

Inorganic Chemistry

M.S.C. / First Semester

(5) Lecturer

2020-2021




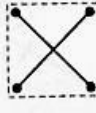



Pro .Dr. Mohammed Hamid

=====

HYBRIDIZATION:-

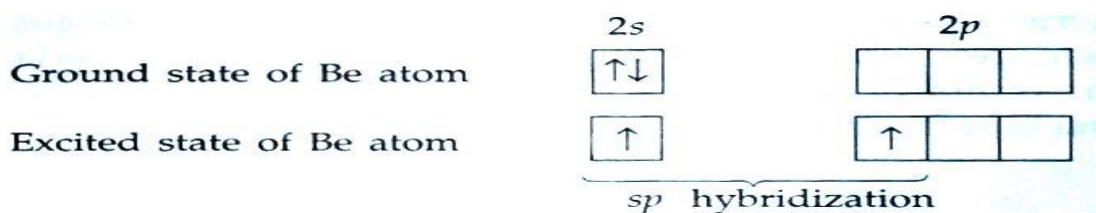
The valence bond theory (overlapping concept) explains satisfactorily the formation of various molecules but it fails to account the geometry and shapes of various molecules. It does not give explanation why BeCl_2 is linear, BF_3 is planar. CH_4 is tetrahedral, NH_3 is pyramidal and water is V-shaped molecule. In order to explain these cases, the valence bond theory has been supplemented by the concept of hybridization. This is a hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called **hybrid orbitals**. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as **hybridization**. The following are the rules of hybridization:

- (i) Only orbitals (atomic) of nearly same energy belonging to same atom or ion can take part in hybridization.
- (ii) Number of the hybrid orbitals formed is always equal to number of atomic orbitals which have taken part in the process of hybridization.
- (iii) Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They may differ from one another in orientation in space.
- (iv) Actually the orbitals which undergo hybridization and not the electrons. For example, for orbitals of nitrogen atom ($2s^2 2p_x^1 2p_y^1 2p_z^1$) belonging to valency shell when hybridize, form four hybrid orbitals, one of which has two electrons (as before) and other three have one electron each.
- (v) The electron waves in hybrid orbitals repel each other and this tend to the farthest apart.
- (vi) Hybrid orbitals form only sigma bonds.
- (vii) Depending on the number and nature of orbitals undergoing hybridization, various types of hybrid orbitals directing towards the corners of specified geometrical figures come into existence. The molecule has a **regular geometry** if all the hybrid orbitals after overlapping contain shared pair of electrons, i.e., there are no orbitals containing lone pairs in the valency shell. If, however, the central atom is surrounded by one or more orbitals containing lone pairs of electrons in the valency shell, the geometry of the molecule is distorted to some extent. Thus, the presence of one or more orbitals with lone pairs affect the bond angle to some extent due to repulsion between lone pair (pairs) with bonded (pairs). This type of observation has been made, for example, in the molecules of ammonia and water. The following table shows the type of hybridization and the geometry of the molecules containing only bond pairs of electrons.

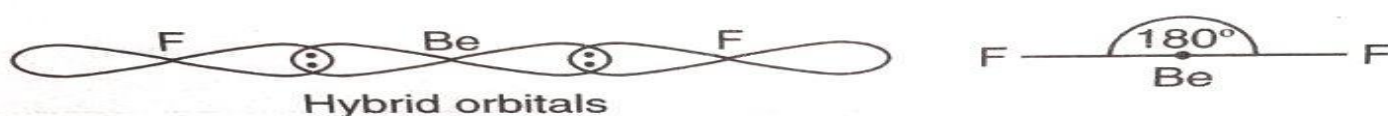
No. of atomic orbitals involved in hybridization	Type of hybridization	No. of hybrid orbitals	Shape of molecules	Bond angles	Examples	
2	sp ($s + p$)	2	Linear		180°	$\text{BeCl}_2, \text{BeF}_2$
3	sp^2 ($s + p + p$)	3	Plane triangular		120°	$\text{BF}_3, \text{BCl}_3$
4	sp^3 ($s + p + p + p$)	4	Tetrahedral		$109^\circ 28'$	$\text{CH}_4, \text{CCl}_4$
4	dsp^2 one 'd' ($d_{x^2-y^2}$) + one 's' + two 'p'	4	Square planar		90°	$[\text{Ni}(\text{CN})_4]^{2-}, [\text{PtCl}_4]^{2-}$
5	dsp^3 or sp^3d one 's' + three 'p' + one d (d_{z^2})	5	Trigonal bipyramid		120° and 90°	PCl_5
6	d^2sp^3 or sp^3d^2 one 's' + three 'p' + two 'd' ($d_{x^2-y^2}, d_{z^2}$)	6	Octahedral		90°	SF_6
7	d^3sp^3 or sp^3d^3 one 's' + three 'p' + three 'd' (d_{xy}, d_{yz}, d_{zx})	7	Pentagonal bipyramid		72° and 90°	IF_7

Some Typical Cases of Hybridization

(i) **BeF₂ molecule** : Beryllium atom has the configuration $1s^2, 2s^2$. Since there are no unpaired electrons in the valency shell, it cannot form any covalent bond. Thus, $2s$ -orbital is first unpaired and an electron is shifted to $2p$ -orbital.



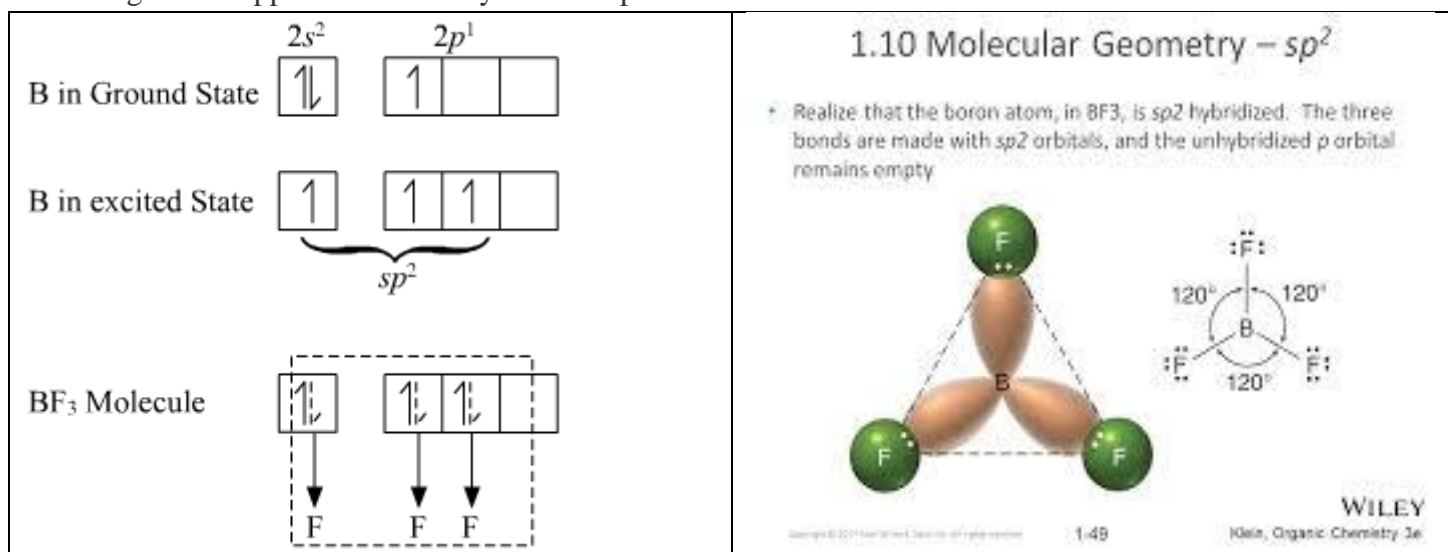
Now, there is hybridization between one s - and one p -orbital. Two orbitals (hybrid) of same shape and energy come into existence. These overlap with p -orbital (singly occupied) each of the two fluorine atoms forming two sigma bonds. The molecule formed is linear with a bond angle 180° .



Formation of BeF₂ Molecule

Hybridization of BF₃ (Boron Trifluoride)

BF₃ has a boron atom with three outer-shell electrons in its ground state and three fluorine atoms containing seven outer electrons. Further, if we observe closely, one boron electron is unpaired in the ground state. During the formation of this compound, the 2s orbital and two 2p orbitals hybridize. Only one of the empty p-orbital is left behind as the lone pair. In short, Boron needs 3 hybridized orbitals to make bonds with 3 atoms of F where the 2p_z orbitals get overlapped with these hybridized sp² orbitals and bonds are formed.



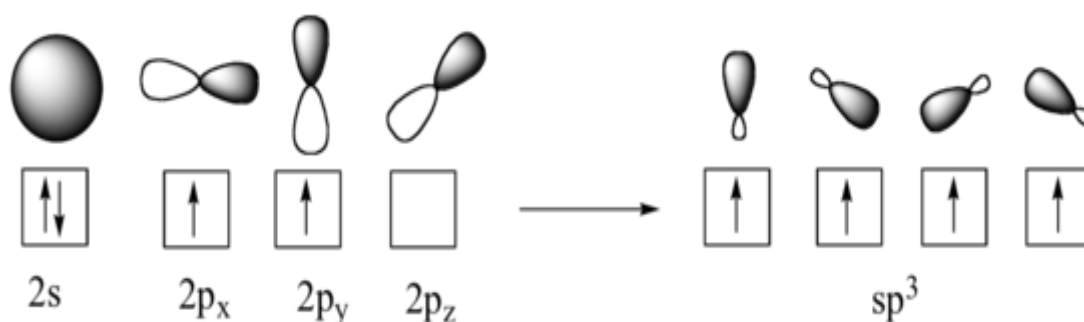
Important Points to Remember

- The three hybridized sp² orbitals are usually arranged in a triangular shape.
- BF₃ molecule is formed by bonding between three sp² orbitals of B and p of 3 F atoms.
- All the bonds in BF₃ are sigma bonds.

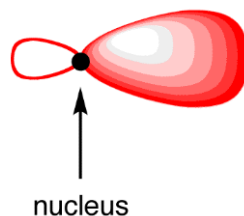
Hybridization of CH₄ (Methane)

In order to understand the hybridization of CH₄ (methane), we have to take a look at the atomic orbitals which are of different shape and energy that take part in the process. The type of hybridization involved with CH₄ is sp³. We will discuss in detail how this hybridization occurs below.

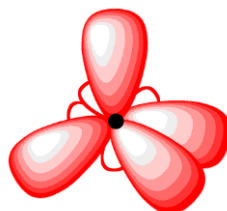
In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2s and three 2p orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named **sp³ orbitals** because they are formed from mixing one s and three p orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp³ orbital creating four unpaired electrons.



The shape of an sp³ hybridized orbital is a combination of s and p atomic orbitals.



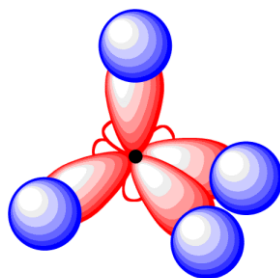
Each sp^3 -hybridized orbital bears an electron, and electrons repel each other. To minimize the repulsion between electrons, the four sp^3 -hybridized orbitals arrange themselves around the carbon nucleus so that they are as far away as possible from each other, resulting in the tetrahedral arrangement predicted by VSEPR. The carbon atom in methane is called an “ sp^3 -hybridized carbon atom.” The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5° .



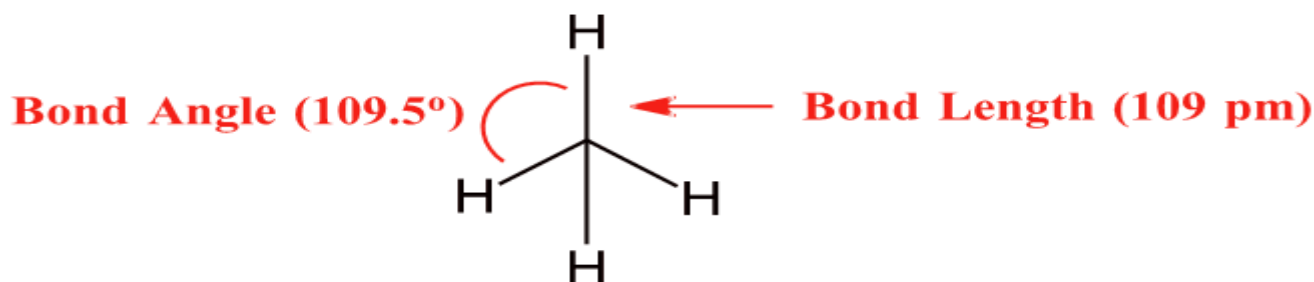
Bonding in Methane

Each C-H bond in methane, then, can be described as an overlap between a half-filled $1s$ orbital in four hydrogen atoms and the larger lobe of one of the four half-filled sp^3 hybrid orbitals form a four equivalent sigma (σ) bond. This orbital overlap is often described using the notation: $sp^3(\text{C})-1s(\text{H})$. The formation of sp^3 hybrid orbitals successfully explains the tetrahedral structure of methane and the equivalency of the the four C-H bonds.

What remains is an explanation of why the sp^3 hybrid orbitals form. When the s and 3 p orbitals in carbon hybridize the resulting sp^3 hybrid orbital is unsymmetrical with one lobe larger than the other. This means the larger lobe can overlap more effectively with orbitals from other bonds making them stronger. Hybridizing allows for the carbon to form stronger bonds than it would with unhybridized s or p orbitals.

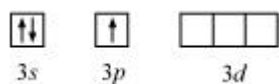


The four carbon-hydrogen bonds in methane are equivalent and all have a bond length of 109 pm (1.09×10^{-10} m), bond strength of of 429 kJ/mol. All of the H-C-H bond angles are 109.5° .

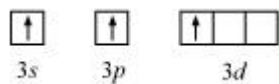


Hybridization of PCl_5

Atomic number of Phosphorous is 15, The Ground state configuration is

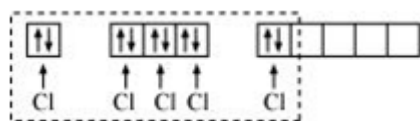


& the excited state configuration is

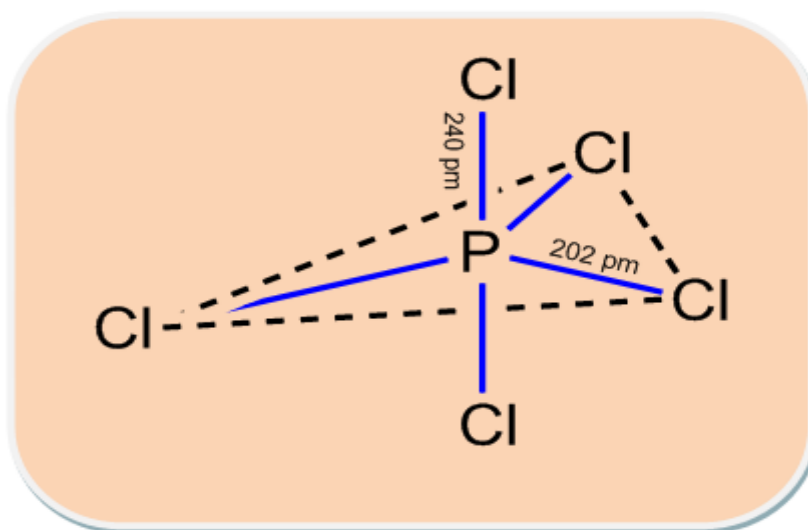


The 5 electrons present in valence shell form bond pairs with the electrons of five chlorine atoms. Phosphorus atom is sp^3d hybridized in the excited state.

PCl_5



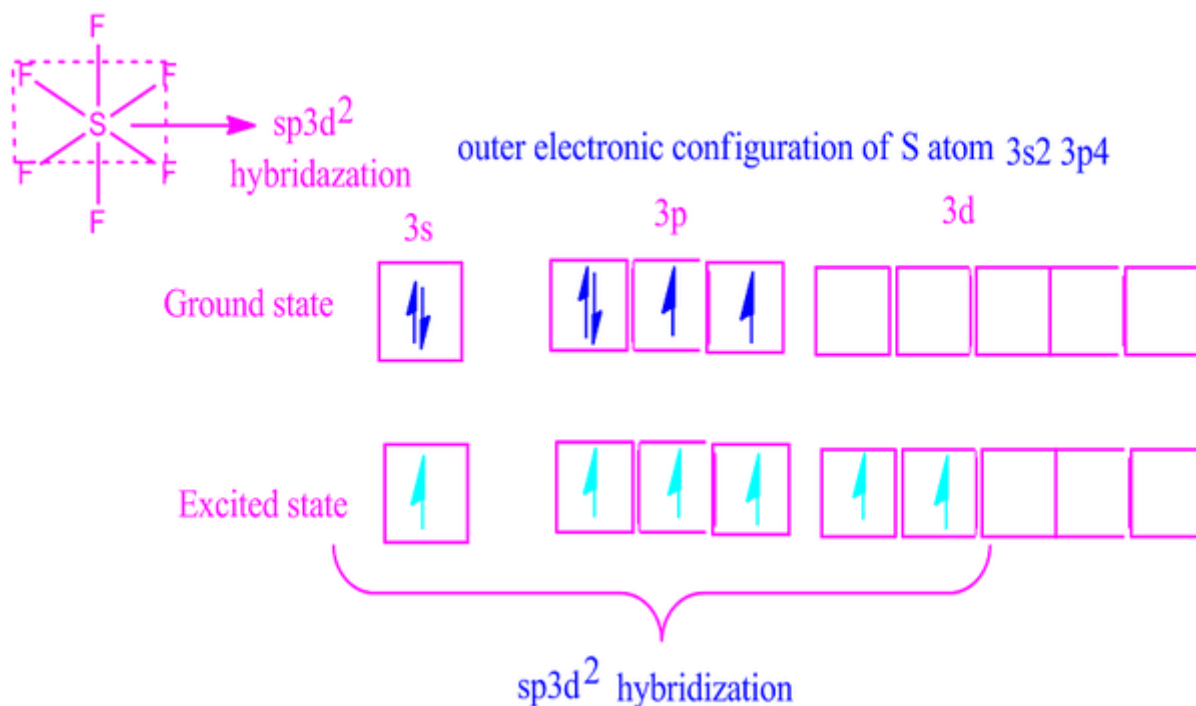
The geometry of PCl_5 is trigonal bipyramidal. The P atom lies in the centre of an equatorial triangle & three P-Cl bonds (equatorial bonds) are directed towards its three corners with 120° bond angle. The remaining two P-Cl bonds (axial bonds) lie above & below the plane of the triangle at bond angle 90° .



The axial bonds are longer than equatorial bonds because the axial Cl atoms suffer from more repulsion than the equatorial Cl atoms, as a result the axial Cl atoms try to reside far away from the equatorial Cl atoms, & hence axial bonds are longer than equatorial bonds.

Hybridization of SF_6

The outer electronic configuration of S atom is $3s^2, 3p^4$. It has also vacant 3d orbital. In excited state by absorbing energy one 3s and one 3p electron shifted to 3d_{xy} and 3d_{yz} orbital. As a result, the number of unpaired electrons is six. Now one S, three P and two 'd' orbitals mixed and form six equivalent new orbitals, each called sp^3d^2 hybridized orbital. So in SF_6 , the hybridization of 'S' is sp^3d^2 .



Geometry of molecules containing lone pairs of electrons

When we travel, we often take a lot more stuff than we need. Trying to fit it all in a suitcase can be a real challenge. We may have to repack or just squeeze it all in. Atoms often have to rearrange where the electrons are in order to create a more stable structure.

Central Atom with One or More Lone Pairs

The molecular geometries of molecules change when the central atom has one or more lone pairs of electrons. The total number of electron pairs, both bonding pairs and lone pairs, leads to what is called the **electron domain geometry**. When one or more of the bonding pairs of electrons is replaced with a lone pair, the molecular geometry (actual shape) of the molecule is altered. In keeping with the A and B symbols established in the previous section, we will use E to represent a lone pair on the central atom (A). A subscript will be used when there is more than one lone pair. Lone pairs on the surrounding atoms (B) do not affect the geometry.

AB₃E: Ammonia, NH₃

The ammonia molecule contains three single bonds and one lone pair on the central nitrogen atom (see figure below).

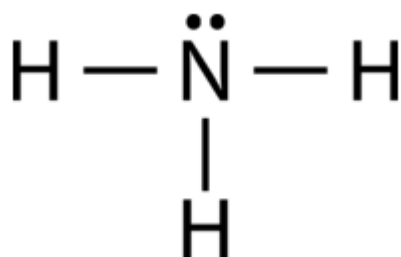


Figure : Lone pair electrons in ammonia.

The domain geometry for a molecule with four electron pairs is tetrahedral, as was seen with CH₄. In the ammonia molecule, one of the electron pairs is a lone pair rather than a bonding pair. The molecular geometry of NH₃ is called trigonal pyramidal (see figure below).

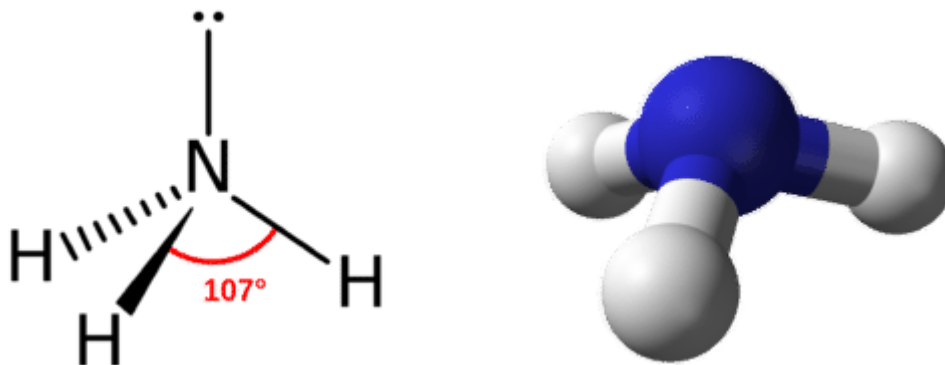


Figure : Ammonia molecule.

Recall that the bond angle in the tetrahedral CH_4 molecule is 109.5° . Again, the replacement of one of the bonded electron pairs with a lone pair compresses the angle slightly. The H-N-H angle is approximately 107° .

AB2E2: Water, H_2O

A water molecule consists of two bonding pairs and two lone pairs (see figure below).

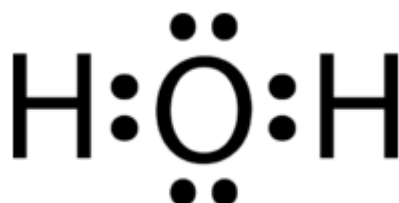


Figure : Lone pair electrons on water.

As for methane and ammonia, the domain geometry for a molecule with four electron pairs is tetrahedral. In the water molecule, two of the electron pairs are lone pairs rather than bonding pairs. The molecular geometry of the water molecule is bent. The H-O-H bond angle is 104.5° , which is smaller than the bond angle in NH_3 (see figure below).

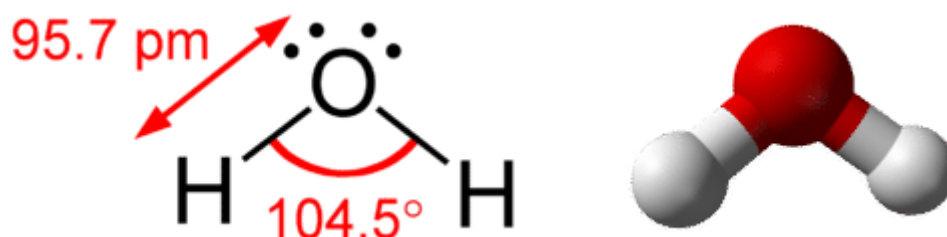


Figure : Water molecule.

AB4E: Sulfur Tetrafluoride, SF_4

The Lewis structure for SF_4 contains four single bonds and a lone pair on the sulfur atom (see figure below).

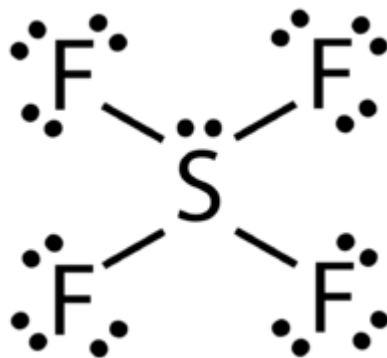


Figure : Lone pair electrons in SF₄.

The sulfur atom has five electron groups around it, which corresponds to the trigonal bipyramidal domain geometry, as in PCl₅PCl₅ (see figure below). Recall that the trigonal bipyramidal geometry has three equatorial atoms and two axial atoms attached to the central atom. Because of the greater repulsion of a lone pair, it is one of the equatorial atoms that are replaced by a lone pair. The geometry of the molecule is called a distorted tetrahedron or seesaw.

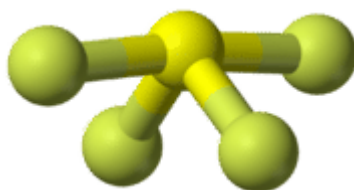


Figure : Ball and stick model for SF₄

Table Geometries in Which the Central Atom Has One or More Lone Pairs					
Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Electron Domain Geometry	Molecular Geometry	Examples
3	2	1	Trigonal Planar	Bent	O ₃
4	3	1	Tetrahedral	Trigonal Pyramidal	NH ₃
4	2	2	Tetrahedral	Bent	H ₂ O
5	4	1	Trigonal Bipyramidal	Distorted Tetrahedron (Seesaw)	SF ₄
5	3	2	Trigonal Bipyramidal	T-shaped	ClF ₃
5	2	3	Trigonal Bipyramidal	Linear	I ₃ ⁻
6	5	1	Octahedral	Square Pyramidal	BrF ₅
6	4	2	Octahedral	Square Planar	XeF ₄

- The presence of lone pair electrons influences the three-dimensional shape of the molecule.

Geometry of molecules involving sigma and pi bonds:-

Our minds can handle two electrons interacting with one another in a sphere of space. But then we start putting in double bonds and triple bonds. The way we draw these bonds suggests we are squeezing more electrons into the same space, and that doesn't work. Electrons don't like to be pushed together (especially since they all have negative charges that repel one another). So we need a more complex picture that works for all these electrons. The hybridization model helps explain molecules with double or triple bonds (see figure below). Ethene (C_2H_4) contains a double covalent bond between the two carbon atoms and single bonds between the carbon atoms and the hydrogen atoms. The entire molecule is planar.

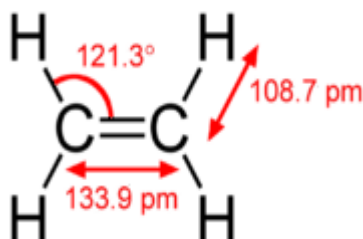


Figure : Geometry of ethene molecule.

As can be seen in the figure below, the electron domain geometry around *each* carbon independently is trigonal planar. This corresponds to sp^2 hybridization. Previously, we saw carbon undergo sp^3 hybridization in a CH_4 molecule, so the electron promotion is the same for ethene, but the hybridization occurs only between the single s orbital and two of the three p orbitals. Thus generates a set of three sp^2 hybrids along with an unhybridized $2p_z$ orbital. Each contains one electron and so is capable of forming a covalent bond.

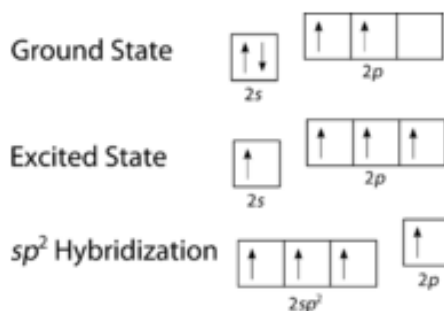


Figure : Hybridization in ethene.

The three sp^2 hybrid orbitals lie in one plane, while the unhybridized $2p_z$ orbital is oriented perpendicular to that plane. The bonding in C_2H_4 is explained as follows. One of the three sp^2 hybrids forms a bond by overlapping with the identical hybrid orbital on the other carbon atom. The remaining two hybrid orbitals form bonds by overlapping with the $1s$ orbital of a hydrogen atom. Finally, the $2p_z$ orbitals on each carbon atom form another bond by overlapping with one another sideways.

It is necessary to distinguish between the two types of covalent bonds in a C_2H_4 molecule. A **sigma bond** (σ bond) is a bond formed by the overlap of orbitals in an end-to-end fashion, with the electron density concentrated between the nuclei of the bonding atoms. A **pi bond** (π bond) is a bond formed by the overlap of orbitals in a side-by-side fashion with the electron density concentrated above and below the plane of the nuclei of the bonding atoms. The figure below shows the two types of bonding in C_2H_4 . The sp^2 hybrid orbitals are purple and the p_z orbital is blue. Three sigma bonds are formed from each carbon atom for a total of six sigma bonds total in the molecule. The pi bond is the "second" bond of the double bonds between the carbon atoms and is shown as an elongated green lobe that extends both above and below the plane of the molecule. This plane contains the six atoms and all of the sigma bonds.

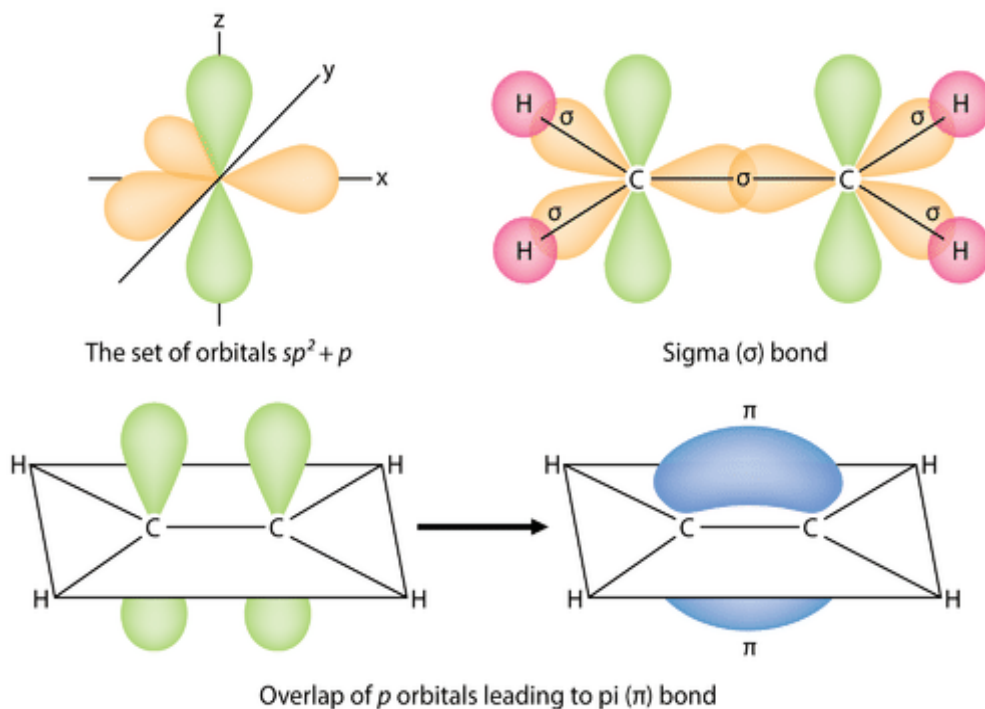


Figure : Sigma and pi bonds.

In a conventional Lewis electron-dot structure, a double bond is shown as a double dash between the atoms as in $C=C$. It is important to realize, however, that the two bonds are different: one is a sigma bond, while the other is a pi bond.

Ethyne (C_2H_2) is a linear molecule with a triple bond between the two carbon atoms (see figure below). The hybridization is therefore sp .



Figure : Ethyne structure.

The promotion of an electron in the carbon atom occurs in the same way. However, the hybridization now involves only the $2s$ orbital and the $2p_x$ orbital, leaving the $2p_y$ and $2p_z$ orbitals unhybridized.

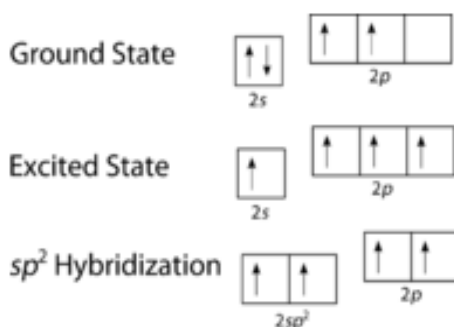


Figure : Hybridization in ethyne.

The sp hybrid orbitals form a sigma bond between each other as well as sigma bonds to the hydrogen atoms. Both the p_y and the p_z orbitals on each carbon atom form pi bonds between each other. As with ethene, these side-to-side overlaps are above and below the plane of the molecule. The orientation of the two pi bonds is that they are perpendicular to one another (see figure below). One pi bond is above and below the line of the molecule as shown, while the other is in front of and behind the page.

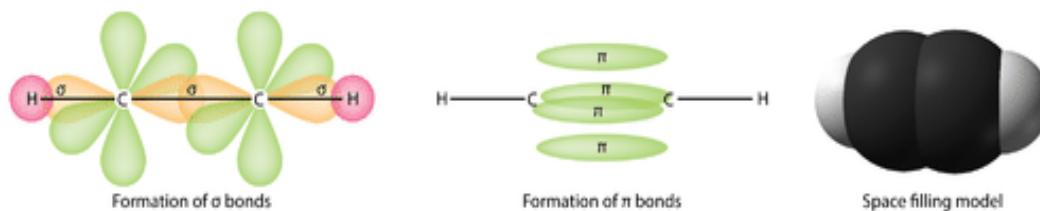
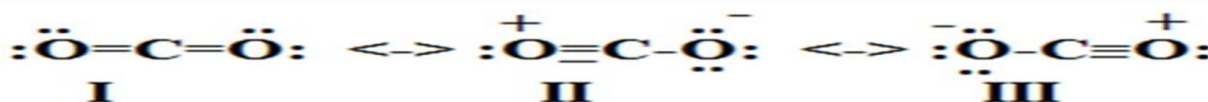


Figure : The C_2H_2 molecule contains a triple bond between the two carbon atoms, one of which is a sigma bond, and two of which are pi bonds.

In general, single bonds between atoms are always sigma bonds. Double bonds are comprised of one sigma and one pi bond. Triple bonds are comprised of one sigma bond and two pi bonds.

Resonance:-

It is generally observed that a single valence bond structure of a molecule cannot correctly account for the properties of the molecule. In such cases, the concept of resonance is introduced. **According to this concept if two or more alternate valence bond structures can be written for a molecule, the actual structure is said to be a resonance or mesomeric hybrid of all these alternate structures.** For example, carbon dioxide molecule can be represented by the following three structures:

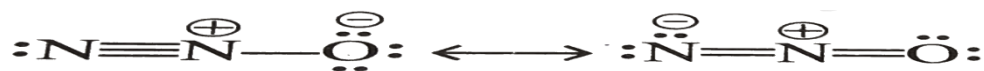


The calculated values of bond distances between carbon and oxygen in $C=O$ and $C\equiv O$ are 1.22 \AA^0 and 1.10 \AA^0 , respectively but the observed bond distance between carbon and oxygen in carbon dioxide is 1.15 \AA^0 . Thus, none of the above structures correctly explains the observed bond length. It is, thus, said that a hybrid form of these structures can provide the exact explanation. The various structures of which the molecule is a resonance hybrid are known as canonical forms or mesomeric forms. **Actually resonance hybrid does not oscillate between the canonical forms of a mixture of these forms but it is a definite form and has definite structure which cannot be written on paper.**

Rules for Selecting Canonical Forms or Mesomeric Forms :

- The relative position of all the atoms in each of the canonical forms must be the same. They should differ only in the position of electrons,
- The number of unpaired and paired electrons in each of the canonical forms must be same.
- The contributing structures should not differ much in energy.
- The contributing structures should be such that negative charge resides on more electronegative and positive charge on the electropositive. Like charges should not reside on atoms close together in the canonical forms.

Formal charges on the atoms in the molecule help us in choosing the most appropriate resonance structure. For example, nitrous oxide molecule is represented by two resonance electron dot structures, one of which has a negative formal charge on the oxygen atom and the other of which has a negative charge on the terminal nitrogen atom.

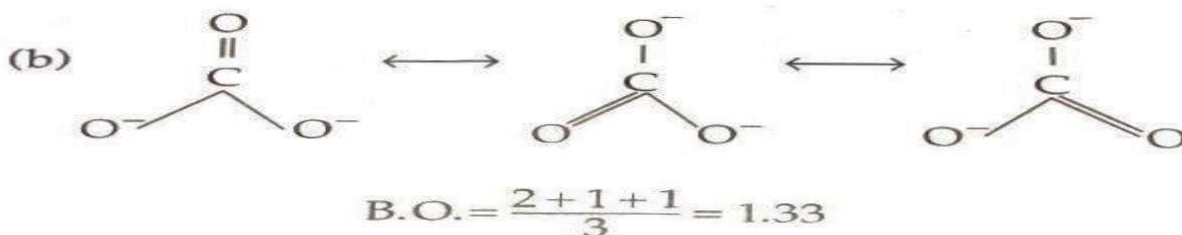


Since oxygen is a more electronegative element than nitrogen, the structure that places a negative formal charge on oxygen is probably lower in energy than the structure that has a negative formal charge on nitrogen. Thus, the actual structure of N_2O is :structure 1



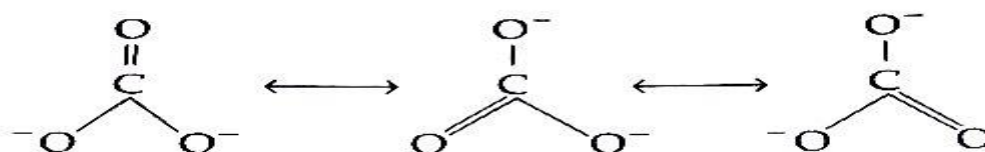
- As a result of resonance, the bond order changes in many molecules or ions.

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$

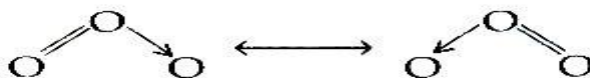


Some Examples Showing Resonance

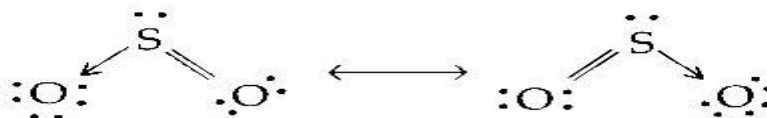
(iii) Carbonate ion : It is the resonance hybrid of the following forms:



(iv) Ozone :



(v) SO₂ molecule :



PREDICTION OF GEOMETRY (SHAPE) OF COVALENT MOLECULES

Geometry of a molecule or ion can be predicted if the state of hybridization at central atom is known. The type of hybridization can be known by the following methods:

First Method: The state of hybridization at central atom in a molecule can be known by counting the number of orbitals involved in co-axial overlappings and the number of orbitals with lone pair of electrons, i.e., by counting the number of σ -bonds and the number of lone pair of electrons at central atom. Adding the two, if the total is 4, the hybridization is sp^3 . If this total is 3, the hybridization is sp^2 and if this total is 2, the hybridization is sp .

A few examples are being given below:

(a) Beryllium chloride (BeCl_2)

No. of σ -bonds at Be atom = 2

No. of lone pair of electrons at Be atom = 0

Total = 2 + 0 = 2 Hybridization is sp , i.e., BeCl_2 is linear and bond angle is 180° .

(b) Boron trichloride (BCl_3)

No. of σ -bonds at B atom = 3

No. of lone pair of electrons at B atom = 0

Total = 3 Hybridization is sp^2 , i.e., BCl_3 is trigonal planar and bond angles are 120° each.

(c) Carbon tetrachloride (CCl_4)

No. of σ -bonds at C atom = 4

No. of lone pair of electrons at C atom = 0

Total = 4 Hybridization is sp^3 , i.e., CCl_4 is tetrahedral and bond angles are $109^\circ 28'$ each.

(d) Ammonia (NH_3)

No. of σ -bonds at N atom = 3

No. of lone pair of electrons at N atom = 1

Total = 3 + 1 = 4 Hybridization is sp^3 Shape is trigonal pyramidal (not tetrahedral) and bond angles are not $109^\circ 28'$ but $106^\circ 45'$

Second Method: Number of electron pairs in the valency shell of the central atom can be determined by applying the following formula:

For neutral molecules:

No. of electron pairs = No. of atoms bonded to it + $1/2$ (Group number of central atom - Valency of the central atom)

No. of electron pairs at the central atom in $CH_4 = 4 + 1/2(4-4) = 4$ (sp^3 hybridization)

No. of electron pairs at the central atom in $PCl_5 = 5 + 1/2(5-5) = 5$ (sp^3d hybridization)

No. of electron pairs at the central atom in $SF_6 = 6 + 1/2(6-6) = 6$ (sp^3d^2 hybridization)

No. of electron pairs at the central atom in $H_2O = 2 + 1/2(6-2) = 4$ (sp^3 hybridization)

For ions :

No. of electron pairs = No. of atoms bonded to it + $1/2$ [Group number of central atom - Valency of the central atom \pm No. of electron]

No. of electron pairs in $NH_4^+ = 4 + 1/2(5 - 4 - 1) = 4$ (sp^3 hybridization)

No. of electron pairs in $SO_4^{2-} = 4 + 1/2(6-8 + 2) = 4$ (sp^3 hybridization)

No. of electron pairs in $BF_4^- = 4 + (3 - 4 + 1) = 4$ (sp^3 hybridization)

Third Method : The number of orbitals involved in hybridization can be determined by the application of the following formula :

$$H = + 1/2[V + M - C + A]$$

where H = number of orbitals involved in hybridization

V = valence electrons of central atom

M = number of monovalent atoms linked with central atom

C = charge on the cation

A = charge on the anion

From the value of H, the type of hybridization can be predicted.

Value of H	2	3	4	5	6	7
Hybridization	sp	sp ²	sp ³	sp ³ d	sp ³ d ²	sp ³ d ³

Type 1. Neutral molecules :

(i) CO₂ : V = 4, M = 0, C = 0, A = 0

H = 1/2 [4 + 0 - 0 + 0] = 2, sp hybridization

(ii) SO₂ or SO₃ V = 6, M = 0, C = 0, A = 0

H = 1/2[6 + 0 - 0 + 0] = 3, sp² hybridization

(iii) BCl₃ : V = 3, M = 3, C = 0, A = 0

H = 1/2 [3 + 3 - 0 + 0] = 3, sp² hybridization

(iv) SiCl₄ : V = 4, M = 4, C = 0, A = 0

H = 1/2 [4 + 4 - 0 + 0] = 4, sp³ hybridization

Type 2. When the species is a cation

(i) NH₄⁺ : V = 5, M = 4, C = 1, A = 0

H = 1/2 (5 + 4 - 1 + 0) = 4, sp³ hybridization

(ii) CH₃⁺ : V = 4, M = 3, C = 1, A = 0

H = 1/2 (4 + 3 - 1 + 0) = 3, sp² hybridization

(iii) NO₂⁺ : V = 5, M = 0, C = 1, A = 0

H = 1/2 (5 + 0 - 1 + 0) = 2, sp hybridization

Type 3. When the species is an anion

(i) CO₃²⁻ : V = 4, M = 0, C = 0, A = 2

H = 1/2 [4 + 0 - 0 + 2] = 3, sp² hybridization

(ii) SO₄²⁻ : V = 6, M = 0, C = 0, A = 2

H = 1/2[6 + 0 - 0 + 2] = 4, sp³ hybridization

(iii) ICl₄⁻ : V = 7, M = 4, C = 0, A = 1

H = 1/2[7 + 4 - 0 + 1] = 6, sp³d² hybridization