KLE Technological University
Creating Value
Leveraging Knowledge

Department of Chemistry

ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 1 - CHAPTER 1: CHEMICAL BONDING

Introduction

Atoms combine to form molecules. 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 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:

- Electrovalent bond or Ionic bond
- Covalent bond
- Coordinate bond or Dative bond

1. Electrovalent or Ionic bond

Ionic bond is proposed by the scientist Arrhenius. An ionic bond 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} : $1S^2\ 2S^2\ 2P^6\ 3S^1$

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

$$Na \longrightarrow Na^+ + e^-$$

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

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

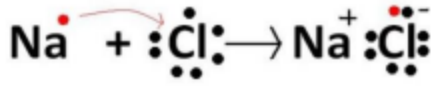
The chlorine atom accepts one electron in its outermost orbital to satisfy the octet formation and forms Cl^- ion.

$$Cl + e^- \longrightarrow Cl^-$$

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

$$Na^+ + Cl^- \longrightarrow NaCl$$

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.

Conditions for the formation of ionic bond:

- Combining two elements should have opposite charges.
- Cations must have low ionization energy.
- Anions must have high electron affinity.
- Electro negativity difference between the cation and anion must be greater than or equal to 1.7
- Ionic molecule formed must have high lattice energy.
- The potential energy of the ionic molecule must be lower than the combining elements.

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.

$Al \longrightarrow Al^{3+} + 3e^-$

Ionization Energy = 5137 kJ/mole

Variation of Ionization Energy:

(a) Down the Group:

The atomic size increases down the group and hence the shielding effect by the inner electrons increases and therefore effective nuclear charge decreases.

Hence, removal of electrons from an element requires less energy. Therefore, ionization energy decreases down the group.

(b) Along the Period:

The atomic size decreases from left to right along the period as electrons are added to the same shell and as such the effective nuclear force of attraction increases and reaches its saturation and do not release or accept addition of electrons.

Hence, removal of electrons from an element requires more energy. Therefore, ionization energy increases along the period.

- **Low ionization energy of metal atoms:**

  Atoms can lose electrons easily when ionization energy is low. Consequently, greater is the easy 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.

Variation of Electron Affinity:

(a) Down the Group:

The atomic size increases down the group and therefore attraction by the nucleus for addition of an electron decreases down the group.

Therefore, electron affinity decreases down the group.

(b) Along the Period:

The atom has greater tendency to receive an electron and more energy is released during the addition of an extra electron.

Therefore, electron affinity increases from left to right along the period.

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 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.

In general, the electro negativity of non-metal atoms is larger than that of metal atoms.

Variation of Electro negativity:

(a) Down the Group:

The capacity of attraction of electron pair towards the atom decreases as the atomic size increases down the group.

Therefore, electro negativity decreases down the group.

(b) Along the Period:

The atomic size decreases from left to right along the period as the electrons are added to the same shell. Therefore, the force of attraction on the electron pair increases.

Hence, electro negativity increases from left to right along the period.

Halogens have very high electro negativity values. Among halogens, fluorine is the most electro negative element.

- 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.

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.

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.

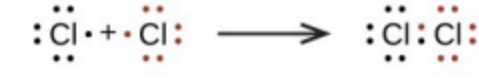
A covalent bond is defined as a force which binds the atoms of same or different elements by mutual sharing of equal number of electrons and both the binding atoms acquire inert gas configuration.

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 '≡'.

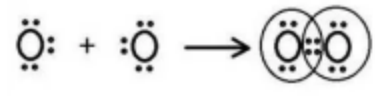
Consider the formation of Cl_2, O_2 and N_2:

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

$Cl + Cl \longrightarrow Cl-Cl$ 

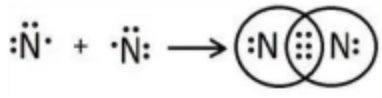
(Stable octet formation in outermost shell)

- Electronic Configuration of O^8 : $1S^2\ 2S^2\ 2P^4$

$O + O \longrightarrow O=O$ 

(Stable octet formation in outermost shell)

- Electronic Configuration of N^7 : $1S^2\ 2S^2\ 2P^3$

$N + N \longrightarrow N\equiv N$ 

(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.

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.

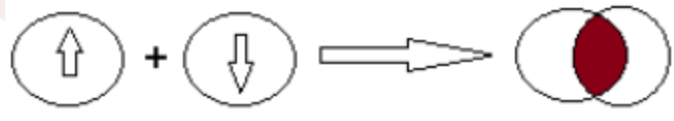
Atomic Orbital Theory

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.

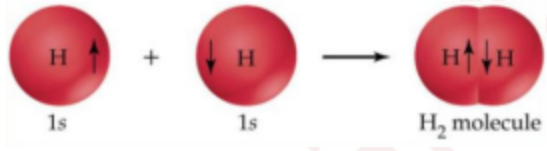
VALENCE BOND THEORY, VBT

Valence Bond Theory was proposed by Heitler and London in the year 1927 and was modified by Pauling and Slater in the year 1931.

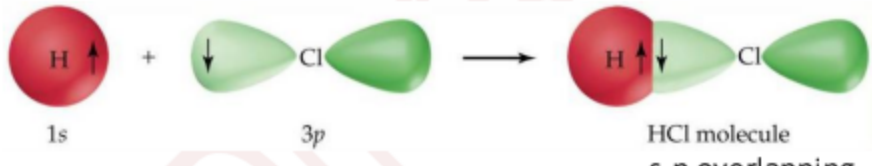
VBT is the theory of chemical bonding that explains the formation of covalent bonds on the basis of overlapping of atomic orbitals and pairing of unpaired electrons with opposite spin.

Features of Valence Bond Theory

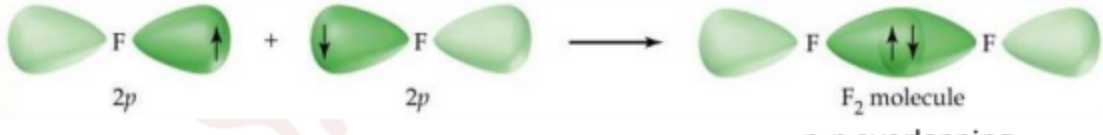
- A covalent bond is formed by overlapping of atomic orbitals, AOs, having two unpaired electrons with opposite spin.
- As a result of covalent bond formation, the energy of the molecule formed decreases and hence provides stability to the molecule.
- Directionally oriented overlapping of atomic orbitals forms stronger bonds whose order is s-s overlapping < s-p overlapping < p-p overlapping.



s-s overlapping

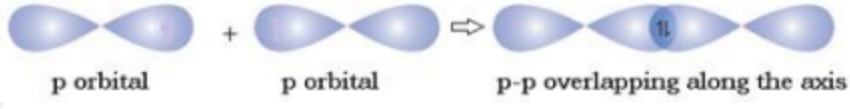


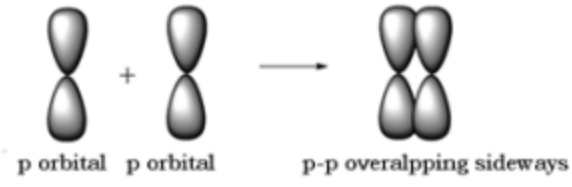
s-p overlapping



p-p overlapping

- Overlapping along the axis is stronger than overlapping on sideways.



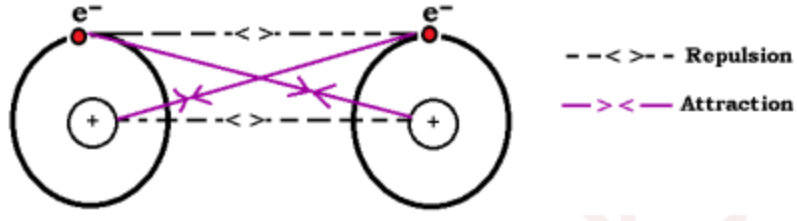


- Axial overlapping forms sigma bond and sideways overlapping forms pi bond.

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.

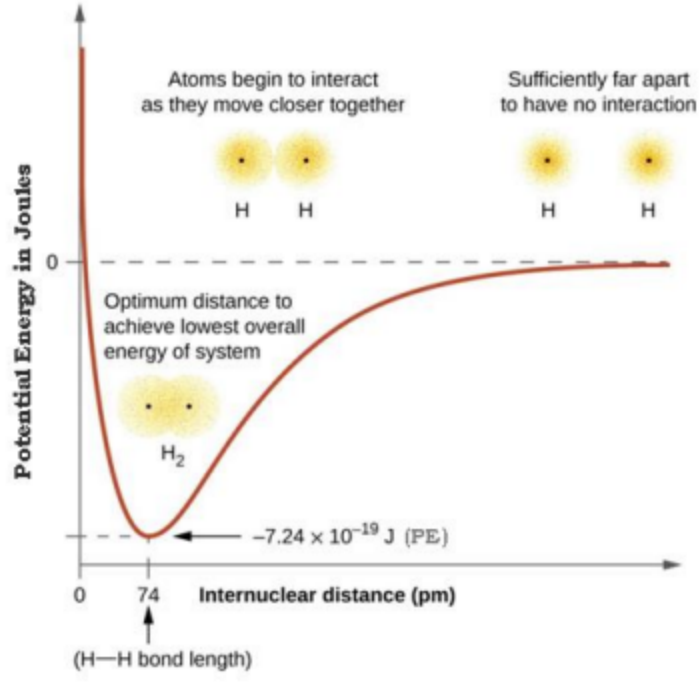
- Attractive forces establish between the nucleus of one atom and electrons of other atom.
- Repulsive forces exist between the two nuclei and as well as between the electrons of the two atoms.



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 are stable.

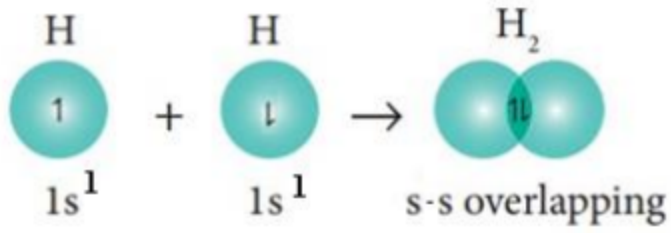
Energy changes during the formation of Hydrogen molecule through covalent bond:

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



Bond length of H_2 molecule = 74 pm = 0.74 Å

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.
- 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 stronger bond in the molecule. Therefore hydrogen molecule formed is stable.

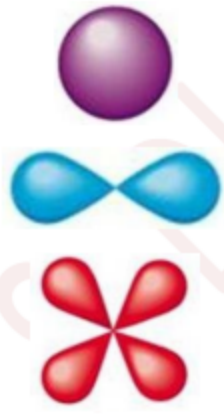
MOLECULAR ORBITAL THEORY, MOT

Molecular Orbital Theory, MOT was proposed by F. Hund and R. S. Mullikan in the year 1932 and was later modified by Lennord Jones and Charles Coulson.

Molecular Orbital Theory is the theory of chemical bonding that explains the formation of covalent bonds on the basis of combination of Atomic orbitals and pairing of unpaired electrons with opposite spin.

Features of Molecular Orbital Theory, MOT:

- When two atomic orbitals, AOs, combine linearly they form Molecular Orbitals, MOs.
- A Molecular Orbital, MO is a region in space around the nuclei wherein the probability of finding electrons is maximum in a molecule.
- When two AOs combine they form two MOs, viz Bonding Molecular Orbital, BMO and Anti-Bonding Molecular Orbital, ABMO.
- A BMO has lower energy and an ABMO has higher energy than the combining AOs.
- MOs are polycentric. That is electrons move under the influence of all the nuclei.
- The shape of MOs depends on the shape of the combining AOs.



s – orbital: Spherical shape

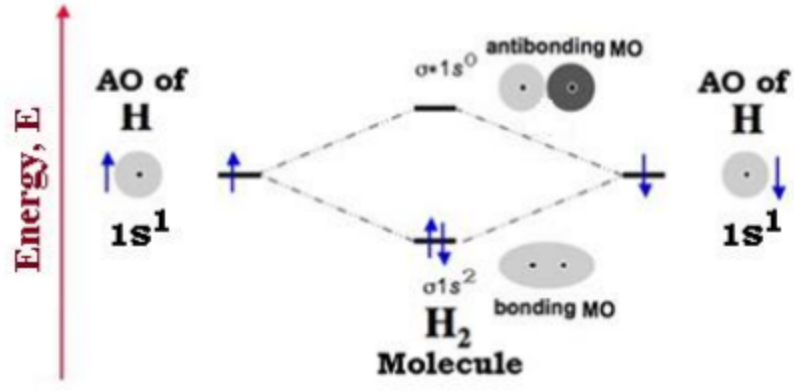
p – orbital: Dumbbell shape

d – orbital: Double dumbbell shape

- Only those AOs having similar energy and proper symmetry can combine to form MOs. s with s, s with p_x, p_y and p_z, p_x with p_x, p_y with p_y, p_z with p_z, etc., but not p_x with p_y, p_x with p_z and p_y with p_z.
- The bonding MOs are represented as σ and π.
- Anti-bonding MOs are represented as σ^* and π^*.
- Each MO can accommodate a maximum of two electrons with opposite spin.
- Electrons are filled in MOs according to Aufbau principle, Hund's rule and Pauli's exclusion principle.

Electronic configuration and Energy level MO diagram of Hydrogen molecule:

- A molecule of H_2 has two hydrogen atoms with one electron each in 1s AO.
- Electronic configuration of H^1 is: $1s^1$
- When two 1s atomic orbital of hydrogen atoms combine, they form one BMO and one ABMO. The two electrons occupy BMO, $\sigma\ 1s^2$.
- Thus the electronic configuration of H_2 molecule is: $\sigma\ 1s^2$.



- **Stability:**

  Since the two electrons are present in BMO and no electrons are present in ABMO, the hydrogen molecule formed is stable.

- **Bond Order:**

  Bond order = (Number of electrons in BMO – Number of electrons in ABMO)/2

  Bond order = (2-0)/2 = 2/2

  - Bond order = 1.

  Hence, two hydrogen atoms are bonded by single covalent bond, H – H.

- Hydrogen molecule is diatomic.

Polar and Non-polar covalent bond:

- **Polar Covalent Bond:**

  When a covalent bond is formed between unlike or 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 and this will result 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, $\mathbf{H^{\delta+} - Cl^{\delta-}}$

- **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, μ = electric charge x Bond length

  That is, **μ = e x d**

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

- **Percentage of Ionic character:**

Molecules like HCl, SO_3 and CH_3Cl 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%.

% of ionic character = (observed dipole moment / calculated dipole moment)*100

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

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

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

3. Coordinate Bond (or) Dative Bond

A coordinate bond is formed when both the electrons are contributed by only one atom.

A Coordinate covalent bond or Dative bond is defined as a force which binds the atoms of same or different elements when one atom shares a lone pair of electrons with another atom lacking such a pair of electrons.

According to orbital theory, a coordinate covalent bond is formed when an orbital containing lone pair of electrons of one atom overlaps with an empty orbital present in another atom.

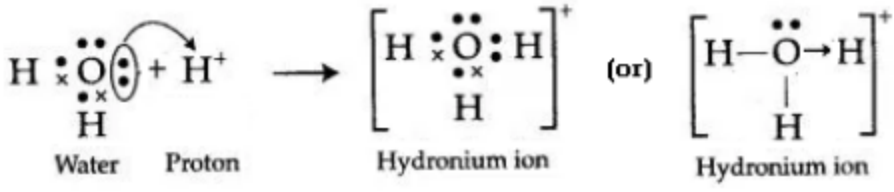
A. Formation of Hydronium ion, $[H_3O]^+$

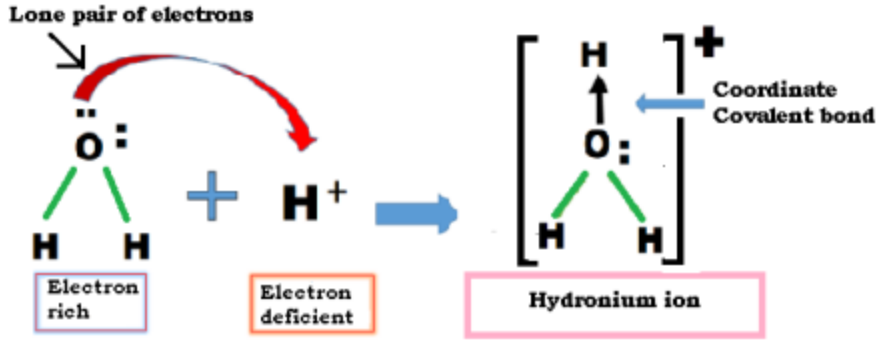
Hydronium ion can be formed when an acid is present in water or simply in pure water. It can also be formed by the combination of H^+ ion with H_2O molecule. Its chemical formula is H_3O^+.

The hydronium ion has a **trigonal pyramidal geometry** and it is composed of three hydrogen atoms and one oxygen atom.

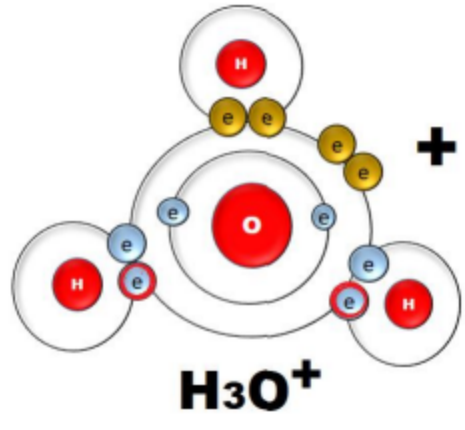
Electronic configuration of H^1: $1s^1$

Electronic configuration of O^8: $1s^2\ 2s^2\ 2p^4$





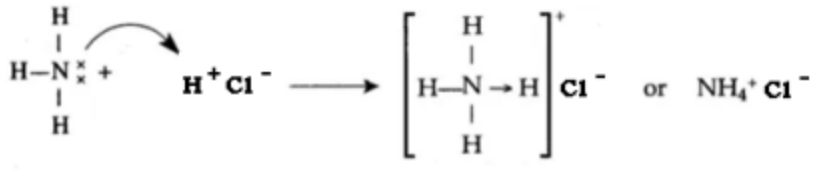
The central atom, oxygen in water molecule has four orbitals; two of these orbitals contain lone pair of electrons, while other two contains bond pair of electrons.



B. Formation of Ammonium ion, $[NH_4]^+$

- **Reaction between ammonia and hydrogen chloride:**
  If these colourless gasses are allowed to mix, a thick white smoke of solid ammonium chloride is formed.

  $NH_3 + HCl \rightarrow NH_4Cl$

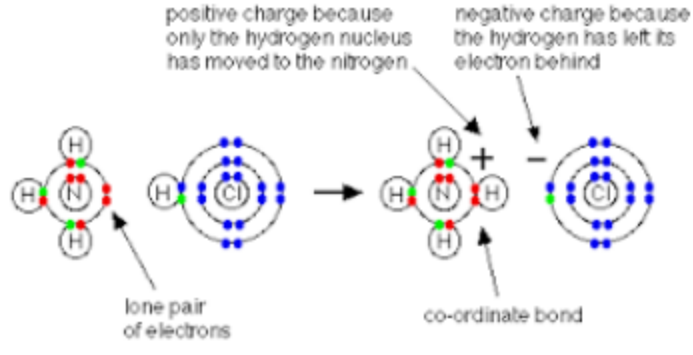


- **Formation of ammonium ion, $[NH_4]^+$:**
  Ammonium ions are formed by the transfer of a hydrogen ion from the hydrogen chloride to the lone pair of electrons on the ammonia molecule.

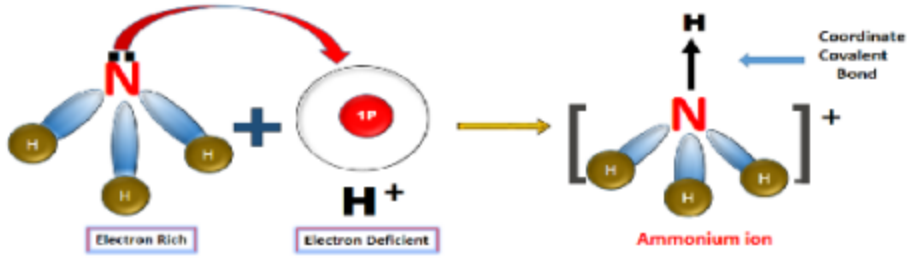
  Electronic configuration of H^1: $1s^1$

  Electronic configuration of N^7: $1s^2\ 2s^2\ 2p^3$

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



When the ammonium ion, NH_4^+, is formed, the fourth hydrogen is attached to nitrogen by a coordinate covalent bond because only the hydrogen's nucleus is transferred from chlorine to the nitrogen. The electron of hydrogen is left behind on the chlorine to form a negative chloride ion.



The central atom nitrogen in ammonia molecule has four orbitals, one of which contains lone pair of electrons while the remaining three orbitals contain bond pair of electrons.