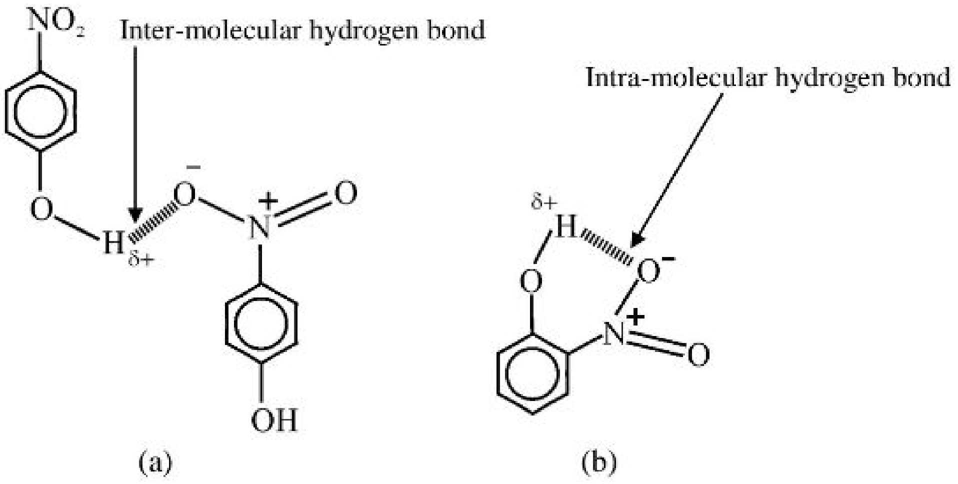


Figure 2.47 Hydrogen bonds in (a) *ortho*-nitrophenol and (b) *para*-nitrophenol

In certain cases, possibility of having hydrogen bond is defined (the strength of a hydrogen bond is less) when the electronegative atom is Cl. Therefore there is another rule including Cl as well. It is called FONCl rule. In general, stronger hydrogen bonds are observed between a polarized hydrogen atom (δ+) and polarized F, O or N atom (δ-).

Ion – induced dipole interactions

Iodine (I_2) is a non-polar molecule which is slightly soluble in water. However, iodine in solid state can be dissolved in an aqueous KI solution. This observation can only be explained with ion –induced dipole interactions. In this case, interaction of an iodide ion (I^-) can induce a dipole on an iodine molecule. The positive pole of induced dipole interacts with I^- ion to combine I_2 molecule in order to form the I_3^- ion. Hence, I_2 dissolves in KI solution.

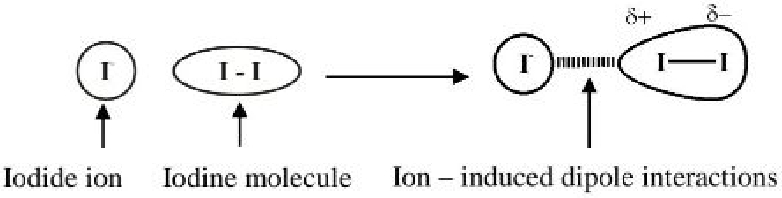


Figure 2.48 Ion –induced dipole interactions

Therefore, ion – induced dipole interactions can make iodine soluble in an aqueous KI solution.

Dipole – induced dipole interaction

This is a weak attractive force that results when a polar molecule induces a dipole in an atom or a nonpolar molecule. The polarization of outer electron cloud of atom or nonpolar molecule takes place as a result of the impact of electrostatic force of the dipole of the polar molecule.

This interaction energy is proportional to 1/ r^6 where "r" is the distance between two molecules. The magnitude of dipole moment of induced dipole depends upon polarizability of nonpolar molecule or atom and the magnitude of the dipole moment of the polar molecule. The interaction between HCl molecule and Ar atom is one example.

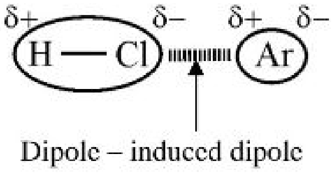


Figure 2.49 Dipole – induced dipole interactions

London interactions (forces) (Instantaneous induced dipole – induced dipole interaction)

Non polar molecules are held together by weak interactions. These interactions are also present in gas, liquid and solid states of inert elements and these weak interactions are called **London forces**. Though the molecule is non-polar, due to continuous movement of electrons, regions of relatively high and low electron densities are created instantaneously. However, location of these two poles can instantaneously change in the next moment. Interaction between a momentarily polarized dipole of a molecule with an oppositely charged such a dipole of another molecule (δ^{+}--- δ^{-}) is a London interactions. They are also called dispersion forces. Molecule has a high probability for forming London interaction when the surface area of the molecule is large. The net strength of interaction between two molecules is significant as they have relatively large surface areas.

London forces exist among all the atoms and molecules irrespective of whether they are polar or non-polar. In determining physical properties of molecules having larger molecular weights, dispersion forces are likely to be more important than dipole – dipole forces exist between them. London forces are the dominant interactions in order to compact the iodine molecules in solid state.

Compacting of iodine molecules in solid state

Iodine is a nonpolar molecule and solid state of iodine is considered to be a molecular crystal. Iodine molecule is a heavy molecule having a large size. Thermal energy at room temperature is not sufficient for molecular movement of iodine molecules in the solid state. London forces hold these molecules in an orderly arrangement in the solid state. Large surface area of the I_2 molecule creates London forces with neighbouring molecules giving rise to a molecular lattice structure. Since I_2 molecules are nonpolar, solubility of iodine is greater in non-polar solvents than in polar solvents.

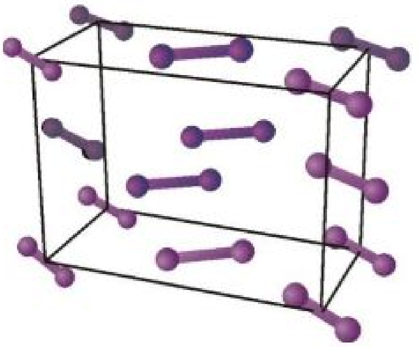


Figure 2.50 Lattice structure of iodine

The following chart shows the variation of boiling points of some simple molecules. The variation of boiling points can be explained using the dipole moment and intermolecular forces.

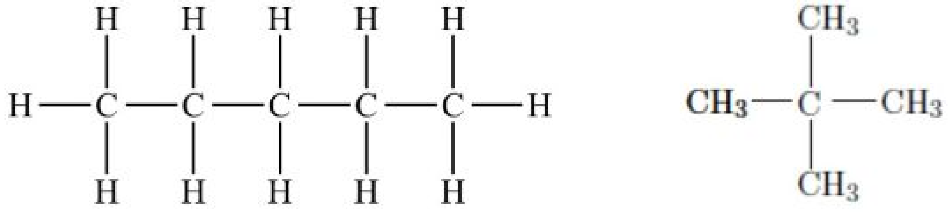
Table 2.7 Variation of boiling points of some simple molecules with dipole moment

Molecule	Molar mass/ g mol^{-1}	Dipole moment/ D	Boiling point/ ^{0}C	Type of dominant interaction
O_2	32	0	-183	London
NO	30	0.153	-152	Dipole-dipole
Kr	83.8	0	-152	London
HBr	81	0.82	-62	Dipole-dipole
Br_2	160	0	59	London
ICl	162.5	1.6	97	Dipole- dipole

Molar masses of NO and O_2 are comparable but boiling point of NO is greater than O_2. Hence, the relative strength of inter molecular interaction forces among NO molecules should be greater than the intermolecular interaction strength among O_2 molecules. The model of dipole moment and polarity of molecule can be used to explain this observation. NO is a molecule with atoms of different electronegativity and hence, it is a polar molecule having a dipole moment (0.153 D). Oxygen molecule is a nonpolar molecule with zero dipole moment. Polar NO has dipole–dipole attractions among the molecules. Nonpolar oxygen molecules have relatively weak London interactions. Hence, liquid NO needs more energy than liquid oxygen in order to break the intermolecular interactions in the liquid state.

Molecules of bromine (Br_2) and iodine monochloride (ICl) are isoelectronic. Bromine molecules are non-polar and liquid Br_2 boils at 59 ^{0}C. ICl consists of polar molecules and boils at 97 ^{0}C almost 40 ^{0}C higher. The boiling point indicates that intermolecular forces among ICl molecules are stronger than those of Br_2. Any substance with strong dipole-dipole forces has to absorb substantially more energy to melt and boil.

The net strength of intermolecular attraction also depends on the molecular shape. Electrons in elongated molecules are easily polarized or distorted. For example, *n*-pentane boils at 36 ^{0}C, whereas *neo*-pentane boils at 9 ^{0}C. Boiling points increase with increasing attraction among molecules. Hence the London forces in *n*- pentane are stronger than those in *neo*-pentane. This is because the spherical shape of *neo*-pentane molecule and the valence electrons in C-C bonds are well shielded from the CH_3 groups whereas *n*-pentane is chain shaped so that valence electrons in C-C bonds are more exposed in order to form London interaction.



(a) (b)

Figure 2.51 Structure of (a) *n*-pentane and (b) *neo*-pentane