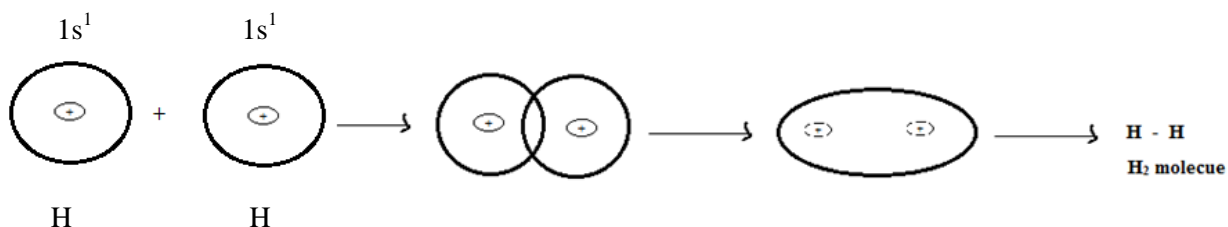


UNIT: I INORGANIC CHEMISTRY

COVALENT BOND

- A covalent bond is a chemical bond which is formed when two atoms mutually share a pair of electron. By doing so, the atoms attain stable octet electronic configuration. In covalent bonding, overlapping of the atomic orbitals having one electron from each of the two atoms takes place resulting in equal sharing of the pair of electrons.
- Generally the orbitals of the electrons in the valency shell of the atoms are used for electron sharing.
- For example, In hydrogen molecule (H_2) a covalent bond is formed by the overlap of the two s orbitals each containing one electron from each of the two H atoms of the molecule. Each H atom attains ' $1s^2$ ' filled K shell.



- A covalent bond can be formed by sharing of s , p , d , f electrons also.
- For example, Consider Cl_2 molecule. The outer shell electronic configuration of atom is $3s^2 3p_x^2 3p_y^2 3p_z^1$. When each chlorine atom mutually share the $3p_z$ unpaired electron contributed from each Cl atom of the molecule, a covalent bond is formed. By doing so, each chlorine atom the atoms attain stable octet electronic configuration.

Characteristics of covalent compounds

- Covalent compounds are formed by the mutual sharing of electrons. There is no transfer of electrons from one atom to another and therefore no charges are created on the atom. No ions are formed. These compounds exist as neutral molecules and not as ions. Although some of the covalent molecules exist as solids, they do not conduct electricity in fused or molten or dissolved state.
- They possess low melting and boiling points. This is because of the weak intermolecular forces existing between the covalent molecules. Some covalent molecules are volatile in nature.
- Covalent bonds are rigid and directional therefore different shapes of covalent molecules are seen.
- Most of the covalent molecules are non-polar and are soluble in non-polar solvents (low dielectric constant) like benzene, ether etc and insoluble in polar solvents like water. Carbon tetrachloride (CCl_4) is a covalent nonpolar molecule and is soluble in benzene.

Structure of the molecules: VSEPR theory

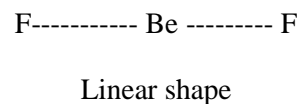
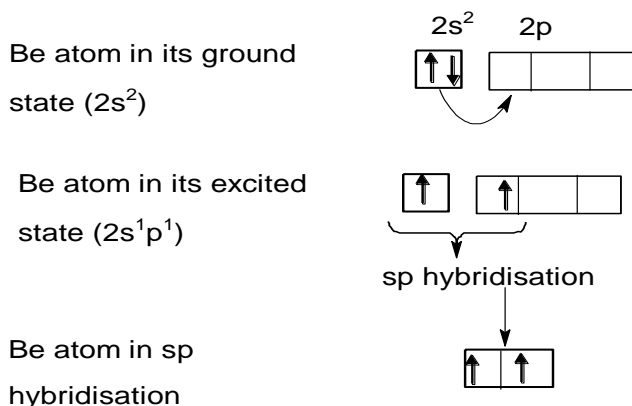
Valence shell electron pair repulsion theory (VSEPR) provides a method for predicting the shape of molecules, based on the electron pair electrostatic repulsion. It was described by Sidgwick and Powell in 1940 and further developed by Gillespie in 1957. The VSEPR method predicts shapes that compare favorably with those determined experimentally.

1. The central atom is identified and its outer most electronic configuration is written.
2. We should know theoretically the number of pi and sigma bonds present around the central atom.
3. The central atom should have unpaired electrons equal to the sum of pi and sigma bonds in the ground state. If the ground state configuration does not possess the required number of unpaired electron, the paired electrons in the valence shell are allowed to excite in order to get the required number of unpaired electrons.
4. The number of unpaired electrons required for pi bonding is rounded off and they should not be allowed to take part in the hybridization.
5. The remaining orbitals having unpaired electrons as well as paired electrons are allowed to undergo hybridization.
6. **The geometry of the molecule is fixed based on the type of hybridization**

Type of hybridization	Geometry	Bond angle
sp	Linear	180°
Sp ²	Trigonal planar	120°
Sp ³	Tetrahedral	109.5°
dsp ²	Square planar	90°
Sp ³ d(sp ² +dp)	TBP	90°, 120°, 180°
dsp ³ (dsp ² +p)	Square pyramidal	90°
Sp ³ d ²	Octahedral	180°, 90°
Sp ³ d ³	Pentagonal bipyramidal	

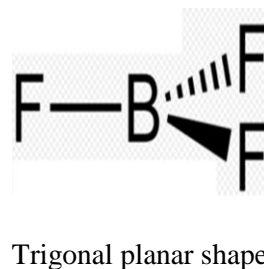
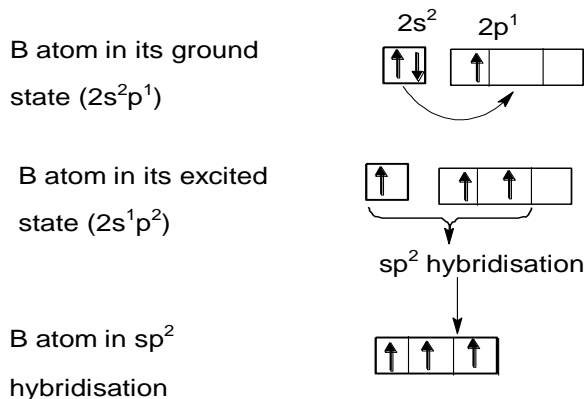
7. The geometries which are derived are based on the hybridization and they are slightly modified based on the Valence shell electron pair repulsion theory.
8. According to this theory, lp-lp interaction is stronger than lp-bp which is stronger than bp-bp interactions.
9. These interactions are repulsive in nature and therefore the molecules tries to minimize the stronger interaction. Thus, the geometry of the molecule is slightly altered giving more space for lone pairs in order to minimizing this interaction. Such modified structure is the real structure of the molecule.

The structure of BeF₂



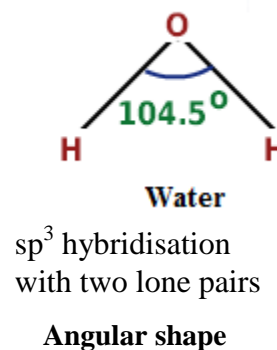
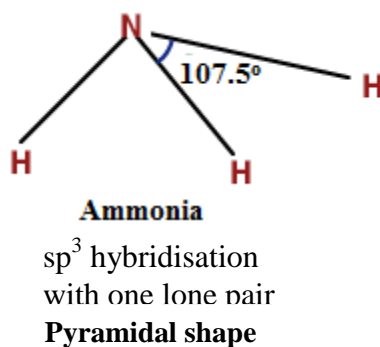
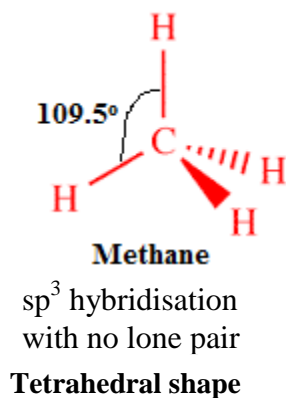
- It has a linear shape. Only sigma bonding is present in this molecule, with no lone pair on the central atom.

The structure of BF_3



- It has a trigonal planar shape. Only sigma bonding is present in this molecule, with no lone pair on the central atom.

The structure of NH_3 , H_2O and CH_4



- The change in the magnitude of bond angle is due to the fact that *lone pair - lone pair repulsion* is greater than *lone pair - bonding pair repulsion*, which in turn is greater than the *bonding pair- bonding pair repulsion*.

(lp - lp) repulsion > (bp - lp) repulsion > (bp - bp) repulsion

- More the number of lone pairs on the central atom, the greater will be the contraction caused in the angle between the bonding pairs. This fact is clear when we compare the bond angles in Methane, ammonia and water molecules.

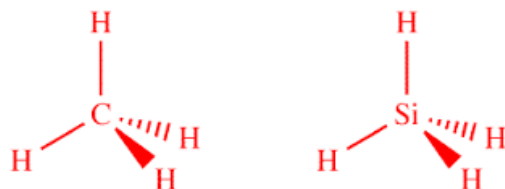
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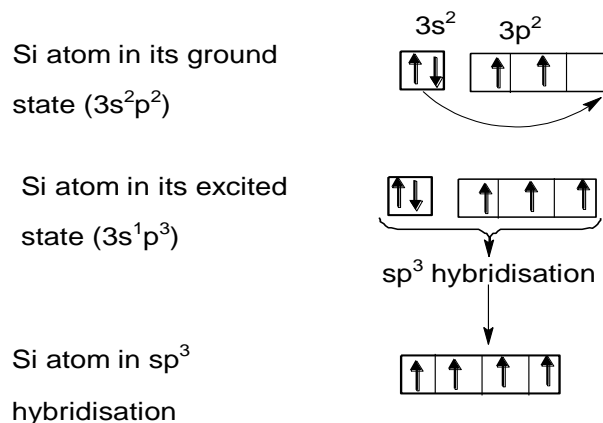
Molecule	Number of lone pair on central atom	Bond angle and contraction in bond angle
CH ₄	0	109.5° (109.5 - 109.5 = 0)
NH ₃	1	107.5° (109.5 - 107.5 = 2°)
H ₂ O	2	104.5° (109.5 - 104.5° = 5°)

- The comparison of bond angles of Ammonia and water with that of methane shows that each of H-O-H bond angles in water is decreased from tetrahedral angle of 109.5° to a greater extent than in ammonia. The greater decrease in case of water is explained as follows.
- In water molecule, we see that O-atom in water molecule has two lone pairs, while Nitrogen atom in ammonia has only one lone pair in it.
- Thus, in water molecule, there are three types of repulsion
 - Lp- lp repulsion.*
 - Bp - lp repulsion and*
 - BP- bp repulsion*
- While in ammonia molecule, we have only two pairs of repulsion:
 - Lp - lp repulsion and*
 - Bp - bp repulsion*
- Therefore, each of the H-O-H bond angles in water molecule is decreased from a tetrahedral angle to a greater extent than in ammonia molecule.

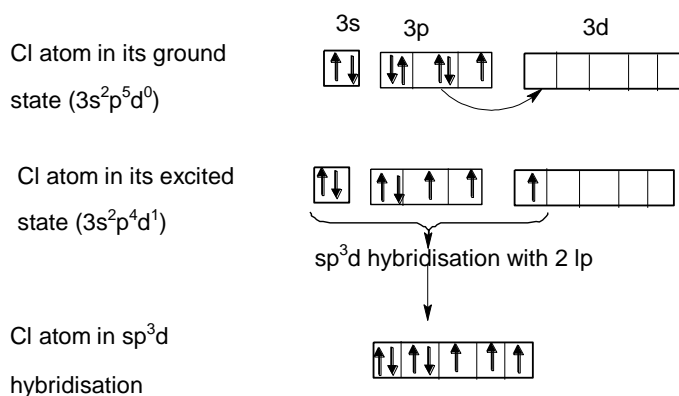
The structure of SiH₄

It has a tetrahedral shape similar to that of methane. Only sigma bonding is present in this molecule, with no lone pair on the central atom.

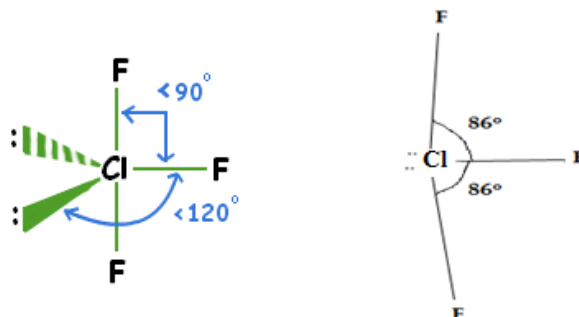




The structure of ClF_3 (Chlorine trifluoride)



- It has sp^3d hybridization and it is **Trigonal bipyramidal** shape and due to the presence of *two lps* in the equatorial position, the shape of ClF_3 gets distorted and becomes **slightly bent T-shape** as shown in the fig (b)



Structure of SF_4 molecule [sulfur tetra fluoride]

It has sp^3d hybridization and it is **Trigonal bipyramidal**, due to the presence of *one lp* in the equatorial position, the shape of SF_4 gets distorted and becomes **distorted tetrahedral or Seesaw structure** as shown in the fig. In this molecule, the axial bonds are longer than equatorial bonds.

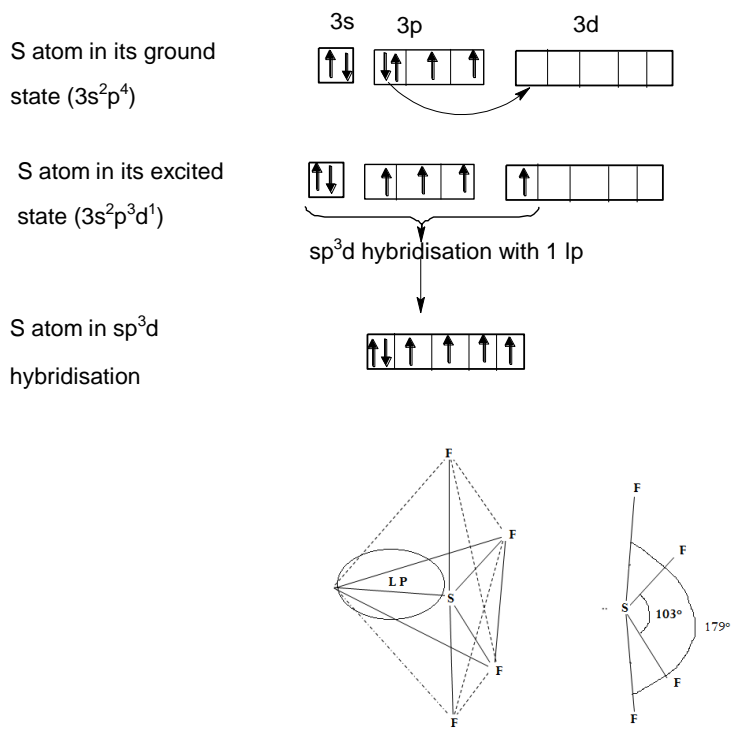
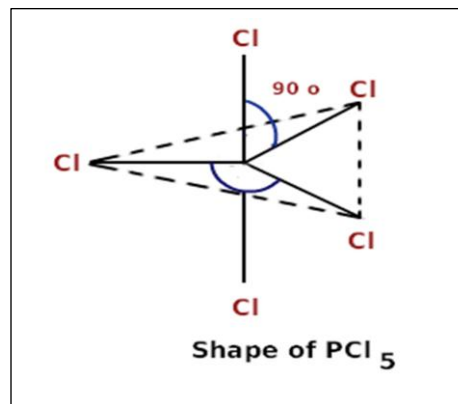
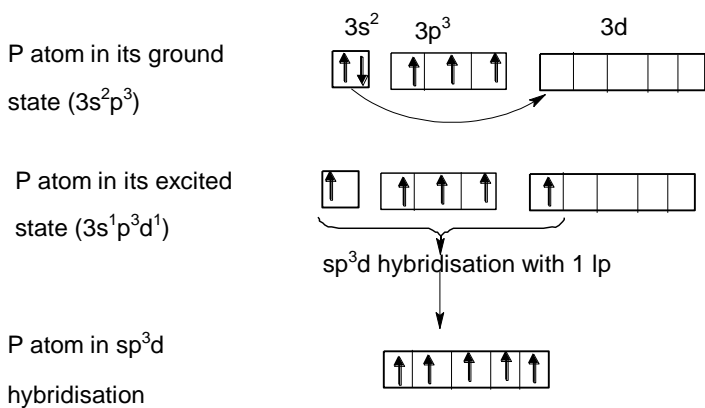


Fig. Sulfur tetrafluoride a) Trigonal bipyramidal structure with equatorial lone pair b) Experimentally determined structure of SF_4

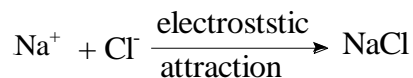
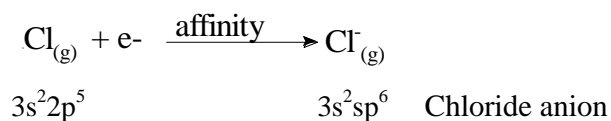
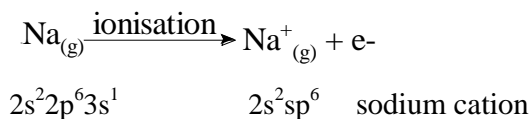
Structure of PCl_5 molecule [phosphorous penta chloride]



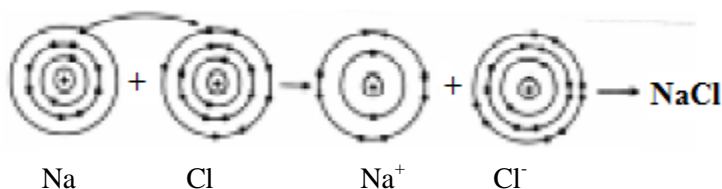
Sp^3d hybridization has trigonal bipyramidal shape with only bonding pairs and no lone pair.

IONIC BOND

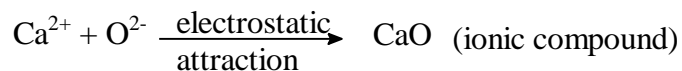
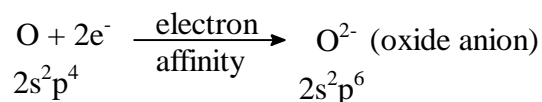
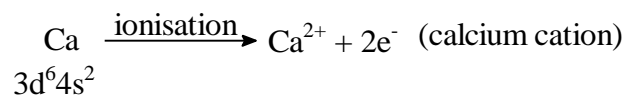
- An ionic bond is formed by the complete transfer of one or more electrons from an atom to the other atom so that both atoms attain the nearest inert gas configuration. *Example:* Formation of NaCl.



Sodium ion Chloride ion ionic/crystalline compound is formed

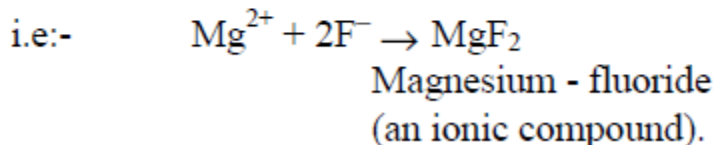
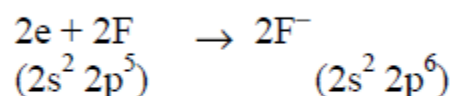
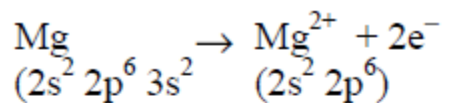


- In CaO, which is an ionic compound, the formation of the ionic bond involves two electron transfers from Ca to O atoms. Thus, doubly charged positive and negative ions are formed.

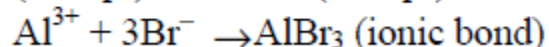
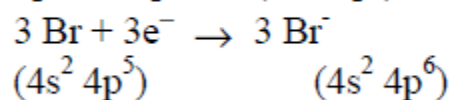
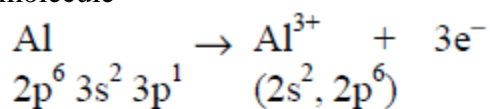


- Ionic bond may be also formed between a doubly charged positive ion with single negatively charged ion and vice versa. The molecule as a whole remains electrically neutral. For example in MgF₂, Mg has two positive charges and each fluorine atom has a

single negative charge. Hence, Mg^{2+} binds with two fluoride (F^-) ions to form MgF_2 which is electrically neutral.



- Similarly in Aluminium bromide (AlBr_3), Aluminium ion has three positive charges and therefore it bonds with three Bromide ions to form AlBr_3 which is a neutral ionic molecule



The characteristics properties of ionic compounds

- Several properties distinguish ionic compounds from covalent compounds. These may be related to the crystal structure of ionic compounds, namely, a lattice composed of positive and negative ions in such a way that the attractive forces between oppositely charged ions are maximized and the repulsive forces between ions of the same charge are minimized.
- Ionic compounds tend to have very low electrical conductivities as solids but conduct electricity quite well when melt. This conductivity is attributed to the presence of ions, atoms charged either positively or negatively, which are free to move under the influence of an electric field. In solid, the ions are bound tightly in the lattice and are not free to migrate and carry electrical current.
- Ionic compounds tend to have high melting points. Ionic bonds usually are quite strong and they are *Omni directional*. The second point is quite important; the ionic bonding was much stronger than covalent bonding –which is not the case. It is known that substances containing strong, multidirectional covalent bonds, such as diamond also have very high melting points. The very high melting point of sodium chloride for example, results from the strong electrostatic attraction between the sodium cation and the chloride anion and from the lattice structure in which each sodium ion attracts six chloride ions, each of this in turn attracts six sodium ions etc through the crystal.

- Ionic compounds usually are hard but brittle substances. The hardness of ionic substances follows naturally from the argument presented above. The tendency towards brittleness results from the nature of ionic bonding. If one can apply sufficient force to displace the ions, the formerly attractive forces become repulsive as anion-anion and cation-cation contacts occur, hence the crystal flies apart. This accounts for the cleavage properties of many minerals.
- Ionic compounds are often soluble in polar solvents with high permittivity (dielectric constant).

Conditions for the formation of ionic compounds (or) factors which influence the formation of ionic compounds

- Simple ionic compounds are formed only between very active metallic elements and very active nonmetals. There are three requirements for the formation of the ionic compounds.
- Lower ionisation potential of the atom which forms cation
- Higher electron affinity of the atom which forms the anion
- High lattice energy of formation of the ionic compound.
- Thus, the requirements for ionic bonding are (i) the atoms of one element must be able to lose one or two (rarely three) electrons without undue energy input and (ii) the atoms of the other elements must be able to accept one or two electrons (almost never three) without undue energy input. This restricts ionic bonding to compounds between the most active metals: *Groups IA (1), IIA(2), part of IIIA(3)* and some lower oxidation states of the transition metals (forming cations) and the most active nonmetals: *Groups VIIA(17), VIA (16)* and nitrogen (forming anions).

ELECTRONEGATIVITY

- *The power of an atom in a molecule to attract electrons to itself is called electronegativity.* It is evident from this definition that electro negativity is not a property of the isolated atom but rather a property of an atom in a molecule, in the environment and under the influence of the surrounding atoms. We must also note that “*power to attract*” is merely another way of describing the “*reluctance to release*” electrons from itself to a more electronegative element.
- Based on the thermo chemical data, Pauling gave the electronegativity scale which is an arbitrary one chosen so that hydrogen is given a value about 2 and the most electronegative element, fluorine, has a value of about 4.
 - i) For noble gases, its value is taken as zero
 - ii) In Periods: Left to right electronegativity decreases.
 - iii) In Groups: down the group electronegativity decreases.

ELECTRONEGATIVITY SCALES

- Electronegativity scale is an arbitrary scale. They are based on various types of experimental data like bond energy, dipole moment, ionisation potential and electron affinity. Most commonly used scales are
 1. Pauling's scale
 2. Mulliken's scale
 3. Sanderson's scale
 4. Alfred and Rochow's scale

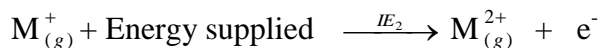
Ionization potential

- Ionization energy of an element is defined as “the minimum amount of energy required to remove the most loosely bound electron from an isolated neutral gaseous atom in its lowest energy state”. The process is represented as Ionisation energy is measured in electron volts per atom (eV/atom), kilo calories per mole (kcal/mole) or kilo joules per mole (kJ/mole).

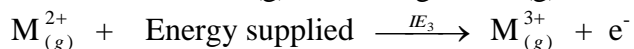


Successive ionization potentials

- In addition to first ionization potential (IE1) defined above, second, third. etc. ionisation potentials are also known. Second ionization potential (I2) is the energy required to remove one more electron from the gaseous cation, $M^+(g)$ to get the doubly positively charged gaseous cation, $M^{2+}(g)$, i.e.,



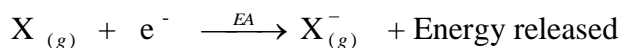
- Similarly, third ionisation potential (IE3) is the energy required to remove still one more electron from $M^{2+}(g)$ cation to get $M^{3+}(g)$ cation, i.e.



- Similarly ionization potentials of higher and higher grades are also known. Each successive ionization potential or energy is greater than the previous one, since the electron must be removed against the net positive charge on the ion.

Electron Affinity or Electron gain enthalpy (E.A.)

- The electron affinity of an element may be defined as “amount of energy which is released when an extra electron enters the valence orbital of an isolated neutral atom to form a negative ion.”

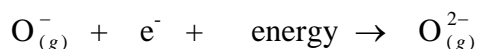


- The greater the energy released in the process of taking up the extra electron, the greater will be the electron affinity. Thus, ionisation potential measures the tendency of an atom

to change into a cation ($M \rightarrow M^+ + e^-$) whereas the electron affinity measures the tendency of an atom to change into anion ($X + e^- \rightarrow X^-$).

Successive Electron Affinities:

- As more than one electron can be introduced in an atom, it is called second electron affinity for the addition of two electrons and so on. The first E. A. of active nonmetals is positive (exothermic) while the second E. A. even for the formation of oxide or sulphide ion is negative (endothermic). In these cases, the energy is absorbed due to repulsion between the anion and the electron. But still it happens in these cases because the stabilization of the compounds after forming the di negative ion is much more than the compound formed by uni negative ion. For example, the overall E.A. for the formation of oxide or sulphide ions has been found to be endothermic to the extent of 640 and 390 kJ mol^{-1} respectively.

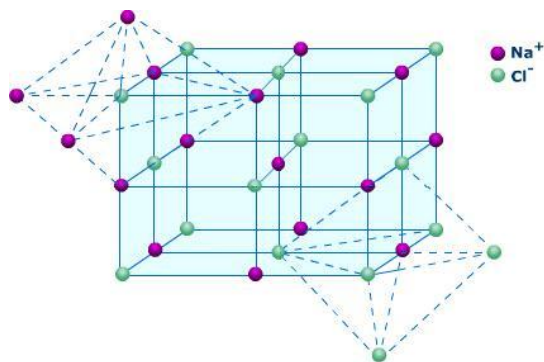


- It is interesting to note that the electron affinity of elements having a $d^{10}s^2$ configuration has been found to be negative. This is so due to the accommodation of the electron in the higher p-orbital ($\text{Zn} = -87 \text{ kJ mol}^{-1}$, $\text{Cd} = -56 \text{ kJ mol}^{-1}$).
- Elements of group 17 possess high electron affinity. The reason for this is that by picking up electron halogens attain the stable noble gas electronic configuration.
- The electron affinity is expressed in kJ mol^{-1} .

What is Lattice Energy?

- It is the energy released when gaseous ions bind to form an ionic solid. Lattice Energy is used to explain the stability of ionic solids.
- A lot of energy is released as the oppositely charged ions interact each other. It is this that causes ionic solids to have such high melting and boiling points.

Structure of NaCl Crystal



Main features

- It has a face centred arrangement (FCC or CCP). Cl⁻ ions occupy the corners and face centers, Na⁺ occupy body centre and edge centers.

- Each Na^+ is surrounded by six Cl^- and each Cl^- is surrounded by 6 Na^+ .
- Therefore it has 6:6 coordination.

Number of NaCl Units per unit cell

- **Number of Cl^- ions**

8 at the corners contribute $\frac{1}{8}$ per unit cell $8 \times \frac{1}{8} = 1$

6 at the corners contribute $\frac{1}{2}$ per unit cell $6 \times \frac{1}{2} = 3$

Total number of Cl^- ions = 4

- **Number of Na^+ ions**

12 at the edge centers contribute $\frac{1}{4}$ per unit cell $12 \times \frac{1}{4} = 3$

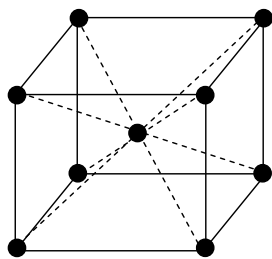
1 at the body center contributes fully = $1 \times 1 = 1$

Total Number of $\text{Na}^+ = 3+1=4$

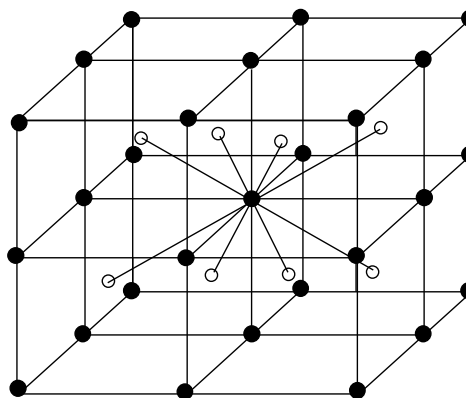
- Therefore, there are 4 NaCl molecules in one Unit cell.
- There are four 4 Chloride ions and 4 Na ions in one unit cell. These are totally 8 ions in one unit cell.

Structure of CsCl Crystal

In this structure, Cs ions are represented by hallow circles whereas Cl ions are represented by solid circles. The crystal structure of CsCl can be discussed as follows.



Unit cell of CsCl



The extended unit cell. 27● Cl^- 8○ Cs^+

Main features of CsCl structure:

- The radius ratio (r^+/r^-) value for **CsCl crystal is 0.884**. Since the value lies in the range 0.732 – 1.000, which suggests that it has a bcc type lattice
- Cl^- ions are at the corners, centers of the faces, centre of the edges and center of the body and Cs ions are present at the centre of the body of individual unit cell.
- Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ions is surrounded by 8 Cs^+ ions. Therefore the crystal has 8:8 co-ordination.

Number of Cl^- ions

Atoms at the corner contribute = $1/8 \times 8 = 1$

Atoms at the centre of the face contributes = $1/2 \times 6 = 3$

Atoms at the centre of the edge contributes = $12 \times 1/4 = 3$

Atoms at the centre of the body contributes = $1 \times 1 = 1$

Hence the total number of Cl ions is 8.

Number of Cs^+ ions

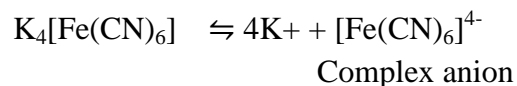
For smaller unit it is 1

For bigger unit it is 8

- Hence the total number of Cl^- and Cs^+ ions is $(8+8)16$.
- Therefore, there are 8 CsCl molecules in one unit cell of CsCl.

COORDINATION COMPOUNDS

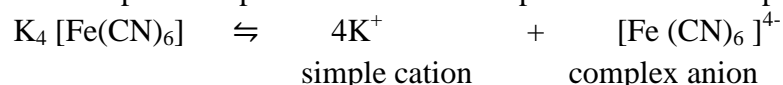
- Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds which do not dissociate into its constituent ions in solution are called coordination compounds. For example



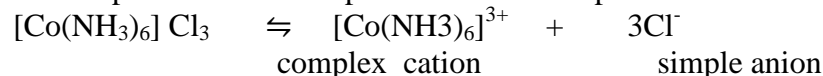
- In $\text{K}_4[\text{Fe}(\text{CN})_6]$ the individual components lose their identity. The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

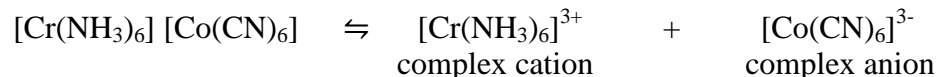
- An anionic complex compound contains a complex anion and simple cation.



- A cationic complex contains complex cation and simple anion



- In the case of a complex compound, $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, it gives both complex cation and complex anion



TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) Lewis Acid

All electron acceptors are Lewis acids.

(b) Lewis Base

All electron donors are Lewis base.

(c) Central metal ion

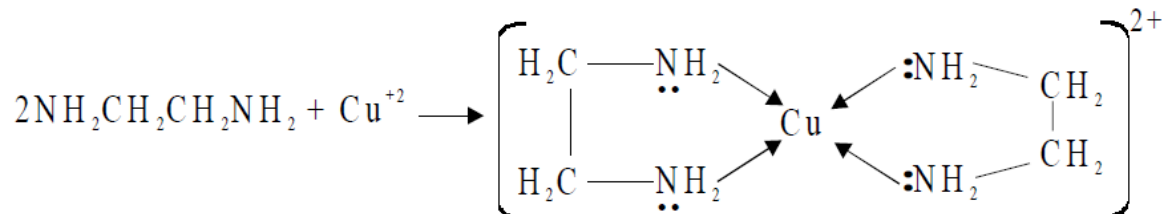
In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation. Hence, central metal cation in a complex serves as a Lewis acid.

(d) Oxidation state

This number denotes the charge, explaining the number of electrons it has lost to form the cation. It is oxidation number that denotes the charge, if the central metal atom would have if all the ligand in the complex were removed along with their electron pairs that were shared with the central atom. It is usually represented by Roman numeral.

Chelates

- If a ligand is capable of forming more than one bond with the central metal atom (or) ion then the ring structures are produced which are known as metal chelates. Hence the ring forming group is described as chelating agents (or) polydentate ligands.

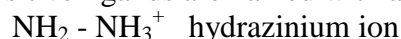


- **Ambidentate ligands:** The ligands which can bond with metal ion through two different atoms are called ambidentate ligands. Ex: NO_2^- , SCN^- , NCS^- etc

Name of the ligands

- **Positive ligands**

The positive ligands are named with an ending -ium.



This ligand, though positive can bind through the uncharged nitrogen

- **Neutral ligands**

The neutral ligands are named as such without any special name. But water is written as 'aqua' : Ammonia is written as ammine. Note that two m's to distinguish from organic amine

CO-Carbonyl,

NO-Nitrosyl,

$\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ -ethylenediamine(en),

Pyridine $\text{C}_5\text{H}_5\text{N}$.

- **Negative Ligands**

Negative ligands end in suffix 'O'.

Example

F⁻-Fluoro, Cl⁻-Chloro, $\text{C}_2\text{O}_4^{2-}$ -Oxalato, CN^- -Cyano, NO_2^- -Nitro, Br⁻-Bromo, SO_4^{2-} -Sulphato, CH_3COO^- acetato, CNS^- -thiocyanato, NCS^- -isothiocyanato, $\text{S}_2\text{O}_3^{2-}$ -thiosulphato.

IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The rules are outlined below

1. In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.
2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).
3. Ligand names generally end with 'O' if the ligand is negative ('chloro' for Cl-, 'cyano' for CN-, 'hydrido' for H-) and unmodified if the ligand is neutral ('methylamine' for MeNH₂).
Special ligand names are 'aqua' for water, 'ammine' for ammonia, 'carbonyl' for CO, 'nitrosyl' for NO.
4. A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead. For example, [Ni(PPh₃)₂Cl₂] is named dichlorobis(triphenylphosphine) nickel(II).
5. A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.
6. If the complex ion is negative, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate etc.
7. If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each. For example, NH₃ (ammine) would be considered as 'a' ligand and come before Cl-(chloro).

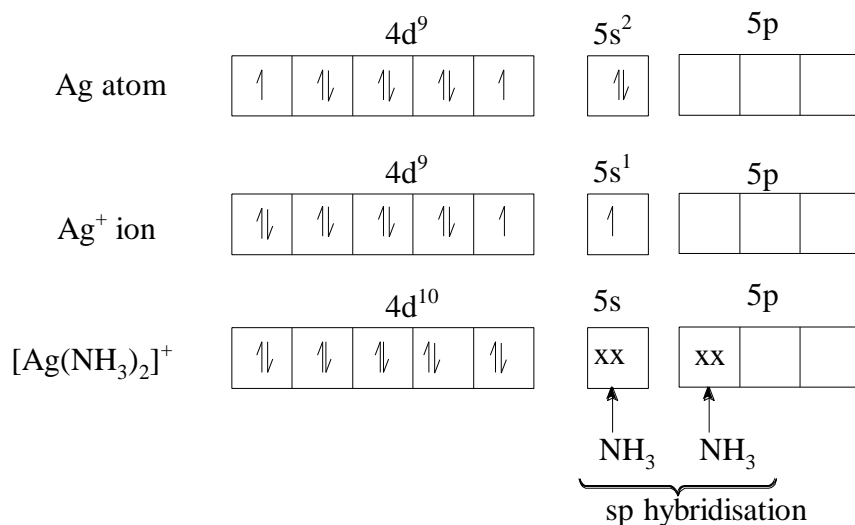
Examples

- | | |
|--|--|
| ➤ [Co(en) ₃]Cl ₃ | Tris(ethylenediamine)cobalt(III) chloride |
| ➤ [Co(NH ₃) ₃ (NO ₂) ₃] | Triamminetrinitrocobalt (III) |
| ➤ K ₂ [CoCl ₄] | Potassiumtetrachlorocobaltate(II) |
| [Note that it is not necessary to enclose the halogens in brackets] | |
| ➤ [Co(NH ₃) ₅ Cl] ²⁺ | pentaamminechlorocobalt(III) ion |
| ➤ [Co(NH ₃) ₆]Cl ₃ | Hexaamminecobalt(III) chloride |
| ➤ [Cr(en) ₃]Cl ₃ | Tris (ethylenediamine)chromium(III) chloride |
| ➤ K ₄ [Fe(CN) ₆] | Potassium hexacyanoferrate(II) |
| ➤ [Ni(CN) ₄] ²⁻ | Tetracyanonickelate(II) ion |
| ➤ [Cu(NH ₃) ₄] ²⁺ | Tetraamminecopper(II) ion |
| ➤ [PtCl ₂ (NH ₃) ₂] | Diamminedichloroplatinum(II) |

[Ag (NH₃)₂]⁺ is a linear complex

Silver atom

Outer electronic configuration 3d⁹ 4s²



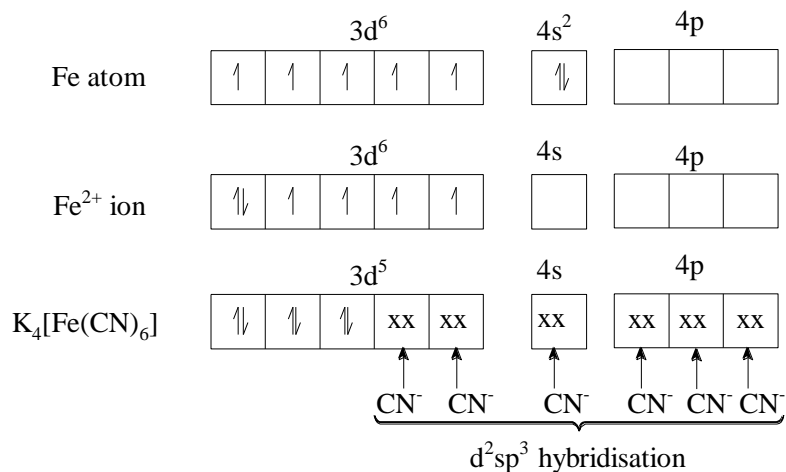
- In Linear complexes one *s* and one *p* orbital are hybridised to form two equivalent orbitals oriented linearly. This is illustrated below for [Ag (NH₃)₂]⁺.
- The Silver is in +1 oxidation state and the ion has the electronic configuration 4d⁹. The hybridisation scheme is as shown in diagram.
- Each NH₃ ion donates a pair of electrons. The compound is diamagnetic since it contains no unpaired electrons.



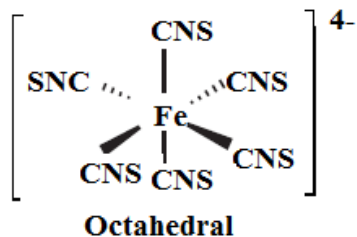
K₄[Fe(CN)₆] Potassium ferrocyanide

Iron atom

Outer electronic configuration 3d⁶ 4s²



Six pairs of electrons, one from each CN molecule, occupy the six hybrid orbitals. Thus, the complex has **octahedral geometry and is diamagnetic** because of the absence of unpaired electron. In the formation of this complex, since the inner *d* orbital (3*d*) is used in hybridisation, the complex is called an **inner orbital** or **low spin** or **spin paired complex**.



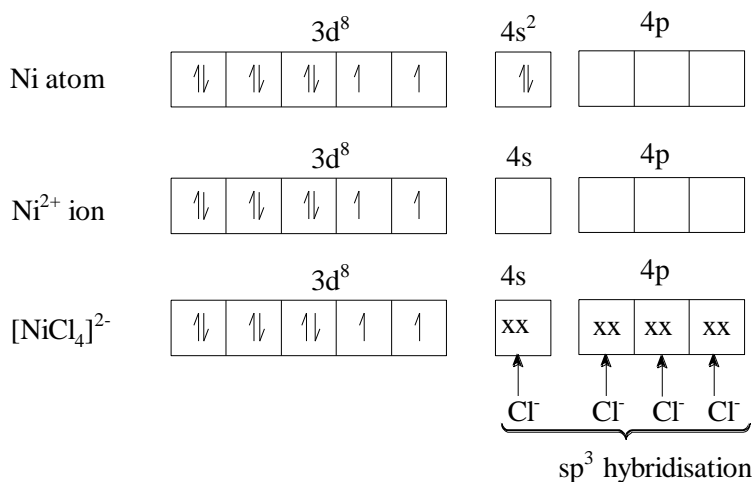
The molecule is diamagnetic since the number of unpaired electron = 0. The geometry of the molecule is inner orbital octahedral complex.

[NiCl₄]²⁻ is tetrahedral complex

In tetrahedral complexes one *s* and three *p* orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for [NiCl₄]²⁻. Here nickel is in +2 oxidation state and the ion has the electronic configuration 3*d*⁸. The hybridisation scheme is as shown in diagram. Each Cl⁻ ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, [Ni(CO)₄] has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

Ni atom

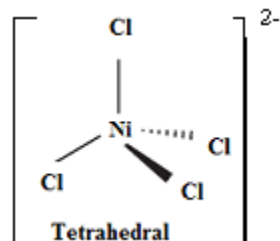
Outer electronic configuration 3*d*⁸ 4*s*²



Number of unpaired electrons = 2

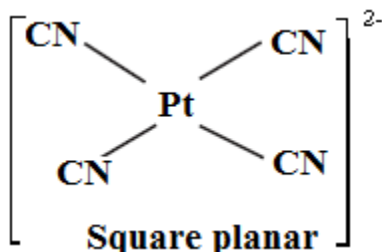
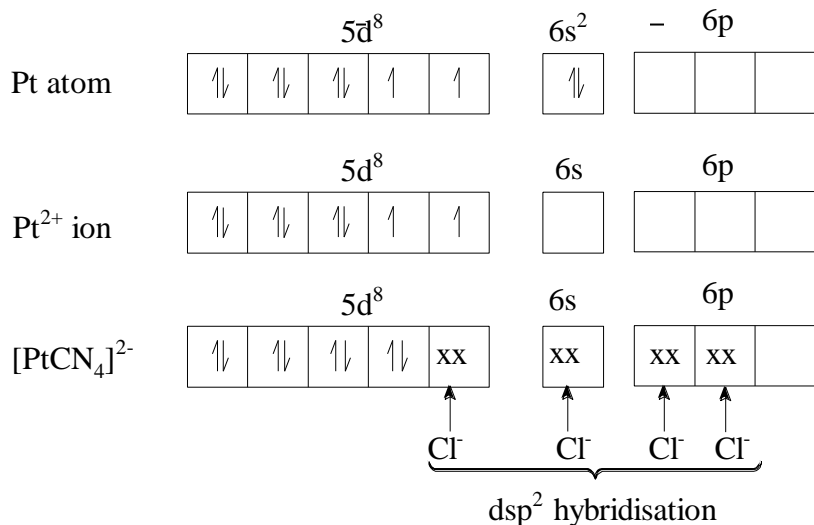
Therefore, $\mu_s = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$

Since the hybridisation is sp³, the geometry of the molecule is tetrahedral



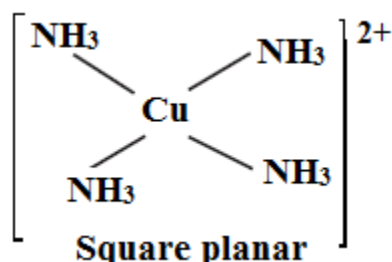
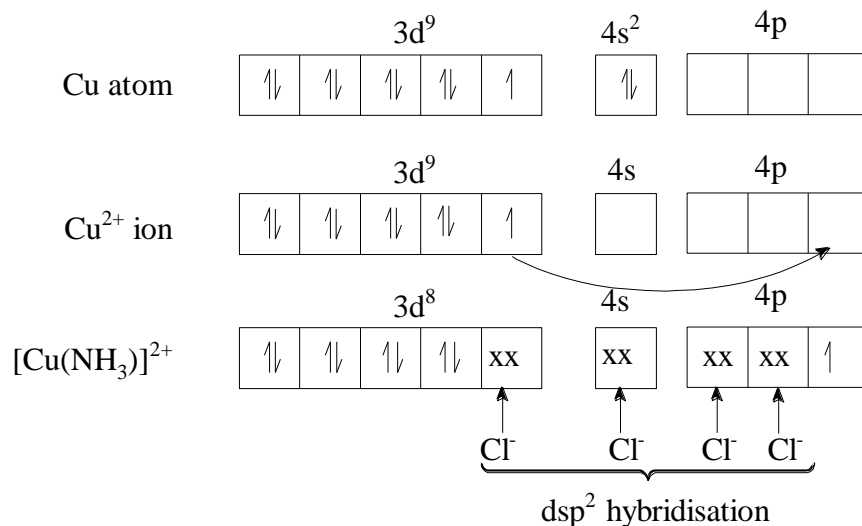
[PtCN₄]²⁻ is square planar complex

In square planar complexes one *s*, two *p* orbitals and one *d* orbitals are hybridised to form four equivalent *dsp*² orbitals oriented in square planar shape. This is illustrated below for [PtCN₄]²⁻. Here Platinum is in +2 oxidation state and the ion has the electronic configuration 5*d*⁸. The hybridisation scheme is as shown in diagram. Each CN⁻ ion donates a pair of electrons. The compound is diamagnetic since it contains no unpaired electrons.



[Cu(NH₃)₄]²⁺ is square planar complex

In square planar complexes one *s*, two *p* orbitals and one *d* orbitals are hybridised to form four equivalent *dsp*² orbitals oriented in square planar shape. This is illustrated below for [Cu(NH₃)₄]²⁺. Here Copper is in +2 oxidation state and the ion has the electronic configuration 3*d*⁹. The hybridisation scheme is as shown in diagram. Each NH₃ ion donates a pair of electrons. The compound is paramagnetic since it contains one unpaired electrons.



Hydrogen bonding

- Hydrogen bonding comes into existence as a result of dipole-dipole interactions between the molecules in which hydrogen atom is covalently bonded to a highly electronegative atom. Therefore, the conditions for the effective hydrogen bonding are
- High electronegativity of the atom bonded to hydrogen atom so that bond is sufficiently polar.
- Small size of the atom bonded to hydrogen so that it is able to attract the bonding electron pair effectively.
- If the atom bonded to hydrogen has low value of electronegativity and/or large atomic size, dipole-dipole interactions are not strong enough to allow effective hydrogen bonding.
- Only nitrogen, oxygen and fluorine form strong hydrogen bonds because they have high value of electronegativity and small atomic size.

Strength of H-bonds

- It is a weak bond because it is merely an electrostatic force and not a chemical bond. Its strength depends upon the electronegativity of atom to which H atom is covalently bonded. Since electronegativity of F > O > N, the strength of H-bond is in the order



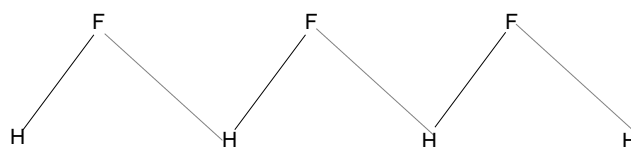
- Hydrogen bonds are much weaker than covalent bonds. The bond strength of different bonds is in the order :

Ionic bond > Covalent bond > Hydrogen bond > dipole-dipole interactions, Vander Waal's (London forces)

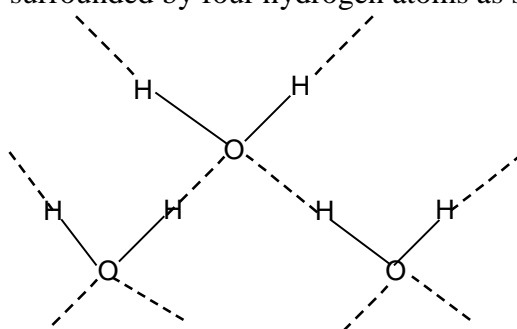
Types of Hydrogen bonds

- There are two different types of hydrogen bonds as :
- **Intermolecular hydrogen bonding.** This type of bond is formed between the two molecules of the same or different compounds. Some examples of the compounds exhibiting intermolecular hydrogen bonds are :

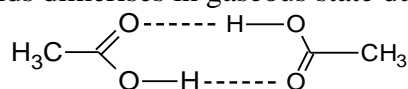
Hydrogen fluoride, $H^{\delta+} - F^{\delta-}$. In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated by hydrogen bonds as shown below.



- Therefore, hydrogen fluoride is represented as $(HF)_n$.
- Water $H^{\delta+} - O^{\delta-} - H^{\delta+}$. In water molecule, the electronegative oxygen atom forms two polar covalent bonds with two hydrogen atoms. The oxygen atom due to its higher electronegativity acquires partial negative charge and the two hydrogen atoms acquire partial positive charge. The negatively charged oxygen forms two hydrogen bonds with two positively charged hydrogen atoms of two Neighbouring molecules. Each oxygen atom is tetrahedrally surrounded by four hydrogen atoms as shown below :

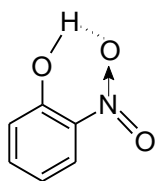


- Hydrogen bonding in water results in a hydrogen bridge (H-O-H) network extending in three dimensions and the associated water molecule may be expressed as $(H_2O)_n$.
- Carboxylic acids dimerises in gaseous state due to H-bonding.

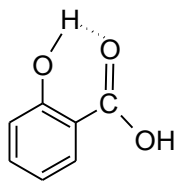


Intramolecular hydrogen bonding

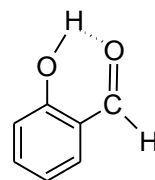
- This type of bond is formed between hydrogen atom and N, O or F atom of the same molecule. This type of hydrogen bonding is commonly called chelation and is more frequently found in organic compounds. Intramolecular hydrogen bonding is possible when a six or five membered rings can be formed.



O-Nitro phenol



Salicylic acid



Salicylaldehyde

- Intramolecular hydrogen bonding (chelation) decreases the boiling point of the compound and also its solubility in water by restricting the possibility of intermolecular hydrogen bonding.

Difference between intramolecular and intermolecular H- bonding

Intermolecular H- bonding	Intramolecular H-bonding
if the hydrogen bonding is formed between the molecule then it is called intermolecular H- bonding	if the hydrogen bonding is formed within the molecule then it is called intramolecular H- bonding
It raises the boiling and melting point. Hence extra energy is needed to break the bond	It lowers the boiling and melting point. Hence low energy is needed to break the bond
If the H-bonding is possible between the solute and solvent, it greatly increases the solubility due to solvation. Hence alcohols, acids and amines are water soluble.	It decreases the solubility
It decreases the acid strength.	It increases the acid strength

Importance or consequences of H-bonding

- Life would have been impossible without liquid water which is the result of intermolecular H-bonding in it.
- The boiling and melting points of Water, Ammonia and hydrogen fluoride are much higher than the hydrides of other elements of V, VI and VII groups.
- H₂O exists as liquid under normal condition whereas H₂S exists as a gas.
- A substance is said to be insoluble in water if it does not form H- bonding with water. Therefore, alkenes, alkynes and alkyne are insoluble in water whereas alcohols and acids are soluble in water.
- Chlorine has the same electronegativity as nitrogen but does not form H-bonding. This is because of the larger size of chlorine.
- Due to H- bonding, Carboxylic acids exist as dimers in gaseous state.

- The substances which can give more extensive H-bonding will have higher viscosity and have high surface tension.

Ex. Ethanol < glycol < glycerol

Higher viscosity and have high surface tension

- Hydrogen bonding increases the rigidity and strength of wood fibres and thus makes it an article of great utility to meet requirements of housing, furniture, etc.
- The cotton, silk or synthetic fibres also own their rigidity and tensile strength to hydrogen bonding.
- Most of our food materials such as carbohydrates and proteins also consist of hydrogen bonding.
- Hydrogen bonding also exists in various tissues, organs, skin, blood and bones