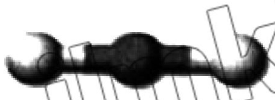
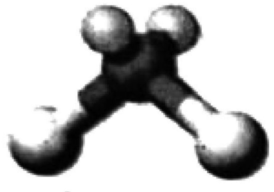
CHAPTER 3

linear



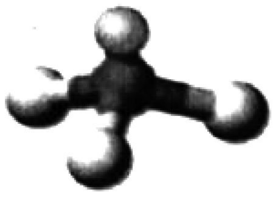
linear

trigonal planar

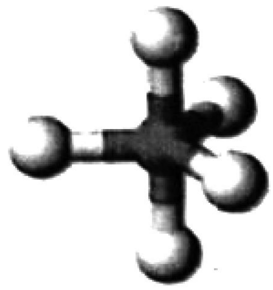


bent or angular

tetrahedral



trigonal pyramidal



trigonal bipyramidal

octahedral

CHEMICAL BONDING

SLOs: After completing this lesson, the student will be able to:

1. DEFINE ELECTRONEGATIVITY as the power of an atom to attract electrons to itself.
2. Explain the factors influencing the electonegativities of elements in terms of nuclear charge, shielding by inner shells and subshells.
3. Explain the trends in electronegativity across a period and down a group of the periodic table.
4. Use the differences in Pauling electronegativity values to predict the formation of ionic and covalent bonds.
5. Describe covalent bonding in molecules using the concept of hybridization to describe sp, sp2, and sp3 orbitals.
6. Use bond energy values and the concept of bond length to compare the reactivity of covalent molecules.
7. Describe the shapes and bond angles in molecules using VSEPR theory (including describing sketching).
8. Predict the shapes, and bond angles in molecules and ions.
9. Explain hybridization and types of hybridization.
10. Explain valence bond theory.
11. Explain the importance of VSEPR theory in the field of drug design by discussing how the shape and bond angles of the molecules help chemist predict their interactions in the body.
12. Explain the salient features of molecular orbital theory.
13. Explain the paramagnetic nature of oxygen molecule in the light of MOT.
14. Calculate bond order of N_2, O_2, F_2, and He
15. Describe the types of Van der Waals` forces.
16. Describe hydrogen bonding limited to molecules including ammonia and water.
17. Use the concept of hydrogen bonding to explain the anomalous properties of water.
18. Use the concept of electronegativity to explain bond polarity and dipole moments of molecules.
19. State that, in general, ionic, covalent, and metallic bonding are stronger than intermolecular forces.
20. Recognize that molecular ions/polyatomic ions can have expanded octets e.g. sulphate and nitrate.
21. Analyze the formation of dative bond in CO, ozone and H_3O^+ ion (resonance structures are not required).

In this chapter, we will discuss how VSEPR theory explains the shapes of molecules. We will also discuss how shapes of molecules effect the polarity in a molecule. Other theories such as Valence Bond Theory and Molecular Orbital Theory have also been discussed, which explain the orbital overlapping and paramagnetism in a molecule. These theories can also be used to explain the chemical and physical properties of molecules.

3.1 ELECTRONEGATIVITY

It is the power of a covalently bonded atom to attract shared pair of electrons towards itself in a molecule.

It is a dimensionless property and has no unit because it is only a tendency. It basically indicates the net result of the tendencies of atoms in different elements to attract the bond-forming electron pairs. We measure electronegativity on several scales. The most commonly used scale was designed by Linus Pauling.

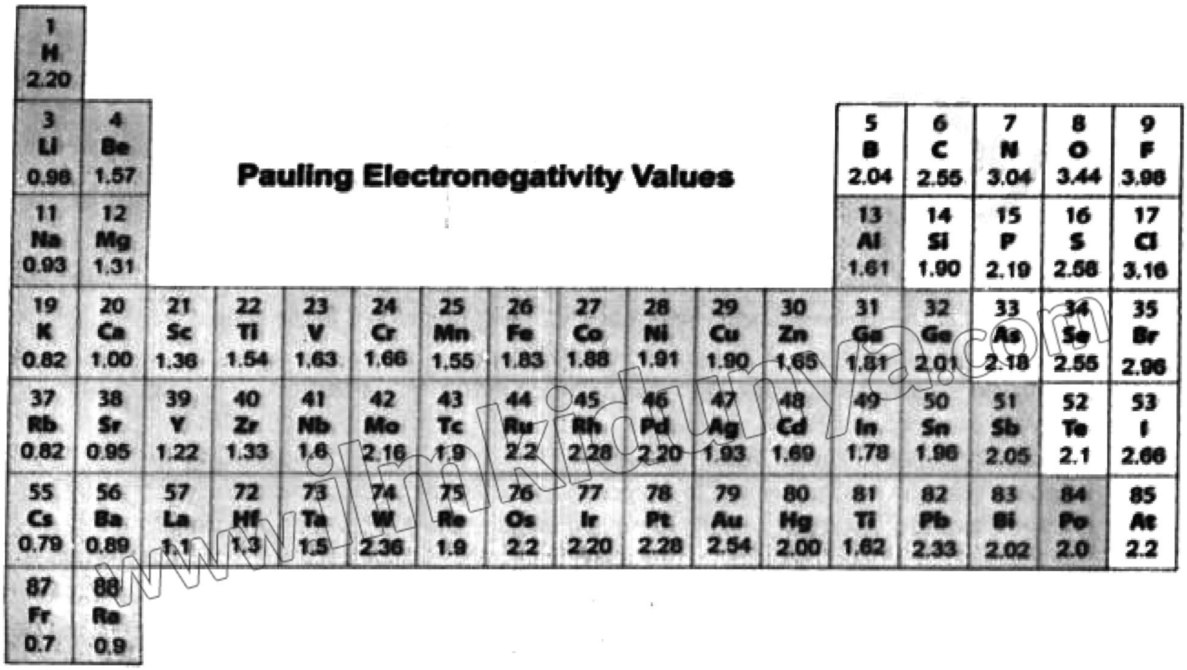
3.1.1 Factors affecting Electronegativity.

Electronegativity depends upon the following factors.

- Size of atom
- Nuclear charge
- Screening by inner electrons

As the number of protons in nucleus increases, the nuclear charge increases. Hence the size of atom decreases causing the attraction of bonded electrons with the nucleus to decreases, resulting in increase of electronegativity. When the number of inner shell electrons increases, the distance between the nucleus and valence electrons increases. So, attraction of bonded electron with the nucleus decreases causing decrease in electronegativity. Table 3.1 represents electronegativity of elements in the periodic table.

Table 3.1: Electronegativity of elements in the periodic table



Pauling Electronegativity Values

1 H 2.20																
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

3.1.2 Trend of Electronegativity in the Periodic Table.

Electronegativity decreases from top to bottom in groups. There is an increase in the atomic number as we move down the group in the modern periodic table. The nuclear charge also increases but the effect of the increase in nuclear charge is overcome by the addition of an extra shell (increase in shielding effect). The attraction of shared electrons with the nucleus decreases. Hence, the value of electronegativity decreases.

For example, in the halogen group as we move down the group from fluorine to astatine the electronegativity value decreases, and it is shown in the figure 3.1.

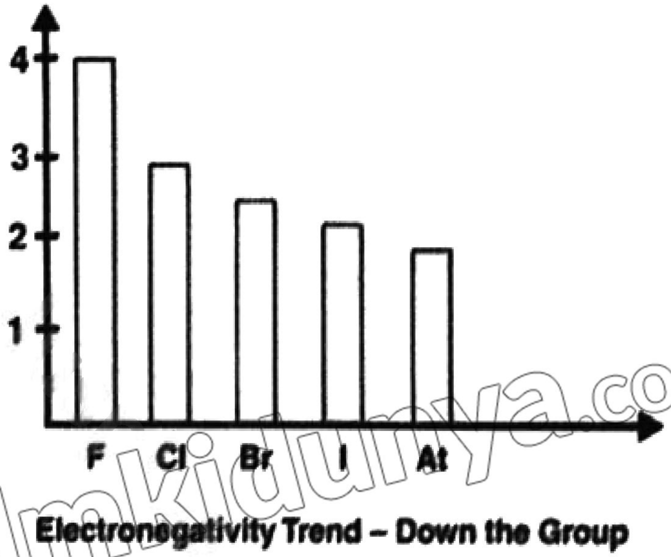


Figure 3.1: Trend of Electronegativity of Halogen down the group.

Electronegativity increases from left to right across a period. When we move from left to right in periods effective nuclear charge increases. Shielding effect remains constant. Hence, the size of atom decreases. The power of atoms to attract shared pair of electron increases.

For example, in the third period from sodium to chlorine the electronegativity value increases, and it is shown in the figure 3.2.

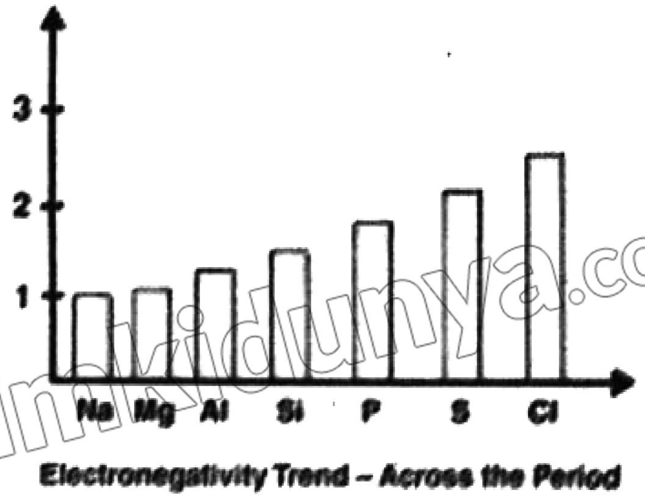


Figure 3.2: Trend of Electronegativity of third period elements.

3.1.3 Nature of Bond in terms of Pauling Electronegativity Values

In ionic bonds, the differences in electronegativity between two atoms is higher than 1.8. Polar-covalent bonds have differences in electronegativity between 1.8 and 0.4. Nonpolar Covalent bonds have differences in electronegativity of 0.4 or lower. In case the electronegativity of both atoms is the same, the pair of electrons will be shared equally.

Example 3.1: Consider the following substances and determine their bond types.

(i) Oxygen molecule (O=O)

(ii) Potassium Chloride (KCl)

(iii) Hydrogen Chloride (HCl)

(i) This molecule consists of two oxygen atoms. Oxygen has an electronegativity value of 3.44. So each atom in this molecule has an electronegativity of 3.44.

The difference in electronegativity is 0, which means that none of the two atoms in the molecule pulls the electrons to itself more strongly than the other. This means that this molecule has a **covalent bond.**

(ii) This compound has a potassium atom with an electronegativity of 0.82 and a chlorine atom with an electronegativity of 3.16.

There is a difference in electronegativity of 2.34 which is greater than 1.8, hence the bond will be ionic.

(iii) This molecule consists of a hydrogen atom with an electronegativity of 2.20 and a chlorine atom with an electronegativity of 3.16.

In this molecule, Chlorine is more electronegative than hydrogen. This means that Chlorine pulls the electrons more closely to itself than the hydrogen atom. The difference between their electronegativities is 0.96 which is between 1.8 and 0.4. Hence the bond will be Polar **Covalent Bond.**

3.1.4 Covalent character in a compound

Covalent character in a molecule depends upon the polarising power of cation which in turn depends on the oxidation state of cation. Higher the polarising power of cation, more will be the covalent character. That is why when we move from left to right in periods covalent character increases.

For example, Aluminium chloride is more covalent in nature as compared to magnesium chloride. In Aluminium chloride oxidation sate of aluminium atom is +3 while in Magnesium chloride oxidation state of magnesium is +2. Because of high polarizing power of Al, it can polarise the anion causing electrons to be shared between the two ions. Hence, covalent character will be developed in the compound.

3.2 DIPOLE MOMENT

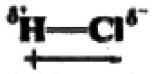
It is the product of the magnitude of positive or negative charges and the distance between them. Mathematically it can be written as

$$\underset{\text{Dipole moment}}{\mu} = \underset{\text{Charge}}{q} \, . \, \underset{\text{Separation distance}}{r}$$

SI unit of dipole moment is debye.1 Debye is equal to 3.335×10^{-30} Cm.

(Cm is coulomb meter).

The difference between the electronegativity of two atoms in a compound determines the overall dipole moment and overall polarity of the compound.



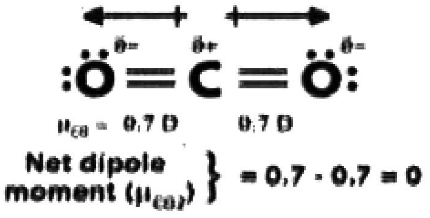
Dipole Moment has a Magnitude and a Direction

Electronegativity difference between two atoms determines the bond polarity of the molecule. Greater the electronegativity difference between two atoms, more will be the bond polar (more ionic nature). But a small difference in electronegativity of two bonded atoms will make bond less polar or more covalent in nature.

3.3 POLAR AND NONPOLAR COVALENT BOND

In polar covalent bond, due to electronegativity difference, one atom which is more electronegative will attract shared electron to itself and bear partial negative charge and other bears partial positive charge. Such molecules are called polar molecules. Polar molecules have dipoles, electric charges of equal magnitude and opposite sign.

Symmetrical polyatomic molecules are non-polar molecules having shape of Linear, Trigonal Planar and Tetrahedral. In these molecules dipole of bond exerts equal and opposite effects and hence cancels the charges. Non-polar molecules have no overall charge. Following diagram represents dipole moment of Carbon dioxide molecule.



Due to electronegativity difference between Carbon and Oxygen C=O bond in CO_2 is polar, but CO_2 is nonpolar because dipole gets canceled with each other.

Concept Assessment Exercise 3.1

1. Are the following molecules polar or non-polar? In each case give a reason for your answer.
(Electronegativity values: F = 4.0, Cl = 3.0, Br = 2.8, S = 2.5, C = 2.5, H = 2.1)

a. Chlorine, Cl_2 **b.** Hydrogen fluoride, HF **c.** The V-shaped molecule, sulfur dichloride, SCl_2 **d.** The tetrahedral molecule, chloromethane, CH_3Cl

e. The tetrahedral molecule tetrabromomethane, CBr_4.

3.4 BOND ENERGY (BOND ENTHALPY)

Energy which is required to break the bond of the same type in one mole of a substance is known as bond energy. Its unit is kJmol^{-1}. Bond energy depends upon the following factors:

(i) Electronegativity difference between two bonded atoms

(ii) Size of atom

(iii) Bond order

(iv) Bond length

The greater the electronegativity difference between two bonded atoms, the more polar will be the bond and the greater will be the bond energy.

Table 3.2: Following table represents the bond energy of hydrogen halide (Hydride of group VII).

Bond	Bond Energy (kJmol^{-1})	Electronegativity difference between bonded atoms
H–F	562	1.8
H–Cl	431	0.9
H–Br	366	0.7
H–I	299	0.4

From the above data we conclude that greater the electronegativity difference, higher will be the value of bond energy, for example HF has greater value of bond energy. Figure 3.3 represents bond enthaply of HX from HF to HI.

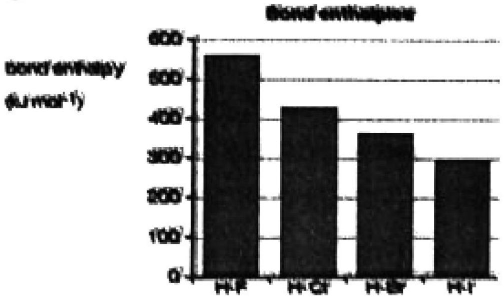


Figure 3.3: Bon enthalpy of Hydrogen halide from HF to HI

Bond Length:

Bond length is the distance between the nuclei of two covalently bonded atoms. It is measured in A° or picometer (Pm). 1pm = 10^{-12} m. Bond length depends upon the size of atom. Smaller the size of atoms, the greater the bond energy due to shorter bond length.

Bond energy of H-H is 436 kJmol^{-1} and that of H-Br is 366 kJmol^{-1}. It is due to the shorter bond length of hydrogen molecule compared to HBr. (Size of Br is greater that hydrogen).

Table 3.3: Following table represents the bond energy and bond length of Halogens.

Bond	Bond Energy ($kJmol^{-1}$)	Bond length (pm)
F—F	158	149
Cl—Cl	242	199
Br—Br	193	228
I—I	151	266

The atomic radius increases from fluorine to iodine. Bond energy decreases from chlorine to iodine molecule, but fluorine molecule has lower value of bond energy than chlorine. It is because of the smaller size of fluorine atoms that their lone pairs repel each other, hence less amount of energy is required to break the bond between fluorine atoms.

Bond energy is also used to predict the reactivity of covalent molecules. Greater the bond energy stronger will be the bond and that molecule will be stable and less reactive. For example, In alkyl halides, alkyl fluorides are less reactive than alkyl chlorides (as bond energy of C-F is greater than C-Cl). Trend of bond length and bond energy of halogen is shown in the following diagram.

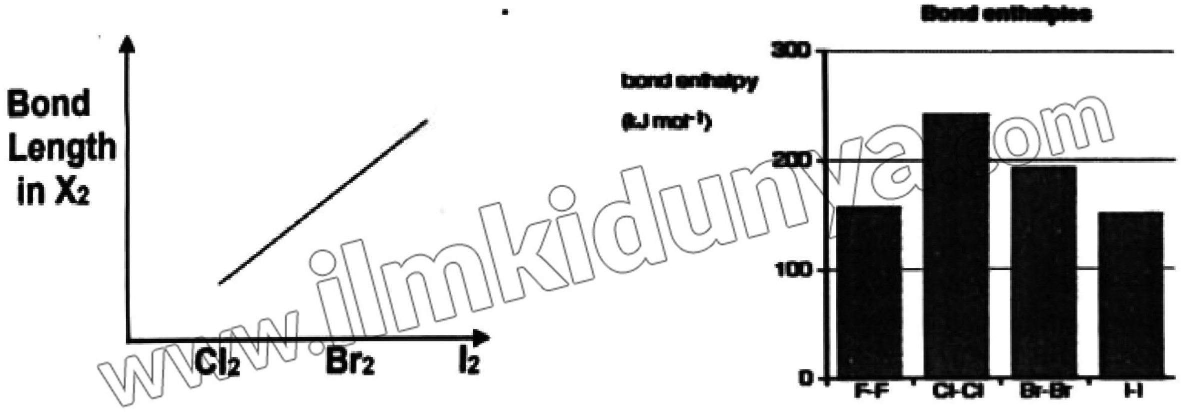


Figure 3.4: (a) Bond length of Halogen from Cl_2 to I_2 (b) Bond enthalpy of Halogen from F_2 to I_2.

3.5 SHAPES OF MOLECULES

Valence Shell Electron Pair Repulsion Theory

This theory is used to determine the shape and bond angle in the molecule.

As electrons are negatively charged particles, they repel each other when close together. So, a pair of electrons in the bonds surrounding the central atom in a molecule will repel other electron pairs. These repulsions between electron pairs force apart until the repulsive forces are minimised.

The shape and bond angles of a covalently bonded molecule depends on the number of pairs of electrons around each atom, whether these pairs are lone pairs or bonding pairs. Lone pairs of electrons have a more concentrated electron charge cloud than bonding pairs of electrons. Their cloud charges are wider and slightly closer to the nucleus of the central atom. This results in a different amount of repulsion between different types of electron pairs.

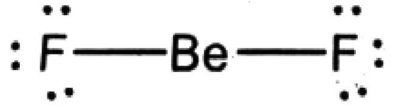
The order of repulsion is lone pair-lone pair (most repulsion) > lone pair-bond pair > bond pair-bond pair (least repulsion).

3.5.1 Shapes of Molecule containing two Electron Pairs

Those molecules where central atom is surrounded by two electron pairs and no lone pairs are linear in shape and of 180°angle.

AX_2: BeF_2

The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



In BeF_2 there are two electron pairs around the central beryllium atom. We see from the above figure that the arrangement that minimizes repulsions places the groups 180° apart.

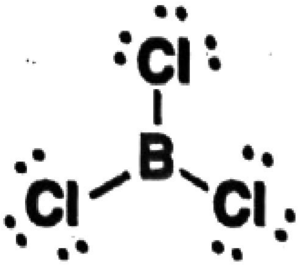
3.5.2 Shapes of Molecule containing three Electron Pairs

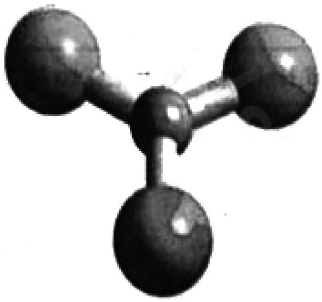
Those molecules where central atom is surrounded by three electron pairs and no lone pair are Trigonal in shape and angle will be 120°.

Three Bonding Pairs

AX_3 : BCl_3

The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure and shape of BCl_3 is shown below:

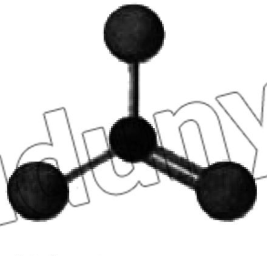




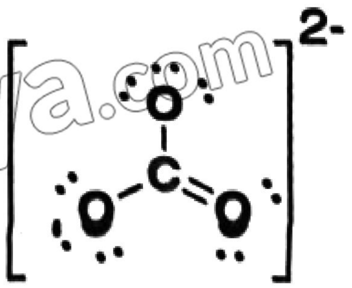
There are three electron pairs around the central atom. To minimize repulsions, the groups are placed 120° apart and geometry is trigonal planar.

AX_3 : CO_3^{2-}

In Carbonate ion, CO_3^{2-}, the central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. There are three bonding pairs around the carbon atom. The molecular geometry of CO_3^{2-} is trigonal planar.



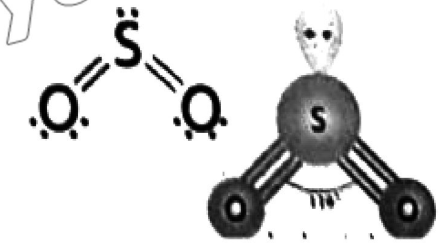
Molecular geometry (trigonal planar)



Two Bonding Pairs and one Lone Pair

AX_2E: SO_2

The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. The Lewis electron structure and shape of SO_2 is shown in the right side.



There are three electron pairs around the central atom, two double bonds and one lone pair. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E.

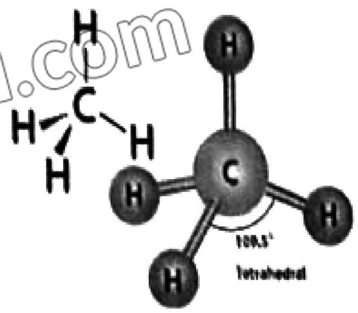
Because a lone pair occupies more space near the central atom than a bonding pair. Thus, bonding pairs and lone pairs repel each other. In SO_2, we have one BP-BP interaction and two LP-BP interactions. Thus, the shape is bent or V shaped and the angle will be less than 120°.

3.5.3 Shapes of Molecule containing four Electron Pairs

Four Bonding Pairs

AX_4 : CH_4

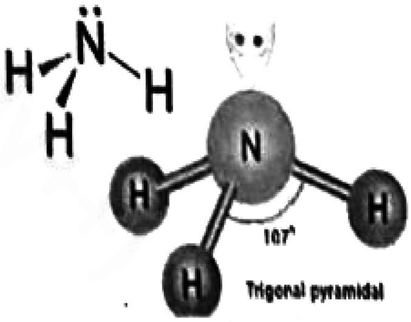
Those molecules where the central atom is surrounded by four electron pairs and no lone pair are tetrahedral in shape with bond angle of 109.5°. For example, In CH_4 carbon atom is surrounded by four electron pairs which are bonding pairs.



Three Bonding Pairs and one Lone Pair

AX_3E: NH_3

Those molecules where the central atom is surrounded by four electron pairs, three bonding pairs and one lone pair are Trigonal pyramidal in shape.

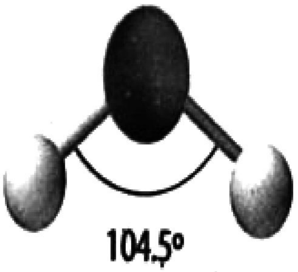


For example in ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron. In ammonia NH_3, nitrogen atom is surrounded by four electron pairs out of which three are bonding pairs and one lone pair. With three bonding pairs and one lone pair, the structure is designated as AX_3E.

There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. However, the H-N-H bond angles are less than the ideal angle of 109.5° because of Lone Pair-Bond Pair repulsions.

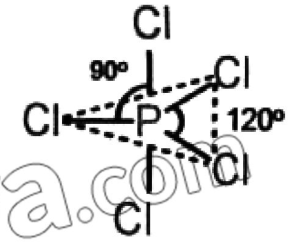
Two Bonding Pairs and Two Lone Pair

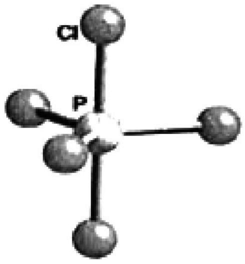
AX_2E_2 : H_2O



Those molecules where the central atom is surrounded by four electron pairs, two bonding pairs and two lone pairs are Bent in shape. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP-LP, LP-BP, and BP-BP interactions, we expect a significant deviation from idealized tetrahedral angles. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is bent, or V shaped, with an H-O-H angle that is even less than the H-N-H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.

3.5.4 Shapes of Molecule containing five Electron Pairs

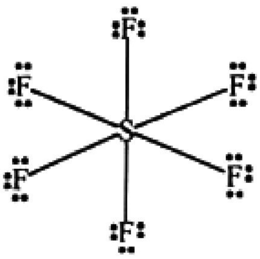


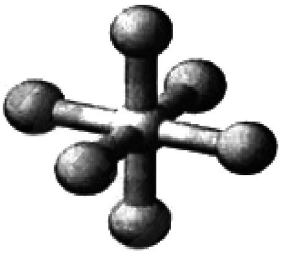


There are some cases in which the electrons around a central atom may not have a noble gas configuration. Those molecules where central atom is surrounded by five electron pairs and no lone pair are trigonal bipyramidal in shape. For example, PCl_5 which has five bonding pairs of electrons and no lone pairs. The repulsion between the electron pairs results in the most stable structure being a trigonal bipyramid. Three of the chlorine atoms lie in the same plane as the phosphorous atom. The bond angles ClPCl within this plane are 120°. Two of the chlorine atoms lie above and below this plane at 90° to it.

3.5.5 Shapes of Molecule containing six Electron Pairs

Those molecules where central atom is surrounded by six electron pairs and no lone pair are octahedral in shape. All angles are 90°. Sulphur hexafluoride, SF_6, has twelve electrons around the central Sulphur atom. We say that the Sulphur atom has an 'expanded octet'.





3.5.6 Expanded Octet/Hypervalency

The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule sometimes, but not always. In larger atoms of 3rd period onwards the valence shell contains additional subshells, d,f and g subshells.

Therefore, atoms of 3rd, 4th ... period elements can have higher valence shell counts by "expanding" into these additional subshells. When atoms contain more than eight electrons in their valence shell, they are said to be hypervalent. This is also called expanded octet. Figure 3.5 represents the molecular ions with expanded octet.

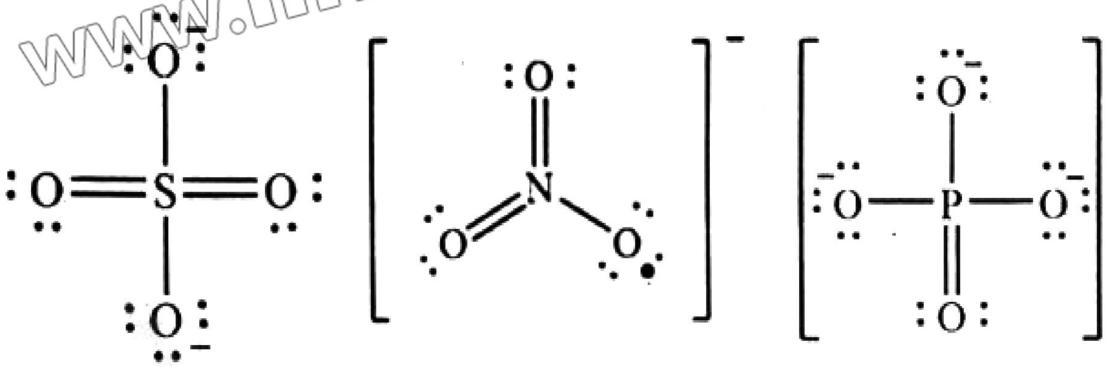


Figure 3.5: Indicates the ions with expanded octet.

Table 3.4: Shapes of Molecules

Summary of Shapes of Molecules

Number of valence electrons	Number of bonding pairs of electrons	Number of lone pairs of electrons	Total number of electron pairs	Arrangement of orbitals	Arrangement of atoms / Angle	Examples
4	2	0	2	Linear	Linear 180°	$BeCl_2$, HCN, CO_2
6	3	0	3	Trigonal planar	Trigonal planar 120°	BF_3, $AlCl_3$, NO_3^{1-}
	2	1	3		Bent 118°	$SnCl_2$
8	4	0	4	Tetrahedral	Tetrahedral 109.5°	CH_4, $SiCl_4$, SO_4^{2-}, NH_4^{1+}
	3	1	4		Trigonal Pyramid 107°	NH_3, PCl_3 ClO_3^{1-}
	2	2	4		Bent 104.5°	H_2O, H_2S
10	5	0	5	Trigonal bipyramid	Trigonal bipyramid 90° and 120°	PCl_5, PI_5
12	6	0	6	Octahedral	Octahedral 90°	SF_6

3.5.7 Working out the shapes of Molecules

Add together the number of valence electrons from the central atom, and the number of electrons contributed to bonding by surrounding atoms. Include the ion charge if there is one.

Divide the total electrons by 2. This gives the number of electron pairs distributed around the central atom.

Example 1	Example 2
Predict the Geometry of NH_3 Valence electrons of nitrogen = 5 Electron from 3 chlorine atoms = 3 Total number of electrons = 8 Number of electron pairs = 4 So, the electron pairs are arranged tetrahedrally. Number of atoms surround the central atom = 3 Number of bonding pairs =3 Number of lone pairs = 1 The molecule is trigonal pyramidal.	Predict the Geometry of NH_4^{1+} Valence electrons of nitrogen = 5 Electron from 4 hydrogen atoms = 4 Electron from molecular charge = 1+ Total number of electrons = 8 Number of electron pairs = 4 So, the electron pairs are arranged tetrahedrally. Number of atoms surround the central atom = 4 Number of bonding pairs = 4 Number of lone pairs = 0 The molecule is tetrahedral.

3.5.8 Importance of VSEPR Theory in the Field of Drug

By predicting molecular shapes and bond angles, VSEPR aids Medicinal chemists in understanding how drug molecules interact in the body.

Shape and dimensions of the molecules being used as drugs also depends upon the length and angles of the bonds between their atoms. Any change in bond angles affect the overall 3D shape of molecules thus affecting their binding ability or permeability through membranes of target cell.

Molecular Shape and Enzymatic Reactions

Enzymes recognize and bind to drug substrates based on their molecular shape. VSEPR helps predict this 3D structure, allowing designers to tailor molecules for optimal interaction with enzyme active sites. Understanding the molecular geometry through VSEPR aids in creating drug with enhanced substrate recognition, facilitating targeted interactions in enzymatic reaction.

Enzyme-Substrate Interaction in Drug Design

Consider the interaction between a drug and the enzyme acetylcholinesterase in neuropharmacology. VSEPR guides the design of drugs with shapes that fit precisely into the enzyme's active site, enhancing efficacy and specificity.

Molecular Geometry in Drug Delivery Systems

VSEPR theory, which predicts molecular shapes and plays a vital role in designing effective drug Carriers. Liposomes, spherical lipid-based vesicles, are extensively used as drug carriers due to their biocompatibility and versatility. VSEPR informs the design of liposomal carriers by predicting the optimal arrangement of electron pairs, influencing their three-dimensional structure. For instance, tailoring liposomes into specific shapes, such as elongated or targeted geometries, enhances their ability to navigate biological barriers and efficiently deliver drugs to the desired tissues.

Now, imagine a drug molecule designed to interact with a specific enzyme. The VSEPR-derived geometry of this drug molecule needs to be considered to ensure optimal binding. If the enzyme's active site has a pocket with a tetrahedral arrangement of binding sites, a drug with a complementary tetrahedral geometry might fit more effectively.

Understanding molecular geometry also helps scientists to understand the shapes of more complex molecules such as proteins and DNA. The shapes of these molecules play incredibly important roles in determining the jobs performed by these molecules in our bodies.

Cisplatin is a neutral complex, $Pt(NH_3)_2Cl_2$,has square planar structure. Cisplatin is one of the most effective anticancer agents widely used in the treatment of solid tumors. It is generally considered as a cytotoxic drug which kills cancer cells by damaging DNA and inhibiting DNA synthesis. Cisplatin-induced DNA damage activates the various signaling pathways to prevent or to promote cell death.

Concept Assessment Exercise 3.2

1. a Predict the shapes of the following molecules.
   - i tetrachloromethane, CCl_4
   - ii beryllium chloride, $BeCl_2$
   - iii phosphorus (III) chloride.

   b Draw dot-and-cross diagrams for the following molecules and then predict their shapes:
   - i hydrogen sulphide, H_2S
   - ii phosphine, PH_3.

2. a Draw a dot-and-cross diagram for a molecule of selenium hexafluoride, SeF_6.

   b Predict the shape of selenium hexafluoride.

   c Draw the shape of the phosphorus(V) chloride molecule

3.6 VALENCE BOND THEORY

This theory was proposed by Heitler and London (1927) and later developed by Pauling. It has successfully explained bond energies, bond lengths and shapes of the covalent molecules.

According to Valence Bond Theory, covalent bonds are formed by the overlapping of partially filled atomic orbital of one atom with a partially filled atomic orbital of the other. Their identity was retained by the two overlapping atomic orbitals. The term overlap means that the two orbitals share the same common region in space.

Main points of VBT

1. A bond between two atoms is formed by the overlap of half-filled atomic orbitals of two atoms. These atomic orbitals retain their identity.
2. Electrons of overlapping orbitals have opposite spin.
3. The number of bonds formed is equal to the number of unpaired electrons present in the outermost shell of the atom.
4. By the overlapping of two orbitals overlap, a single bond which is sigma bond is formed. By the overlapping of additional orbitals, multiple bonds are formed (double and triple).
5. In order to form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis.

   "A line joining the nuclei of two bonded atoms is called bond axis".
6. Energy is released by the overlapping of orbitals. The greater the overlap between the orbitals, the greater is the energy released and the stronger will be the bond formed.

Types of Overlapping and Nature of Covalent Bonds

The two main types of covalent bonds obtained by overlapping are as follows:

- Sigma bond (σ)
- Pi Bond (π)

Sigma Bond

When there is a single bond between two atoms, the bond will be sigma bond. Sigma bond is formed by the head on overlapping of atomic orbital.It is formed between s-s, s-px, s-py, s-pz, px-px overlap.

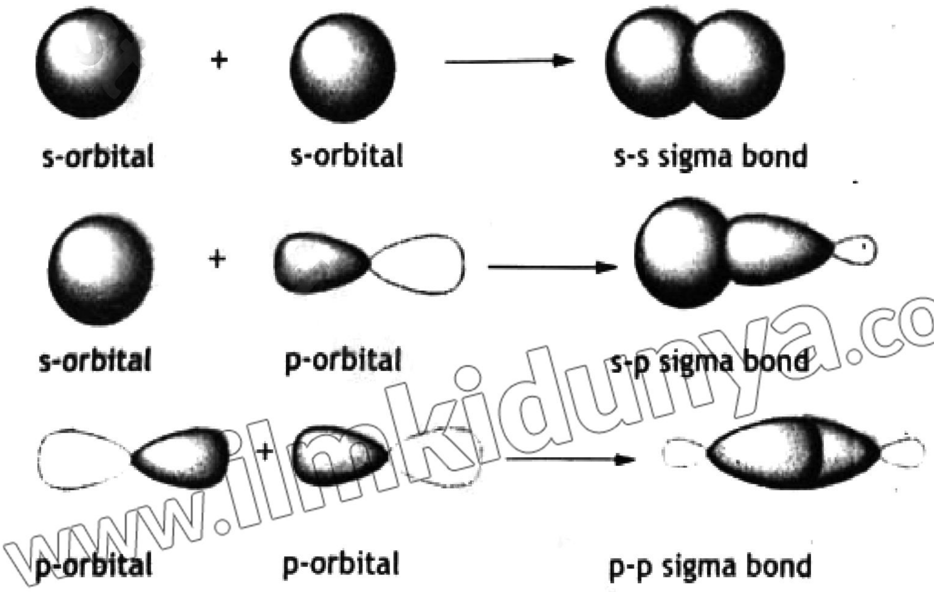


Figure 3.6: Formation of sigma bond due to (a) The s-s overlap (b) the s-p overlap (c) The p-p overlap.

Pi Bond

Pi bond is formed by the parallel overlapping of P orbitals. (Between Py—Py and Pz—Pz)

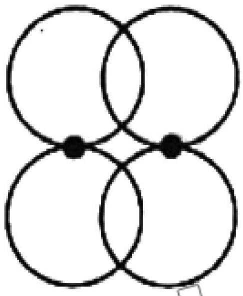


Figure 3.7: Parallel Overlapping of Orbitals (Formation of π Bond)

When there is double bond between two atoms, one should be sigma and the other should be Pi bond. When there is triple bond between two atoms, there is one sigma and two Pi bonds.

Structure of Ethene

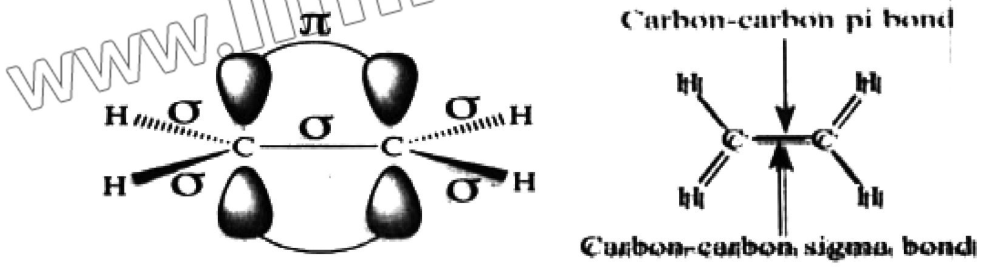


Figure 3.8: Structure of Ethene

Strength of Sigma and Pi Bond

Sigma bond is stronger than Pi bond because in sigma bond electron density is in between the line joining the two nuclei while in pi bond electron density is above and below the plane. Hence it is more diffuse bond and less amount of energy is required to break this bond.

3.6.1 Applications of Valence Bond Theory

Single Bond Formation

a) Formation of H_2 Molecule

Electron configuration of hydrogen atom is $1s^1$. Each half-filled s orbital of hydrogen atoms overlaps to form H-H bond where electron density is in between the line joining the two nuclei so bond formed is a sigma (σ) bond.

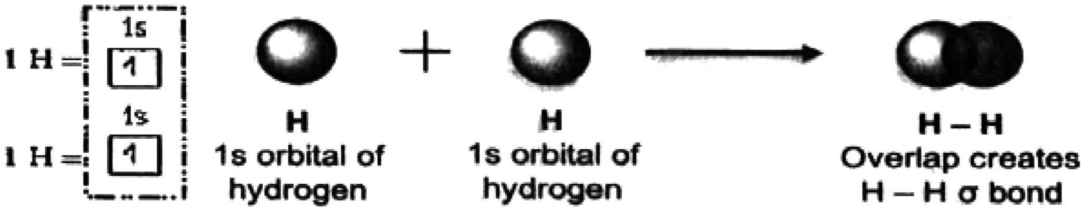


Figure 3.9: Orbital Diagram of H_2 Molecule

b) Formation of F_2 Molecule

The electronic configuration of fluorine is $1s^2\ 2s^2\ 2p^5$. Half-filled 2pz orbital of each fluorine atom head on overlap to form F-F bond which is sigma bond.

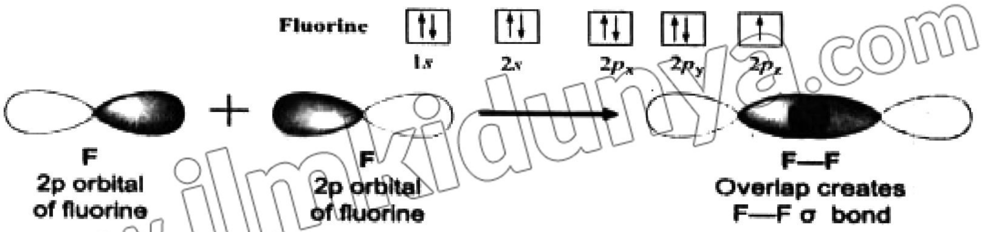
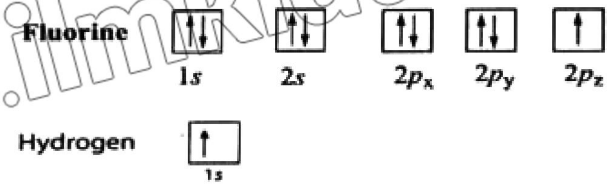


Figure 3.10: Orbital Diagram of F-F Molecule

Formation of HF Molecule

The electronic configurations of F and H atoms are:



In the formation of HF molecule, the half-filled 1s orbital of H atom overlaps with the half-filled $2p_z$ orbital of F to form H-F σ bond.

Figure 3.11: Orbital Diagram of H-F Molecule

Formation of O_2 Molecule

In Oxygen molecule, each oxygen atom contains two half-filled 2py and 2pz orbitals so according to Valence Bond Theory two bonds are formed. One due to head on overlap of two half-filled p orbitals which is sigma bond and the other bond is formed due to parallel overlap of half-filled p orbitals which is pi bond. Electronic configuration of an oxygen atom and orbital overlapping in O_2 molecule is shown in figure 3.12.

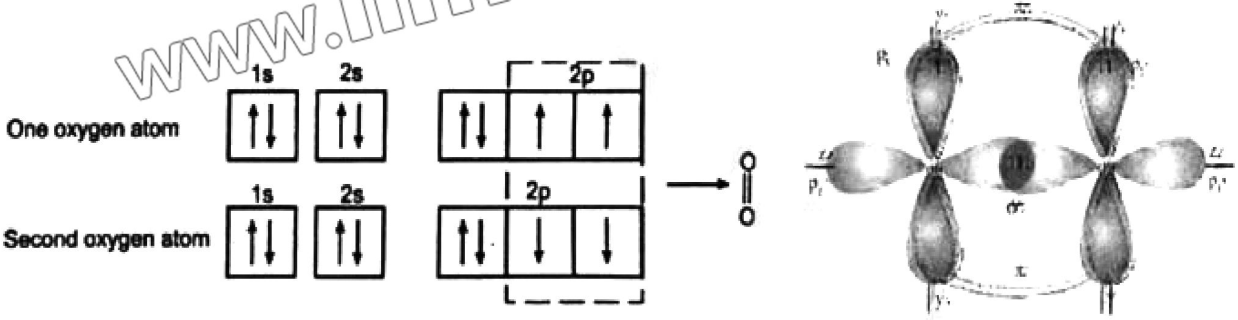


Figure 3.12: Formation of σ and π bonds in O_2 Molecule

Formation of N_2 Molecule

Nitrogen molecule contains two nitrogen atoms. Each nitrogen atom contains three half-filled p orbitals. According to VBT three bonds are formed. Half-filled 2px orbitals of nitrogen atoms head on overlap with each other and sigma bond is formed, while half-filled orbitals of 2py and 2pz of each nitrogen atom parallel overlap with each other so two pi bonds are formed. Hence triple bond is formed between two nitrogen atoms.

The electronic configuration of N atom and orbital overlapping in nitrogen molecule is shown figure 3.13.

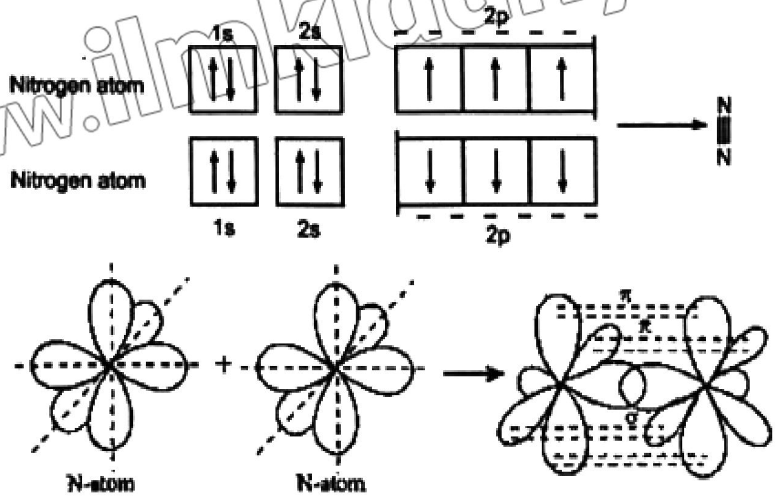


Figure 3.13: Orbital Diagram of N_2 Molecule

3.7 HYBRIDIZATION

Hybridization is the concept of mixing of atomic orbitals of different energies and different shapes to produce a new set of orbitals of the same energies and same shape called new hybrid orbitals and this process is known as hybridization.

During the process of hybridization, the electrons which are present in the ground state structure are promoted to the excited state due to which number of unpaired electrons increases. Energy which is required for the excitation of electron is compensated by the amount of energy which is released during the bond formation. There is number of types of hybridization depending upon the nature of different atomic orbitals i.e s, p d and f. Hybrid orbitals are very useful in the explanation of molecular geometry and atomic bonding properties.

Types of Hybridization

There are many types of hybridization.

For example, sp, sp^2, sp^3, dsp^2, dsp^3, d^2sp^3, d^3sp^3 hybridization. We will discuss only three types of hybridization.

3.7.1 sp Hybridization

Intermixing of one s and one p orbital of different energies and different shapes to produce two new sets of hybrid orbitals of the same energies and same shapes is known as sp hybridization. sp-hybridized orbital has 50% s-character and 50% p-character. The sp-hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

Examples of sp Hybridization

1. Beryllium Chloride ($BeCl_2$)

The electronic configuration of Be in ground state is $1s^2\ 2s^2$. Since there are no unpaired electrons, it undergoes excitation by promoting one of its 2s electrons into an empty 2p orbital. Thus, in the excited state, the electronic configuration of Be is $1s^2\ 2s^1\ 2p^1$. In the excited state, the beryllium atom undergoes 'sp' hybridization by mixing a 2s and one 2p orbitals. One electron from 2s orbital is promoted to 2p to form two new hybridized orbitals which are arranged linearly.

When the two beryllium sp hybrid orbitals overlap with p orbitals of chlorine atoms, the bonding is as shown in figure 3.12. Thus, $BeCl_2$ is linear in shape with the bond angle of 180°.

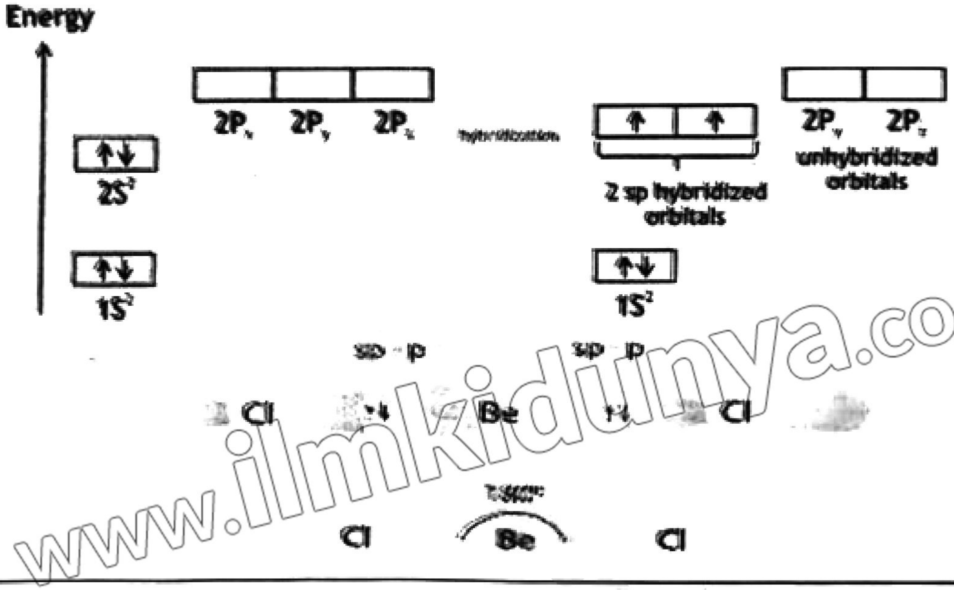
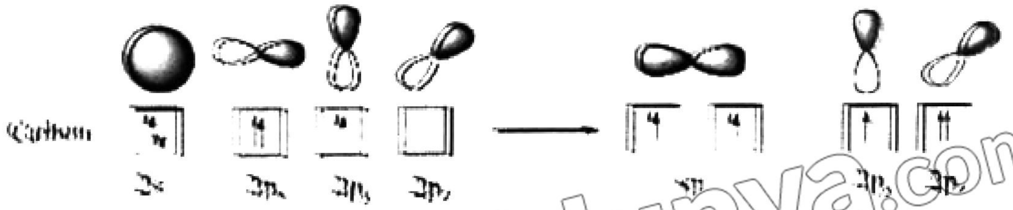


Figure 3.14: Hybridization in $BeCl_2$, a Linear Molecule

2. Acetylene (C_2H_2)

In acetylene the central atom is carbon. The ground state electronic configuration of 'C' is $1s^2\ 2s^2\ 2p_x{}^1 2p_y{}^1$. There are only two unpaired electrons in the ground state. However, the valency of carbon is four i.e., it forms 4 bonds. To form four bonds, there must be four unpaired electrons. Hence carbon promotes one of its 2s electrons into the empty $2p_z$ orbital in the excited state. Thus, in the excited state, the electronic configuration of carbon is $1s^2\ 2s^1$ $2Px^1 2Py^1 2Pz^1$.



Each carbon atom undergoes 'sp' hybridization by using a 2s and one 2p orbitals in the excited state to give two half filled 'sp' orbitals, which are arranged linearly. The two carbon atoms form a σ sp-sp bond with each other by using sp-orbitals. However, there are also two unhybridized p orbitals i.e, $2p_y$ and $2p_z$ on each carbon atom which are perpendicular to the sp hybrid orbitals. These orbitals form two π bonds between the two carbon atoms.

Thus, a triple bond (including one σ sp-sp bond and two π bonds) is formed between carbon atoms. Each carbon atom formed a sigma bond with the hydrogen atom by the overlapping of sp-s. Thus, acetylene molecule is linear with 180° of bond angle.

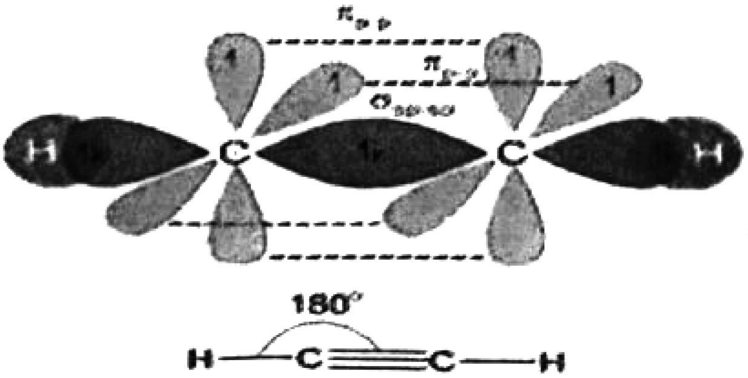


Figure 3.15: Hybridized Orbital Diagram and Linear structure of Acetylene Molecule.

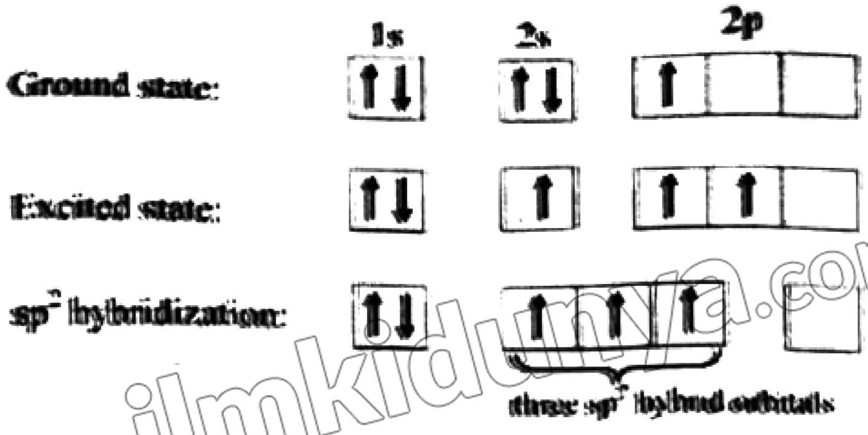
3.7.2 sp² Hybridization

It is the intermixing of one s and two p orbitals having different energy and different shape to produce three hybridized orbitals of the same energy and same shape and this phenomenon is known as sp² hybridization.

Examples of sp² Hybridization.

1. Boron trichloride (BCl_3)

The electronic configuration of 'B' in ground state is $1s^2\ 2s^2\ 2p^1$ with only one unpaired electron. Since the formation of three bonds with chlorine atoms require three unpaired electrons, there is promotion of one of 2s electron into the 2pz orbital by absorbing energy. Excited state electronic configuration of boron after absorbing energy is $1s^2\ 2s^2\ 2p_x^1 2p_y^1$. In the excited state, Boron undergoes sp² hybridization by using a 2s and two 2p orbitals to give three half-filled sp² hybrid orbitals which are oriented in trigonal planar symmetry.



In BCl_3, three sp^2 hybridized orbitals of boron atom overlap with three p orbitals of three chlorine atoms and forms three σ sp^2-p bonds. Thus, the shape of BCl_3 is trigonal planar with bond angles equal to 120°.

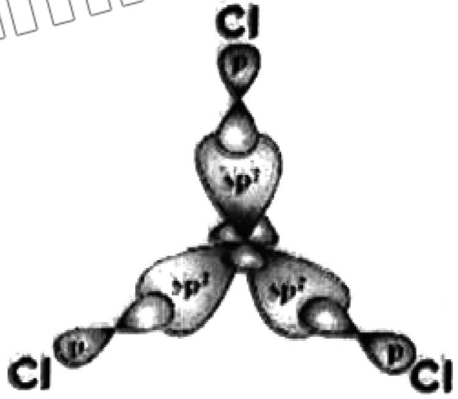
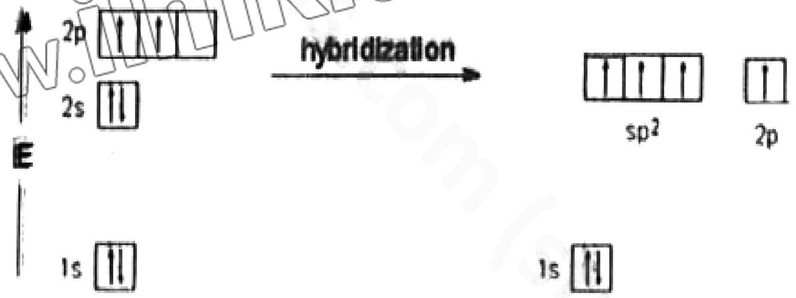


Figure 3.16: BCl_3, Trigonal Planar Molecule.

2. Ethylene (C_2H_4)

During the formation of ethylene molecule, each carbon atom undergoes sp^2 hybridization in its excited state by mixing 2s and two 2p orbitals to give three half-filled sp^2 hybrid orbitals oriented in trigonal planar symmetry. There is also one half filled unhybridized 2p orbital on each carbon perpendicular to the plane of sp^2 hybrid orbitals.



The carbon atoms form a σ bond with each other by using sp^2 hybrid orbitals. A π bond is also formed between them due to the parallel overlapping of unhybridized $2p_z$ orbitals. Thus, there is a double bond (σ and π) between two carbon atoms. Each carbon atom also forms two σ between sp^2orbital of carbon atom and s orbitals of two hydrogen atoms.

Thus, ethylene molecule is planar with HCH and HCC bond angles equal to 120°. All the atoms are present in one plane.

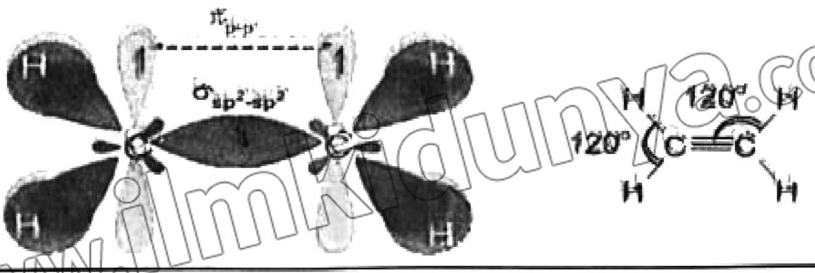
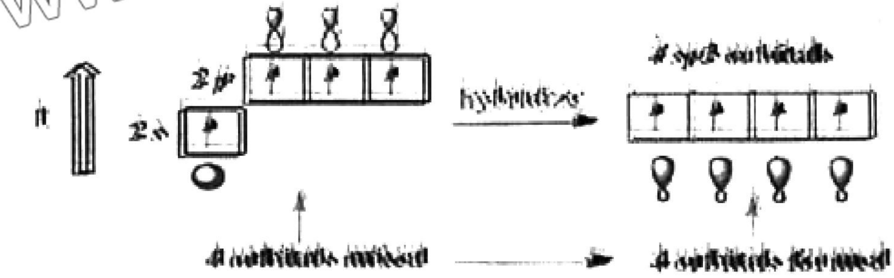


Figure 3.17: C_2H_4, Trigonal Planar Molecule

3.7.3 sp^3 Hybridization

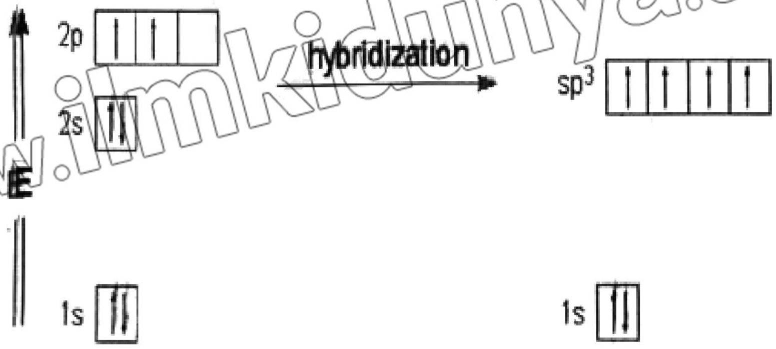
It is the intermixing of one s and three p orbitals having different energy and different shape to produce four hybridized orbitals of the same energy and same shape and this phenomenon is known as sp^3 hybridization.



Examples of sp^3 Hybridization

1. Methane (CH_4)

During the formation of methane molecule, the carbon atom undergoes sp^3 hybridization. In the excited state by mixing one '2s' and three 2p orbitals, four half-filled sp^3 hybrid orbitals are formed which are oriented in tetrahedral symmetry in space around the carbon atom.



Each of these sp^3 hybrid orbitals forms form sigma bond with s orbital of hydrogen atom. Thus, carbon forms four σ sp^3-s bonds with four hydrogen atoms. Methane molecule is tetrahedral in shape with 109°.5' bond angle.

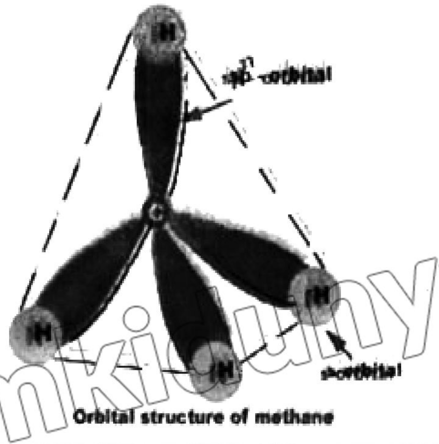


Figure 3.18: CH_4, a Tetrahedral Molecule

2. Ethane (C_2H_6)

Just as in methane molecules, each carbon atom undergoes sp^3 hybridization in the excited state to give four sp^3 hybrid orbitals in tetrahedral geometry. The two carbon atoms form a σ sp^3-sp^3 bond with each other due to overlapping of sp^3 hybrid orbitals along the inter-nuclear axis. While the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1s orbitals of hydrogen atoms. All of these are sigma bonds.

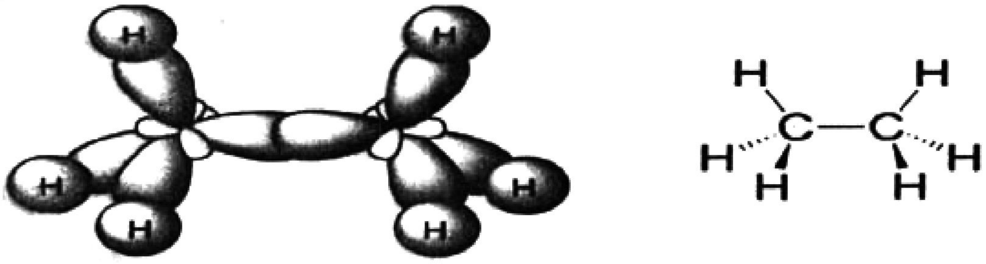


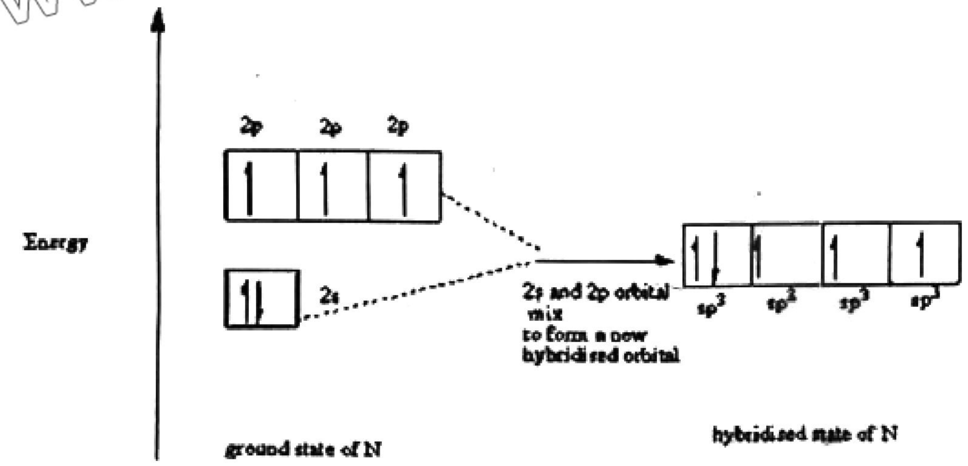
Figure 3.19: C_2H_6, Tetrahedral Molecule

3. Ammonia (NH_3)

The ground state electronic configuration of nitrogen atom is $1s^2\ 2s^2\ 2p_x^1 2p_y^1 2p_z^1$. Since there are three unpaired electrons in the 2p sublevel, the nitrogen atom can form three bonds with three hydrogen atoms.

In ammonia, nitrogen atom undergoes sp^3 hybridization of a 2s and three 2p orbitals to give four sp^3 orbitals, which are arranged in tetrahedral symmetry. This arrangement will give more stability to the molecule due to minimization of repulsions.

Among them three are half filled and one is full filled.



3 sp^3 orbital of Nitrogen atom overlap with s orbital of three hydrogen atoms by using three half-filled sp^3 hybrid orbitals. There is also a lone pair on nitrogen atom belonging to the full filled sp^3 hybrid orbital. It occupied more space than the bond pairs. However, the HNH bond angle is not equal to normal tetrahedral angle i.e. 109.5°. The reported bond angle is 107°. The

observed decrease in the bond angle is due to the repulsion caused by the lone pair over the bond pairs. That is why ammonia molecule is trigonal pyramidal in shape.

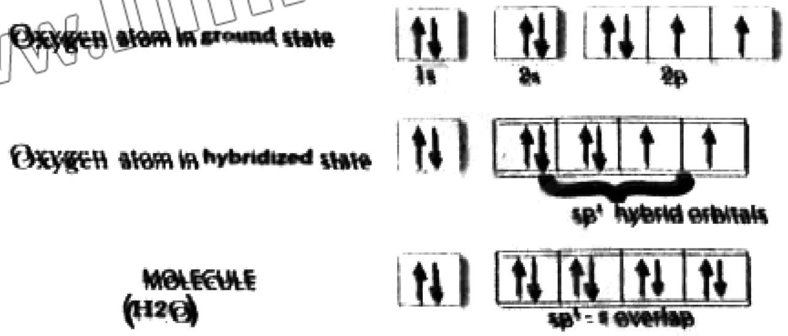
Figure 3.20: NH_3, Trigonal Pyramidal Molecule

4. Water Molecule (H_2O)

The electronic configuration of oxygen is $1s^2\ 2s^2\ 2p_x^2 2p_y^1 2p_z^1$. There are two unpaired electrons in oxygen atom which may form bonds with hydrogen atoms. The experimental bond angles reported were equal to 104.5°. To account this, sp^3 hybridization before the bond formation was proposed.

During the formation of water molecule, the oxygen atom undergoes sp^3 hybridization by mixing a 2s and three 2p orbitals to furnish four sp^3 hybrid orbitals oriented in tetrahedral geometry.

Among them, two are half filled and the remaining two are completely filled.



Now the oxygen atom forms two σ sp^3-s bonds with hydrogen atoms by using half-filled hybrid orbitals. Bond angle between HOH in water molecule is 104.5. It is again due to repulsions caused by two lone pairs on the bond pairs. Thus, water molecule gets angular shape (V shape).

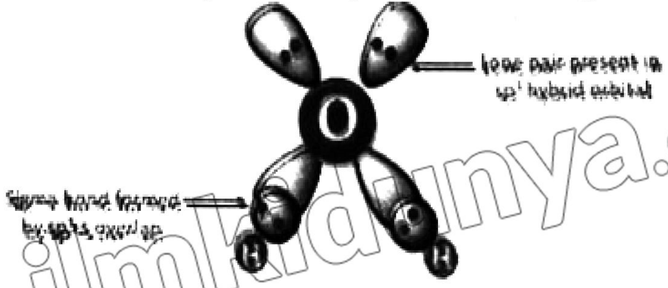


Figure 3.21: Hybridization in H_2O Molecule

3.8 CO-ORDINATE COVALENT BOND

A Co-ordinate Covalent Bond (or dative covalent bond) is formed when one atom provides both the electrons needed for a covalent bond or shared paired of electron is donated by one atom only. For dative covalent bonding we need:

One atom having a lone pair of electron and the second atom having an unfilled empty orbital to accept the lone pair (an electron-deficient atom/molecule).

During the formation of hydronium ion, water containing lone pair of electrons donate a pair of electrons and form dative bond with the electron deficient hydrogen ion.

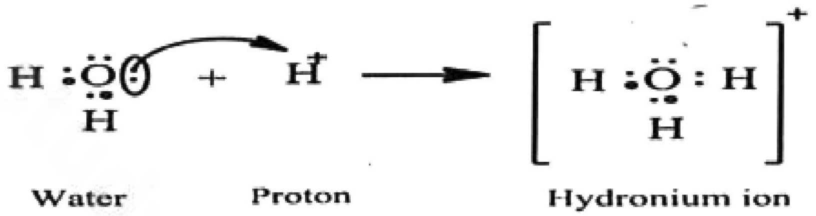
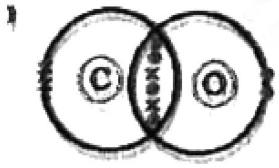


Figure 3.22: Formation of Coordinate Covalent Bond in Hydronium ion

In Ozone (O_3) molecule, central oxygen atom donates its electron pair with other oxygen atom and form dative bond.

Coordinate covalent bond is also present in carbon monoxide molecule.



$C \equiv O$ or $C \equiv O$

In this molecule oxygen atom form coordinate covalent bond with carbon atom.

Concept Assessment Exercise 3.3

1. Draw dot-and-cross diagrams to show the formation of a co-ordinate bond between the following:
   i boron trifluoride, BCl_3, and ammonia, NH_3, to form the compound Cl_3BNH_3
   ii phosphine, PH_3, and a hydrogen ion, H^+, to form the ion PH_4^+
2. Draw the displayed formulae of the products formed in part a. Show the co-ordinate bond by an arrow.

3.9 INTERMOLECULAR FORCES (FORCES BETWEEN MOLECULES)

Intermolecular forces are those forces which are present between the Covalent molecules. Physical properties such as melting point, boiling point, density etc can be explained on the basis of intermolecular forces.

3.9.1 Types of Intermolecular Forces.

There are three types of intermolecular forces

- Permanent Dipole-Dipole forces
- Instantaneous dipole induced dipole forces
- Hydrogen bonding

1. Permanent dipole-dipole Forces

These forces are present between polar molecules. Polar molecules are those molecules where due to electronegativity difference one atom bears partial positive charge and the other, which is more electronegative, bears partial negative charge.

Some molecules with polar bonds have an overall dipole (e.g. $\overset{\delta+}{H}-\overset{\delta-}{Cl}$), Although not all do e.g. In CCl_4 the individual dipoles cancel each other out, so CCl_4 is non polar molecule. There are attractions between these permanent dipoles in neighboring molecules e.g. between H-Cl molecules. $\overset{\delta+}{H}-\overset{\delta-}{Cl}\cdots\overset{\delta+}{H}-\overset{\delta-}{Cl}$

Stronger the dipole-dipole forces, higher will be the value of melting point, boiling point, heat of vaporization and heat of sublimation of particular compound.

2. Instantaneous Dipole induced Dipole Forces

Those forces which are present between nonpolar molecules are called Instantaneous dipole induced dipole forces.

Even in molecules with no polar bonds, there are temporary dipoles. It is because of uneven electron distribution due to the constant movement of electrons. This induces a temporary dipole in a neighboring molecule, producing a temporary dipole induced dipole forces of attraction.

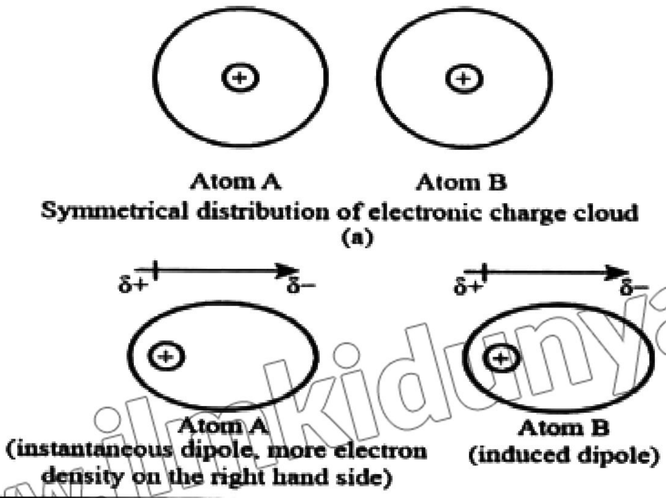


Figure 3.23: Instantaneous Dipole induced Dipole Forces.

Strength of Permanent dipole-dipole forces and Instantaneous dipole induced dipole forces (Vander waal,s forces) depends upon the following factors.

- Molecular size
- Atomic size
- Molecular mass
- No of electron in the molecule

The bigger the molecule i.e., more the electrons, larger the size or higher the relative molecular mass, greater will be the van der Waals' forces. The following table represents the boiling point of Alkanes.

Table 3.5: Boiling point of first four members of alkane

Name	Molecular formula	Boiling point (°C)
Methane	CH_4	-164
Ethane	C_2H_6	-89
Propane	C_3H_8	-42
Butane	C_4H_{10}	-1

For example, the above table shows that the boiling point of propane (C_3H_8) is greater than that of ethane (C_2H_6). It is because molecular mass of C_3H_8 is 44 which is greater than Mr of C_2H_6 which is 30.

3. Hydrogen Bonding

This is a special case of permanent dipole-dipole forces - It is present between those molecules where hydrogen is covalently bonded with higher electronegative elements such as F, N and O. There is a strong attraction from the lone pair on the N, O or F of one molecule to the exposed Hydrogen nucleus of another molecule. This is simply a strong intermolecular force - it is **NOT** a bond. Those covalent compounds which form hydrogen bonding with water molecules are water soluble. For example, ammonia is soluble in water. Figure 3.24 is represents the hydrogen bonding between ammonia and water molecules.

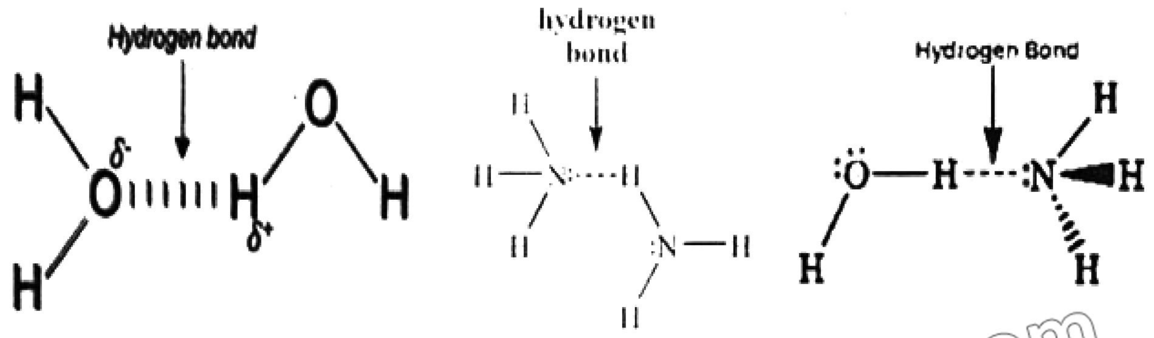


Figure 3.24: Hydrogen Bonding between Ammonia and Water Molecules.

3.9.2 Peculiar Behaviour of Hydrogen Bonding

Ice is less dense than water.

Most of the solids are denser than their liquids. This is because in solid state, the molecules are more closely packed. But this is not true of water. In ice, there is a three-dimensional hydrogen bonded network of water molecules. This produces a rigid lattice in which each oxygen atom is surrounded by a tetrahedron of hydrogen atoms. This 'more open' arrangement, due to the relatively long hydrogen bonds, allows the water molecules to be slightly farther apart than in the liquid (Figure 3.25). Hence water in solid state occupy more space. So, the density of ice is less than that of liquid water. That is why ice floats on water.

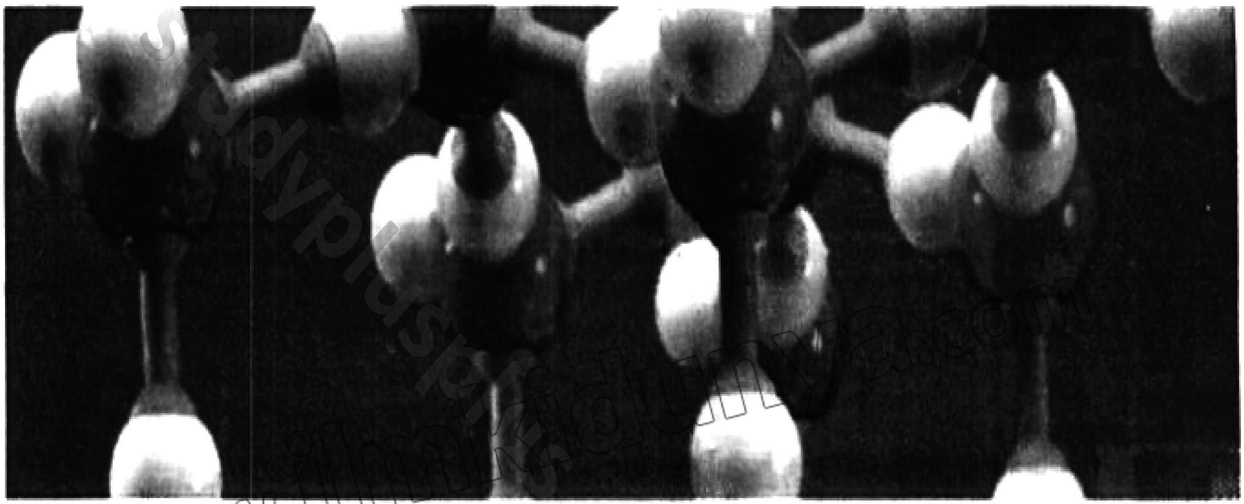


Figure 3.25: A model of ice. Oxygen Atoms are Red, Hydrogen atoms are white, Hydrogen Bonds are Lilac. This Hydrogen Bonded arrangement makes ice less dense than Water

The strength of intermolecular forces

H-bonding > permanent dipole-dipole > Instantaneous dipole induced dipole forces

Table 3.6: Comparison of boiling point of different compounds

Molecule	CH_4	HCl	H_2O
Boiling Points (°C)	−162	−85	100
Intermolecular forces	Instantaneous dipole induce dipole forces	Permanent dipole dipole forces	Hydrogen bonding

Melting and boiling points of covalent molecules depend upon the intermolecular forces not on the covalent bonds in the molecule. Covalent bonds are very strong (values in hundreds of kJ mol^{-1}). The forces between molecules are much weaker than covalent bond. Figure 3.26 represents boiling points of hydrides of Groups 4, 5, 6 and 7.

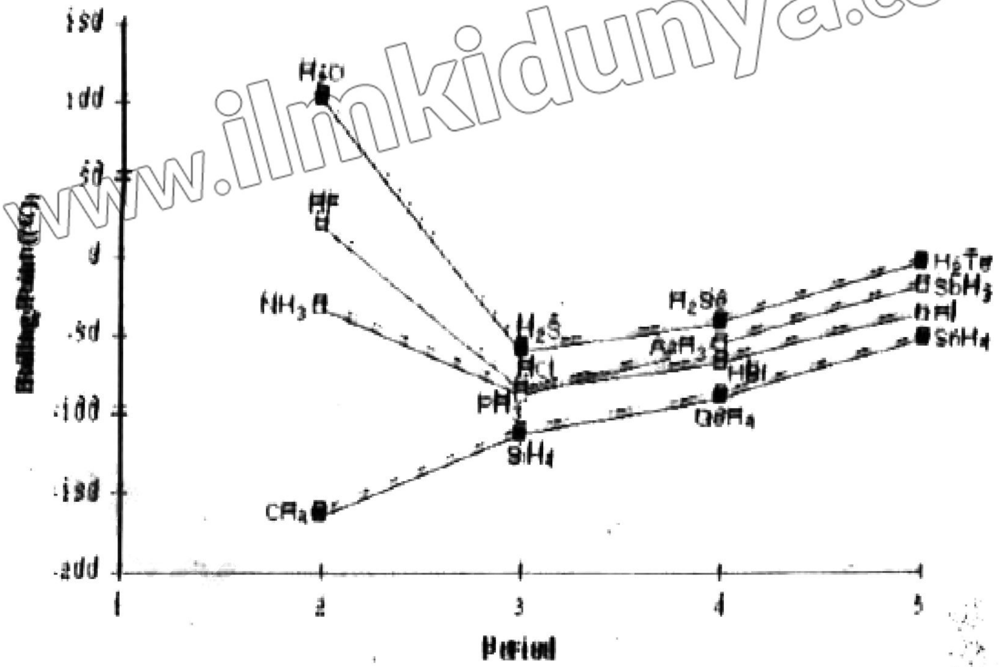


Figure 3.26: Boiling Points of Hydrides of Group 4, 5,6 and 7 Elements

Concept Assessment Exercise 3.4

1 a The boiling points of the halogens are

Fluorine	−188°C	Chlorine	−35°C
Bromine	+59°C	Iodine	+184°C

Explain the trend in these boiling points.

b The table lists the formulae and boiling points of some alkanes. Explain this trend.

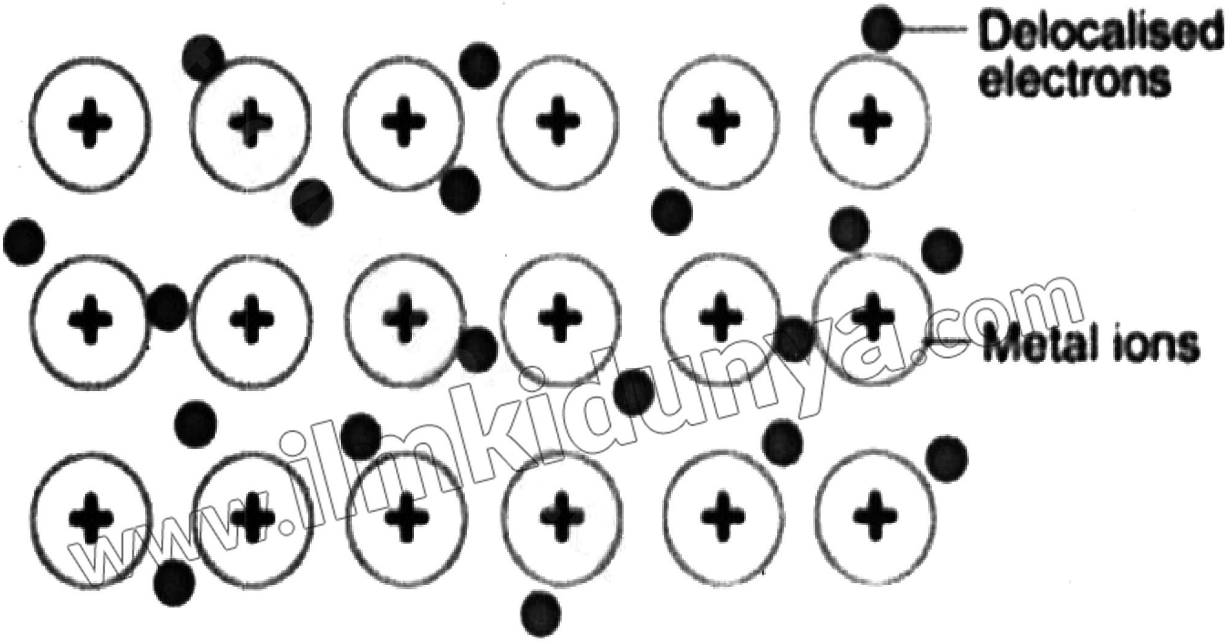
	Structural formula	Boiling point / °C
Methane	CH_4	−164
Ethane	CH_3CH_3	−88
Propane	$CH_3CH_2CH_3$	−42
Butane	$CH_3CH_2CH_2CH_3$	0

2. Bromine, Br_2, and iodine monochloride, ICl, have the same number of electrons. But the boiling point of iodine monochloride is nearly 40°C higher than the boiling point of bromine. Explain this difference.

3. Draw diagrams to show hydrogen bonding between the following molecules:
a Ethanol and water b Ammonia and water c Two HF molecules

3.9.3 Comparison of strength of Ionic, Covalent, metallic bonding and intermolecular forces

The strength of a bond depends on the specific elements involved. Ionic bonds contain strong electrostatic forces of attraction between positive and negative ions. Metallic bonds occur between atoms within a metal, where electrons are shared and free to move throughout the material. This creates a "sea" of delocalized electrons that hold the metal atoms together. Covalent bonds are formed by sharing of electrons. This sharing of electrons results in the formation of a strong bond between the atoms. The electrons are held in the region between the nuclei of the bonded atoms and the positive nuclei are attracted to these shared electrons. This leads to a stable and strong bonding interaction.



Intermolecular forces are weaker than ionic, covalent and metallic bonding and occur between molecules, not within a single molecule. These forces are responsible for holding molecules together in a substance but are much weaker as compared to the forces within a molecule (covalent bonds).

Table 3.7: Following table represents mp/bp of ionic, simple covalent, giant covalent and metallic substances.

Substance	Bonding / structure	Melting point/°C	Boiling Point/°C
Sodium Chloride	Ionic (Electrostatic forces)	801	1465
Diamond	Giant Covalent (Covalent bond)	4000	4830
Iron	Metallic (electrostatic forces)	1538	2862
Methane	Simple Covalent (Intermolecular forces)	–182	–161.6

It is obvious from the above table that the melting point/boiling point of methane is lower than that of other substances because it contains weak intermolecular force which requires less amount of energy to break.

3.10 Molecular Orbital Theory

The molecular orbital theory was proposed by Hund and Mullikan in 1932. According to this theory, linear combination of atomic orbitals form new orbitals called molecular orbitals which are characteristics of the whole molecule. During this process identity of both atomic orbitals is lost. After the combination of atomic orbitals different types of molecular orbitals are formed which differ in energy. One of lower energy, is called bonding molecular orbital (BMO) while other of high energy is called anti-bonding molecular orbital (ABMO).

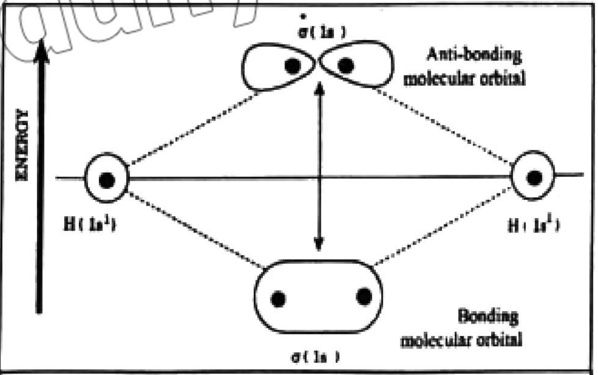


Figure 3.27: Energy diagram of bonding and anti-bonding molecular orbitals

Paramagnetic or diamagnetic nature of the molecule can be explained on the basis of molecular orbital theory as given below.

- Molecules having unpaired electrons in the molecular orbitals are paramagnetic in nature and can be attracted by magnetic field.
- Molecules having no unpaired electrons in the molecular orbitals are diamagnetic in nature and cannot be attracted by magnetic field. They repel magnetic field.

3.10.1 Bonding and Antibonding Molecular Orbitals

A bonding molecular orbital (BMO) is formed by the overlap of atomic orbitals. BMO has high electron density in the region between the two nuclei which is responsible for the stability of bond. Each electron in the BMO contributes to attraction between the two atoms. They are designated as σ and π BMO.

An antibonding molecular orbital (ABMO) is formed by the subtraction overlap of atomic orbitals. It has zero electron density in between two nuclei and the concentration of electron density is on the opposite side. Each electron in ABMO contributes to repulsion between two atoms. They are designated as $\sigma^*$and π^* $ABMO$.

The number of Molecular orbitals formed is equal to the number of atomic orbitals that are combined. Electrons in the molecular orbitals are influenced by all nuclei but in atomic orbital an electron is influenced by one nucleus.

The filling of electrons into the molecular orbitals occur according to

- Aufbau Principle
- Pauli's Exclusion Principle
- Hund's Rule

There are two types of overlapping in molecular orbital theory.

i. Head on approach (linear overlapping) or linear combination

ii. Sideways approach (parallel overlapping)

Head on approach or linear overlapping takes place by the combination of s-s, s-p and p_x-p_x

Orbitals. When "s" atomic orbitals overlap with each other two molecular orbitals σs of low energy and $\sigma^{*}s$ of high energy molecular orbital is formed.

Sideways approach or parallel overlapping of atomic orbital takes place between p_y-p_y and $p_z p_z$ orbitals. When two p orbitals py or pz atomic orbitals overlap with each other two molecular orbitals $\pi py = \pi pz$ of low energy and $\pi^{*}py = \pi^{*}py$ of high energy molecular orbital is formed.

When three 2p atomic orbitals (p_x, p_y and p_z) of one atom overlap with three 2p atomic orbitals of other atom, six molecular orbitals (three bonding and three anti-bonding) are formed. These molecular orbitals according to the energy are

$$\sigma 2p_x > \pi 2p_y = \pi 2p_z > \pi^{*}2p_y = \pi^{*}2p_z > \sigma^{*}2p_x$$

3.10.2 Bond Order (No. of Bonds)

It is the total number of bonds formed when two atoms of atomic orbitals overlap with each other. It half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No.of electrons in BMOs} - \text{No.of electrons in ABMOs}}{2}$$

The number of bonds formed in hydrogen molecule may be calculated as follows.

No. of electrons in the Bonding orbitals = 2

No. of electrons in the anti-bonding orbitals = 0

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

If bond order is zero, the molecule is unstable, and it does not exist. A positive value of order reveals that the molecule exits and is stable.

3.10.3 Relative Energies of the Molecular Orbitals

Spectroscopic measurements determine the relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals.

a) The following increasing order of energy shows the molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions.

$$\sigma 1s < \sigma^{*}1s < \sigma 2s < \sigma^{*}2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^{*}2p_y = \pi^{*}2p_z < \sigma^{*}2p_x$$

b) The diatomic molecule such as H_2, He_2, B_2, C_2, and N_2 (lighter molecules) show slightly different energy order.

$$\sigma 1s < \sigma^{*}1s < \sigma 2s < \sigma^{*}2s < \pi 2p_y = \pi 2p_z < \sigma 2p_x < \pi^{*}2p_y = \pi^{*}2p_z < \sigma^{*}2p_x$$

Elements of second period having atomic number 3 to 7 (prior to oxygen) have a relatively small difference in energy between the 2s and 2p orbitals. As the energy difference between 2s and 2p atomic orbitals is small, as a result, $\sigma 2s$ and $\sigma^* 2s$ MO do not retain pure s- character (hybridization of A.O.). Mixing of 2s and 2p orbitals is the primary cause of the difference in the molecular orbitals of nitrogen and oxygen, which is influenced by the initial atomic orbital energies. Hence energy of $\sigma 2p_x$ is greater than $\pi 2p_y$ and $\pi 2p_z$.

3.10.4 Molecular Orbital Diagram of Homo Nuclear Diatomic Molecules

After having discussed the basic principles of molecular orbital theory, we are now able to take up the electronic structures and bonding properties of some homo-nuclear diatomic molecules.

1. Hydrogen Molecule H_2

Hydrogen molecule is formed from the overlap of 1s atomic orbitals of two hydrogen atoms. They give rise to two molecular orbitals σ 1s and σ^*1s. The molecule has two electrons which occupy the lower energy σ1s orbital as shown in the figure 3.28.

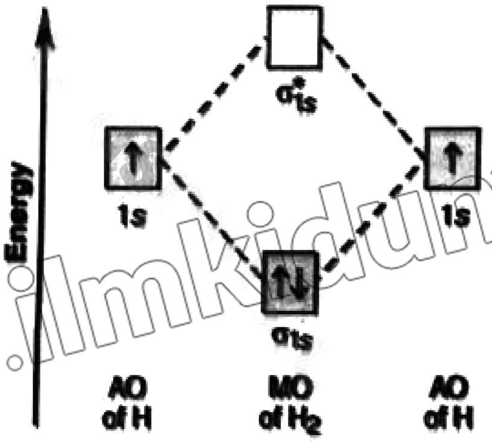


Figure 3.28: Energy Diagram of BMO and ABMO of H_2

Total number of electrons = 2

Electronic configuration of hydrogen atom is $1s^1$

$H_2 = \sigma 1s^2, \sigma^* 1s^0$

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

Magnetic character = Diamagnetic (having no unpaired electron)

2. Helium Molecule (Hypothetical) He_2

The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons occupying the anti-bonding σ^*1s orbital as shown in the figure 3.29.

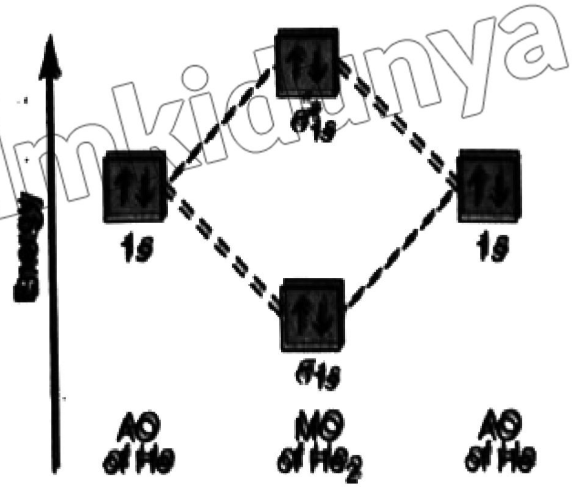


Figure 3.29: Energy Diagram of BMO and ABMO He_2

Total number of electrons = 4

Electronic configuration of helium is $1s^2$

$He_2 = \sigma 1s^2, \sigma^* 1s^2$

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

Magnetic character: As there is no unpaired electron in the molecular orbitals of He_2 molecule, it is diamagnetic.

As bond order of He_2 is zero so molecule is unstable, and it does not exist. Helium exist only as mono-atomic molecules.

3. Nitrogen Molecule N_2

Nitrogen contains three unpaired electrons in 2p orbitals.

Electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

Total number of electrons in N_2 molecule = 14

The following diagram represents the molecular orbitals of nitrogen molecule.

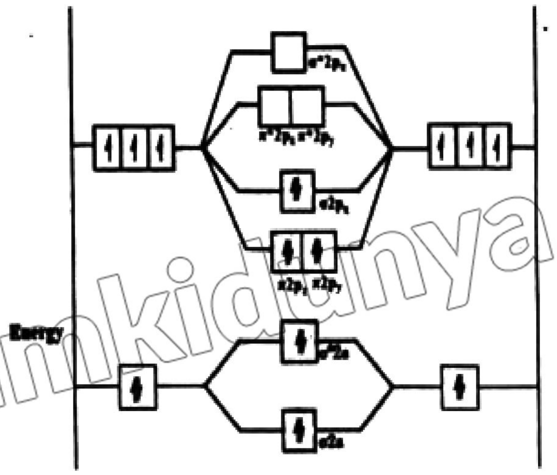


Figure 3.30: Energy Diagram of BMO and ABMO of N_2

Distribution of electrons in the molecular orbitals of nitrogen molecule is.

$N_2 = (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_y)^2 = (\pi 2p_z)^2(\sigma 2p_x)^2$

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

Magnetic character: As there is no unpaired electron in the molecular orbitals of N_2 molecule, it is diamagnetic.

Bond order of N_2 is three. Two N-atoms are bonded through triple bond. N_2 molecule is very stable molecule and has a very high bond energy 946 kJ mol^{-1}, It is diamagnetic in nature and possesses a very short bond length.

4. Oxygen Molecule O_2

Electronic configuration of oxygen is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Oxygen contains two unpaired electrons in 2p orbitals i.e. $2P_y$ and $2P_z$.

Total number of electrons in O_2 molecule = 16

The following diagram represents the molecular orbitals of oxygen molecule.

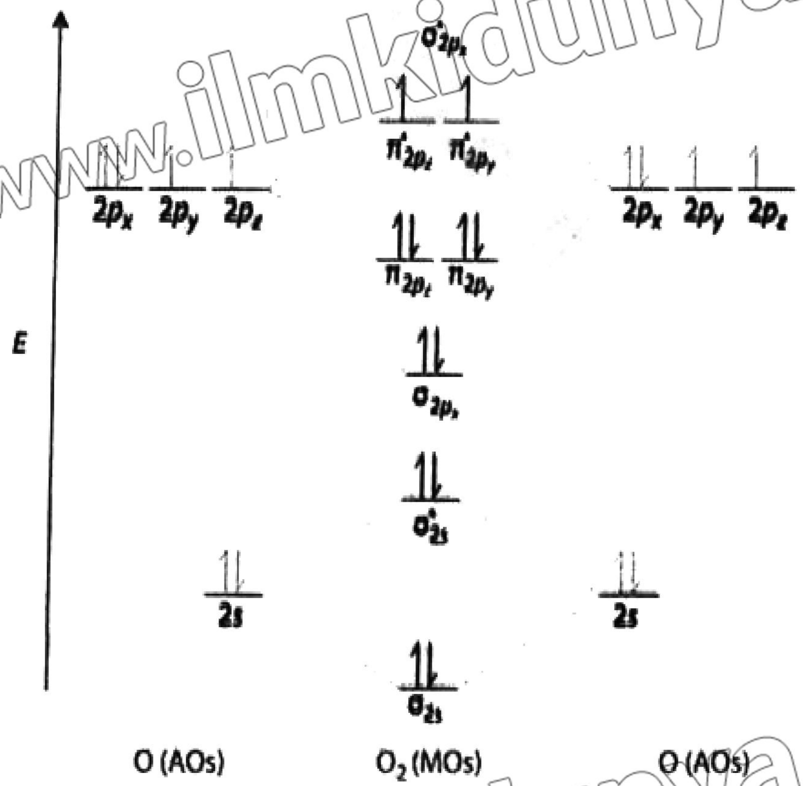


Figure 3.31: Energy Diagram of BMO and ABMO of O_2

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

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

Paramagnetic Nature of Oxygen molecule

It is found from molecular orbital diagram of oxygen molecule that the electrons present in the two π* orbitals are unpaired. The two unpaired electrons reside in the degenerate anti-bonding orbitals π^*2p_y and π^*2p_z. These unpaired electrons not only go around the atom in their orbitals, but they also spin, which creates a magnetic field. Unpaired electrons spin in the same direction as each other which increases the magnetic field effect. Due to the presence of these unpaired electrons, O_2 is found to be paramagnetic in nature.

Paramagnetic behavior of O_2 molecule is not explained by Valance Bond Theory. It is obvious that the two oxygen atoms are bonded through a double bond. So, we conclude that the molecule should be very stable as it possesses high bond energy i.e.498 kJ mol^{-1} with bond length 1.21 $A°$.

5. Fluorine Molecule F_2

Electronic configuration of Fluorine is $1s^2\ 2s^2\ 2p_x{}^2\ 2p_y{}^2\ 2p_z{}^1$

Total number of electrons in F_2 molecule = 18

The following diagram represents the molecular orbitals of fluorine molecule.

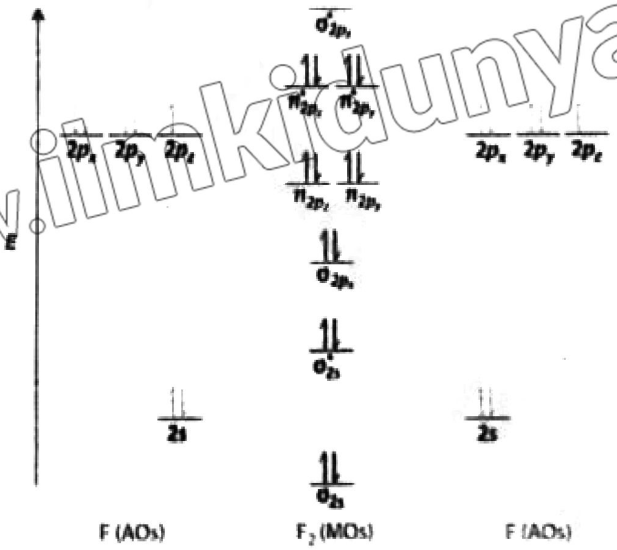


Figure 3.32: Energy Diagram of BMO and ABMO of F_2

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

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

Magnetic character: As there is paired electron in the molecular orbitals of F_2 molecule, it is diamagnetic.

Bond order of F_2 is one. Two F-atoms are bonded through a single bond. The F-F bond distance is longer (1.43A^0) than the bond distance for O_2 (1.21 A^0) and N_2 (1.09 A^0) molecules. The bond energy of F_2molecule is quite low (159kJ mol^{-1}). It is diamagnetic in nature because it has no unpaired electrons.

Key Points

- Electronegativity is the power of an atom to attract shared paired of electron to itself in a molecule. Nonmetals have higher value of electronegativity compared to metals.
- Valence shell electron repulsion theory is used to predict the geometry of molecules.
- Valence bond theory based on the overlapping of atomic orbitals in order to form a chemical bond.
- By predicting molecular shapes and bond angles, VSEPR aids Medicinal chemists in understanding how drug molecules interact in the body.
- According to Molecular orbital theory the number of molecular orbitals produced is always equal to the number of atomic orbitals of atoms in the molecules that have combined. In these molecular orbitals bonding molecular orbitals are lower in energy from their parent atomic orbitals, and the antibonding molecular orbitals are higher in energy. This theory is used to explain the paramagnetic character of the molecule.
- Intermolecular forces are present between the molecules while intramolecular forces are present within the molecules i.e. covalent bonds.
- Hydrogen bonding is the strongest dipole dipole forces. Covalent compounds which form hydrogen bonding with water molecules are soluble in water.
- Wander Waals forces depends on the molecular mass, no of electrons present in the molecule and molecular size.
- Bond energy is the amount of energy required to break the bond of same type in one mole of bonds. It depends upon the electronegativity difference between two bonded atoms and bond length.
- Dipole moment is the product of the magnitude of charges and distance between them.

References for Further Information

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Exercise

1. Choose the correct answer

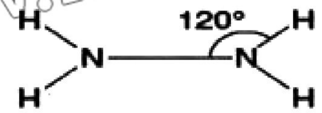
(i) Which of the following molecules is nonpolar?

a. CCl_2F_2 b. $CHCl_3$
c. C_2Cl_4 d. C_2H_5Cl

(ii) Which is the most likely shape of hydrazine, N_2H_4?

A


B


C


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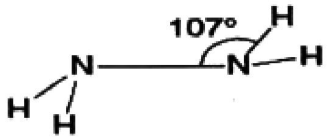


(iii) Which molecule contains only six bonding electrons?

a. C_2H_4 b. C_2F_6
c. H_2O d. NF_3

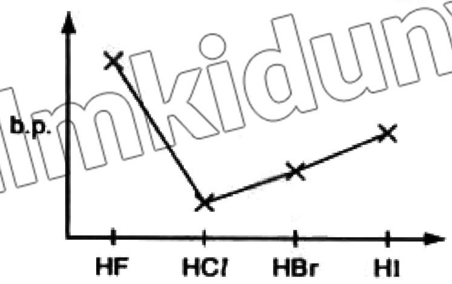
(iv) Which molecule is trigonal planar in shape?

a. NF_3 b. C_2Cl_4
c. C_3H_6 d. C_3H_8

(v) Which of the following orbitals overlap with each other in the PH_3 molecule?

a. sp^2 - s b. sp - s
c. sp^3-p d. sp^3 - s

(vi) The diagram shows the variation of the boiling points of the hydrogen halides.

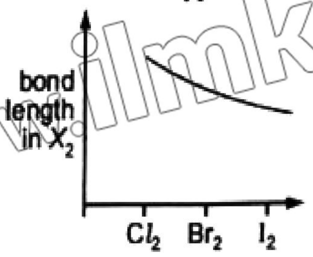


What explains the higher boiling point of hydrogen fluoride?

a. The bond energy of HF molecules is greater than in other hydrogen halides.
b. The effect of nuclear shielding is much reduced in fluorine which polarizes the HF molecule.
c. The electronegativity of fluorine is much higher than for other elements in the group.
d. There is hydrogen bonding between HF molecules.

(vii) Which graph correctly describes a trend found in the halogen group?

A



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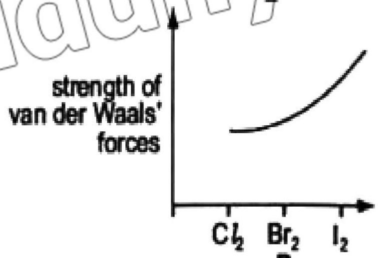

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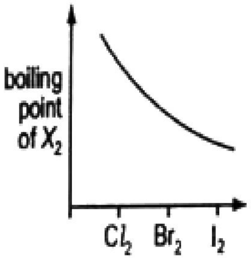

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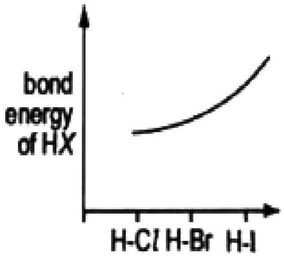


(viii) Sp^3 hybridization is not important in describing the bonding in;

a. NH_4^+ b. CCl_4

c. H_2O d. AgCl

(ix) In the formulation of N_2^+ from N_2, the electron is removed from;

a. $\sigma 2p_x$ orbital b. $\sigma^* 2p_x$ orbital

c. $\pi 2p_y$ orbital d. $\pi^* 2p_y$ orbital

(x) In which process are hydrogen bonds broken?

a. $H_2(l) \rightarrow H_2(g)$ b. $NH_3(l) \rightarrow NH_3(g)$

c. $2HI(g) \rightarrow H_{2(g)} + I_{2(g)}$ d. $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$

(xi) The CN1- ion is widely used in the synthesis of organic compounds.

What is the pattern of electron pairs in this ion?

	bonding pairs of electrons	lone pairs on carbon atom	lone pairs on nitrogen atom
A	2	1	1
B	2	2	1
C	3	1	1
D	3	1	2

(xii) Which chlorine compound has bonding that can be described as ionic with some covalent character?

a. NaCl b. $MgCl_2$

c. $AlCl_3$ d. $SiCl_4$

(xiii) Gaseous nitrogen is less reactive than gaseous fluorine. What is the reason for this difference in reactivity?

a. The boiling point of nitrogen is lower than that of fluorine.
b. The relative molecular mass of nitrogen is lower than that of fluorine.
c. The atomic radius of nitrogen is greater than that of fluorine.
d. The bond strength in the molecule is greater in nitrogen than in fluorine.

2. The table shows the atomic number and boiling points of some noble gases.

Gas	helium	neon	argon	krypton	Xenon
Atomic number	-12	-110	-118	-136	-154
Boiling point / °C	-253	-246	-186	-152	-107

a Explain this trend in boiling points. b Xenon forms a number of covalently bonded compounds with fluorine. i Draw a dot-and-cross diagram for xenon tetrafluoride, XeF_4.

iii Suggest a shape for XeF_4. Explain why you chose this shape.

3. Aluminium chloride, $AlCl_3$, and ammonia, NH_3, are both covalent molecules.

A Draw a diagram of an ammonia molecule, showing its shape. Show any lone pairs of electrons. Also State the bond angle HNH in the ammonia molecule.

b What type of forces are present in ammonia molecule. Draw diagram to show forces between ammonia molecules.

c An ammonia molecule and an aluminium chloride molecule can join together by forming a co-ordinate bond. i Explain how a co-ordinate bond is formed.

ii Draw a dot-and-cross diagram to show the bonding in the compound formed between ammonia and Aluminium chloride, H_3NAlCl_3.

4. Electronegativity values can be used to predict the polarity of bonds.

a Explain the term electronegativity.

b The electronegativity values for some atoms are given below: H = 2.1, C = 2.5, F = 4.0, Cl = 3.0, I = 2.5 Use these values to predict the polarity of each of the following bonds by copying the bonded atoms shown below and adding δ+ or δ- above each atom.

i H—I
ii F—I
iii C—Cl

c Describe the shape of this ICl3molecule. Also mention bond angle in it.

d The boiling points of the hydrogen halides are shown in the table.

Hydrogen halide	HF	HCl	HBr	HI
Boiling point / °C	+20	–85	–67	–35

i Explain the trend in boiling points from HCl to HI.

ii Explain why the boiling point of HF is so much higher than the boiling point of HCl.

e Tetrachloromethane, CCl_4, is a non-polar molecule. Draw a diagram to show the shape of this molecule. Explain why this molecule is non-polar.

5. a. Hydrogen sulphide, H_2S, is a covalent compound. Explain the type of hybridization also write bond angle in HSH. Also show on your diagram the partial charges on each atom as $\delta+$ or $\delta-$ and an arrow showing the exact direction of the dipole in the molecule as a whole.

b. Oxygen, O, sulphur, S, and selenium, Se, are in the same group in the Periodic Table.

i Explain why hydrogen selenide, H_2Se, has a higher boiling point than hydrogen sulphide, H_2S. ii Explain why the boiling point of water is so much higher than the boiling point of hydrogen sulphide.

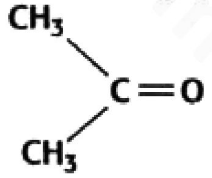
6. a. Describe the shape of the carbon dioxide molecule.

b. Bromine is a liquid at room temperature. Weak van der Waals' forces hold the bromine molecules together. Describe how van der Waals' forces arise.

7. Water is extensively hydrogen bonded. This gives it anomalous (peculiar) properties.

a Explain why ice is less dense than liquid water. Also State two other anomalous properties of water.

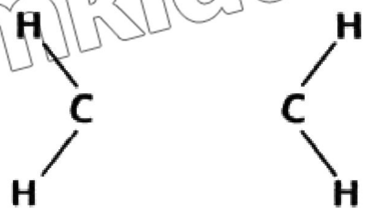
b Propanone has the structure shown below.



When propanone dissolves in water, it forms a hydrogen bond with water. Draw a diagram to show a propanone molecule and a water molecule forming a hydrogen bond.

c (i) Propanone has a double bond. One of the bonds is a σ bond (sigma bond). The other is a π bond (pi bond). Explain the difference between a σ bond and a π bond in terms of how they are formed.

ii Copy the diagram, then complete it to show the shapes of the electron clouds in the σ bond and the π bond between the carbon atoms in ethene. Label your diagram.



8. Energies of orbitals can be explained by molecular orbital theory. It has been observed that in case of Nitrogen molecule $\sigma 2p_x$ is higher in energy than $\pi\ 2p_y$ and $\pi\ 2p_z$

   a Draw molecular orbital energy diagram for nitrogen molecule.

   b Give reason why the $\sigma\ 2p_x$ energy is greater than $\pi 2p_y$ and $\pi 2p_z$.

9. Carbon can make a bond with hydrogen to form ethyne. Bond energy of C-H is same although 2s and 2p orbitals are involved which have difference in energies. Explain the formation of ethyne molecule on the basis of hybridization with the help of diagram.

10. Explain the magnetic properties of O_2, O_2^+ and N_2 by applying molecular orbital theory.

11. Differentiate between a sigma bond and a pi bond.