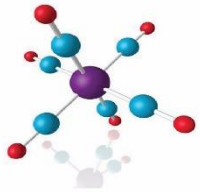
3 CHAPTER

CHEMICAL BONDING



Chemical bond

A chemical bond is the force that holds together two or more atoms, molecules or ions. The properties of a substance depend on the type of the chemical bond between its atoms.

The term chemical bond includes ionic, covalent, dative, metallic bonds, as well as intermolecular forces, i.e. van der Waals forces. However, being weak enough, van der Waals forces are usually not termed as pure chemical bonds.

In this chapter, we shall discuss the types of bonds in the light of electronegativity and its effect on the nature of bonding, dipole moment, and polarity. Then, the modern bonding theories such as VSEPR, VBT, Hybridization, and MOT will be discussed in detail. The intermolecular forces, i.e. van der Waals forces will also be considered. Finally, a comparison of the chemical bonds and intermolecular forces will be presented in terms of bond energies.

NaCl has ionic bond and is solid, but water is a covalent compound and liquid

3.1 TYPES OF BONDING

Lewis concept of bonding gives a simple explanation of the formation of all types of bonds. According to this theory, atoms make bonds to complete their outermost shells to have noble gas like configuration. This is mostly attained through the formation of an octet in the valence shell.

3.1.1 Ionic Bond

Definition

"According to the Lewis theory, the ionic bond is formed by the complete transfer of electrons from an atom with low ionization energy to another atom with high electron affinity."

Formation of NaCℓ

(i) The Na atom ($_{11}$Na = 2,8,1) tends to lose the outermost electron to form Na^+ (2, 8) ion, which has the electron configuration of $_{10}$Ne, a noble gas nearest to it.

(ii) Chlorine atom Cl (2,8,7) gains one electron to form the chloride ion, Cl^- (2,8,8), also gaining the next noble gas electron arrangement.

(iii) The oppositely charged Na^+ and Cl^- ions are held together by strong ionic bond in the crystal of NaCl. A similar type of bond is expected between group 1and 2 metals and groups 16 and 17 non-metals.

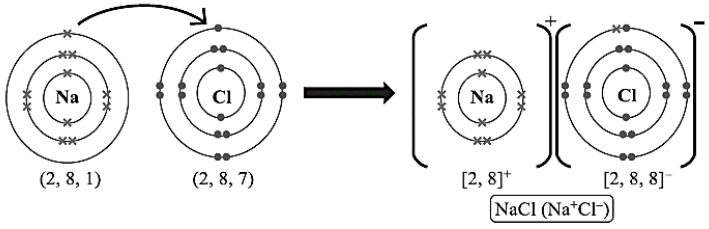


Fig. (3.1) Ionic bond formation between Na and Cl

3.1.2 Covalent Bond (Electron Pair Bond)

Definition

"A covalent bond is formed by the mutual sharing of electrons between two atoms."

Purpose

While sharing electrons, each atom completes its valence shell and attains the nearest noble gas configuration.

Example

The bond formation between two Cl atoms is shown below (Fig. 3.2).

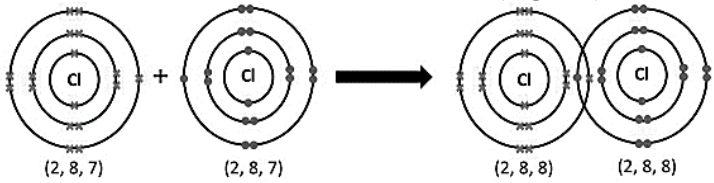


Fig (3.2) Formation of a covalent bond between two Cl atoms

Types of covalent bond

A covalent bond may be non-polar or polar in character.

(i) Non-polar covalent bond

The bond between two Cl atoms is purely covalent and non-polar. The electronegativity of the two atoms is exactly the same, due to which, the bonded atoms remain electrically neutral and there is no charge on either atom.

Examples

H_2, F_2, Br_2 and I_2.

(ii) Polar covalent bond

The electronegativity of the two atoms is different due to which, the bonded atoms develop partial charges on atoms.

Examples

H–Cl, H-Br and H_2O.

SHORT QUESTION

Define coordinate covalent bond with an example.

3.1.3 Dative Bond (Coordinate Covalent Bond)

Definition

"A dative bond is formed between two atoms when the shared pair of electrons is donated by one of the bonding atoms."

Explanation

This bond is formed by overlapping of one completely filled orbital with one *empty orbital*. An atom that donates a pair is called donor atom **(Lewis base)** and one that accepts a pair is called acceptor **(Lewis acid)**. This bond is represented by an arrow pointing from donor to acceptor.

Example 1

Let us consider the of bond formation between H_2O and a proton (H^+). H_2O has two covalent bonds and there are two lone pairs of electrons on the oxygen atom. On the other hand, the proton is deficient in electrons. Therefore, the oxygen atom can donate its lone pair of electrons to the acceptor H^+, and this results in the formation of a dative bond as in the following diagram (Figure 3.3(a).

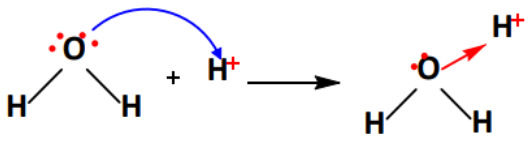


Fig (3.3) (a) Dative bond formation between water and hydrogen

Example 2

Carbon monoxide also contains a dative bond between oxygen and carbon atoms. Oxygen shares its two valence shell electrons with the carbon atom to make a normal double covalent bond. However, the valency of carbon is not satisfied with these bonds. It needs one more pair of electrons to complete its octet. Oxygen atom donates one of its lone pairs for the formation of a covalent bond, which is a dative bond as exhibited in Figure 3.3(b).

Fig (3.3) (b) Carbon monoxide

Example 3

The structure of ozone molecule is presented in Figure 3.3(c). It is formed by a reaction between the oxygen molecule with an oxygen atom (a free radical (O). One of the oxygen atoms in the molecule donates a pair of electrons to make a coordinate covalent bond with this free radical. Therefore, the central atom has total three bonds including a double covalent bond on one side and a coordinate covalent bond on the other. It carries a positive charge, while the oxygen atom that accepts the lone pair carries a negative charge.

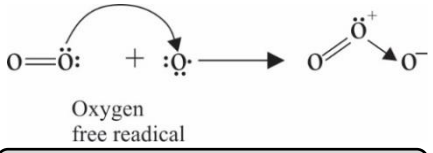


Fig (3.3) (c) Ozone molecule

QUICK CHECK 3.1

(a) Draw the Lewis structures of N_2 and CS_2 molecules.

Ans. The Lewis structure of N_2 molecule is $\ddot{N} \equiv \ddot{N}$

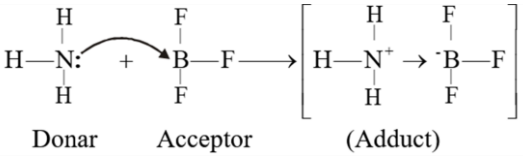
The Lewis structure of CS_2 molecule is $\ddot{S} = C = \ddot{S}$

(b) How many electrons are there in the valence shell of B in BF_3? Does it have the ability to accept a lone pair of electrons?

Ans. Yes. Since boron has only 6 valence electrons, it can accept a lone pair to complete its octet. Hence BF_3 can act as Lewis acid.

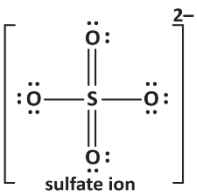
(c) Show the formation of a dative bond between NH_3 and BF_3.

Ans. Nitrogen atom in $\ddot{N}H_3$ have lone pair and it donates it to boron in BF_3 (which is electron deficient of octet) to form a co-ordinate covalent bond.



3.1.4 Expanded Octet in Polyatomic Ions

Polyatomic ions are the ions composed of more than one type of atoms.



Formal charge

Formal charge is the net charge on them which is calculated based on the number of electrons in their valence shells after the formation of bonds.

Example

With the exception of ammonium ion (NH_4^+), these ions mostly carry a negative charge.

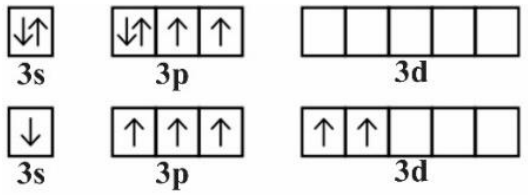
- Carbonate (CO_3^{2-})
- Sulfate (SO_4^{2-})
- Nitrate (NO_3^{3-}) ions
- In some polyatomic ions, the central atom violates the octet rule by expanding its electron density to the higher orbitals. These are said to have expanded octets.
- Some prominent examples are SO_4^{2-}, ClO_4^- , PO_4^{3-}. From the Lewis structures of SO_4^{2-}, we can calculate the number of electrons around the central S atom.
- The number of electrons in the valence shell of S atom can be calculated as:
  No of valence electrons = 2 × (double bond electrons) + 2 × (single bond electrons) = 2 (4) + 2(2) = 12
- Thus, S has 12 electrons in its valence shell and it exceeds the octet by 4 electrons.

SHORT QUESTION

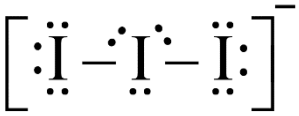
Define octet rule. Give two examples in which octet rule is not followed.

Expansion of octet

The expansion of octet is caused by the involvement of the d orbital in bonding, which can accommodate the extra electrons. The following electronic configuration of native S(0) atom shows that it has two unpaired electrons in the p orbitals. The presence of d-orbital allows this configuration to extend to 4 unpaired electrons by the transfer of one electron from 3s and one from the 3p electron pair. It explains not only the variable oxidation states of S, but also the possibility of accepting extra electrons in its d orbital.



In the same way, we can calculate the number of valence electrons around the central iodine atom in the tri-iodide ion. The Lewis structure of the ion is given by:



The number of valence electrons of the central atom can be calculated as follows,
No of valence electrons = 2 × (no. of single bond electrons) + 2 × (no. of lone pairs) = 2 (2) + 2 (3) = 10
The central iodine atom in tri-iodide ion (I_3^-) has 10 electrons in the valence shell and the octet expands by two electrons.

MULTIPLE CHOICE QUESTIONS

(i) Coordinate covalent bond is present in

(A) H_2O **(B) H_3O^+** (C) HCI (D) CH_4^+

(ii) Which one of the following has no tendency to form coordinate covalent bond with H^+?

(A) NH_3 (B) H_2O **(C) CH_4** (D) CH_3-OH

EXTENSIVE QUESTION

What do you mean by coordinate covalent bond? Write its examples.

QUICK CHECK 3.2

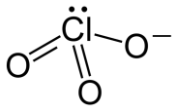
(a) Can the elements of period 2 of the periodic table have expanded octet? Explain why or why not.

Ans. No, elements of period 2 cannot have an expanded octet. Elements in period 2 (like C, N, O, F) have their valence electrons in the 2nd energy level, where only s and p orbitals are available. The maximum number of electrons that can be accommodated in the 2nd shell is 8 (2 in 2s and 6 in 2p). They lack d-orbitals in their valence shell, so they cannot expand their octet beyond 8 electrons. Therefore, period 2 elements are strictly limited to the octet rule.

(b) Predict and explain the expanded octets in the following ions: ClO_3^-, PO_4^{3-}

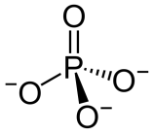
ClO_3^- (Chlorate ion)

Ans. Chlorine (Cl) belongs to period 3. Chlorine has access to 3d orbitals, so it can expand its octet. In ClO_3^-, Cl forms 3 Cl–O bonds, and one of them is typically a double bond in resonance. Cl ends up surrounded by more than 8 electrons showing expanded octet.



PO_4^{3-} (Phosphate ion)

Phosphorus (P) belongs to period 3. Phosphorus also has 3d orbitals and can accommodate more than 8 electrons. In PO_4^{3-}, P forms 3 P–O single bond and 1 P=O double bond in resonance with each other. Phosphorus is surrounded by 10 electrons. So, phosphorous has expanded octet in PO_4^{3-}.



3.2 ELECTRONEGATIVITY AND THE TYPE OF BOND

Effect of electronegativity type of bonding

i. The difference in electronegativity of two bonded atoms provides an approximate measure of the bond polarity and an indication of the type of bond.

ii. When this difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic.

iii. The following figure graphically depicts the change in the nature of bond with electronegativity difference.

iv. Two atoms having electronegativity difference less than 0.4 are said to make a pure covalent bond. An electronegativity difference between 0.4 and 1.8 corresponds to a polar covalent bond, whereas, above this value the bond between two atoms will be ionic in nature.

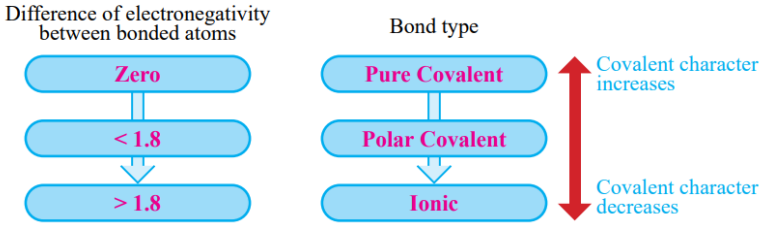


Fig (3.4) Variation of the nature of bond with the electronegativity difference

v. The electronegativity differences between the atoms in the bonds such as H–H, H–Cl, and NaCl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. This is why H-H bond is purely non-polar, H-Cl a polar covalent bond, whereas NaCl is an ionic compound.

SHORT QUESTIONS

(i) Why ionic bonds are non- directional?
(ii) No bond in chemistry is 100% ionic in nature why?

QUICK CHECK 3.3

(a) Predict with the help of electronegativity values whether the bonds in these compounds would be non-polar covalent, polar covalent, or ionic.
(i) HF (ii) KI (iii) CaF_2 (iv) ICl (v) Br_2

Ans.

(i) HF
ΔE.N = 4.0 − 2.1 = 1.9 Highly polar covalent (mostly polar covalent)

(ii) KI
ΔE.N = 2.5 − 0.8 = 1.7 Ionic

(iii) CaF_2
ΔE.N = 4.0 − 1.0 = 3.0 Ionic

(iv) ICl
ΔE.N = 3.0 − 2.5 = 0.5 Polar covalent

(v) Br_2
ΔE.N = 2.8 − 2.8 = 0 Non-polar covalent

3.2.1 Dipole Moment and Polarity of Molecules

Dipole moment in HF molecule

In compounds such as HF, where the bonded atoms are from different elements, the electronic distribution between the atoms is uneven. Due to this reason, one atom carries causes partial positive and the other negative charge.

Polarity is related to dipole moment

A molecule with δ+ charge on one part and δ- charge on the other part is called a dipole and such a molecule is said to have a dipole moment. It is a quantitative measurement of the polarity of a bond or a molecule. Higher dipole moment indicates high polarity in a molecule.

Direction of dipole moment

The dipole moments of diatomic molecules like HF, HCl, HBr, HI, NO, etc. are directed from the positive ends (δ^+) to negative ends (δ^-) as in Fig. 3.5.

Dipole moment for

(a) Diatomic molecules

In diatomic molecules (HF, HCl, HBr, CO, NO), dipole moment is directed from the positive ends (δ^+) to negative ends (δ^-).

(b) Polyatomic molecules

Poly atomic molecules contains more than one dipole moments. Net dipole moment is the resultant of vector addition of individual dipole moments.

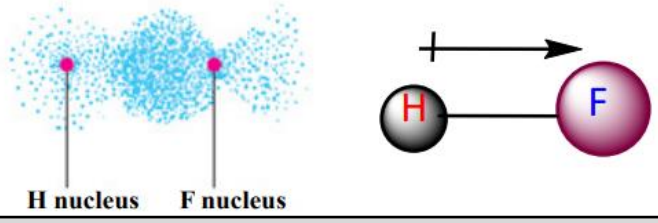


Fig (3.5) Electron density in HF is higher near the F atom and the dipole moment is directed from H to F

Unit

Dipole moment is measured in Debye unit (D).

$$1D = 3.336 \times 10^{-30} \text{ mC}$$

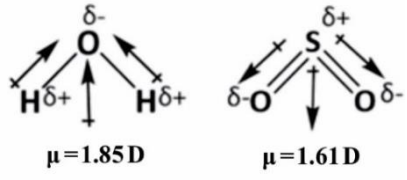
Dipole moment and structure of poly atomic molecule

For compounds having more than two atoms, the dipole moment depends on the structure of the molecule. The dipole moment of water is 1.85 D which is directed from the end having two hydrogen atoms to the end with the oxygen atom as in the structure shown in Fig. 3.6.

SHORT QUESTION

What is dipole moment? How it is measured also give its units?

A linear H_2O molecule (H-O-H) would have zero dipole moment. The non-zero dipole moment value shows that water is a non-linear molecule. Experiments reveal that the water molecule has a V-shaped structure. In contrast, SO_2 has a dipole moment of 1.61 D and in opposite direction to that in water. H_2S is also a non-linear molecule as the individual bonds are polar, but they do not cancel each other's dipole moment and the overall molecule has some dipole moment.



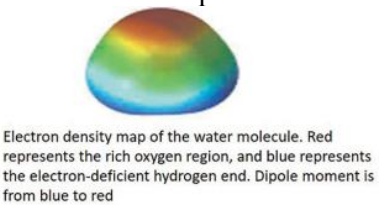


Fig (3.6) Vector addition of individual bond moments in angular H_2O and SO_2 molecules

NOTE: However, some molecules have zero dipole moments as the symmetry in their structures causes the cancellation of the individual bond moments.

$BeCl_2$ structure

It is a linear molecule having two similar Cl atoms on both sides of the central atom at 180°. The individual Be-Cl bond moments are cancelled out as they are opposite in direction and equal in amount.

CCl_4 structure

CCl_4 has four C-Cl bonds which are expected to have high polarity due to a large electronegativity difference between C and Cl atoms. The bond moments associated to the four C-Cl bonds are directed in such a way that they cancel each other. The net dipole moment of the CCl_4 molecule is zero making it a non-polar molecule. The CCl_4 molecule is perfectly tetrahedral.

BF_3 structure

BF_3 has a trigonal planar symmetrical structure and its dipole moment is also zero. As a rule, the molecules that have same ligands (atoms or groups of atoms with the central atom) in a regular geometry, the individual dipole moments may not be zero, but overall molecule has zero dipole moment. Such a molecule is said to be non-polar.

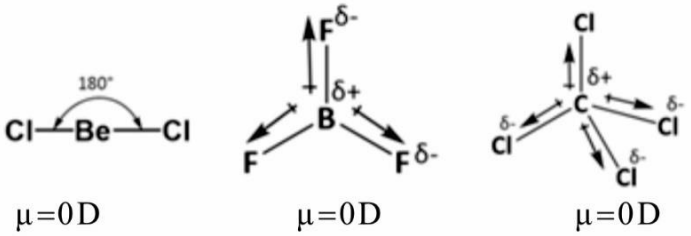


Fig (3.7) The individual bond moments in symmetrical molecules; $BeCl_2$, BF and CH_4 are cancelled out to give zero net dipole moment.

QUICK CHECK 3.4

(a) Can you explain why CO has a dipole moment but CO_2 does not have any?

Ans. CO_2 molecule has linear structure and two dipoles are acting in opposite direction so net effect will be zero. But in case of CO there is only one dipole acting from carbon to oxygen. So that is why CO molecule has dipole moment 0.12 Debye.

(b) Do you think that the bonds in CCl_4 are polar? Explain in terms of the electronegativity difference. What about the polarity of overall CCl_4 molecule?

Ans. Yes, the individual C–Cl bonds in CCl_4 are polar.

Electronegativity of C (carbon) = 2.5
Electronegativity of Cl (chlorine) = 3.0
Difference (ΔEN) = 3.0 – 2.5 = 0.5

This makes each C–Cl bond polar.

However, CCl_4 (carbon tetrachloride) has a tetrahedral shape. The four polar bonds are arranged symmetrically, and the dipole moments cancel out. Therefore, CCl_4 molecule is non-polar.

(c) Are these molecules polar or non-polar? Briefly give reasons. HF, CH_2Cl_2,O_2, H_2S.

Ans.

1. HF

ΔEN = 4.0 (F) – 2.1 (H) = 1.9

Electronegativity difference shows that it is a highly polar bond

2. CH_2Cl_2 (Dichloromethane)

In CH_2Cl_2, C–Cl and C–H bonds are polar in nature due to electronegativity difference and there is an asymmetrical tetrahedral structure and dipoles do not cancel out each other. Thus, it a polar molecule.

3. O_2 (Oxygen gas)

The difference of electronegativity between two oxygen atoms is zero. So, O_2 molecule is non-polar.

4. H_2S

The both S–H bonds are polar due to electronegativity difference. molecules have bent shape in which dipole moment do not cancel each other. So, H_2S is a polar molecule.

MULTIPLE CHOICE QUESTIONS

(i) If the electronegativity difference between bonding atom is zero then the bond formed will be

(A) Ionic **(B) Non-polar covalent** (C) Covalent (D) Polar covalent

(ii) Which factor does NOT affect electronegativity?

(A) Size of the atom (B) Nuclear charge
(C) Screening by inner electrons **(D) Atomic mass**

(iii) How does electronegativity generally change as you move from left to right across a period in the periodic table?

(A) It decreases **(B) It increases**
(C) It remains constant (D) It fluctuates randomly

EXTENSIVE QUESTION

Write a detailed note on dipole moment.

3.3 INTERMOLECULAR FORCES

Intermolecular forces

"The forces of attraction present between the molecules of a substance are called intermolecular forces."

Features

- Intermolecular forces are also considered as binding forces just like chemical bonds.
- However, the attraction between the molecules is much weaker than the chemical bonds.

SHORT QUESTION

Intermolecular forces are stronger than intramolecular forces. Why?

Van der Waals forces

"These forces are believed to exist between all kinds of atoms and molecules when they are sufficiently close to each other. Such intermolecular forces are called van der Waals forces".

These intermolecular forces bring the molecules close together and give particular physical properties to the substances in gaseous, liquid, and solid states.

Types of intermolecular forces

Three types of such forces are mentioned here:

(i) Instantaneous dipole-induced dipole forces or London dispersion forces
(ii) Permanent dipole-permanent dipole forces
(iii) Hydrogen Bonding

The detailed discussion on these forces will be made in the chapter on states and phases of matter

3.4 BOND ENERGY AND BOND LENGTH

1. Bond energy

"The bond energy is the average amount of energy required to break all bonds of a particular type in one mole of a substance".

- It is determined experimentally by measuring the heat involved in a chemical reaction.
- Bond energy is a measure of the strength of a bond and its reactivity.

Unit of bond energy

The unit of energy is kJ mol^{-1}.

Factors affecting bond energy

Bond energy depends upon the following factors:

(i) Electronegativity difference between two bonded atoms
(ii) Size of atom

Table 3.1 Average bond energies of some selected bonds in kJ mol^{-1}

Single Bonds						Multiple Bonds	
H – H	432	C – l	240	F – F	154	C = C	614
H – F	565	C – Cl	339	Cl – Cl	239	C ≡ C	839
H – Cl	427	C – N	305	Br – Br	193	O = O	495
H – Br	363	C – O	358	I – I	149	C = O	745
H – I	295	N – H	391	S – S	266	N ≡ N	941
C – H	413	N – O	201	Si – Si	340	C ≡ N	615
C-C	347	O – H	467	Si – O	452	N = O	607

Effect of electronegativity difference on bond energy

SHORT QUESTION

What is bond energy? Write factors affecting it.

Let us consider the role played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I. The data show that the bond energy of a bond rises with the increasing electronegativity difference between the bonded atoms. As the difference in electronegativity increases, the bond polarity also becomes greater and this gives rise to additional attractive force for binding

the atoms. This is why the bond energy for HF is higher (565 kJ mol^{-1}) than for HI (295 kJ mol^{-1}). It may be noted that energies of multiple bonds are greater than those of single bonds

$$C \equiv C > C = C > C - C$$

2. Bond length

"Bond length is the distance between the nuclei of two atoms forming a covalent bond".

Measurement

The bond lengths are experimentally determined by physical techniques,

(i) Electron diffraction,

(ii) X-ray diffraction, or Spectral studies.

Factors effecting bond length

The bond length of a bond is governed by many factors which are given below

(i) Electronegativity between bonded atoms

(ii) Size of bonded atoms

(iii) The nature of the covalent bond (single, double, or triple).

Some selected bond lengths are given in Table 3.2.

Table 3.2 Bond lengths of some selected bonds

Bond	Bond length (pm)	Bond	Bond length (pm)
H – H	74	Si – F	155
H – Br	144	C – F	135
C – C	154	C – Cl	180
C = C	133	C – Br	196
C ≡ C	120	C –l	214
C = O	122	B – F	130
Si – H	146	B – Cl	275

Effect of atomic size on bond length

With an increase in size of the atoms, the covalent bond length also increases. The C-Cl bond length is about 180 pm, whereas the C-F bond length is 135. This is because the Cl atom is much larger.

Effect of electronegativity difference between bonded atoms

With the rise in electronegativity difference between the bonded atoms, the bond becomes shortened.

Example

Si-F bond length in SiF_4 is found to be near 155 pm, whereas the calculation of Si-F bond from the covalent radii of Si and F (Si=117 pm and F=64 pm) is 181 pm.

SHORT QUESTION

How polarity affects bond length of molecule?

The electronegativity difference causes an ionic character in the covalent bond. The ionic character results in shortening of the bond length due to the additional attraction between the bonded atoms.

MULTIPLE CHOICE QUESTIONS

(i) What type of intermolecular force is the strongest?

(A) Hydrogen bonding (B) Permanent dipole-dipole forces

(C) Instantaneous dipole-induced dipole forces (D) Ion-dipole forces

(ii) The strongest acid among halogen acids is

(A) HCl (B) HBr **(C) HI** (D) HF

EXTENSIVE QUESTION

Explain the factors affecting bond length.

QUICK CHECK 3.5

(a) **HI is a stronger acid and a robust reducing agent, whereas HF is a weaker acid. Explain.**

Ans. HI is a strong acid because the H–I bond is very weak (~295 kJ/mol), so it easily breaks to release H^+. On the other hand, the H–F bond is extremely strong (~565 kJ/mol), so it's hard to break and release H^+. F^- is very small and highly electronegative, making it very basic and less stable in solution. Hence HF is a weak acid.

HI is a strongest reducing agent because iodine has a larger atomic radius and lower electronegativity, so it loses electrons more readily.

$$2I^- \rightarrow I_2 + 2e^-$$

I^- is much more able to donate electrons (i.e., be oxidized), making HI a strong reducing agent, while HF is not.

(b) **Acetylene ($HC \equiv CH$) is more stable than ethene ($H_2C=CH_2$). Can you explain why?**

Ans. Acetylene has triple bond; its bond energy is 839 $kJmol^{-1}$ which is higher than bond energy of ethene that is 614 $kJmol^{-1}$ due to double bond. Higher bond energy makes molecule more stable. Hence acetylene is more stable than ethene.

3.5 A COMPARISON AMONG IONIC, COVALENT, METALLIC BONDS AND INTERMOLECULAR FORCES

Effect of chemical bonding on chemical properties

Chemical bonds, i.e. ionic, covalent, and metallic bond are usually termed as true chemical bonds, as they affect the chemical properties of a substance.

Table 3.3 Relative strengths of chemical bonds and intermolecular forces

Bond Type	Bond Energy ($kJ\ mol^{-1}$)
Ionic bond in NaCI	760
O-H bond in water	464
Hydrogen bonding	20-50
Permanent dipole- Permanent dipole force	5-20
Van der Waals forces	1-20

Reason

Firstly, chemical bonds result in the formation of new species through transfer and sharing of electrons.

Physical properties

Intermolecular forces act to bring molecules closer and influence the physical properties. However, such a clear distinction between the chemical bonds and intermolecular forces is not possible.

Bond Strength

The distinctive feature of the chemical bonds and intermolecular forces is their bond strength. The strength of a force is measured by the bond energy. Table 3.4 provides a comparison among different chemical bonds and intermolecular forces.

Stronger ionic bond than covalent bond

The bond energy of ionic bond (sodium chloride, 760 kJ mol^{-1}) is highest, followed by covalent bond (O-H = 464 kJ mol^{-1}), and average hydrogen bond energy (20-25 kJ mol^{-1}). It shows that the ionic bond is the strongest form of chemical bonding.

Weaker LDF than chemical bond

It also reveals that chemical bonds are generally much stronger than intermolecular forces. The permanent dipole-dipole forces (5-20 kJ mol^{-1}) and London dispersion forces (1-20 kJ mol^{-1}) are even weaker as indicated by their low bond energies.

Strength of metallic bond

The metallic bond is mostly elaborated in terms of electrostatic forces, although some theories suggest that it may be of covalent nature. In any case, the metallic bond is weaker than both the ionic and covalent bonds. The average bond energy of the metallic bond is 100-150 kJ mol^{-1}. A satisfactory argument for the low strength of metallic bond is extensive delocalization of electrons within the metallic crystal.

3.6 VALENCE BOND THEORY (VBT)

Shape of molecules

VBT is concerned with both the formation of bonds and the shapes of molecules. This method of describing a covalent bond considers a molecule as a combination of atoms.

Postulates of VBT

The main postulates of VBT are given below

SHORT QUESTION

Describe formation of F_2 molecule.

i. A covalent bond is formed when half-filled orbitals in the valence shells of two atoms with similar energy overlap.

ii. A greater overlap of the orbitals results in a stronger bond.

iii. Covalent bonds are directional. The direction of the bond is determined by the shape and mode of the overlapping orbitals.

3.6.1 Formation of Sigma Bond

A sigma bond is formed by the linear overlap of two half-filled atomic orbitals on adjacent atoms. The orbitals approach each other on the nuclear axis. Both s and p orbitals can overlap head-on to form sigma bonds.

1. s-s Overlap (Formation of H_2 molecule)

The 's' orbital of one atom overlaps with the s-orbital of the other to give a bond orbital. This type of overlap occurs during the formation of the H_2 molecule, where each hydrogen atom has a half-filled 's' orbital.

After the bond formation, the electrons are paired up and the electron density in this molecule is symmetrical around the two nuclei as in Figure 3.8.

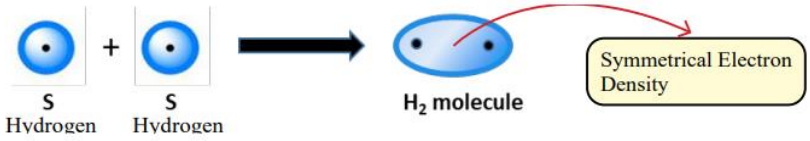


Fig (3.8) Overlap between s orbitals of two hydrogen atoms to form the H_2 molecule

2. s-p Overlap (Formation of HCl molecule)

The s orbital of one atom can overlap with the p orbital of the other to form a covalent bond (σ).

Example

In HCl molecule, a half-filled s orbital of hydrogen overlaps with a halffilled p orbital of chlorine as shown in Figure 3.9. The electron density is higher close to the Cl atom due to its

higher electronegativity value. *This is why HCl is a polar molecule.*

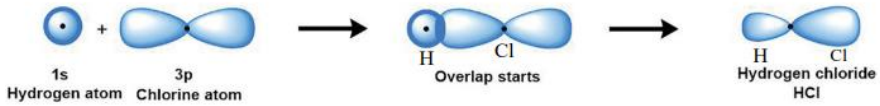


Fig (3.9) Formation of σ bond by s-p overlap

3. p – p Overlap (Formation of Cl_2 molecule)

p – p Overlap is an example of this type of overlap is the formation of the Cl_2 molecule where 'p' orbitals of two chlorine atoms overlap on the nuclear axis. The electron density is symmetrical around the nuclei of the two Cl atoms, making it non-polar molecule because both have same value of electronegativity.

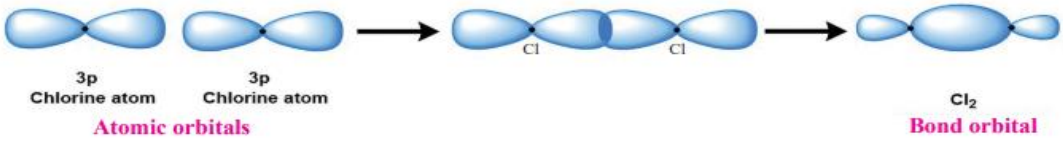


Fig (3.10) Overlap of p and p orbitals to form $C1_2$ molecule according to VBT

Interesting Information

The bond angle in H_2O is 104.5°, whereas in H_2S, it is 92°. This is because the orbitals of S are larger and the lone pair exerts a stronger repulsion.

Formation of H_2S molecule

The H_2S molecule is a non-linear molecule which is formed by the combination of one sulfur and two hydrogen atoms. The two 3p (say $3p_y$ and $3p_z$) orbitals of sulfur containing one electron each can overlap with the 1s orbitals of two hydrogen atoms. A V-shaped molecule is thus formed having a bond angle of 92° as in Fig. 3.11.

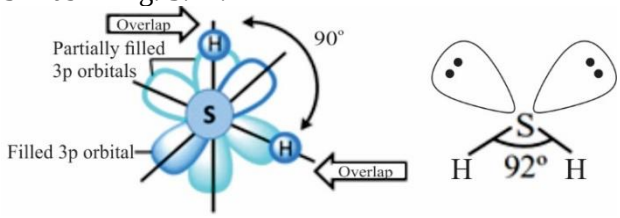


Fig (3.11) The formation of H_2S molecule by H and S orbitals overlap

Formation of π bond: (Formation of O_2 molecule)

Consider the formation of a double covalent bond between oxygen atoms (O=O).

- There are two unpaired electrons on each atom in perpendicular p orbitals (say p_x and p_y).

SHORT QUESTION

π Bonds are more diffused than σ bond. Explain it.

- The p_x orbitals on the two oxygen atoms are oriented in such a way that they overlap end-to-end linearly. The linear overlap of the p_x orbitals gives a σ bond.
- However, the unhybridized p_y orbitals on both atoms are aligned parallel to each other. They overlap in a parallel way so that the two p lobes overlap above the plane of the nuclei and the other two lobes below the plane as shown in Figure 3.12. This results in the formation of π bond. the oxygen atoms are doubly bonded through σ and π bonds.

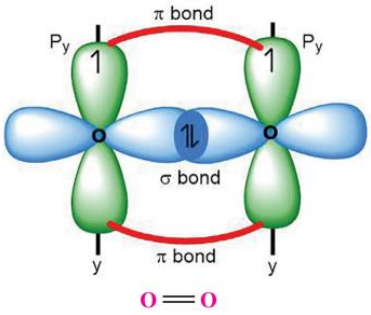


Fig (3.12) Formation of double bond (σ and π) between oxygen atoms

KEEP IN MIND

Hybridization is a process of mixing of orbitals in a single atom (or ion). Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals. The number of mixing orbitals is always equal to the number of the resulting hybrid orbitals.

(i) Identify the strongest overlapping of atomic orbital

(A) s–s (B) p–p (C) s–p (D) p–d

(ii) Overlapping of atomic orbital always produce

(A) Sigma bond (B) Pi bond (C) Dative bond (D) Ionic bond

EXTENSIVE QUESTION

Explain different types of overlapping for the formation of sigma bond.

QUICK CHECK 3.6

(a) Draw the orbital structures of H_2O and N_2 molecules.

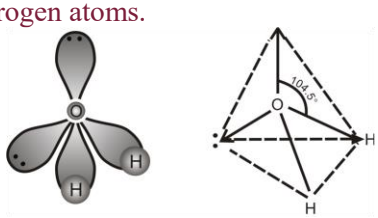
Ans. Formation of the H_2O molecule

The electronic configuration of oxygen (central atom) is

$_8O = 1s^2, 2s^2, 2p^2_x, 2p^1_y, 2p^1_z$ (Ground state configuration)

$_8O = 1s^2, (sp^3)^2, (sp^3)^2, (sp^3)^1, (sp^3)^1$ (Hybridized state)

In the valence shell of oxygen, two orbitals (2s and $2p_x$) are filled and two orbitals ($2p_y$ and $2p_z$) are half–filled. Four orbitals (One 2s and three 2p) undergo "sp^3" hybridization to form four "sp^3" hybrid orbitals. Two "sp^3" orbitals are filled having lone pairs. The rest of two "sp^3" orbitals are half filled and overlap separately with two "1s" orbitals of two hydrogen atoms.

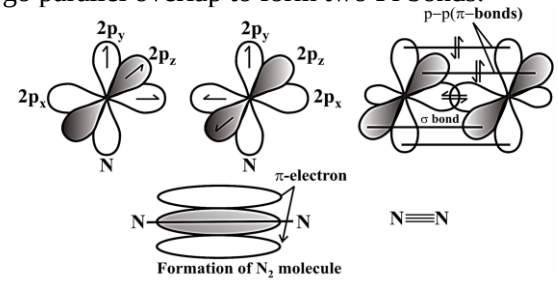


N_2-molecule (p-p linear and overlapping)

The electronic configuration of nitrogen atom is

$_7N = 1s^2, 2s^2, 2p^1_x, 2p^1_y, 2p^1_z$

Nitrogen atom has three partially filled p-orbitals. First set of p-orbitals i.e. $2p_x$ (one from each atom) undergo Linear overlapping to form a sigma bond. Second set ($2p_y$ i.e. one from each atom) and third set ($2p_z$ i.e. one from each atom) of p-orbitals separately undergo parallel overlap to form two Pi bonds.

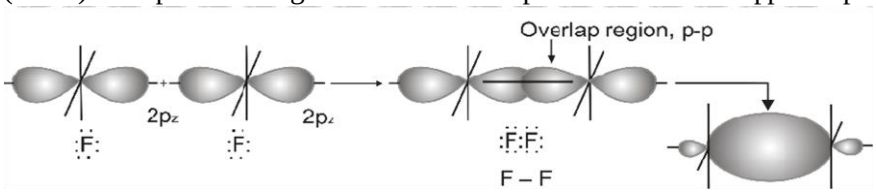


QUICK CHECK 3.6

(b) Draw the orbital overlap to show the formation of F_2 and HF molecules

Ans. The electronic configuration of F is ${}_9F = 1s^2, 2s^2, 2p^2_x, 2p^2_y, 2p^1_z$.

"$2p_z$" orbitals of both fluorine atoms are half filled and undergo head to head (Linear) overlap to form a sigma bond. The two unpaired electrons with opposite spin form a pair.



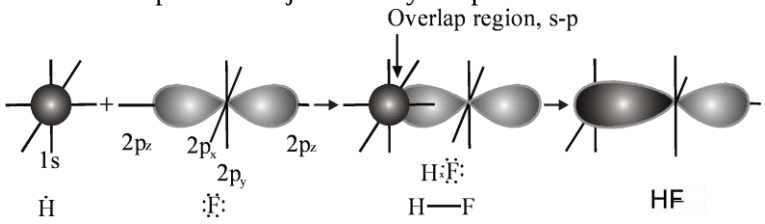
HF molecule (s-p overlapping)

The electronic configuration of both atoms are

${}_1H = 1s^1$

${}_9F = 1s^2, 2s^2, 2p2x, 2p^2_y, 2p^1_z,$

The requirements for bond formation are met by overlapping the half-filled "1s" orbital of hydrogen with the half-filled "2p" orbital of fluorine. There are then two orbitals plus two electrons whose spins can adjust so they are paired.



3.7 ATOMIC ORBITAL HYBRIDIZATION

A process in which atomic orbitals of slightly different energies and shapes are mixed together to form a new set of equivalent orbitals of same energy and same shape is called hybridization.

3.7.1 Types of Hybridization (sp, sp^2, sp^3)

1. sp–hybridization

"In sp hybridization, ones (low energy and spherical) and one p orbital (high energy and dumb-bell shaped), intermix to give a new set of two hybrid orbitals of same energy and same shape called sp hybrid orbitals".

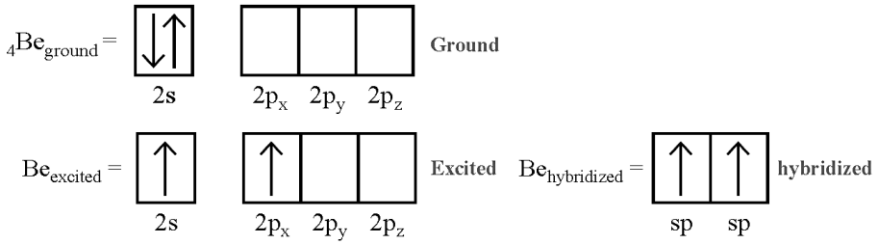
These sp hybrid orbitals are arranged in linear geometry and oriented at 180°.

SHORT QUESTION

Define sp-hybridization. Give example.

Formation of $BeCl_2$

The electronic configuration of the outermost shell of Be is as follows:



- The two sp hybrid orbitals lie linearly as in the following diagram Fig. 3.16
- The sp hybridization explains the geometry of linear molecules such as beryllium chloride, $BeCl_2$. It is formed when two sp hybrid orbitals of Be atom overlap with the half-filled p-orbitals of chlorine atoms.

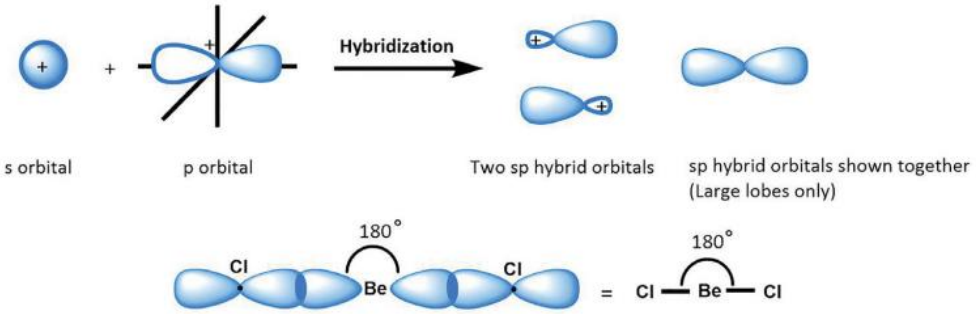


Fig (3.13) Mixing of s and p orbitals to give two hybrid sp orbitals and the formation of $BeCl_2$

2. sp^2–hybridization

"In sp^2 hybridization, one s and two p atomic orbitals of an atom intermix to form three orbitals called sp^2 hybrid orbitals."

Orbital diagram

The three half-filled sp^2 hybrid orbitals are arranged in a trigonal planar geometry with bond angles of 120°.

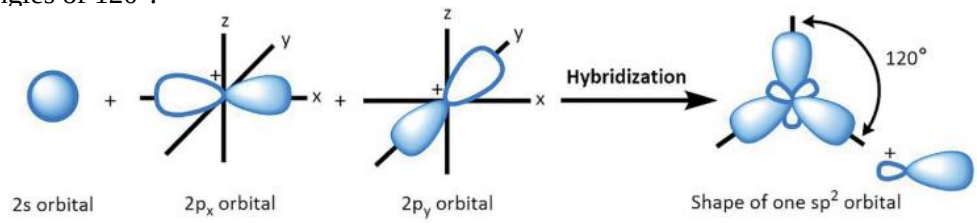
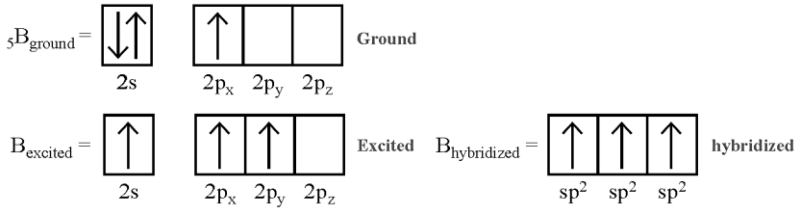


Fig (3.14) Formation of sp^2 hybrid orbitals from atomic orbitals

BF_3 molecule

- The sp^2 hybridization explains the geometry of planar molecules such as BF_3. Electronic configuration of $_5B$ is:



- The three outermost orbitals of B mix together to give three sp^2 hybrid orbitals. On the other hand, one of the p orbitals of fluorine is half filled (e.g. $2p_z$). BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms. The structure is triangular planer with each bond angles equal to 120° as in Figure 3.15.

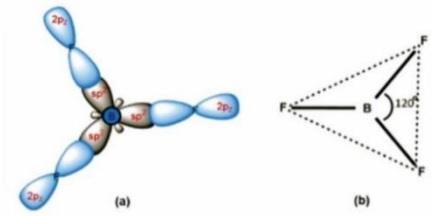


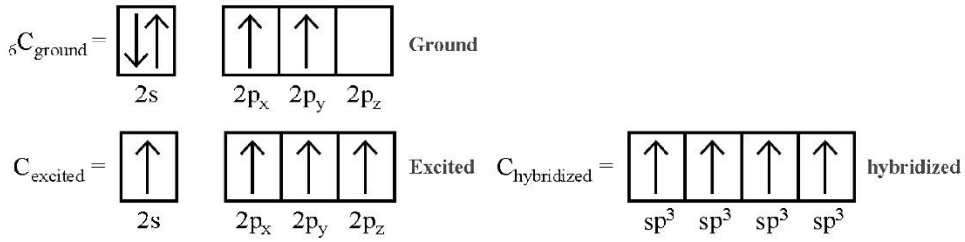
Fig (3.15) Formation of BF, molecule through sp^2-p overlap

3. sp^3–hybridization

"In sp^3 hybridization, one s-orbital (low energy and spherical) and three p-orbitals (high energy and dumbbell shaped), intermix to give a new set of four hybrid orbitals of same energy and same shape."

Example

The electronic configurations of valence shell of $_6C$ in its excited and hybridized states are given as follows:



- The energies of hybrid orbitals are lower than un-hybrid orbitals. Figure 3.16 shows the outermost four atomic orbitals of carbon mix up to give four hybrid orbitals of same energy and same shape.
- The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon nucleus at the center.
- The methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds.
- The four C-H bonds, which result from sp^3-s overlaps, are directed towards the corners of a regular tetrahedron.

SHORT QUESTION

Identify hybridization in H_2O and CO_2.

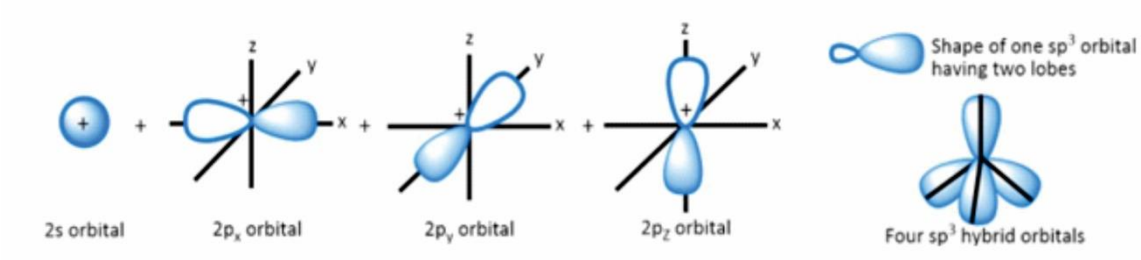
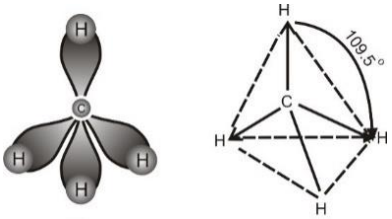


Fig (3.16) Formation of sp^3 hybrid orbitals of C in methane

The four C-H bonds, which result from sp^3-s overlaps, are directed towards the corners of a regular tetrahedron.



Did You Know?

Each sp^3 hybrid orbital consists of two lobes, one larger and the other smaller. For the sake of simplicity, the smaller lobe is usually not shown while representing sp^3 hybrid orbitals together.

(i) **Which of the following molecules exhibits sp^2 hybridization?**
(A) CH_4 (B) **BF_3** (C) H_2O (D) NH_3

(ii) **In a molecule with sp^3 hybridization, what is the approximate bond angle between the hybrid orbitals?**
(A) 90° (B) **109.5°** (C) 120° (D) 180°

(iii) **In nitrogen molecule each nitrogen atom contributes in sharing for formation of bond**
(A) One electron (B) Two electron (C) **Three electron** (D) Four electron

EXTENSIVE QUESTION

What is atomic hybridization? Why it is needed to explain the formation of ethene according to this concept.

3.8 VALENCE SHELL ELECTRON PAIR REPULSION MODEL (VSEPR)

Introduction

The VSEPR model describes the shapes of molecules based on the electron pairs that surround the central atom. This model was presented by Sidgwick and Powell in 1940.

Basic assumptions

It assumes that a molecule will take a shape such that the electronic repulsions among the valence electrons of that atom are minimum. In order to have the minimal repulsions, the electron pairs arrange themselves at farthest possible distances.

This arrangement of the electron pairs determines the geometry of the resulting molecule.

Postulates

i. Both the lone pairs (non-bonded) as well as the bond pairs participate in determining the geometries of molecules.

ii. The electron pairs are arranged around the central atom so as to remain at maximum distance apart to avoid repulsions.

SHORT QUESTIONS

(i) Write down any two pasulates of VSEPR theory.
(ii) Why the lone pair of electrons occupy more space.

iii. The electrons of lone pairs occupy more space than the bond pairs. As a result, the non- bonding electron pairs exert greater repulsive forces on bonding electron pairs and, thus, tend to compress the bond pairs.

Order of electron pair repulsion

The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:

Lone pair- lone pair (lp-lp) > lone pair -bond pair (lp-bp) > bond pair - bond pair (bp-bp)

An electron pair shared by two nuclei occupies less space than a lone pair bound by a single nucleus

iv. The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density, but they are regarded as single pairs.

v. The presence of highly electronegative atoms with the central atom results in decreased electronic repulsions between the bond pairs, but stronger repulsion by the lone pair.

Predicting the shapes of molecules

In order to illustrate this model, the central atom is named 'A'. The electron pairs around 'A' are designated as 'B'.

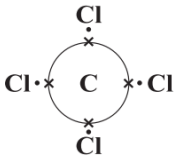
There may be different number of electron pairs around the central atom depending upon its valency. It gives rise to various types of molecules, such as AB_2, AB_3, AB_4, etc. The electron pair geometry of a molecule is determined by the total number of electron pairs around 'A'. Whereas, the actual shape of the molecule is determined by the atoms excluding the lone pairs. Following

Table 3.4 Possible Shapes of Different Types of Molecules

No. of electron pairs around central atom	No. of lone pairs	Electron pair geometry	Shape with respect to atoms	Angular separation of atoms	Examples
2	0	Linear	Linear	180°	CO_2, $BeCl_2$
3	0	Trigonal	Trigonal	120°	BCl_3, SO_3
3	1	Trigonal	Angular, V- shaped	Less than 120°	SO_2, $SnCl_2$
4	0	Tetrahedral	Tetrahedral	109.5°	CH_4, CCl_4
4	1	Tetrahedral	Pyramidal	Less than 109.5°	NH_3, H_3O^+
4	2	Tetrahedral	Angular, V- shaped	Less than 109.5°	H_2O, OF_2
5	0	Trigonal bipyramidal	Trigonal bipyramidal	120° , 90°	PCl_5, I_3^-
6	0	Octahedral	Octahedral	90°	SF_6

Steps to determine the shapes of molecules.

The following steps are followed to predict the shape of a molecule.



- The least electronegative atom or the element with the least number of atoms is mostly selected as the central atom. For example, in CCl_4, the carbon atom is the central atom.
- The total number of electron pairs around the central atom are counted (including bond pairs and lone pairs). For example, in CCl_4, the total number of bond pairs around the C atom are 4 and it has no lone pair.
- The total number of electron pairs determines the electron pair geometry (as in the above table) of the molecule. For example, CCl_4 has total four electron pairs and its geometry is tetrahedral.
- Finally, the actual shape of the molecule is determined excluding the lone pairs (if any).

Keep in Mind!

Number of electron pairs around the central atom are calculated as in the following example:
In NH_3,
Valence electrons in N = 5
Electrons shared by 3H = 3 x 1 = 3
Total number of electrons = 5 + 3 = 8
Total number of electron pairs $= \frac{8}{2} = 4$

Calculation for lone pairs on N
No. of lone pairs on N = Total no. of pairs – no. of bond pairs
No. of lone pairs on N = 4 – 3 = 1
Thus, N has 1 lone pair in NH_3.

1. AB_2 type Molecules (Linear geometry)

In such molecules, two electrons pairs around the central atom are arranged at an angle of 180° to minimize repulsions between them. Thus, they form a linear geometry as shown in Figure 3.17

Fig (3.17) Linear shape of the $BeC1_2$ molecule

Example

$BeCl_2$ molecule is of AB_2 type with Be as the central atom and two bond pairs around it, but no lone pair.

2. AB_3 type (Trigonal planar geometry)

In AB_3 type molecules, the central atom is surrounded by three electron pairs, which are arranged at maximum distance apart at an angle of 120° giving a trigonal geometry.

Example

BF_3 molecule has a trigonal planar shape with each F-B-F bond angle of 120° Figure 3.18. The similar geometries are expected in the hydrides of group 13–A, i.e. AlH_3, GaH_3, BH_3, etc.

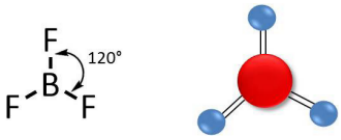


Fig (3.18) BF_3 is an AB_3 system having triangular planar geometry

AB_3 type molecule with one lone pair

In $SnCl_2$, the Sn atom has 4 electrons in its outermost shell. It makes two bonds with two Cl atoms and the remaining two electrons exist as a lone pair (Figure 3.19 below). One of the corners of the triangle is occupied by this lone pair, giving rise to a distorted trigonal electron pair geometry (in vapour phase). The actual shape of $SnCl_2$ is V-shaped and bond angle less than 120° due to the presence of a lone pair on Sn atom.

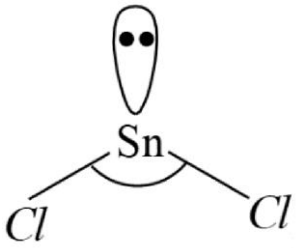


Fig (3.19) V shape of $SnCl_2$ molecules

AB_3 Type with multiple bonds

The molecule of SO_3 has all the three regions occupied by S=O bonds. The structure of SO_3 is perfectly trigonal with each angle equal to 120°. On the other hand, in SO_2, one corner of the triangle is occupied by a lone pair and the other two corners each by a double bond (S=O). Thus, it makes an angular or V-shaped structure just as $SnCl_2$ does as in Fig 3.20.

SHORT QUESTION

Explain the shape of SO_2 and $SnCl_2$ according to VSEPR theory.

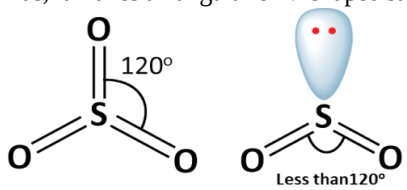


Fig (3.20) Shape of SO_2 and SO_3 molecules

3. AB_4 type molecule (Tetrahedral geometry)

In this type of molecules, the charge clouds due to four electron pairs avoid their electrostatic repulsions by being farthest apart to form the shape of a regular tetrahedron. Each of the bond angles is of 109.5°.

Shapes of CH_4

The four bonded electron pairs are directed from the center towards the corners of a regular tetrahedron, as following Fig 3.21 with each corner representing a hydrogen nucleus. This arrangement permits a non-planar geometry of electron pairs. Each H-C-H bond angle is perfectly 109.5°. On the same grounds, SiH_4, GeH_4, CCl_4 possess the similar shape

SHORT QUESTION

What is the shape and geometry of $PbCl_4$. Explain.

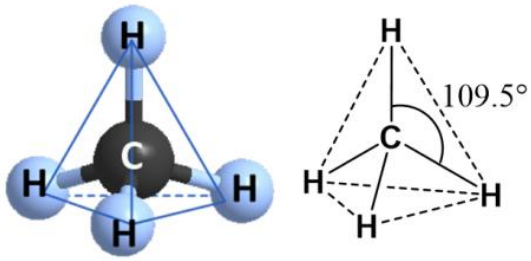


Fig (3.21) Regular tetrahedral shape of the CH_4 molecule

EXTEND YOUR KNOWLEDGE

The tetrahedral shape has four corners, four faces, six edges and six bond angles. Ideally it has bond angles of 109.5° each.

Example

Each of the four valence electrons of carbon pair up with the sole electron of a hydrogen atom in methane.

Shape of NH_3

In the ammonia molecule (NH_3), there are three atoms attached to the nitrogen atom having one lone pair. Due to a lone pair the ideal angel 109.5° is reduce to 107° as in Figure 3.22.

This effect compels ammonia to assume a triangular pyramidal shape with reduced bond angles, instead of a tetrahedral. The substitution of hydrogen in NH_3 with electronegative atoms like F or Cl further reduces the bond angles.

SHORT QUESTION

(i) Bond angle in NF_3 is 102° is less than in NH_3 107.5. Justify.
(ii) Why H_2O is liquid while H_2S is a gas?

Bond angle and NF_3

Take the example of NF_3, which contains three highly electronegative F atoms bonded to the N atom. The bond angles are further compressed to 102.5°. The first reason being the strong polarity of N-F bond, due to which N atom pulls the lone pair closer to its nucleus. This, in turn, exerts a stronger repulsion over bonding electrons. Moreover, the bond pairs (N-F bonds) are closer to F atoms than N atom. The increased distances in these bond pairs make their repulsions weaker and allow the bonds to come closer.

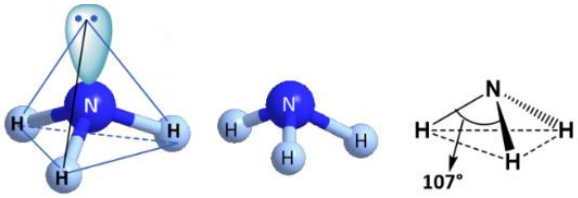


Fig (3.22) Distorted geometry and pyramidal shape of the NH_3 molecule

Shape of H_2O

Experiments reveal that the water molecule (H_2O) is angular or V-shaped, although it has four electron pairs around the central atom. Two of the corners of the tetrahedron are occupied by two lone pairs and the remaining two by bond pairs. But, due to the greater repulsions of the lone pairs, the bond angle is reduced to 104.5° as in Fig 3.23.

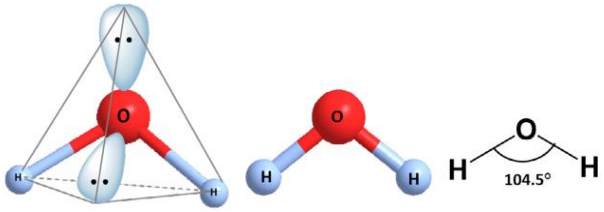


Fig (3.23) Water molecule has two lone pairs and is v-shaped with suppressed bond angle

Shape of H_3O^+

The VSEPR model also explains the shapes of ions. The hydronium ion $[H_3O]^+$ is formed when a water molecule captures a proton. The hydronium ion belongs to AB_4 type with one lone pair and possesses a trigonal pyramidal shape just like the ammonia molecule. The amide ion $[NH_2]^-$ is also

AB_4 type as it is surrounded by two lone pairs and two bond pairs. Its geometry is tetrahedral, but it has a bent shape (v-shape) similar to the water molecule (Figure 3.24)

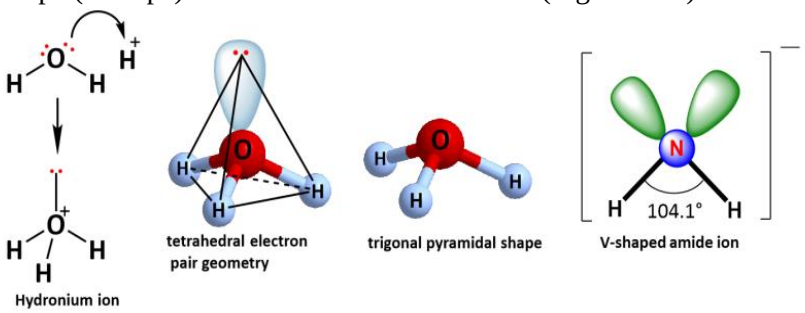


Fig (3.24) Shapes of hydronium and amide ions (NH_2^-)

QUICK CHECK 3.7

(a) Calculate number of lone pairs on central atom in following H_2O, ICl_3, I_3^{-1}

Ans. **H_2O**

Central atom = oxygen
Group number = 6
Number of bonds = 2
Valence electrons = 6

$$\text{Number of lone pairs} = \frac{\text{No. of valence electron} - \text{No. of bonds}}{2}$$

$$= \frac{6-2}{2} = 2$$

ICl_3

Central atom = Iodine
Group number = 17
Valence electrons = 7
Number of bonds = 3

$$\text{Number of lone pairs} = \frac{\text{No. of valence electron} - \text{No. of bonds}}{2}$$

$$= \frac{7-3}{2} = 2$$

I_3^{-1}

Central atom = Iodine
Group number = 17
Valence electrons = 7
Total electrons = 7 + 1 = 8
Number of bonds = 2

$$\text{Number of lone pairs} = \frac{\text{No. of valence electron} - \text{No. of bonds}}{2}$$

$$= \frac{8-2}{2} = 3$$

(b) Calculate the number of bond pairs and lone pairs in SiH_4, H_2Se, and PH_3.

Ans.

1. SiH_4 (Silane)
Si has 4 valence electrons.
It forms 4 single bonds with H atoms.
Bond pairs = 4, Lone pairs = 0

2. H_2Se (Hydrogen selenide)
Se has 6 valence electrons.
It forms 2 single bonds with H atoms.
Remaining electrons: 6 − 2 = 4 electrons
= 2 lone pairs
Bond pairs = 2, Lone pairs = 2

3. PH_3 (Phosphine)
P has 5 valence electrons.
It forms 3 single bonds with H atoms.
Remaining electrons: 5 − 3 = 2 electrons
= 1 lone pair
Bond pairs = 3, Lone pairs = 1

QUICK CHECK 3.7

(c) Predict the shapes and angles in SiH_4, H_2Se, and PH_3

Ans.

1. **SiH_4**
Shape: Tetrahedral
Bond angle: ~109.5°

2. **H_2Se**
Shape: Bent/V-shaped (like H_2O, due to 2 lone pairs)
Bond angle: < 104.5°

3. **PH_3**
Shape: Trigonal pyramidal
Bond angle: < 107°

(d) Predict how the bond angle in H_2S would be different from that in H_2O.

Ans. H_2O has bond angle 104.5° where as that of H_2O is 92°. The reason is that
Size of s atom is move than O.
Lone pair electrons of S experience nuclear attraction so is much expanded.
Bond length of S–H is more than O–H.
Thus, lone pair cause more repulsion leading to decrease in bond angle.

4. AB_5 type (Trigonal bipyramid geometry)

In AB_5 type molecules, repulsions between the five electron pairs can be minimized by an even distribution of electrons among the corners of a trigonal bipyramid geometry. In a trigonal bipyramid, three positions lie along the corners of the planar triangle, whereas, the other two positions lie along an axis perpendicular to the plane.

Angle

The angles within the plane are 120° and that between the axial atom and a planar atom is 90°.

Example

This is evident from the geometry of the PCl_5 molecule given in Figure 3.25.

Geometry of the PCl_5 molecule

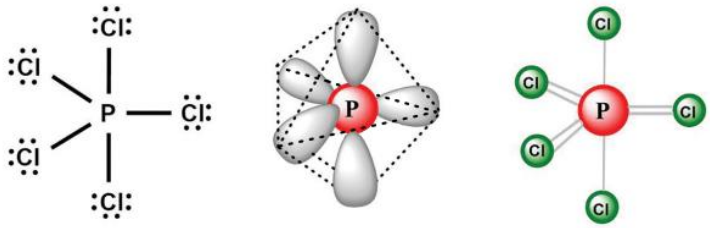


Fig (3.25) Lewis structure and shape of PCl_5 molecule

Tri-iodide ion $[I_3]^-$ is linear, although it is an AB_5 system. The central atom in this ion is the iodine atom. There are five electron pairs around the iodine atom including two bond pairs and three lone pairs. Therefore, it is an AB_5 type molecule with three lone pairs and possesses trigonal bipyramidal geometry. The lone pairs occupy the corners of the trigonal region and the iodine atoms occur on the apices, one being above and the second below the plane. However, the actual shape of the tri-iodide ion is linear and the iodine atoms are at an angle of 180° as in Figure 3.26.

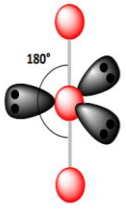


Fig (3.26) Shape of tri-iodide ion $[I_3^{-1}]$

5. AB_6 type molecules (Octahedral Geometry)

- AB_6 type molecules have 6 electron pairs around the central atom. The repulsions between the electron pairs can be minimized by assuming an octahedral geometry.
- In this geometry, four electron pairs are at the corners of a planar square and the other two lie along an axis perpendicular to the square.

Structure of SF_6

All the ABA angles in this type of geometry are of 90°. The Lewis structure of SF_6 is given in Figure 3.26, it shows that this is an AB_6 type molecule.

SHORT QUESTION

Describe geometry of H_2S and SF_6.

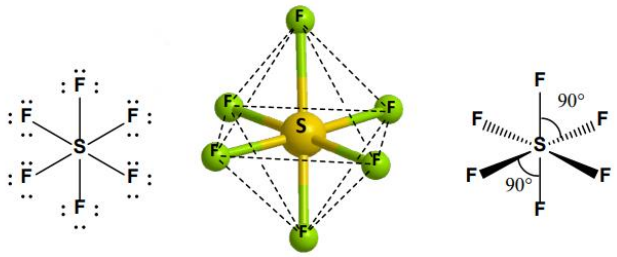


Fig (3.27) Lewis structure and octahedral shape of SF_6 with each angle of 90°

Geometry of XeF_4

XeF_4 is an AB_6 type molecule with four bond pairs and two lone pairs. the two lone pairs remain at farthest distance at angle of 180°. Excluding the lone pairs, the actual shape of XeF_4 is square planar with all F-P-F angles equal to 90° as in figure 3.28.

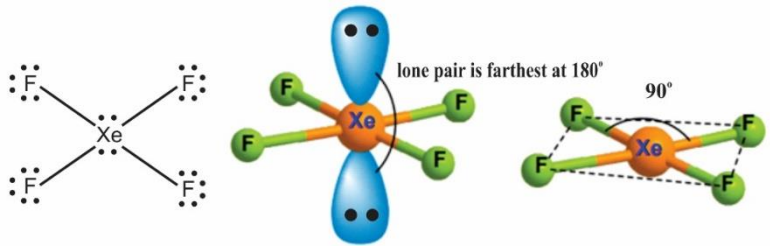
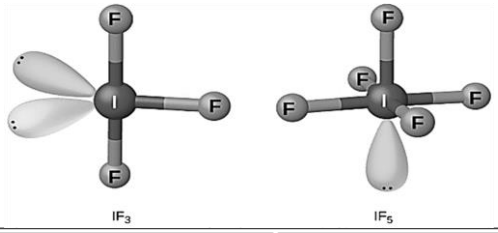


Fig (3.28) Lewis structure and square planar shape of XeF_4

QUICK CHECK 3.8

Draw the Lewis structures for IF_3 and IF_5 and predict their geometry with reference to the VSEPR model.

Ans.



Molecule	Lewis Structure Summary	Electron Domains	Shape (VSEPR)
IF_3	3 bonds, 2 lone pairs on I	5	T-shaped
IF_5	5 bonds, 1 lone pair on I	6	Square pyramidal

3.8.2 Applications of VSEPR Model in Drug Designing

SHORT QUESTION

What do you mean by receptor? Give example.

(i) Drugs

Drugs are chemical substances that prevent, diagnose, or treat a disease.

(ii) Substrates

Drugs interact with human body at specific points, or with specific processes called targets or substrates.

(iii) Ligands

Those bio active molecules through which drug interact with human body at specfic point with a specfic process are called ligands.

(iv) Receptor

A receptor is mostly a protein that receives and responds to a ligand through binding.

The examples of targets in the body are receptors, such as enzymes, proteins, nucleic acids, and cellular pathways.

(v) Specificity of a drug or a ligand

Each drug interacts with a specific target in the body to a different degree, this feature is called specificity of a drug or a ligand.

- Molecular shape is an important feature that determines how a drug interacts with a biological target.
- Only the ligands with suitable shape can fit in the active sites of a biological target as a specific key fits in a specific lock.

Application of VSEPR in biological system

VSEPR model is successfully applied in determining the shapes of various biological systems, such as substrate recognition, ligand specificity or selectivity, and antibody recognition.

Examples

- Aspirin is an analgesic drug (painkiller) used for relief from pain as a primary medicine. It interacts with an enzyme COX (cyclooxygenase) by binding to its active site through the acetyl group (-$OCCH_3$).
- The shape of COX active site and that of acetyl group on Aspirin are compatible with each other as in fig. 3.29 . Therefore, the binding is successful to block COX, which is a cause of the pain in the body.

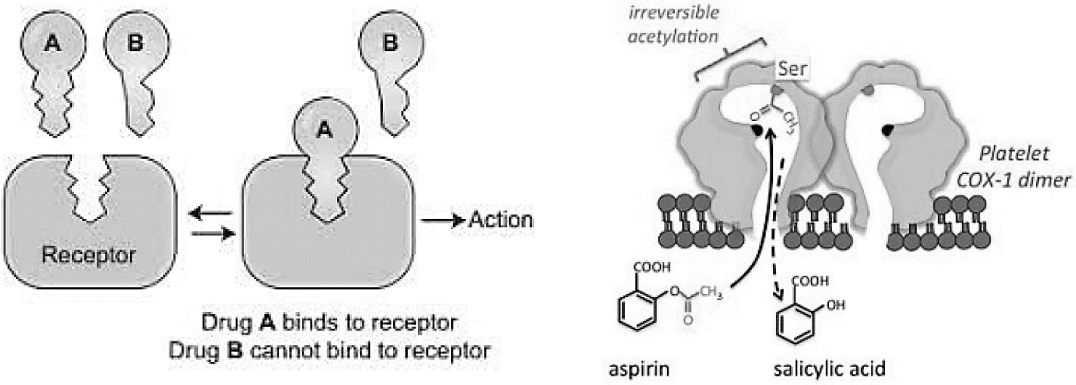


Fig (3.29) An interaction of Aspirin with COX (Published after permission from Tulane University Press)

MULTIPLE CHOICE QUESTIONS

(i) **What is the shape of a molecule with two bond pairs and no lone pair around the central atom?**
(A) Bent (B) **Linear** (C) Trigonal planar (D) Tetrahedral

(ii) **In the VSEPR theory, which type of electron pair repulsion is strongest?**
(A) Bond pair - Bond pair (B) Lone pair - Bond pair
(C) Lone pair - Lone pair (D) All repulsions are equal

(iii) **What is the molecular geometry of NH_3 according to VSEPR theory?**
(A) Tetrahedral (B) Trigonal planar **(C) Trigonal pyramidal** (D) Linear

EXTENSIVE QUESTION

What are the main postulates of VSEPR theory?

3.9 MOLECULAR ORBITAL THEORY (MOT)

The molecular orbital approach explains the results of quantum mechanical calculations for covalent bonding.

Postulates

Postulates this theory are given below

i. During the formation of a molecule, the atomic orbitals of the combining atoms overlap to form new orbitals called '**molecular orbitals**', which are characteristic of the whole molecule.

ii. The atomic orbitals overlap with the lobe having suitable sign of the wave function of the orbital. For example, one lobe of a p orbital is given the '+' sign and the other is marked with '-' sign.

iii. Two atomic orbitals overlap to form two sets of molecular orbitals.

(a) When same sign orbitals overlap, the **bonding molecular orbital** (σ or π) is formed that has lower energy than the parent atomic orbital.

(b) While with opposite signs, high energy **anti-bonding molecular orbital** (σ* or π*) is formed, that has higher energy than the parent atomic orbitals.

iv. The number of bonds formed between two atoms after the atomic orbitals overlap, is called the **bond order** and is taken as half of the difference between the number of bonding electrons (say a) and anti-bonding electrons (say b).

$$\text{Bond order} = \frac{a-b}{2}$$

SHORT QUESTION

Define bond and anti-bonding molecular orbitals.

s-s Overlap (Formation of H_2 molecule)

In the formation of H_2 molecule, two s orbitals of H atoms combine to give two molecular orbitals. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (nuclear axis), while the anti-bonding molecular orbital has the electron density away from the nuclei of the overlapping atoms as in Fig 3.30. The p orbitals of an atom can combine to give sigma bond.

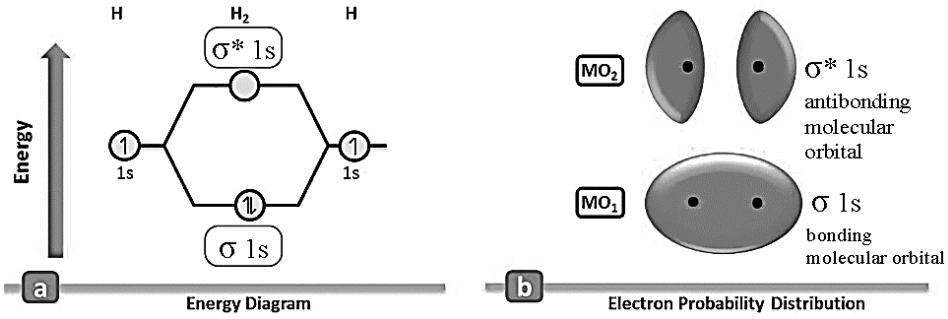


Fig (3.30) Formation of bonding and anti-bonding orbitals for the H_2, molecule

(a) Head on approach

Here, the p-orbitals of the two atoms approach along the same axis (say x-axis) as shown in Figure 3.31. This combination of atomic orbitals gives rise to σ ($2p_x$) bonding and σ* ($2p_x$) antibonding molecular orbitals.

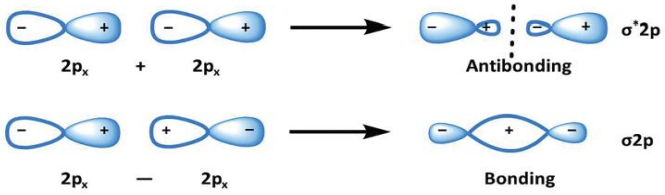


Fig (3.31) Head on overlap of p orbitals

(b) Sideways approach

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form π molecular orbitals as shown in the diagram Figure 3.32. The bonding molecular orbitals π($2p_y$) or π($2p_z$) have zero electron density on the nuclear axis (called the nodal plane). On the other hand, anti-bonding molecular orbitals π * ($2p_y$) and π * ($2p_z$) have the least electron density in the inter-nuclear region

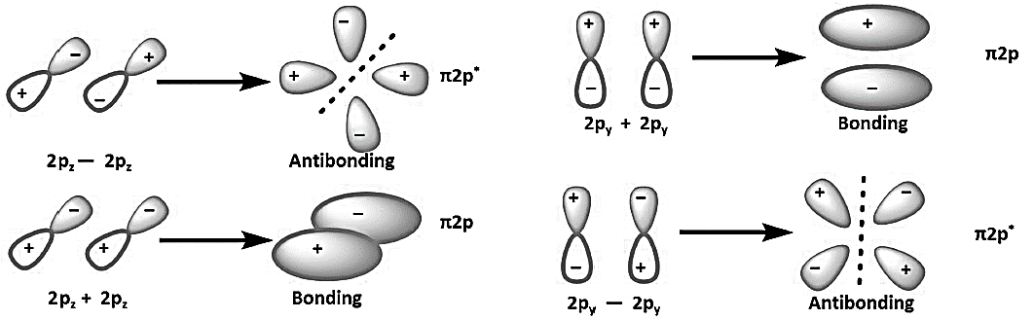


Fig (3.32) Formation of σ and π MOs from p_x, p_y and p_z orbitals

3.6.1 Molecular orbital diagrams of some diatomic molecules and their bond orders

(i) Helium

The electron configuration of He is $1s^2$. For a successful formation of He_2 molecule, 1s orbitals of two He atoms must combine to form bonding (δ1s) and anti-bonding (δ*1s) orbitals as shown in Figure 3.33. Out of four electrons, two enter the bonding molecular orbital δ (ls) and the remaining two occupy the antibonding δ*(1s) molecular orbital. But on calculation we discover that the bond order for He is zero. Hence, He_2 molecule is not formed.

SHORT QUESTION

How molecular orbital theory justifies that helium can't form He_2?

$$\text{Bond order of } He_2 = \frac{2-2}{2} = \mathbf{0}$$

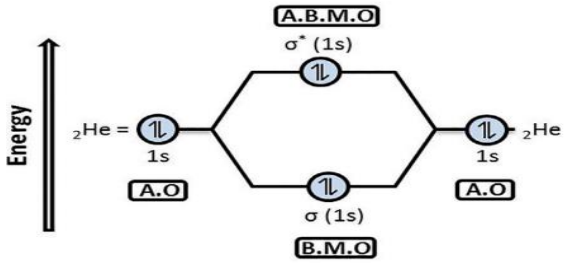


Fig (3.33) Molecular orbital diagram of He_2 molecule

(ii) Nitrogen (N_2)

Electronic configuration of N is, $_7N$: $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$

The molecular orbital diagram of N_2 based on this electron configuration is shown in the figure below (Figure. 3.34). The valence shell 2s on both N atoms give σ2s and σ* 2s orbitals; whereas, 2p orbitals give six molecular orbitals which are arranged in the increasing order of energy as:

SHORT QUESTION

Why N_2 molecules is diamagnetic?

σ (1s)< σ* (1s) σ(2s) < σ*(2s) < π(2p_y) = π(2p_z) < σ(2p_x) < π*(2p_y) = π*(2p_z) < σ*(2p_x)

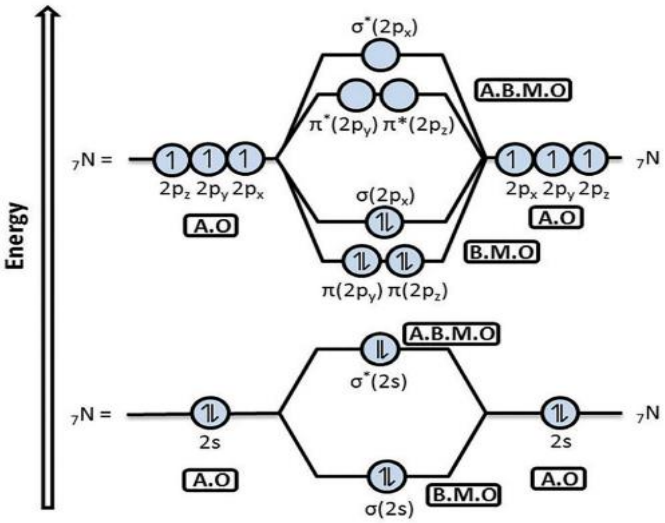


Fig (3.34) Molecular orbital diagram of N_2 Molecule

The bond order for N_2 can be calculated from its orbital diagram as:

Bond order of N_2 molecule

The bond order of oxygen = $\frac{6-0}{2} = \frac{6}{2} = 3$

Therefore, there are three covalent bonds between the nitrogen atoms in this molecule. One of these is a σ bond while the other two are π bonds. Nitrogen molecule has a triple bond between its atoms.

Liquid oxygen is attracted and gets suspended between the poles of a strong magnet

(iii) Oxygen, O_2

The formation of molecular orbitals in oxygen molecule is shown as follows in figure 3.35. The bond energy of the MOs can be arranged as

σ(1s)<σ*(1s)σ(2s)<σ* (2s)<σ (2p_x)<π(2p_y)=π(2p_z)<π *(2p_y) = π* (2p_z)<σ*(2p_x)

The bond order of O_2 molecule

The bond order of oxygen = $\frac{6-2}{2} = \frac{4}{2} = 2$

It shows the presence of one σ and one π bond between the oxygen atoms, i.e. they are linked by a double bond (O=O).

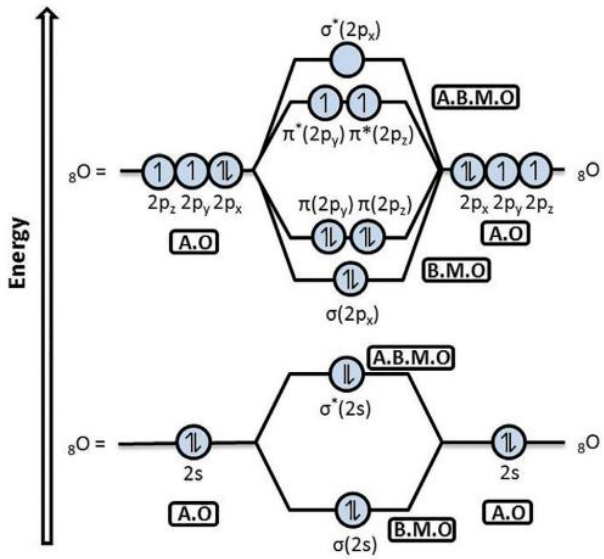


Fig (3.35) Molecular orbital diagram of O_2 Molecule

Magnetic behaviour

Oxygen molecule is paramagnetic in nature, which means it is attracted by a magnetic field. Paramagnetic substances have one or more unpaired electrons in them.

SHORT QUESTIONS

(i) Why MOT is superior to VBT?
(ii) Why O_2 molecules is paramagnetic?

Paramagnetism

"*A substance with large number of unpaired electrons is strongly attracted by magnetic field is called Paramagnetic substance and phenomenon is called Paramagnetism".*

NOTE: MOT successfully explains the paramagnetic behavior of oxygen molecule.
The MO diagram of oxygen shows the presence of two unpaire d electrons, one in π*(2py) and π*(2pz) each. Due to the presence of these unpaired electrons, oxygen molecule has a net magnetic field, which interacts with the external magnetic field.

MULTIPLE CHOICE QUESTIONS

(i) **_____ is not a paramagnetic.**
(A) O_2^{-2} (B) O_2 (C) N_2^{-2} (D) O_2^{-1}

(ii) **What is the main principle of molecular orbital theory?**
(A) Electrons are shared equally between atoms
(B) Atomic orbitals combine to form molecular orbitals
(C) Molecules are held together by ionic bonds
(D) Electrons exist in fixed energy levels

(iii) **Which of the following molecules is paramagnetic according to molecular orbital theory?**
(A) N_2 **(B) O_2**
(C) F_2 (D) He_2

EXTENSIVE QUESTIONS

(1) **Discuss and compare MOT diagram of O_2 and N_2.**
(2) **Discuss paramagnetic character of oxygen according to MOT.**

TEXT BOOK EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Choose the correct one from the given options.

(i) Chemical bond formation takes place when

(A) Force of attraction are equal to the force or repulsion
(B) Force of repulsion is greater than force of attraction
(C) Force of attraction overcomes force of repulsion
(D) None of these

(ii) An ionic compound A^+B^- is most likely to be formed when

(A) The ionization energy of A is high and electron affinity of B is low
(B) The ionization energy of A is low and electron affinity of B is high
(C) Both the ionization energy of A and electron affinity of B are high
(D) Both the ionization energy of A and electron affinity of B are low

(iii) Which of the following molecules has zero dipole moment?

(A) NH_3 **(B)** $CHCl_3$
(C) H_2O **(D)** BF_3

(iv) The numbers of σ and π bonds in the N_2 molecule are

(A) One σ and one π bonds
(B) One σ and two π bonds
(C) Three σ bonds only
(D) Two σ and one π

(v) Which of the following species has unpaired electrons in antibonding molecular orbitals?

(A) O_2^{2+} **(B)** N_2^{2-}
(C) B **(D)** F_2

(vi) The shape of ICl_3 according to the VSEPR model is

(A) Tetrahedral
(B) Trigonal planar
(C) Trigonal bipyramidal
(D) T-shape

(vii) Which of the following molecules has a dipole moment?

(A) CO_2 **(B)** CS_2
(C) SO_2 **(D)** CCl_4

(viii) How many electrons are present in the valence shell of P in PO_4^{3-}?

(A) 8 **(B)** 10
(C) 12 **(D)** 14

(ix) How many extra electrons than a normal octet are there in the valence shell of I in ICl_5?

(A) 2 **(B)** 3
(C) 4 **(D)** 5

(x) What is the type and shape of $[ICl_4]^-$ according to the VSEPR model?

(A) AB_4, tetrahedral
(B) AB_4, pyramidal
(C) AB_5, trigonal bipyramidal
(D) AB_6, square planar

(xi) Which of the following molecules has a central atom with sp^3 hybridization and a tetrahedral electron pair geometry?

(A) BF_3 **(B)** SO_2
(C) CCl_4 **(D)** PCl_5

(xii) Which of the following species contains a dative bond?

(A) CH_4 **(B)** NaCl
(C) NH_4^+ **(D)** O_2

ANSWER KEY

i	*C*	*ii*	*B*	*iii*	*D*	*iv*	*B*	*v*	*B*
vi	*D*	*vii*	*C*	*viii*	*B*	*ix*	*C*	*X*	*D*
xi	*C*	*xii*	*C*						

SHORT QUESTIONS

Q.2 Answer the following short questions.

a) Define the following

(i) Dipole

Ans. A molecule with δ^+ charge on one part and δ^- charge on the other part is called a dipole.

(ii) Bond order

Ans. The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order and is taken as half of the difference between the number of bonding electrons (say a) and anti-bonding electrons (say b).

Bond order = a – b/ 2

(iii) Permanent dipole- permanent dipole force

Ans. The force of attraction between the positive end of a polar molecule and the negative end of a nearby polar molecule is called permanent dipole-permanent dipole force.

(iv) London dispersion force

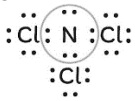
Ans. The momentary force of attraction between an instantaneous dipole and an induced dipole is called instantaneous dipole-induced dipole force or London dispersion force.

b) Draw the Lewis (electron dot) structures for the following species:

(i) HCN

Ans. H:C:::N:

(ii) NCl_3

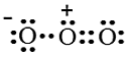


Ans.

(iii) CO

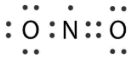
Ans. :C::O:

(iv) O_3



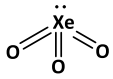
Ans.

(v) NO_2



Ans.

c) Xenon is a noble gas (group 18); xenon trioxide has the following structure:



i. By counting electron pairs around the central atom, explain why xenon trioxide has this shape.

Ans. Shape of xenon trioxide

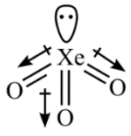
Xenon has 8 electrons in its valence shell. In xenon trioxide, each oxygen forms double bonds with xenon. As double bond behaves as a single bond in determining geometry. Therefore, 4 electron pairs are present around central atom (3 bonding pairs + 1 lone pair).

Using VSEPR theory:

- 4 electron pairs around Xe → tetrahedral electron geometry
- With 1 lone pair → trigonal pyramidal molecular shape

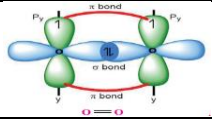
ii. Draw a structure of xenon trioxide showing partial charges on the atoms and the direction of the dipole in the molecule.

Ans.

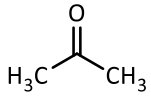


d) Explain the difference between the formation of σ and π bonds in term of VBT.

Ans.

σ bond	π bond
A sigma bond is formed by the linear overlap of two half-filled atomic orbitals on adjacent atoms.	A pi bond is formed by the sideways overlap of two half-filled atomic orbitals on adjacent atoms.
Both s and p orbitals can overlap head-on to form sigma bonds.	p orbitals can overlap sideways to form pi bond.
	

e) The structure of propanone (acetone) is:



i. Show how the central carbon atom forms σ and π bonds through hybridization.

Ans. Hybridization at central atom

The central carbon atom is sp^2 hybridized. It uses three sp^2 hybrid orbitals to form σ bonds with:

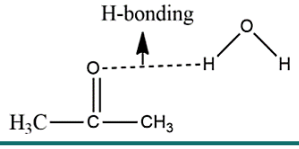
- The carbon of one CH_3 group,
- The carbon of the other CH_3 group,
- The oxygen atom (σ component of the C=O double bond).

The unhybridized p orbital on the carbon overlaps with a p orbital on the oxygen to form the π bond in the C=O.

ii. Can propanone make a hydrogen bond with water when both are intermixed?

Ans. Hydrogen bonding in propanone

Yes, propanone can form hydrogen bonds with water. The oxygen atom in propanone has lone pairs, and it's electronegative. Water has hydrogen atoms bonded to oxygen (O–H), making them slightly positive. The hydrogen of water can form a hydrogen bond with the lone pair on the oxygen in propanone.



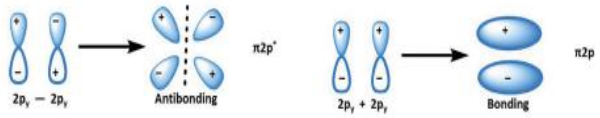
f) Predict the shapes of sulfate ($[SO_4]^{2-}$), borate ($[BH_4]^-$) and tri-iodide ions ($[I_3]^-$) according to the VSEPR model.

Ans. Shapes

Molecule	Electron Pairs	Electronic geometry	Shape (VSEPR)
$[SO_4]^{2-}$	4	Tetrahedral	Tetrahedral
$[BH_4]^-$	4	Tetrahedral	Tetrahedral
$[I_3]^-$	2 bond pair, 3 lone pair	Trigonal bipyramidal	Linear

g) Sketch the molecular orbital pictures of π(2p) and π*(2p).

Ans. Molecular orbital pictures



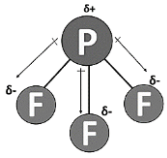
h) Sketch the hybrid orbitals and bond formation in PCl_3, $SiCl_4$, and NH_4^+.

Ans. (For answer to this question, see article 3.5).

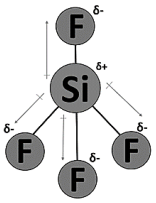
i) The structures of PF_3 and SiF_4 are given below. Redraw these with partial charges and state which is polar and which is non-polar.

Ans.

PF_3 is polar molecule

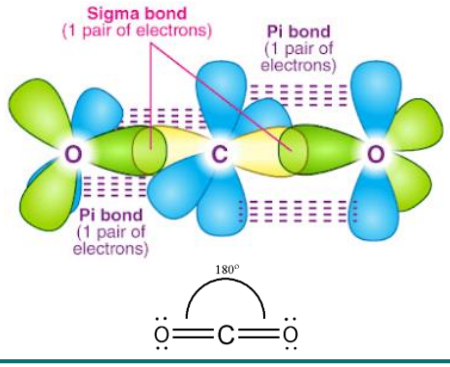


SiF_4 is non-polar molecule



j) Draw the orbital structures of the CO_2 molecule in terms of VBT.

Ans. Orbital structures

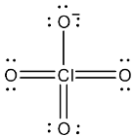


k) Draw the Lewis structures and tell whether these ions involve expanded octets?

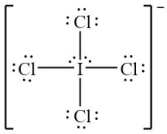
i) ClO_4^- ii) ICl_4^- iii) NH_4^+ iv) I_3^-

Ans.

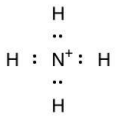
i) ClO_4^- has expanded octet



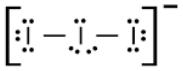
ii) ICl_4^- has expanded octet



iii) NH_4^+ has octet



iv) I_3^- has expanded Octet



l) The bond between K and Cl is ionic but that between Si and Cl is polar covalent. Explain why.

Ans. Reason

Potassium (K) is alkali metal having low ionization energy, tends to lose electron to complete its octet. So, potassium forms cation While chlorine is non-metal having high electron affinity, tends to gain electron. So it forms anion. The force is a ionic bond between metal cation and non-metal anion.

Silicon is metalloid has high ionization energy then alkali metals so it prefers to share electron instead of cation formation. Similarly, chlorine is non-metal prefer to share electron. The force is a covalent bond between Si and Cl because of less electronegativity difference than 1.8.

m) SO_2 is a polar molecule but SO_3 not. Justify.

Ans. Justification

SO_2 is triatomic molecule, and it is a bent structure due to lone pair, So the electronic charge on it is not equally distributed, its dipole moment is 1.61D and it is a polar molecule while in case of SO_3, there are three oxygen atoms and have trigonal structure and electronic charge is equally distributed so dipole moment is zero and it is a non-polar molecule.

n) Which of O_2^{2+}, and O_2^{2-} would be paramagnetic? Give reason in the light of MOT.

Ans. Reason for paramagnetic property

Oxygen atom has 8 electrons so O_2, O_2^{2+} and O_2^{2-} have 16, 14, 18 electrons, respectively. Fillings the MOs with electrons, O_2 ends up with 2 unpaired electrons in π^* orbitals so it is paramagnetic. In O_2^{2+}, 2 electrons are removed from π^* orbitals. Now, all electrons are paired so it is diamagnetic. In O_2^{2-}, 2 electrons are added in π^* orbitals. Now all electrons are paired so it is also diamagnetic.

o) Which of the following bonds would be most polar?

i) C-Cl ii) Si-F iii) Se-F

Ans. Nature of bond

ΔEN of C-Cl = 3 – 2.5 = 0.5

ΔEN of Si-F = 4 – 1.8 = 1.2

ΔEN of Se-F = 4 – 2.5 = 1.5

Greater the electronegativity difference, greater will be the polarity. Since, Si-F bond has highest ΔEN so, it will be the most polar bond.

p) Compare the bond energies of single, double, and triple bonds between the same two atoms (e.g., H-H, O=O, N≡N). Explain the trend in terms of the number of shared electrons.

Ans. Comparison

The bond energies of single, double, and triple bonds vary significantly due to the number of shared electron pairs between the same two atoms. H-H bond energy is 436 kJ/mol, O=O bond energy is 498 kJ/mol and N≡N Bond energy is 945 kJ/mol.

Trend explanation

The bond energy increases as the number of shared electrons increases. More electron pairs mean stronger electrostatic attraction between the nuclei and the bonding electrons, which leads to greater bond strength and shorter bond length. This is why breaking a triple bond requires significantly more energy than breaking a single bond.

DESCRIPTIVE QUESTIONS

Q.3 How the bonding in the following molecules can be explained with respect to valence bond theory?

(i) Cl_2 (ii) O_2

(iii) N_2 (iv) HF

(v) H_2S

Ans. (For answer to this question, see article 3.6).

Q.4 What are the postulates of VSEPR model? Discuss the structures of the following species with reference to this theory.

(i) CH_4 (ii) NH_3

(iii) H_3O^+ (iv) PCl_5

(v) SO_2 (vi) SF_6

Ans. (For answer to this question, see article 3.8)

Q.5 Explain the orbital hybridization for CH_4, NH_3, BF_3, and $BeCl_2$.

Ans. (For answer to this question, see article 3.7).

Q.6 Draw the molecular orbital diagrams of the following molecules. Calculate their bond orders?

(i) H_2 (ii) He_2

(iii) N_2 (iv) O_2

Ans. (For answer to this question, see article 3.9).

Q.7 Discuss the formation of F_2 molecule in the light of Lewis concept, VBT, and MOT.

Ans. (For answer to this question, see article 3.6 and 3.9).

SELF IMPROVEMENT TEST

Time: 35 Minutes **OBJECTIVE TYPE** **Total Marks: 25**

Q.No.1 Choose the Correct Answer by Filling the Circle. **(7 × 1 = 7)**

1. Which of the following pairs is most likely to form an ionic bond?

Ⓐ Hydrogen and Oxygen Ⓑ Sodium and Oxygen

Ⓒ Carbon and Hydrogen Ⓓ Nitrogen and Oxygen

2. Identify the species which do not have extended octet:

Ⓐ ClO_4^{-1} Ⓑ PO_4^{-3} Ⓒ NH_4^+ Ⓓ PCl_5

3. A molecule with high dipole moment is likely to be

Ⓐ Polar Ⓑ Non-polar Ⓒ Neutral Ⓓ Inert

4. The shape of ICl_3 according to the VSEPR model is

Ⓐ Tetrahedral Ⓑ Trigonal planar

Ⓒ Trigonal bipyramidal Ⓓ T-shape

5. Bonding in NH_4Cl is

Ⓐ Ionic Ⓑ Covalent Ⓒ Dative Ⓓ All of these

6. Which of the following molecular shape corresponds to a central atoms surrounded by four bonding pairs?

Ⓐ Trigonal planar Ⓑ Tetrahedral Ⓒ Bent Ⓓ Linear

7. Which type of hybridization of C occurs in HCN?

Ⓐ sp^3 Ⓑ sp^2 Ⓒ sp Ⓓ dsp

Q.No.2 Write Short Answer. **(5 × 2 = 10)**

(i) Discuss the factors affecting electronegativity.

(ii) CCl_4 has polar bonds but zero dipole moment. Justify.

(iii) Differentiate between sigma and pi bond.

(iv) Draw the structure of acetone by using the hybridization concept.

(v) How does the type of covalent bond (single, double, triple) influence bond length?

SECTION II

Q.No.3 Extensive Questions. **(2 × 4 = 8)**

(a) Why He_2 is not exist unlike O_2? Justify your answer with the help of their Molecular Orbital diagram. **(4)**

(b) Write down the postulates of VSEPR theory. **(4)**