

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Introduction

Atoms combine to form molecules. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a **Chemical bond**. The combining power of atoms to form molecules is called **Valency** (Latin word Valencia: meaning Strength). With the advancement of knowledge about atomic structure, it was realized that electrons in an atoms were primarily involved in chemical combinations.

According to '**Lewis Octet Rule**', atoms of all elements have a tendency to acquire an electronic configuration similar to that of inert gases because it represents the most stable electronic configuration. All atoms having unstable or incomplete outer shell have a tendency to gain or lose electrons so as to acquire an electronic configuration of the nearest inert gas in the periodic table.

Thus, according to '**Electronic Theory of Valency**', a chemical bond is formed as a result of electronic interactions. It may be noted that a molecule is formed only when electrons of the constituent atoms interact in such a way that the potential energy is lowered. Greater the lowering of potential energy, greater is the strength of the bond.

Types of Bond

According to electronic theory of valency, the interaction of extra nuclear electrons leads to the formation of following type of bonds:

- Ionic bond or Electrovalent bond
- Covalent bond
- Coordinate covalent bond
- Hydrogen bond
- Metallic bond

Dr. S. Dhananjay

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

1. Electrovalent or Ionic bond

Ionic bond is proposed by the scientist **Arrhenius**. It is formed by the complete transfer of one or more electrons from the outermost shell of one atom to the outermost shell of another atom and the combining atoms acquire inert gas configuration.

The atom which loses electrons acquires a positive charge, referred to as **cations** and the other atom which gains electrons becomes negatively charged and is referred to as **anions**. These **cations** and **anions** are held together by **electrostatic force of attraction** and the **bond** formed between them is called **electrovalent or ionic bond**. The compound thus formed is called as an **electrovalent or ionic molecule**.

Hence, **ionic bond** is defined as the electrostatic force of attraction between the oppositely charged ions formed by the transfer of electrons.

This electrostatic force of attraction causes decrease in potential energy between the ions and therefore the molecule formed is stable.

Consider the formation of NaCl:

Electronic Configuration of Na^{11} : $1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^1$

The sodium atom loses one electron of its outermost orbital to satisfy octet formation and forms Na^+ ion.



Electronic Configuration of Na^+ : $1\text{S}^2 2\text{S}^2 2\text{P}^6$ (stable octet formation in outermost shell)

Electronic Configuration of Cl^{17} : $1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^2 3\text{P}^5$

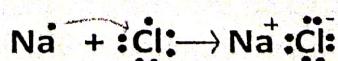
The chlorine atom accepts one electron in its outermost orbital to satisfy the octet formation and forms Cl^- ion.



Electronic Configuration of Cl^- : $1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^2 3\text{P}^6$ (stable octet formation in outermost shell)



The sodium ion and chloride ion are held together by electrostatic force of attraction to form ionic molecule, NaCl .



The presence of ionic crystals in the ionic molecule is confirmed by X-ray and spectroscopic studies.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Factors influencing the formation of Ionic bond

An ionic bond is made up by a metal ion (cation) and a non-metal ion (anion) and is governed / favoured by the following factors.

A. Ionization Energy

The minimum amount of energy required to remove an outermost electron from an isolated gaseous neutral atom is called as Ionization Energy and is expressed in kJ/mole.

↳ Low ionization energy of metal atoms:

Atoms can lose electrons easily when ionization energy is low. Consequently, greater is the ease of formation of cations.

Hence, low ionization energy of metal atoms favours the formation of ionic bond.

B. Electron Affinity (or) Electron Gain Energy

It is defined as the amount of energy released when an electron is added to an isolated gaseous neutral atom of an element and is expressed in kJ/mole.

The electron affinity of inert gases is zero because of their completely filled 's' and 'p' sub-levels.

↳ High electron affinity of non-metal atoms:

Atoms can gain electrons easily when an electron affinity is high. That is greater the electron affinity, higher is the tendency to form anions.

Hence, high electron affinity of non-metal atoms favours the formation of ionic bond.

- Thus, low ionization energy of a metal atom and high electron affinity of a non-metal atom facilitates the formation of an ionic bond between them.
- Large radius of metal atoms and small radius of non-metal atoms favours the ionic bond formation between them.

C. Electro negativity:

It is defined as the ability of an atom in a molecule to attract a shared pair of electrons towards itself.

The electro negativity of non-metal atoms is larger than that of metal atoms. Halogens have very high electro negativity values.

- The electro negativity difference between the cation and anion must be greater than or equal to 1.7 will favour the formation of ionic bond.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

D. Potential Energy

The potential energy of the ionic molecule must be lower than that of combining elements.

- Lower the potential energy of the resulting ionic compound then greater will be the stability of the so formed molecule.

E. Lattice Energy

The amount of energy released when the required number of oppositely charged gaseous ions present at infinite distances come close and form one mole of ionic crystalline solid is known as the lattice energy of the compound.

(or)

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into its gaseous constituent ions.

For example, the lattice enthalpy of NaCl is -786 kJ/mol . This means that 786 kJ of energy is required to separate one mole of solid NaCl into one mole of $\text{Na}^{+}_{(g)}$ and one mole of $\text{Cl}^{-}_{(g)}$ to an infinite distance.

Lattice energy is directly proportional to the product of Z^+ and Z^- and inversely proportional to the sum of the radii of cation and anion.

$$\text{Lattice energy} \propto (Z^+ * Z^-) / (r_c^+ + r_a^-)$$

where Z^+ is charge on cation and Z^- is charge on anion; r_c^+ is radii of cation and r_a^- is radii of anion.

- Born-Haber cycle is used to calculate the lattice energy.
- Lattice energy increases as cation or anion size decreases.
- Greater the charge on ions more is lattice energy.

- Higher the lattice energy of the resulting ionic compound then greater will be the ease of its formation and also more is its strength, stability and melting point.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Born Haber Cycle

The Born–Haber cycle is an approach used to analyze reaction energies. It was named after the two German scientists **Max Born** and **Fritz Haber**, who developed it in 1919. It was also independently formulated by **Kasimir Fajans**.

Born Haber cycle is a cycle of enthalpy change of process that leads to the formation of a solid crystalline ionic compound from the elemental atoms in their standard state and of the enthalpy of formation of the solid compound such that the net enthalpy becomes zero.

Born-Haber cycles are primarily used in calculating the lattice energy. **The lattice energy is the enthalpy change involved in the formation of ionic solids from gaseous ions or the energy involved in breaking the ionic solids into gaseous ions.**

Energy level diagram is used to present the Born Haber Cycle.

Born Haber cycle: Calculation of Lattice Energy of sodium chloride, NaCl

The solid sodium chloride is formed from its element, solid sodium and gaseous chlorine. The heat change that takes place in the reaction is -411.0 kJ/mol and the reaction is represented as



The above reaction is considered to take place in five stages

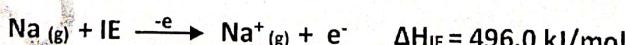
(1) Sublimation of $\text{Na}_{(s)}$ to $\text{Na}_{(g)}$

In this step, one mole of solid Na absorbs energy equal to its sublimation energy and Na is converted into a gaseous state. It is an endothermic reaction.



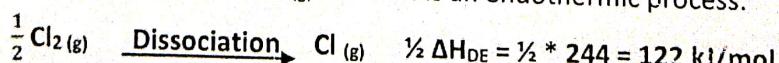
(2) Ionisation of $\text{Na}_{(g)}$ in to $\text{Na}_{(g)}^+$

Each $\text{Na}_{(g)}$ atom absorbs energy equal to its ionization energy and eliminates its outermost electron to form $\text{Na}_{(g)}^+$. It is an endothermic reaction.



(3) Dissociation of $\frac{1}{2}$ mole of $\text{Cl}_{2(g)}$ to give gaseous Cl atom

In this step $\frac{1}{2}$ mole of chlorine absorbs energy equal to the $\frac{1}{2}$ of dissociation energy and $\text{Cl}_{2(g)}$ gas is converted into $\text{Cl}_{(g)}$ atom. It is an endothermic process.



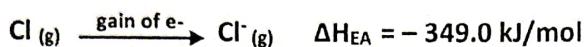
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(4) Conversion of $\text{Cl}_{(g)}$ into $\text{Cl}^{-}_{(g)}$

$\text{Cl}_{(g)}$ atom takes the electron given by $\text{Na}_{(g)}$ in step 2 to form $\text{Cl}^{-}_{(g)}$. In this process, energy released is equal to its electron affinity. It is an exothermic reaction.

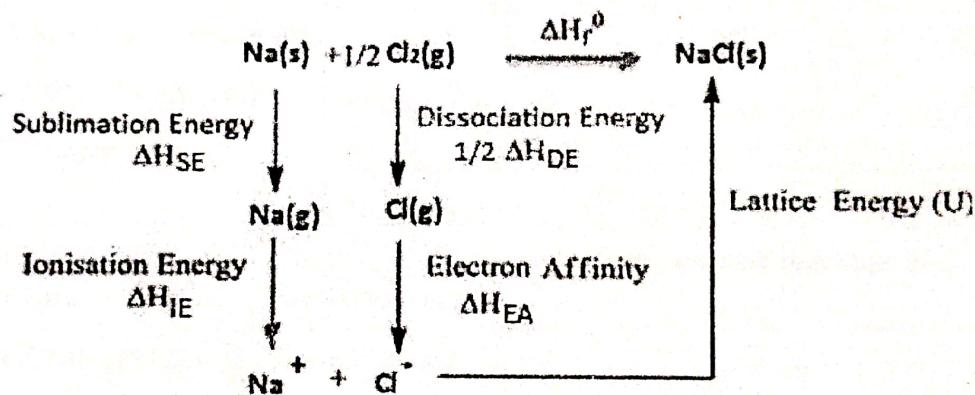


(5) Combination of $\text{Na}^{+}_{(g)}$ and $\text{Cl}^{-}_{(g)}$ to form $\text{NaCl}_{(s)}$

This is the final step in the formation of $\text{NaCl}_{(s)}$. Here $\text{Na}^{+}_{(g)}$ formed in step 2 and $\text{Cl}^{-}_{(g)}$ formed in step 4 are combined to form one mole of NaCl solid. In this process, the energy released is equal to lattice energy. This is also an exothermic reaction.



Born Haber Cycle for Sodium Chloride



But according to Hess's law, the heat of formation of NaCl should be the same whether it takes place directly (single step) or stepwise (as 5 steps above).

Hence, $\Delta H_f^0 = \Delta H_{SE} + \Delta H_{IE} + \frac{1}{2} \Delta H_{DE} + \Delta H_{EA} + U$

Therefore, Lattice Energy, $U = \Delta H_f^0 - \Delta H_{SE} - \Delta H_{IE} - \frac{1}{2} \Delta H_{DE} - \Delta H_{EA}$

Substituting the various values, we have

$$\text{Lattice Energy, } U = -411.0 - 108.0 - 496.0 - 122.0 - (-349.0)$$

$$\text{Lattice Energy, } U = -788.0 \text{ kJ/mole}$$

The negative sign of Lattice Energy, U indicates that energy is released.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Numerical Problems on calculation of Lattice Energy

- (1) Calculate the lattice energy of NaBr crystal with the help of the Born-Haber cycle from the data given below.

- Heat of formation of NaBr (ΔH_f^0) = - 360 kJ/mol
- Sublimation energy of Na (ΔH_{SE}) = 108 kJ/mol
- Ionisation energy of Na (ΔIE) = 496 kJ/mol
- Bond dissociation energy of Br₂ (ΔH_{DE}) = 192 kJ/mol
- Electron affinity of gaseous Br atom (ΔEA) = - 325 kJ/mol

Solution:

$$\Delta H_f^0 = \Delta H_{SE} + \Delta IE + \frac{1}{2} \Delta H_{DE} + \Delta EA + U$$

$$U = \Delta H_f^0 - \Delta H_{SE} - \Delta IE - \frac{1}{2} \Delta H_{DE} - \Delta EA$$

$$U = -360 - 108 - 496 - \frac{1}{2}(192) - (-325)$$

∴ $U = -735 \text{ kJ/mol}$

- (2) Draw Born-Haber cycle for the formation of KCl crystal with relevant reactions and calculate its lattice energy with the following data.

- Heat of formation of KCl (ΔH_f^0) = - 438 kJ/mol
- Sublimation energy of K (ΔH_{SE}) = 89 kJ/mol
- Ionisation energy of K (ΔIE) = 418 kJ/mol
- Dissociation energy of Cl₂ (ΔH_{DE}) = 244 kJ/mol
- Electron affinity of Cl gas (ΔEA) = - 352 kJ/mol

Solution:

$$\Delta H_f^0 = \Delta H_{SE} + \Delta IE + \frac{1}{2} \Delta H_{DE} + \Delta EA + U$$

$$U = \Delta H_f^0 - \Delta H_{SE} - \Delta IE - \frac{1}{2} \Delta H_{DE} - \Delta EA$$

$$U = -438 - 89 - 418 - \frac{1}{2}(244) - (-352)$$

∴ $U = -715 \text{ kJ/mol}$

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(3) Using Born-Haber cycle of NaCl, calculate the electron affinity of chlorine.

- Lattice Energy of NaCl (U) = -788 kJ/mol
- Heat of formation of NaCl (ΔH_f^0) = -411.3 kJ/mol
- Sublimation energy of Na (ΔH_{SE}) = 108.7 kJ/mol
- Ionisation energy of Na (ΔH_{IE}) = 495 kJ/mol
- Bond Dissociation energy of Cl₂ (ΔH_{DE}) = 244 kJ/mol

Solution:

$$\Delta H_f^0 = \Delta H_{SE} + \Delta H_{IE} + \frac{1}{2} \Delta H_{DE} + \Delta H_{EA} + U$$

$$\Delta H_{EA} = \Delta H_f^0 - \Delta H_{SE} - \Delta H_{IE} - \frac{1}{2} \Delta H_{DE} - U$$

$$\Delta H_{EA} = -411.3 - 108.7 - 495 - \frac{1}{2}(244) - (-788)$$

$$\therefore \Delta H_{EA} = -349 \text{ kJ/mol}$$

Properties of Ionic compounds:

- Ionic compounds are more soluble in water but partially soluble in organic solvents.
- The melting point and boiling points of ionic compounds are high.
- Ionic compounds are low volatile.
- Ionic compounds do not conduct electricity in solid state.
- Ionic compounds conduct electricity in the molten state.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

2. Covalent Bond

G.N. Lewis in the year 1916, proposed the concept of covalent bond. According to him, the atoms may combine with other atoms by sharing equal number of electrons in their valence shells and hence the combining atoms attain the stable octet structure in their valence shells.

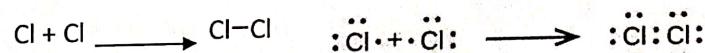
A covalent bond is defined as a force which binds the atoms of same or different elements by mutual sharing of equal number of electrons and both the binding atoms acquire inert gas configuration.

If one pair of electrons is shared, the bond formed is called single bond whereas sharing of two or three pairs of electrons leads to the formation of double bonds or triple bonds respectively.

A single covalent bond is represented by ‘-’; double bond by ‘=’ and triple bond by ‘≡’.

Consider the formation of Cl₂, O₂ and N₂:

- Electronic Configuration of Cl¹⁷: 1S² 2S² 2P⁶ 3S² 3P⁵



(Stable octet formation in outermost shell)

- Electronic Configuration of O⁸: 1S² 2S² 2P⁴



(Stable octet formation in outermost shell)

- Electronic Configuration of N⁷: 1S² 2S² 2P³



(Stable octet formation in outermost shell)

Factors favouring the formation of covalent bond:

- Atomic orbital of the valence shells should contain unpaired electrons with opposite spin.
- The combining atoms should obtain stable octet structure by mutual sharing of one or more electrons.
- The combining atoms should have small difference in their electro negativity values.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

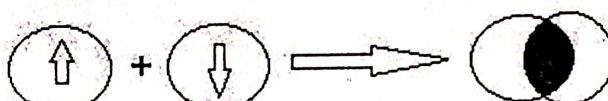
Atomic Orbital Theory

An orbital can have maximum of two electrons with opposite spin and such atomic orbital do not involve during chemical combination.

If only single electron is present in an orbital of outermost shell, then it will have a tendency to combine with an electron having opposite spin present in another atomic orbital and results in the formation of covalent bond between those combining two atoms.

Thus, according to **Atomic Orbital Theory**, formation of a covalent bond between two atoms takes place by coupling of electrons with opposite spin belonging to an orbital of outermost shells of two atoms.

The covalent bond formation leads to the decrease in potential energy of the so formed molecule and thus the molecule formed is stable.



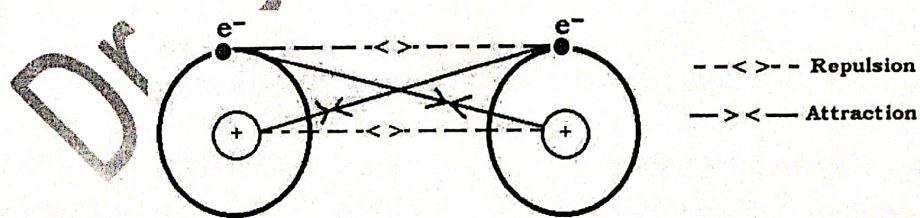
Formation of covalent bond due to overlapping of atomic orbitals

Greater the overlapping, greater is the energy released and stronger is the bond formed.

Formation of Hydrogen molecule:

Consider the formation of hydrogen molecule from two hydrogen atoms through covalent bond. When two hydrogen atoms approach each other there are attractive forces as well as repulsive forces.

- Attractive forces establish between the nucleus of one atom and electrons of other atom.
- Repulsive forces exist between the two nuclei and as well as between the electrons of the two atoms.



Experimentally it is evidenced that when two atoms approach each other, the magnitude of attractive forces is greater than the magnitude of repulsive forces. Hence, potential energy decreases and the molecule formed is stable.

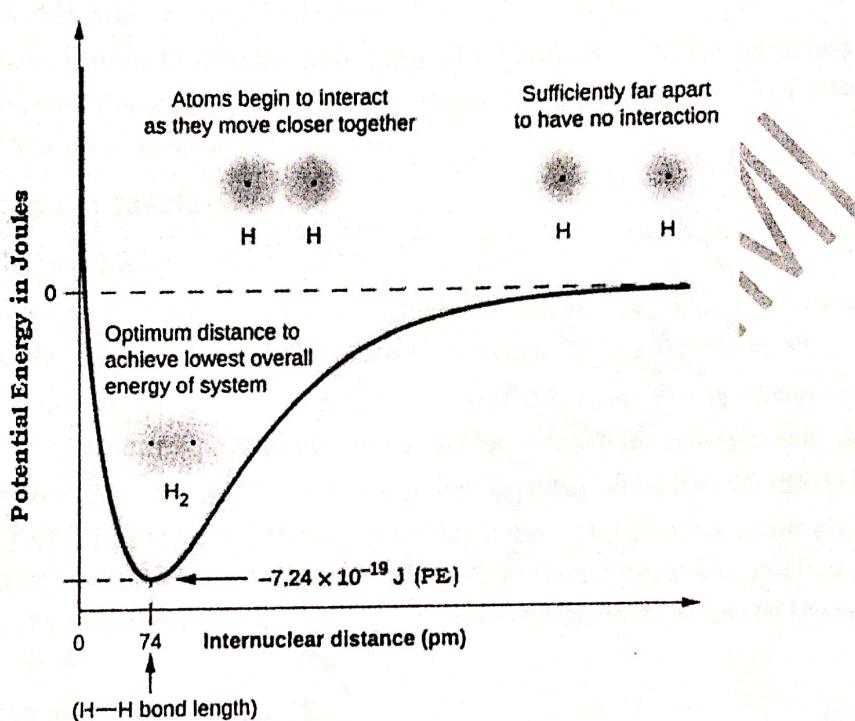
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

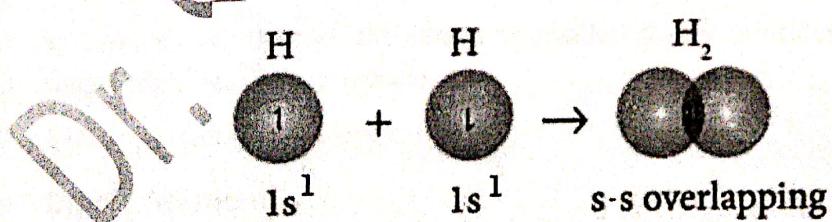
Energy changes during the formation of Hydrogen molecule through covalent bond:

A graph of potential energy, PE verses intermolecular distance of the combining atoms confirms the formation of stable molecule.



$$\text{Bond length of } H_2 \text{ molecule} = 74 \text{ pm} = 0.74 \text{ \AA}$$

Each hydrogen atom has only one electron and its electronic configuration is $1s^1$. The $1s$ atomic orbital of hydrogen is occupied by only one electron. Therefore, it needs one more electron to complete the 's' orbital.



Stability:

- During the formation of hydrogen molecule, the two hydrogen atoms share a pair of electrons between them. Hence, a covalent bond is formed between two hydrogen atoms and the hydrogen molecule acquires a stable inert gas "He" configuration.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

- The shared electrons are located in the region of space between the nuclei of two hydrogen atoms. The shared electrons are therefore attracted by both the nuclei. Hence the potential energy of the system decreases and the hydrogen molecule formed is stable.
- Here covalent bond is formed by overlapping of s - orbitals along the same axis. This type of axial overlapping leads to the formation of sigma bond which is stronger. Therefore hydrogen molecule formed is stable.

Polar and Non-polar covalent bond:

- **Polar Covalent Bond:**

When a covalent bond is formed between dissimilar atoms, the bonding electrons will not be equally shared and the resulting bond is known as **polar covalent bond**.

The shared electrons will be shifted more towards the atom having higher electro negativity. This results in the accumulation of partial negative (δ^-) charge on it. At the same time, the other atom will carry an equivalent partial positive (δ^+) charge on it.

Consider the formation of HCl through covalent bond. The chlorine atom acquires small amount of negative charge because of its higher electro negativity and hydrogen atom has got an equivalent small amount of positive charge on it. So the HCl molecule is polar molecule.

Example: HCl molecule, $H^{\delta^+} - Cl^{\delta^-}$

- **Non Polar Covalent Bond:**

When a covalent bond is formed between atoms of the same element, the bonding electrons are equally shared on account of equal electro negativity of both the atoms and the resulting bond is known as **non-polar covalent bond**.

In case of such a bond, the centre of positive charge coincides with the centre of negative charge in the molecule.

Example: Hydrogen molecule, $H-H$.

- **Dipole Moment, μ**

Dipole moment is defined as the product of the magnitude of the electric charge and the inter-atomic distance (bond length) between the atoms in the molecule.

Dipole moment, $\mu = \text{Electric charge} \times \text{Bond length}$

That is, $\mu = e \times d$

where 'e' is electric charge and 'd' is inter atomic distance (or) bond length.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

- **Percentage of Ionic character:**

Molecules like HCl, SO₃ and CH₃Cl are polar molecules with definite dipole moments. The atoms forming polar bonds develop partial positive and partial negative charges on the combined atoms. This indicates that polar molecules have a partial ionic character.

A molecule is considered as ionic if the percentage of ionic character is greater than 50% and the molecule is considered as covalent if its percentage of ionic character is less than 50%.

$$\% \text{ of ionic character} = (\text{observed dipole moment} / \text{calculated dipole moment}) * 100$$

$$\text{Percentage of ionic character} = (\mu_{\text{obs}} / \mu_{\text{cal}}) \times 100$$

$$\mu_{\text{cal}} = \mu_{\text{ionic}} = e \times d$$

where 'e' is electric charge and 'd' is inter atomic distance (or) bond length.

Numerical Problems on percentage of ionic character

1. The dipole moment of HCl molecule is 1.03D. For complete transfer of electrons, the charge on H⁺ & Cl⁻ ions would be equal to 4.8×10⁻¹⁰ esu. The bond length of HCl is 1.275×10⁻⁸ cm. Calculate the % of ionic character in HCl molecule.

Given:

Dipole moment of HCl, $\mu_{\text{obs}} = 1.03 \text{ D}$ *Given*

Electric charge, $e = 4.8 \times 10^{-10} \text{ esu}$

Bond length of HCl, $d = 1.275 \times 10^{-8} \text{ cm}$

Solution:

Dipole moment of HCl molecule, $\mu_{\text{cal}} = \text{electric charge} \times \text{bond length}$

$$\mu_{\text{cal}} \text{ of HCl} = e \times d = 4.8 \times 10^{-10} \times 1.275 \times 10^{-8} = 6.12 \times 10^{-18} \text{ esu cm}$$

Note: $10^{-18} \text{ esu cm} = 1 \text{ Debye unit}$

∴ $\mu_{\text{cal}} \text{ of HCl} = 6.12 \text{ D}$

$$\text{Percentage of ionic character in HCl} = (\mu_{\text{obs}} / \mu_{\text{cal}}) \times 100$$

$$\text{Percentage of ionic character in HCl} = (1.03 / 6.12) \times 100$$

∴ **Percentage of ionic character in HCl molecule = 16.83%**

The percentage of ionic character is less than 50%, hence the chemical bond present in HCl molecule is **covalent bond**.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

2. The dipole moment of HF molecule is 1.98D. When HF molecule forms H^+ and F^- ions by complete transfer of electrons, the charge on the ion is 4.8×10^{-10} esu and bond length is 0.98×10^{-8} cm. Calculate the percentage of ionic character in HF molecule.

Given:

Dipole moment of HF, $\mu_{\text{obs}} = 1.98$ D

Electric charge, $e = 4.8 \times 10^{-10}$ esu

Bond length of HF, $d = 0.98 \times 10^{-8}$ cm

Solution:

Dipole moment of HF molecule, $\mu_{\text{cal}} = \text{electric charge} \times \text{bond length}$

$$\mu_{\text{cal}} \text{ of HF} = e \times d = 4.8 \times 10^{-10} \times 0.98 \times 10^{-8} = 4.704 \times 10^{-18} \text{ esu cm}$$

∴ $\mu_{\text{cal}} \text{ of HF} = 4.704$ D

$$\text{Percentage of ionic character in HF} = (\mu_{\text{obs}} / \mu_{\text{cal}}) \times 100 = (1.98 / 4.704) \times 100$$

∴ Percentage of ionic character in HF molecule = 42.09%

The percentage of ionic character is less than 50%, hence the chemical bond present in HF molecule is **covalent bond**.

3. The dipole moment of LiH is 1.964×10^{-29} coulomb meter. When LiH forms Li^+ and H^- ions by complete transfer of electrons, the charge on the ion is 1.602×10^{-19} coulombs and bond length is 1.596×10^{-10} m. Calculate the percentage of ionic character in Li-H.

Given:

Dipole moment of Li-H, $\mu_{\text{obs}} = 1.964 \times 10^{-29}$ coulomb meter = 1.964 D

Electric charge, $e = 1.602 \times 10^{-19}$ coulombs;

Bond length of Li-H, $d = 1.596 \times 10^{-10}$ m

Solution:

Dipole moment of Li-H molecule, $\mu_{\text{cal}} = \text{electric charge} \times \text{bond length}$

$$\mu_{\text{cal}} \text{ of Li-H} = e \times d = 1.602 \times 10^{-19} \times 1.596 \times 10^{-10} = 2.557 \times 10^{-29} \text{ coulomb meter}$$

∴ $\mu_{\text{cal}} \text{ of Li-H} = 2.557$ D

$$\text{Percentage of ionic character in Li-H} = (\mu_{\text{obs}} / \mu_{\text{cal}}) \times 100 = (1.964 / 2.557) \times 100$$

Percentage of ionic character in Li-H molecule = 76.8%

The percentage of ionic character is greater than 50%, hence the chemical bond present in Li-H molecule is **ionic bond**.

HBr, $\mu_{\text{obs}} = 0.78$ D

14/35

$$e = 4.8 \times 10^{-10} \text{ esu} \quad \therefore \text{IC} = \underline{11.5\%}$$

$$d = 1.41 \times 10^{-8} \text{ cm}$$

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

4. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is a highly polar molecule. The charge on the ion is 1.602×10^{-19} coulombs and inter-atomic distance between K^+ and Cl^- ions in this molecule is 2.6×10^{-10} m. Determine the dipole moment of KCl molecule, if there were opposite charges of one fundamental unit located at each nucleus. Also, calculate the percentage of ionic character in KCl molecule.

Given:

Dipole moment of KCl, $\mu_{\text{obs}} = 3.336 \times 10^{-29}$ coulomb meter = 3.336 D

Note: 10^{-29} coulomb meter = 1 Debye unit

Electric charge, $e = 1.602 \times 10^{-19}$ coulombs

Bond length of KCl, $d = 2.6 \times 10^{-10}$ m

Solution:

Dipole moment of KCl molecule, $\mu_{\text{cal}} = \text{electric charge} \times \text{bond length}$

$$\mu_{\text{cal}} \text{ of KCl} = e \times d = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10} = 4.1652 \times 10^{-29} \text{ coulomb meter}$$

$$\mu_{\text{cal}} \text{ of KCl} = 4.1652 \text{ D}$$

$$\text{Percentage of ionic character in KCl molecule} = (\mu_{\text{obs}} / \mu_{\text{cal}}) \times 100$$

$$\text{Percentage of ionic character in KCl molecule} = (3.336 / 4.1652) \times 100$$

Percentage of ionic character in KCl molecule = 80.09%

The percentage of ionic character is greater than 50%, hence the chemical bond present in KCl molecule is **ionic bond**.

Properties of covalent compounds:

- Covalent compounds are generally soluble in organic solvents.
- Covalent compounds exist in solid, liquid or gaseous state with low boiling point and melting point.
- They are generally soft, easily fusible and volatile.
- Covalent compounds do not conduct electricity since they exist as molecules and not as ions.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Hybridization

Definition: The phenomenon of mixing up of atomic orbitals of similar energies and formation of equivalent number of entirely new orbitals of identical shape and energy is known as "hybridization" and the new orbitals so formed are called as "hybrid orbitals".

Key features of hybridization:

- Atomic orbitals with equal energies undergo hybridization.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals that participate in hybridization process.
- Covalent bonds in polyatomic molecules are formed by the overlap of hybrid orbitals or of hybrid orbitals with unhybridized ones.
- It is not necessary that all the half-filled orbitals must participate in hybridization. Even completely filled orbitals with slightly different energies can also participate.
- Hybridization happens only during the bond formation and not in an isolated gaseous atom.
- The shape of the molecule can be predicted if the hybridization of the molecule is known.

Types of Hybridization:

Sl. No.	Type of atomic orbitals used	hybridization	Orientation of hybrid orbitals	Examples
1.	1 s + 1 p	sp	Linear	BeF ₂ , BeCl ₂ , C ₂ H ₂
2.	1 s + 2 p	sp ²	Trigonal planar	BF ₃ , C ₂ H ₄
3.	1 s + 3 p	sp ³	Tetrahedral	CH ₄ , CCl ₄ , SiF ₄
4.	1 s + 3 p + 1 d	sp ³ d	Trigonal bipyramidal	PF ₅ , PCl ₅
5.	1 s + 3 p + 2 d	sp ³ d ²	Octahedral	SF ₆
6.	1 s + 3 p + 3 d	sp ³ d ³	Pentagonal Bipyramidal	IF ₇
7.	1 d + 1 s + 2 p	dsp ²	Square planar	[Ni(CN) ₄] ²⁻ , [PtCl ₄] ²⁻

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECCHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(1) Sp hybridization:

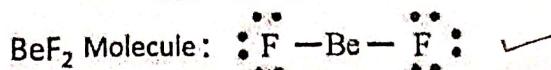
- sp hybridization is observed when one 's' and one 'p' orbital in the same main shell of an atom mix to form 2 new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals**.
- sp hybridization is also called as **diagonal hybridization**.
- It forms a **linear molecules** with an angle of **180°**.
- Each **sp hybridized orbital** has an equal amount of 's' and 'p' character, that is 50% 's' and 50% 'p' character.

Example:

- All compounds of **Beryllium** like BeF_2 , BeH_2 , BeCl_2 .
- All compounds of **Carbon** containing triple bond like C_2H_2 .

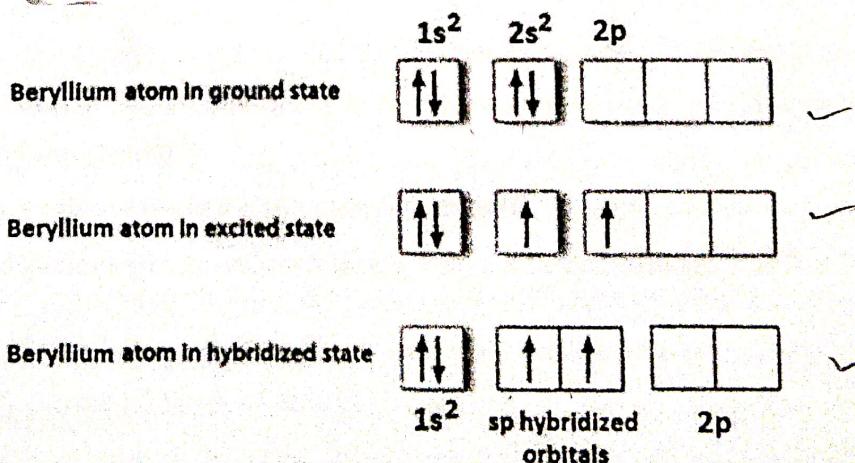
~~✓ sp hybridization and Geometry of Beryllium fluoride, BeF_2 molecule:~~

Beryllium atom can form 2 covalent bonds with 2 fluorine atoms to give a molecule of Beryllium fluoride. In BeF_2 molecule, the sp-hybridized orbitals of beryllium atom overlaps with the half-filled 'p' orbitals of two fluorine atoms and gives a **linear geometry**.



~~Electronic configuration of Be^4- : $1s^22s^2$~~

Beryllium atom has no unpaired electrons in the ground state but in the excited state, it has 2 unpaired electrons and undergoes hybridization as shown below. That is, one 's' and one 'p' orbital of Beryllium atom hybridized to give **two sp hybrid orbitals of equivalent energy**.

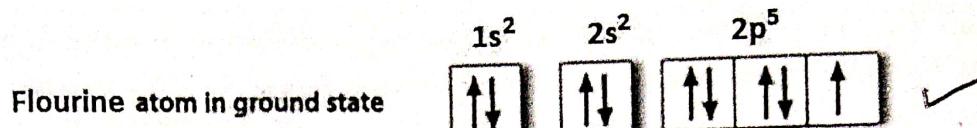


Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

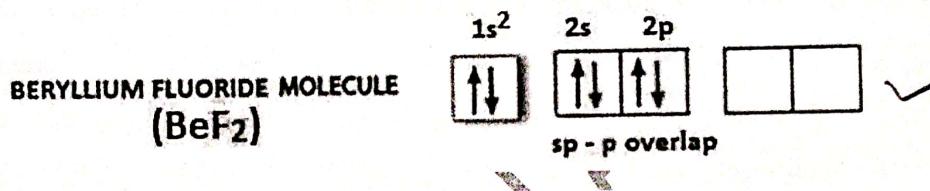
Electronic configuration of F⁹: 1s²2s²2p⁵ ✓



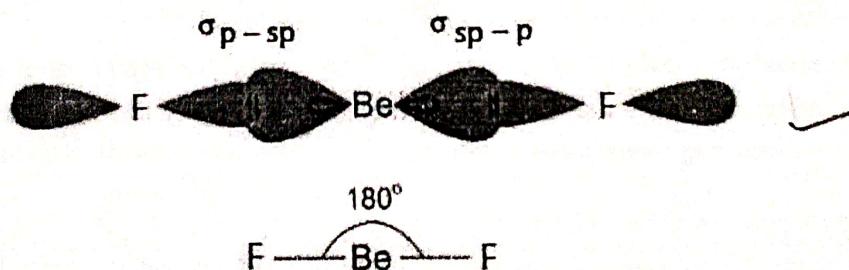
In Fluorine atom, one of the 'p' orbital is only half filled.

Formation of Beryllium fluoride, BeF₂ molecule: ✓

The half-filled sp hybridized orbitals of the Beryllium atom overlaps with the half-filled 'p' orbitals of two fluorine atoms to give sp hybridization resulting in the formation of Beryllium fluoride, BeF₂ molecule.



Shape and Geometry of BeF₂:



Linear geometry of BeF₂

In Beryllium fluoride, BeF₂ molecule, the sp hybridized orbitals are oriented at an angle of 180°, when two sp hybridized orbitals of Beryllium atom overlaps with the half-filled 'p' orbitals of two fluorine atoms.

Two sigma (σ) bonds are formed with bond angle of 180°. ✓

The shape and geometry of Beryllium fluoride, BeF₂ molecule is Linear. ✓

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(2) sp^2 hybridization:

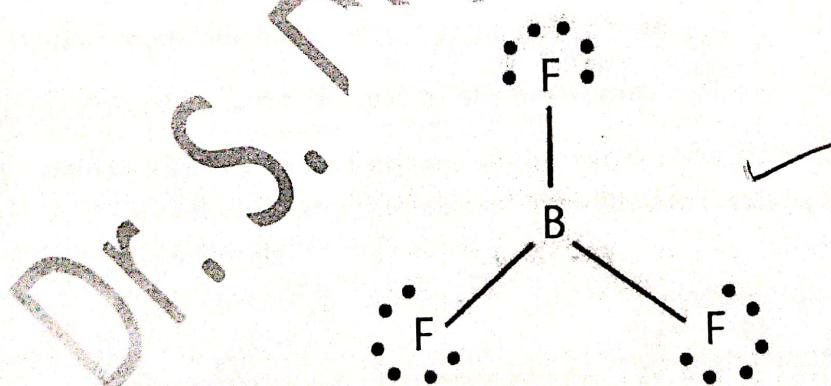
- sp^2 hybridization is observed when one 's' and two 'p' orbitals of the same shell of an atom mix to form 3 equivalent orbitals. The new orbitals formed are called sp^2 hybrid orbitals.
- A mixture of 's' and 'p' orbitals results in trigonal symmetry. Hence sp^2 hybridization is also called as trigonal hybridization.
- All the three hybrid orbitals remain in one plane and linked to a central atom of a molecule and forms a triangular planar shape with an angle of 120° with one another.
- Each hybrid orbitals formed has a 33.33% 's' character and 66.66% 'p' character.

Example:

- All the compounds of **Boron** like BF_3 , BH_3
- All the compounds of **Carbon** containing double bond like C_2H_4 .

sp^2 hybridization and Geometry of Boron trifluoride, BF_3 molecule

Boron atom can form 3 covalent bonds with 3 fluorine atoms to give a molecule of Boron trifluoride. In BF_3 molecule, the sp^2 -hybridized orbitals of boron atom overlaps with the half-filled 'p' orbitals of three fluorine atoms and gives a trigonal planar geometry.



BF_3 Molecule

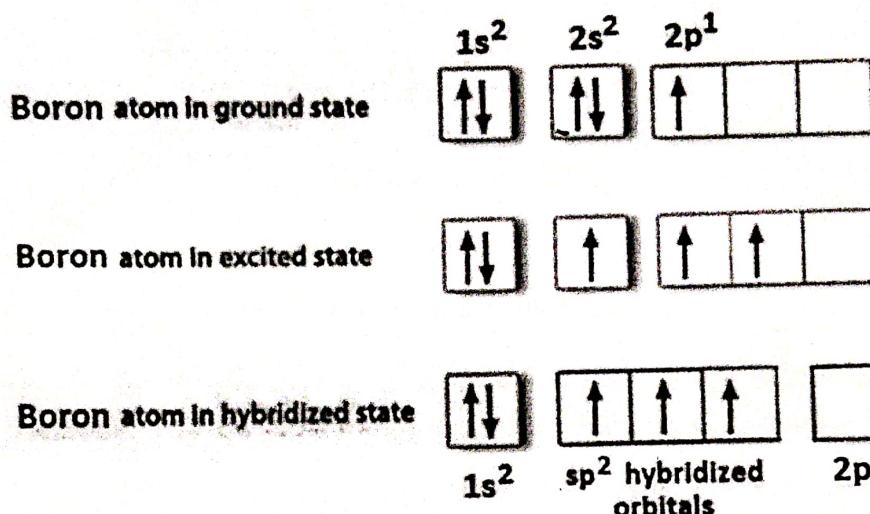
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

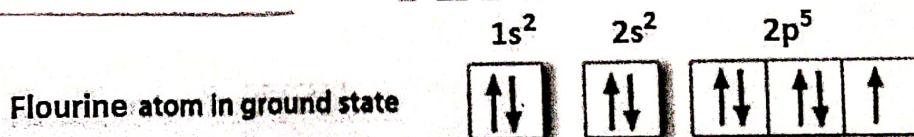
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Electronic configuration of B⁵: 1s²2s²2p¹ ✓

Boron atom has one unpaired electron in the ground state but in the excited state, it has 3 unpaired electrons and undergoes hybridization as shown below. That is, one 's' and two 'p' orbitals of Boron atom hybridized to give three sp² hybrid orbitals of equivalent energy.



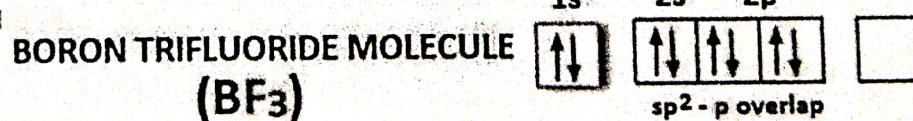
Electronic configuration of F⁹: 1s²2s²2p⁵ ✓



In Fluorine atom, one of the 'p' orbital is only half filled.

Formation of Boron trifluoride, BF₃ molecule:

The half-filled sp² hybridized orbitals of the Boron atom overlaps with the half-filled 'p' orbitals of three fluorine atoms to give sp² hybridization resulting in the formation of Boron trifluoride, BF₃ molecule.

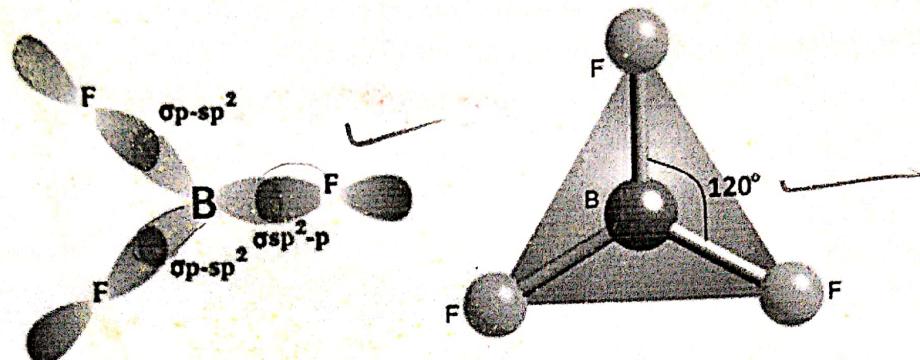


Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Shape and Geometry of BF_3 :



Trigonal planar geometry of BF_3

In BF_3 molecule, the sp^2 hybridized orbitals are oriented at an angle of 120° , when three sp^2 hybridized orbitals of Boron atom overlaps with the half-filled 'p' orbitals of three fluorine atoms.

Three sigma (σ) bonds are formed with bond angle of 120° .

The shape and geometry of Boron trifluoride, BF_3 molecule is Trigonal planar.

(3) sp^3 hybridization:

- sp^3 hybridization is observed when one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form 4 new equivalent orbitals. The new orbitals formed are called sp^3 hybrid orbitals.
- Sp^3 hybridization is also called as tetrahedral hybridization.
- These hybrid orbitals are directed towards the four corners of a regular tetrahedron and make an angle of 109.5° with one another.
- Each sp^3 hybrid orbital has 25% 's' character and 75% 'p' character.

Example:

- CH_4 and C_2H_6 molecules.

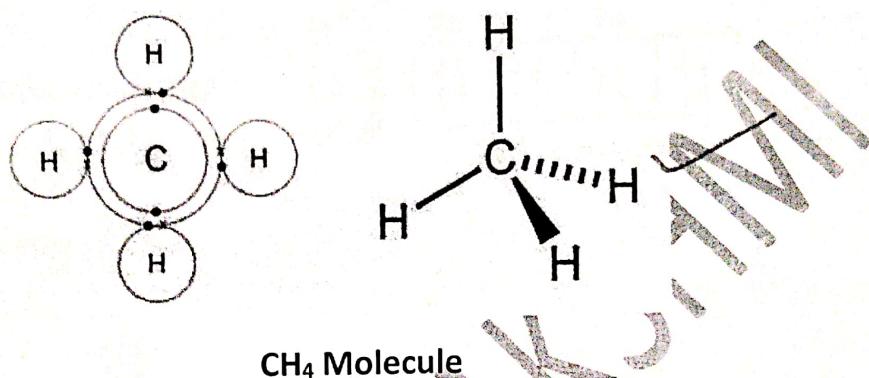
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

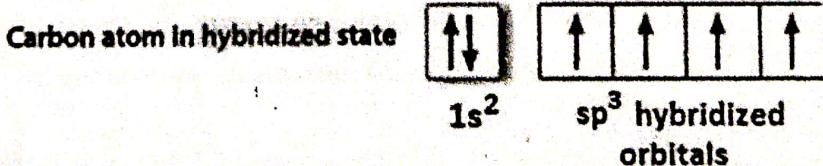
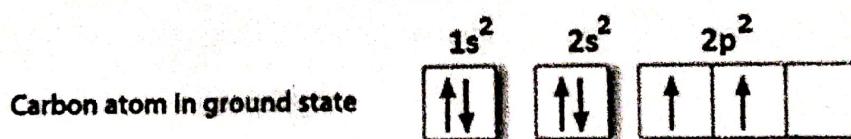
sp³ hybridization and Geometry of Methane, CH₄ molecule:

Carbon atom can form 4 covalent bonds with hydrogen atoms to give a molecule of Methane. In CH₄ molecule, the sp³-hybridized orbitals of carbon atom overlaps with the half-filled 's' orbitals of four hydrogen atoms and gives a tetrahedral geometry.

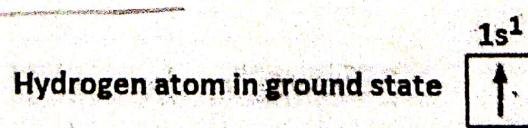


Electronic configuration of C⁶: 1s²2s²2p²

Carbon atom has two unpaired electrons in the ground state but in the excited state, it has 4 unpaired electrons and undergoes hybridization as shown below. That is, one 's' and three 'p' orbitals of Carbon atom hybridized to give four sp³ hybrid orbitals of equivalent energy.



Electronic configuration of H¹: 1s¹



In Hydrogen atom, the 's' orbital is only half filled.

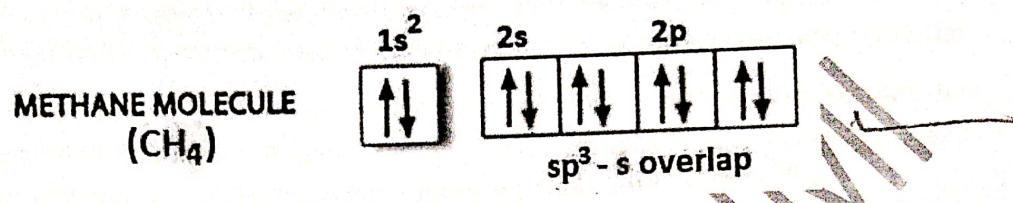
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

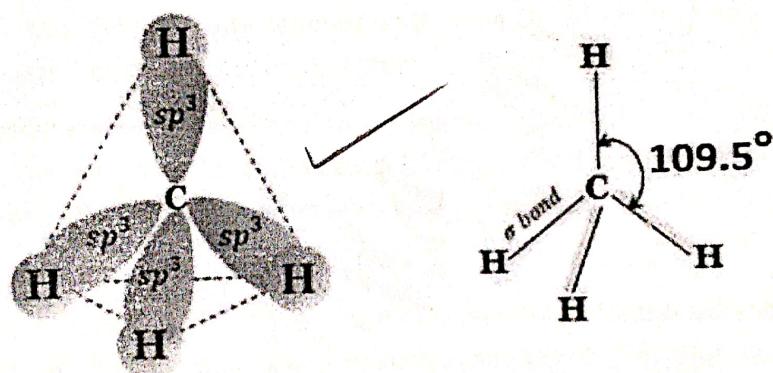
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Formation of Methane, CH₄ molecule:

The sp^3 hybridized orbitals of the Carbon atom overlaps with the half-filled 's' orbital of four hydrogen atoms to give sp^3 hybridization resulting in the formation of Methane, CH₄ molecule.



Shape and Geometry of CH₄:



Tetrahedral geometry of CH₄

In CH₄ molecule, the sp^3 hybridized orbitals are oriented at an angle of 109.5° , when four sp^3 hybridized orbitals of Carbon atom overlaps with the half-filled '1s' orbital of four Hydrogen atoms.

Four sigma (σ) bonds are formed with bond angle of 109.5° .

The shape and geometry of Methane, CH₄ molecule is Tetrahedral.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis concept is unable to explain the shape of molecules. We know that during the formation of covalent bond, orbitals get occupied with electron pairs. When a central atom forms more than one covalent bonds then there will be more than one such orbital surrounding the central atom and the electrons experience electrostatic repulsion from one another and the orbitals containing electrons also experience similar electrostatic repulsion.

Therefore, the orbitals tend to keep away as far as possible from one another so that they may experience minimum repulsion and the molecule shows maximum stability. This leads to a theory called **Valency Shell Electron Pair Repulsion Theory (VSEPR)**.

In the year 1940, Sidgwick and Powell proposed the **VSEPR Theory** based on the repulsive interactions of the electron pairs in the valence shell of the atoms. According to **VSEPR Theory**, the geometry of a molecule depends on the number of electron pairs in the valence shell (bonded or non-bonded) of the central atom.

The Valence-Shell-Electrons-Pair-Repulsion Theory (VSEPR), proposes that the stereochemistry of an atom in a molecule is determined primarily by the repulsive interactions among all the electron pairs in its valence shell.

(or)

VSEPR Theory states that the orbitals containing electrons in the valence shell of the central atom should be arranged in space in such a way that the orbitals lie as far away as possible from one another and due to such an arrangement, the force of repulsion between the orbitals minimizes and the molecule shows maximum stability.

Later, in the year 1957, Nyholm and Gilliespie developed and refined the **VSEPR model** by explaining the important difference between the lone pair and the bond pair of electrons.

The lone pairs are localised on the central atom and each bonded pair is shared between two atoms.

As a result, the lone pair of electrons in a molecule occupy more space as compared to the bond pair of electrons. This results in greater repulsion between lone pair of electrons as compared to the lone pair – bond pair and bond pair – bond pair repulsions.

These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Postulates of VSEPR Theory:

- 1 The shape and geometry of the molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
If the central atom is surrounded by only bond pairs of electrons the molecule has a **regular geometry**. In addition to bond pairs of electrons, if the central atom has one or more lone pairs of electrons, then the molecule has **irregular geometry**.
- 2 Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- 3 These pairs of electrons have a tendency to occupy positions in space in such a way that it minimizes the electron-electron repulsion between them and maximizes the distance between them.
- 4 The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- 5 A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus while the bond pair is shared by two nuclei.
- 6 It follows that repulsion between two lone pairs is greater than the repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. The repulsive interactions decrease in the order:

$$\text{LP-LP} > \text{LP-BP} > \text{BP-BP}$$

Further, the magnitude of repulsion between bond pair of electrons depend on the electronegativity difference between the central atom and the other atoms.

Repulsive forces decrease sharply with increasing bond angle between the electron pairs. Example: BF_3 molecule.

- 7 In VSEPR theory, the number of electron pairs in single bond (or) double bond (or) triple bond (or) dative bond is viewed as a single electron pair because all the electron pairs in the same bond are oriented in the same direction.
- 8 The VSEPR model applies to any structure that has two or more resonance structures that can represent a molecule.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Regular and irregular geometry

It has been observed that if the central atom is surrounded by only bond pairs of electrons then the molecule has a **regular geometry**.

In addition to bond pairs of electrons, if the central atom has one or more lone pairs of electrons, then the molecule has **irregular geometry**. This is because the repulsion between the lone pair- lone pair is greater than the lone pair- bond pair and which is greater than bond pair- bond pair.

Thus, the presence of one or more orbitals with lone pair of electrons will decide the shape and geometry of molecules.

For the prediction of geometrical shapes of molecules with the help of **VSEPR Theory**, it is convenient to divide the molecules into two categories as:

- Molecules in which the central atom has no lone pair
Example: BeCl_2 , BF_3 , CH_4 , PCl_5 , SF_6
- Molecules in which the central atom has one or more lone pairs
Example: SnCl_2 , NH_3 , H_2O , SF_4 , BrF_5

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

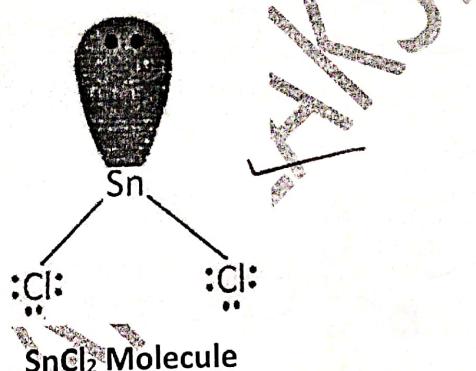
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Geometry of molecules containing bond pair as well as lone pair of electrons

(1) Stannous chloride, SnCl_2 molecule

The Tin, Sn atom can form covalent bonds with two chlorine atoms to give a molecule of stannous chloride, SnCl_2 . The sp^2 - hybridized orbitals of Tin atom overlaps with the half-filled 'p' orbitals of two chlorine atoms and gives SnCl_2 molecule.

According to VSPER Theory, the stannous chloride molecule has bent (or) angular (or) V shape and distorted Trigonal planar geometry. This is due to the presence of a single non-bonding pair of electrons on the Tin atom, which acts as a repulsive force on the bonding orbitals.

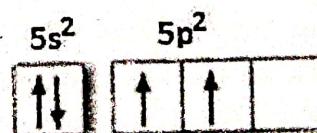


Electronic configuration of Sn^{50} :

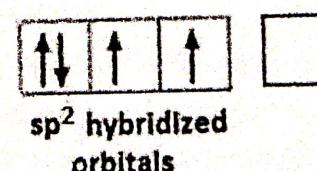
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$ (or) $\text{Kr} [4d^{10} 5s^2 5p^2]$

The Tin, Sn atom in ground state and hybridized state is shown below. One 's' and two 'p' orbitals of Tin atom hybridized to give three sp^2 hybrid orbitals of equivalent energy.

Tin atom in ground state



Tin atom in hybridized state



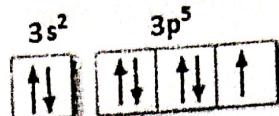
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Electronic configuration of Cl^{17} : $1s^2 2s^2 2p^6 3s^2 3p^5$ ✓

Chlorine atom in ground state

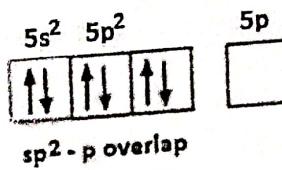


In Chlorine atom, one of the 'p' orbital is only half filled.

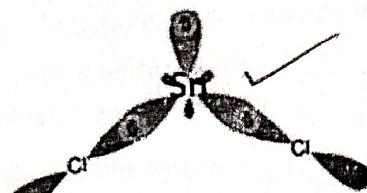
Formation of Stannous chloride, SnCl_2 molecule:

The sp^2 hybridized orbitals of the Tin atom overlaps with the half-filled 'p' orbital of two chlorine atoms to give sp^2 hybridization resulting in the formation of stannous chloride, SnCl_2 molecule.

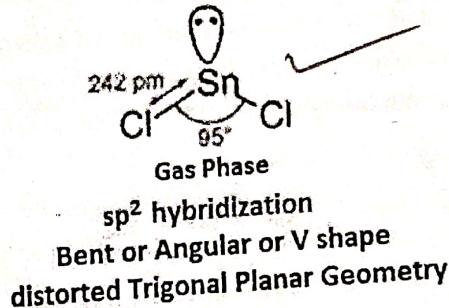
STANNOUS CHLORIDE MOLECULE
 (SnCl_2)



Shape and Geometry of SnCl_2 :



2 bond pairs and 1 lone pair
Orbital overlap in SnCl_2



The outer electronic configuration of central atom Tin is $5s^2 5p^2$ and that of chlorine is $3s^2 3p^5$. According to Hund's rule, there are 2 unpaired electrons in the $5p$ orbitals of Tin atom and these are sufficient to form two sigma bonds with half-filled $3p$ orbital of two Cl atoms to give SnCl_2 molecule without having any excitation of electrons of the Sn atom.

The stannous chloride molecule with 2 bonding orbitals should have linear geometry and the molecule should be symmetrical but actual it is not so.

From X-ray analysis, it is found that, stannous chloride molecule is not linear and the central atom, Tin is surrounded by 3 orbitals and not 2. That is, the central atom, Tin is surrounded by two orbitals containing a bond pair of electrons and the third orbital containing a lone pair of electrons.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

It has been postulated that one 's' and two 'p' orbitals of Tin atom hybridized to give **three sp^2 hybrid orbitals of equivalent energy** and two sigma (σ) bonds are formed with two chlorine atoms to give $SnCl_2$ molecule.

The so formed stannous chloride, $SnCl_2$ molecule should have **trigonal planar geometry** with bond angle of 120° . But, the presence of **lone pair of electrons** on Tin atom causes greater repulsion to the **bond pairs** since the force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between two bond pairs.

As a result, the two **Sn-Cl bonds** move very closer and therefore, the molecule gets a **distortion** and the bond angle decreases from 120° to 95° . Therefore, the stannous chloride molecule in gas phase has **bond angle of 95° with Sn-Cl bond length of 242 pm**.

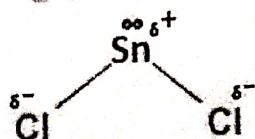
Based on VSPER Theory, due to the presence of lone pair of electrons, the shape of $SnCl_2$ molecule is bent (or) angular (or) V shape and the geometry of $SnCl_2$ molecule is distorted

Trigonal planar.

Why BeF_2 is linear molecule and $SnCl_2$ is angular molecule?

In BeF_2 molecule, hybridization is sp and it doesn't have any lone pairs, so the **shape and geometry of Beryllium fluoride molecule is linear**. But in $SnCl_2$ molecule, the hybridization is sp^2 with one lone pair of electrons, so the shape of stannous chloride molecule is **bent (or) angular (or) V shape and the geometry of $SnCl_2$ molecule is distorted Trigonal planar**.

Is $SnCl_2$ Polar or Non-polar?



Due to difference in electronegativity between Tin atom and Chlorine atoms, the electrons of the Tin atom get pulled towards the electrons of the Chlorine atoms. This causes the Tin atom to have a slightly more positive charge and the Chlorine atoms to be more negative. This slight difference of charge in a molecule is called polarity.

Polarity of any molecule depends upon the orientation of its substituent atoms also. If the bond angle between two Sn-Cl bonds is 180° , then the dipole moment of each of the bond will be cancelled out and the net dipole moment will be zero.

But in $SnCl_2$, both the Sn-Cl bonds are angular with each other. Thus, the dipole moment of one Sn-Cl bond cannot be cancelled by each other. Hence, due to the orientation of two Sn-Cl bonds, $SnCl_2$ is a polar molecule having permanent dipole moment.

Department of Chemistry

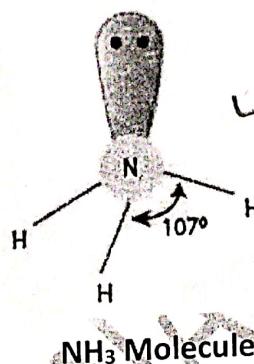
ENGINEERING CHEMISTRY, 22ECCHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(2) Ammonia, NH₃ molecule

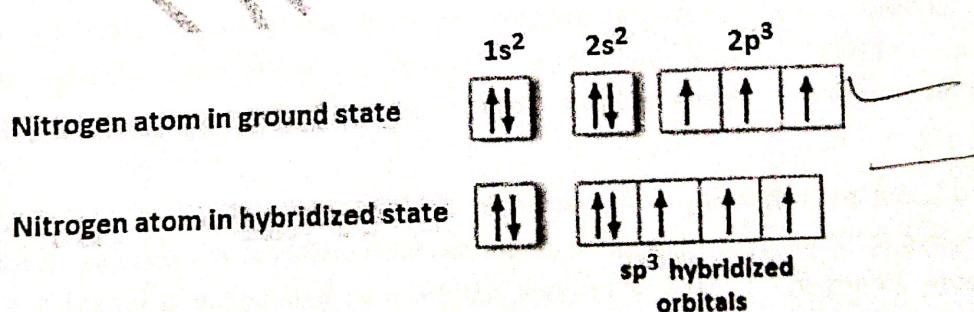
Nitrogen atom can form covalent bonds with three Hydrogen atoms to give a molecule of ammonia, NH₃. The sp³- hybridized orbitals of Nitrogen atom overlaps with the half-filled 's' orbital of three Hydrogen atoms and gives NH₃ molecule.

According to VSPER Theory, the geometry of ammonia molecule is distorted tetrahedral and the shape of ammonia molecule is trigonal pyramidal. This is due to the presence of a single non-bonding pair of electrons on the Nitrogen atom, which acts as a repulsive force on the bonding orbitals.

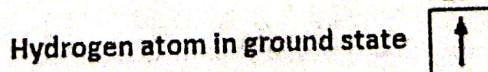


Electronic configuration of N⁷: 1s²2s²2p³

The Nitrogen, N atom in ground state and hybridized state is shown below. One 's' and three 'p' orbitals of Nitrogen atom hybridized to give four sp³ hybrid orbitals of equivalent energy.



Electronic configuration of H¹: 1s¹



In Hydrogen atom, the 's' orbital is only half filled.

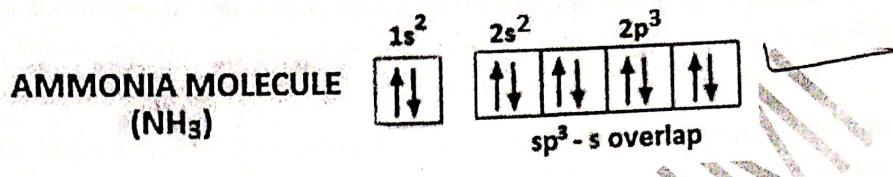
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

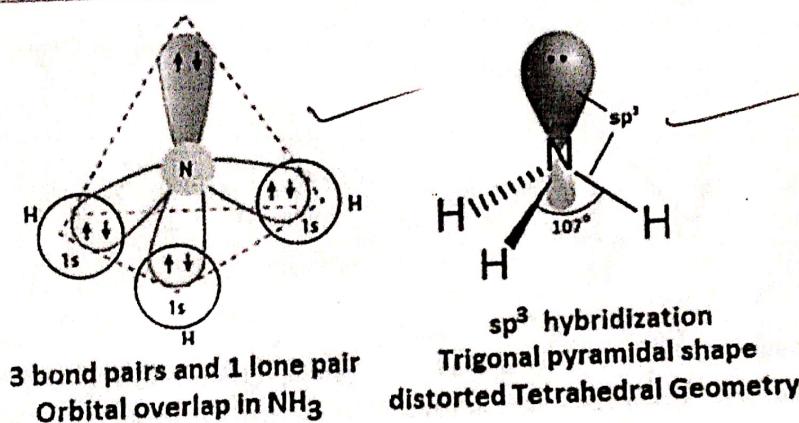
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Formation of Ammonia, NH₃ molecule: ✓

The sp^3 hybridized orbitals of the Nitrogen atom overlaps with the half-filled 's' orbital of three hydrogen atoms to give sp^3 hybridization resulting in the formation of Ammonia, NH₃ molecule.



Shape and Geometry of NH₃:



The electronic configuration of central atom Nitrogen is $1s^22s^22p^3$ and that of Hydrogen atom is $1s^1$. According to Hund's rule, there are 3 unpaired electrons in the $2p$ orbitals of Nitrogen atom and these are sufficient to form three sigma bonds with half-filled $1s$ orbital of three hydrogen atoms to give ammonia molecule without having any excitation of electrons of the Nitrogen atom.

The ammonia molecule with 3 orbitals should have trigonal planar geometry but actual it is not so. From X-ray analysis, it is found that Ammonia molecule is asymmetrical and the central atom Nitrogen is surrounded by 4 orbitals and not 3. That is, the central atom, Nitrogen is surrounded by three orbitals containing a bond pair of electrons and the fourth orbital containing a lone pair of electrons.

It has been postulated that one 's' and three 'p' orbitals of Nitrogen atom hybridized to give four sp^3 hybrid orbitals of equivalent energy and three sigma (σ) bonds are formed with three hydrogen atoms to give NH₃ molecule.



Scanned with OKEN Scanner

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

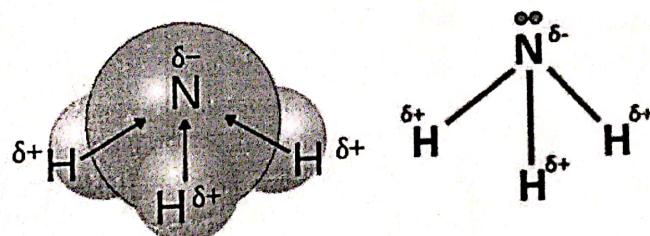
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

The so formed ammonia, NH_3 molecule should have **Tetrahedral** shape with bond angle of 109.5° . But, the presence of **lone pair of electrons** on **Nitrogen** atom causes greater repulsion to the bond pairs since the force of repulsion between a lone pair and a bond pair is greater than the force of repulsion between two bond pairs.

As a result, the three **N-H bonds** move slightly closer and therefore, the molecule gets a little distortion and the bond angle decreases from 109.5° to 107° . Therefore, the ammonia molecule has **H-N-H bond angle of 107°** and **N-H bond length of 101.2 pm**.

Based on **VSPER Theory**, due to the presence of **lone pair of electrons**, **shape of ammonia molecule is trigonal pyramidal** and the **geometry of ammonia molecule is distorted tetrahedral**.

Why NH_3 is highly polar?



Due to difference in electronegativity between Nitrogen atom and Hydrogen atoms, the electrons of the hydrogen atoms get pulled towards the electrons of the Nitrogen atom. This causes the Nitrogen atom to have a slightly more negative charge and the hydrogen atoms to be more positive. This slight difference of charge in a molecule is called polarity.

NH_3 is a **polar molecule** because, in NH_3 molecule, it has three dipoles because of **three N-H bonds** and these dipoles do not cancel out each other. The reason ammonia, NH_3 is a polar molecule is due to its uneven distribution of charges.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

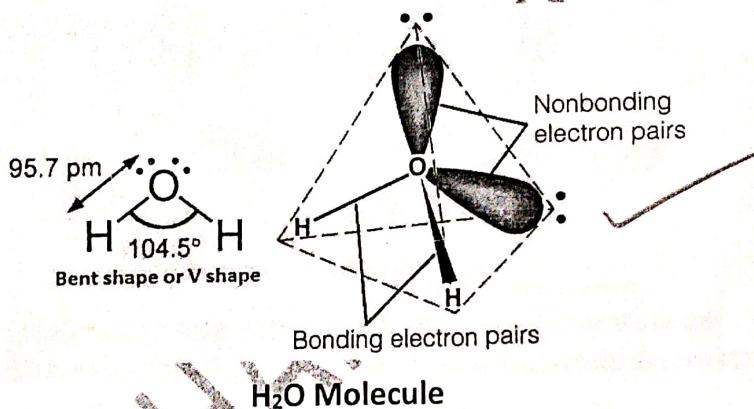
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

(3) Water, H₂O molecule

Oxygen atom can form covalent bonds with two Hydrogen atoms to give water, H₂O molecule. The sp³- hybridized orbitals of **Oxygen** atom overlaps with the half-filled 's' orbital of two **Hydrogen** atoms and gives Water molecule.

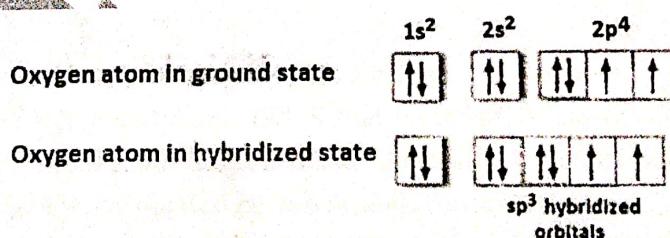
According to **VSPER Theory**, the water molecule has **bent** (or) **angular** (or) **V shape**. This is due to the presence of two non-bonding pairs of electrons on the **Oxygen** atom, which acts as a repulsive force on the bonding orbitals.

The **geometry** of water molecule is **distorted tetrahedral**. That is, the electron groups are **tetrahedrally** arranged with two corners occupied by lone pairs of electrons and two corners occupied by hydrogen atoms.

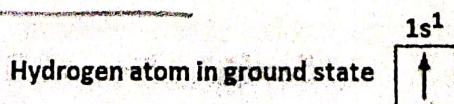


Electronic configuration of O⁸: 1s²2s²2p⁴

The Oxygen atom in ground state and hybridized state is shown below. One 's' and three 'p' orbitals of Oxygen atom hybridized to give four sp³ hybrid orbitals of equivalent energy.



Electronic configuration of H¹: 1s¹



In Hydrogen atom, the 's' orbital is only half filled.

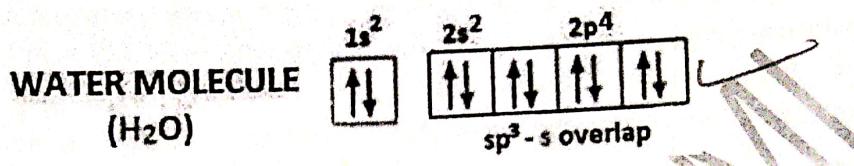
Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

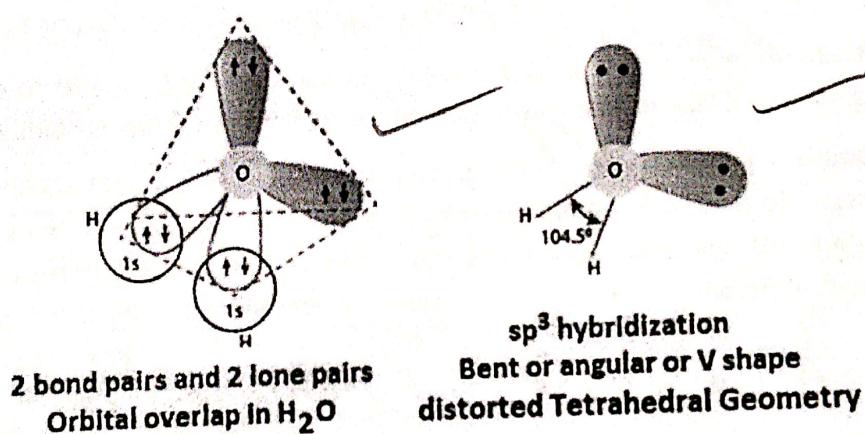
UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Formation of Water, H₂O molecule:

The sp³ hybridized orbitals of the Oxygen atom overlaps with the half-filled 's' orbital of two hydrogen atoms to give sp³ hybridization resulting in the formation of Water, H₂O molecule.



Shape and Geometry of H₂O:



The electronic configuration of central atom Oxygen is 1s²2s²2p⁴ and that of Hydrogen atom is 1s¹. According to Hund's rule, there are 2 unpaired electrons in the 2p orbitals of oxygen atom and these are sufficient to form two sigma bonds with half-filled 1s orbital of two hydrogen atoms to give water molecule without having any excitation of electrons of the Oxygen atom.

The water molecule with 2 orbitals should have a linear geometry and nonpolar like BeF₂ but actual it is not so. It is found from studies that water molecule is highly polar with bent structure and the central atom Oxygen is surrounded by 4 orbitals but not 2. That is, the central atom, Oxygen is surrounded by two orbitals containing a bond pair of electrons and other two orbitals containing a lone pair of electrons.

It has been postulated that one 's' and three 'p' orbitals of Oxygen atom hybridized to give four sp³ hybrid orbitals of equivalent energy and two sigma (σ) bonds are formed with two hydrogen atoms to give H₂O molecule.

Department of Chemistry

ENGINEERING CHEMISTRY, 22ECHB102

UNIT 1 - CHAPTER 1: CHEMICAL BONDING AND MOLECULAR STRUCTURE

Hence, the so formed water, H_2O molecule should have tetrahedral shape with bond angle of 109.5° with two corners occupied by lone pairs of electrons and the other two corners occupied by a hydrogen atoms.

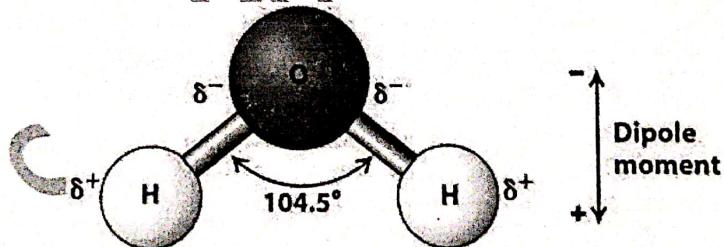
But, the presence of 2 sets of lone pair of electrons on Oxygen atom causes greater repulsion to the bond pairs since the force of repulsion between the two lone pairs of the electrons is more than the force of repulsion between the lone pair and bond pair and which in-turn is greater than the force of repulsion between the two bond pairs of electrons. So greater distortion in geometrical structure is observed in water molecule.

As a result, the two O-H bonds move very closer and the molecule gets a greater distortion and the bond angle decreases from 109.5° to 104.5° . Hence, the water molecule has H-O-H bond angle of 104.5° with O-H bond length of 95.7 pm.

Further, the distortion observed in water molecule is greater than in ammonia. Hence, the H-O-H bond angle in water molecule is smaller than H-N-H bond angle in ammonia.

Based on **VSPER Theory**, due to the presence of lone pair of electrons, **shape of water molecule is bent (or) angular (or) V shape**. Further, water has 4 regions of electron density around the central Oxygen atom (2 bond pairs and 2 lone pairs) and these electrons are arranged in a distorted tetrahedral structure. That is, water molecule has distorted tetrahedral geometry.

Why water molecule is highly polar?



Due to angular shape of water molecule and the difference in electronegativity between Oxygen atom and Hydrogen atoms, the electrons of the hydrogen atoms get pulled towards the electrons of the oxygen atom.

This causes the oxygen atom to have a slightly more negative charge and the hydrogen atoms to be more positive. This slight difference of charge in a molecule is called polarity and this causes the water molecule to be highly polar.