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দাগানো

TEXT BOOK



Chemistry
1st Paper



UNMESH

Medical & Dental Admission Care

Chemical bond : The chemical bond may be defined as the process of getting more stable electronic configuration by those atoms similar to their nearest inert gas elements either by **donation-acceptance of electron** or **sharing of electrons**. The electrons of the outermost energy level or valence electrons express the periodicity of the element. So the chemical bond formation by the elements with one another is the periodic property of the elements.

According to '**Octet theory**', ionic bond and covalent bond formation can be explained as follows :

metal + non-metal \rightarrow ionic bond formation

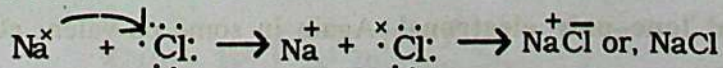
non-metal + non-metal \rightarrow covalent bond formation

Ionic Bond : When metal and non-metal come in contact then metal atoms **donate their valence electrons** and non-metal atoms **accept** those electrons to get nearest inert gas electron distribution. As a result metal atoms become positive ions and non-metal atoms become negative ions. The oppositely charged ions get bonded by electrostatic force known as **ionic bond or electrovalent bond**.

Group based relation to form ionic bond : The alkali metals of group-1 and alkaline earth-metals of group-2 in periodic table contain ns^1 and ns^2 valence electrons respectively. On the otherhand, the elements of group-17 and group-16 contain $ns^2 np^5$ and $ns^2 np^4$ valence electrons respectively.

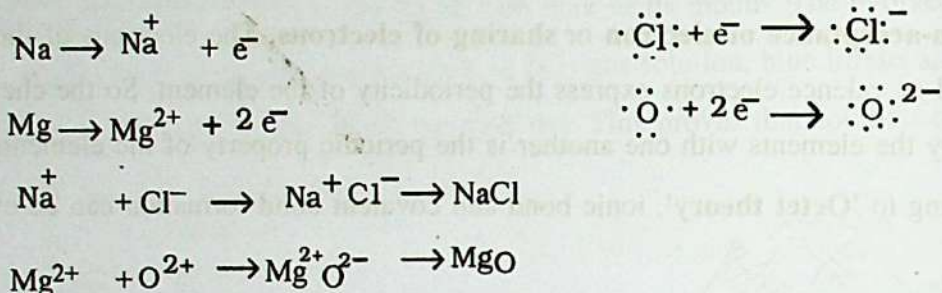
Again the ionisation energies of alkali metals or group -1 elements are the lowest i. e. they have highest tendency to give up or donate valence electrons to other nonmetal atoms and the elements of group -17 or halogens have highest electron affinity or tendency to accept electron to get octet set of electrons.

Thus it is clear that metals of group-1, in contact of nonmetal, give up their ns^1 valence electron easily to form M^+ ion and the elements of group-17 accept that electron to form negative ion X^- . For example, in terms of **Lewis symbol**, the ionic bond between Na atom and Cl atom to form NaCl molecule is shown as follows :



Similarly, elements of group-2 give up their ns^2 electron to form divalent positive ion M^{2+} and elements of group-16 accept those electrons to form divalent negative ion X^{2-} . Each of these ions M^+ , M^{2+} , X^- , X^{2-} has obtained octet set of electrons similar to its nearest inert gas.

Finally, the positive ions and negative ions combine according to their charge number to form ionic compounds like MX and MX₂ etc.

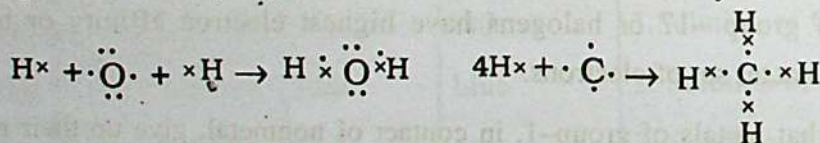


In a group going from up to downwards, according to atomic number of the elements, the sizes of the ions of those elements increase gradually. With the increase of ionic sizes, the ionic bond attraction decreases.

The energy necessary to remove one or two or three electrons of metal atoms is available from reaction surrounding. But to remove 3 or 4 electrons from atoms much more energy is required, which is not available from reaction surrounding. So atoms of many elements get their more stable octet set of electrons similar to their nearest inert gases by the sharing of electron pair. This is called covalent bond

Co-valent Bond : The chemical bond which is formed between two atoms by sharing of electron pair coming equally from both the non-metal atoms is called co-valent bond. The compounds formed by covalent bond are called covalent compounds.

For example, H and O atoms combine to form covalent water (H₂O) molecule by sharing of electron pair. Methane (CH₄) molecule is also formed similarly as follows : •



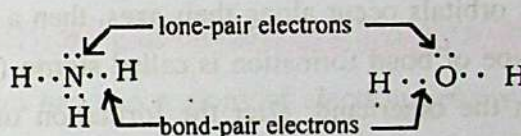
Generally the elements of group-14, group-15, group -16 and group-17 form covalent compounds by sharing of electrons.

Note : As per 'octet rule', in most covalent compounds, the central 'Lewis symbol' contains both 'bond pair electrons' and 'lone-pair electrons'. Again in some co-valent co-valent compounds, the central atom has only bond pair electrons but no lone-pair electrons. For example, in H₂O molecule, the central O atom has two bond-pair electrons on two sides and two lone-pair electrons on O atom above and below (H · · $\ddot{\text{O}}$ · · H) . But in methane (CH₄) four bond-pair electrons are present and no lone-pair.

Bond-pair electrons : In a covalent molecule, the electron-pair which binds two atoms together and is attracted by both the nuclei of two atoms, is called **bond-pair electrons**. For example, in water ($\text{H} \cdot \cdot \text{O} \cdot \cdot \text{H}$) molecule, there are two bond-pair electrons and in CH_4 molecule, there are four bond-pair electrons.

Lone-pair electrons : In a covalent molecule, the electron-pair which is counted in octet set and remains attracted by single atom nucleus, is called **lone-pair electrons**.

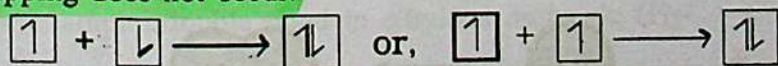
For example, in ($\text{H}_2 \ddot{\text{O}}$) molecule two lone-pair electrons are present on O-atom but in ammonia ($\ddot{\text{N}}\text{H}_3$) molecule one lone pair is present on N-atom.



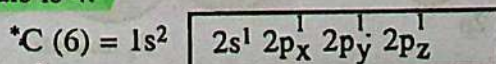
3.8 Orbital Overlapping : Valence Bond (VB) Theory of Covalent Bond

What is a covalent bond and source of bond strength? How we can explain molecular shapes from the interactions of atomic orbitals? To answer these questions, a quantum mechanical model called **Valence bond (VB) theory** has been developed. According to VB theory formation of covalent bond with overlapping of atomic orbitals is explained at first below.

* Atomic orbitals overlapping is the basic principle of VB theory. A covalent bond forms when two atoms approach each other closely enough so that a singly occupied valence orbital on one atom spatially overlaps a singly occupied valence orbital on the other atom. The new-paired up electrons in the overlapping orbitals are in opposite spins and are attracted by the nuclei of both atoms, and thus bond the two atoms together. Here before overlapping like spins of electrons, if any, must be turned into opposite spins; otherwise two orbitals overlapping does not occur.



* The total number of half-filled orbitals in the outermost energy level of an atom is its valence-orbitals. For example, for an excited carbon atom (C^*), total number of half-filled valence orbitals is 4.



* The bond strength depends on the attraction of the nuclei for the shared electrons. So greater the orbital overlapping, the stronger (more stable) is the bond. Again extent of orbitals-overlap depends on the shapes and directions of the orbitals. After overlapping of two orbitals of two atoms, the electron cloud density remains maximum which binds the two

nuclei, forming the maximum bond strength. It is called molecular orbital. At this stage, attraction of the two nuclei on the molecular orbital is maximum and potential energy is minimum. Then the covalent bond will be more stable with low potential energy.

3.8.1 Classification of Covalent Bonds

Overlapping of two orbitals of two atoms to form covalent bond may be either along their orbital axes i. e. head-on orbital overlap or side to side overlap. When overlapping of two atomic orbitals occur along their axes, then a bond with maximum electron density is formed. This type of bond formation is called **sigma (σ) bond**.

On the otherhand, after the formation of a sigma bond between two atoms, when two parallel p-orbitals of these two atoms are close enough to overlap side to side with less electron density, then a bond with less electron density is formed. This type of bond formation is called **pi (π) bond**.

As in both the cases, a bond is formed with overlapping of two singly occupied valence orbitals, so both the sigma bond and pi-bond are basically covalent bonds. Hence covalent bonds are of two types :

- (i) sigma-bond, and (ii) pi-bond

(A) Sigma (σ) Bond : When two singly occupied valence orbitals on two atoms overlap head to head or end-to-end along their axes, then the covalent bond formed with maximum overlapping of bonding orbitals is called **sigma (σ) bond**.

An s-orbital is spherical, but p and d orbitals have more electron density in one direction than in another. Thus whenever possible, a bond involving p or d orbitals will be oriented in the direction that maximizes overlap. Commonly two s orbitals (s-s), one s-orbital and one p-orbital (s-p) and two p-orbitals (p-p) can overlap head to head along their axes to form **sigma bond**. In Fig-3.16, three types of orbital overlapping are shown :

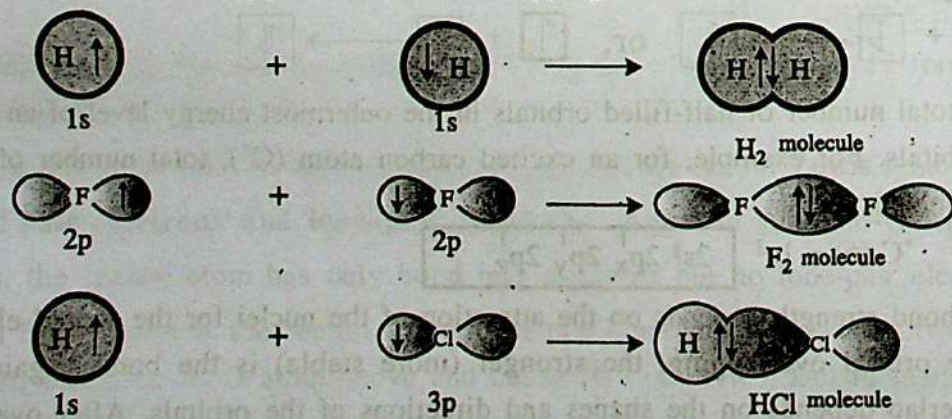


Fig-3.16 : Formation of H₂, F₂ and HCl with sigma bond.

In Fig-3.16, H_2 molecule is formed with s-s sigma bond; F_2 molecule is formed with p-p sigma bond; and HCl molecule is formed with s-p sigma bond. Besides these, different hybrid orbitals of an atom can form sigma (σ) bond.

(B) Pi (π) Bond : Two atoms, after formation of a sigma bond, become close enough and if they have two parallel p-orbitals then the p-orbitals can overlap side-to-side partially. This type of bond formed by partial side-wise overlapping of orbitals, is called pi (π) bond. Pi -bond is weaker than sigma bond. The pi-bond has two regions of electron density, one above and one below the sigma bond axis. One pi-bond holds two electrons that occupy both regions of the bond. In Fig-3.17, after formation of sigma (σ) bond between the two atoms, the side wise overlapping of two parallel p-orbitals forming a pi (π) bond with two lobes above and below regions of two electrons is shown.

Double bond and Triple bond formation with pi (p) bond : When a double bond exists between two atoms in a molecule, it consists of one sigma (s) bond and one pi (p) bond. Again a triple bond between two atoms consists of a sigma (s) bond and two pi (p) bonds.

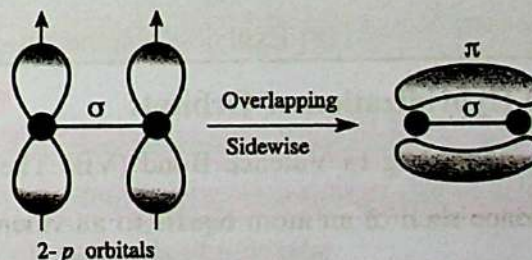


Fig-3.17 : Formation of pi (π) bond

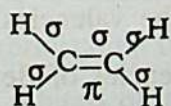


Fig-3.18 : Double bond in ethylene

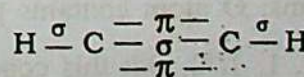


Fig-3.19 : Triple bond in acetylene molecule

For example, double bond in ethylene molecule ($H_2C = CH_2$) consists of one sigma (σ) bond and one pi (π) bond; all the C-H bonds are sigma bonds. Again triple bond in acetylene molecule ($HC \equiv CH$) consists of one sigma (σ) bond and two pi (π) bonds (Fig-3.19]

Characteristics of pi (π) bond

(*) pi (π) bond can only be formed by side-wise partial overlap of parallel p-orbital of two atoms already bonded with a sigma bond.

* The electron density at the partial orbital overlapping remains lower, hence pi (π) bond is weaker than sigma (σ) bond

* Pi (π) bond does not occur with hybrid orbitals but occurs with other normal orbitals except s-orbital.

* Extent of overlap influences bond strength. Because side-to-side overlap is not as extensive as head-to-head overlap, hence pi (π) bond is weaker than a sigma (σ) bond. Thus, a double bond strength is not twice as strong as a single sigma bond.

Student's Work : 3.11 : Chemical Bond Based :

Problem -3.25 (a) : What is co-valent bond,

(b) Explain : (i) Bond pair electron, (ii) Lone pair electron.

(c) What is sigma bond; explain. [Ctg. B. 2015]

(d) Sigma bond is basically covalent bond; explain. [R. B. 2015]

(e) What is pi (π) bond; explain.

(f) Pi (π) bond is weaker than sigma bond; explain why.

(g) Explain : whether pi (π) bond can form between p_y and p_z orbitals.

3.9 Hybridization of Orbitals

According to Valence Bond (VB) Theory, the total number of half-filled orbitals of the valence shell of an atom equals to its valency. In other words, half filled orbital in an atom is essential to form a covalent bond. For example, H and Cl atoms contain one half-filled orbital in their atoms; O atom contains two half-filled orbitals, So the valencies of H, Cl, O are respectively, 1, 1, 2, But this concept can not explain the valencies of Be, B, C with their electron configurations. Their electron configurations are as follows :

Be (4) = $1s^2 2s^2$: Note, no half-filled orbital in Be atom

B (5) = $1s^2 2s^2 2p_x^1$: Note, one half-filled orbital in B atom

C (6) = $1s^2 2s^2 2p_x^1 2p_y^1$: Note, two half filled orbitals in C atom

But these elements form BeCl_2 , BCl_3 , CH_4 etc, which indicate the valencies of Be, B and C are 2, 3 and 4 respectively. To explain this reality, scientists proposed that during the chemical reactions, these atoms absorb required energy to be excited to transfer one electron from $2s^2$ to vacant $2p$ orbital in their valence shells. As a result, number of half-filled orbital increases as follows at their excited states :

$\text{Be}^* (4) = 1s^2 2s^1 2p_x^1$ Note, Be contains 2 half-filled orbitals

$\text{B}^* (5) = 1s^2 2s^1 2p_x^1 2p_y^1$ Note, B contains 3 half-filled orbitals

$\text{C}^* (6) = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ Note, C contains 4 half-filled orbitals

This concept supports the valencies 2, 3, 4 for Be, B and C respectively. But for each, the bond strength and bond angle of the covalent bond formed with the orbital $2s^1$, $2p_x^1$, $2p_y^1$, $2p_z^1$, can not be equal, because $2s^1$ orbital electron contains less energy than other three orbitals. On the otherhand, experimental observation with CH_4 molecule, the facts reveal that four C-H covalent bonds are of equal strength of 415 kJ/mol and four bond angle $\angle\text{HCH}$ are equal with value $109^\circ 28'$.

To explain such facts, in 1931 Linus Pauling proposed that **the valence atomic orbitals in the molecule are different from those in the isolated atoms.** Indeed, quantum mechanical calculations show that if we mix specific combinations of orbitals mathematically, we obtain new atomic orbitals'. **The spatial orientations of these new orbitals lead to more stable bonds and are consistent with observed molecular shapes.**

The process of mixing of different orbitals of different energies to form same number of orbitals with equivalent energy in valence shell of an atom during reaction, is called orbital hybridization; the new atomic orbitals formed are called hybrid orbitals.

The key points of orbital hybridization are as follows :

- * Orbital hybridization occurs in a separated atom only.
- * Generally orbitals of different subshells in a main energy level undergo hybridization.
- * The number of hybrid orbitals with equivalent energy obtained 'equals' the number of atomic orbitals.

[This explains the formation of different covalent bonds with *same bond energy*.]

- * The hybrid orbitals with equivalent energy repel among themselves maintaining equal distances among themselves with spatial direction.

[This explains the formation of *equal bond angle*.]

- * The type of hybrid orbitals obtained 'varies' with the types of atomic orbitals mixed.

[Such as spherical s orbital, dumbbell-shaped p-orbitals and cloverleaf shaped d-orbitals].

- * Electrons enter into hybrid orbitals with spin parallel (Hund's rule) to create stable bond. Each hybrid orbital accomodate two electrons like pure atomic orbital.
- * Covalent bonds with hybrid orbitals attain more bond energy due to more orbital overlapping than covalent bond with pure orbitals.

3.9.1 Different Types of Hybrid Orbitals

Depending on the types of pure atomic orbitals like s, p, d-orbitals and their number taking place in hybridization, different types of hybrid orbitals are produced. Following types of hybrid orbitals are found in main-group elements and d-block elements :

1. sp^3 hybridization : Example, CH_4 , NH_3 , H_2O : tetrahedral
2. sp^2 hybridization : Example, $CH_2=CH_2$, BCl_3 : plane triangular
3. sp hybridization : Example, $CH \equiv CH$, $BeCl_2$: linear structure
4. sp^2d hybridization : Example, $[Cu(NH_3)_4]^{2+}$: plane square
5. sp^3d hybridization : Example, PCl_5 , SF_4 : triangular bipymide
6. sp^3d^2 hybridization : Example, SF_6 , $[Co(H_2O)_6]^{2+}$: octahedral
7. sp^3d^3 hybridization : Example, IF_7 , : pentagonal bipyramide
8. $d^2 sp^3$ or, sp^3d^2 hybridization : Example, $[Cr(H_2O)_6]^{3+}$: octahedral

[*Recent quantum mechanical calculations indicate, however, that main-group compounds do not use d-orbitals in hybridization but instead use a more complex bonding pattern that is not easily explained by valence bond theory.

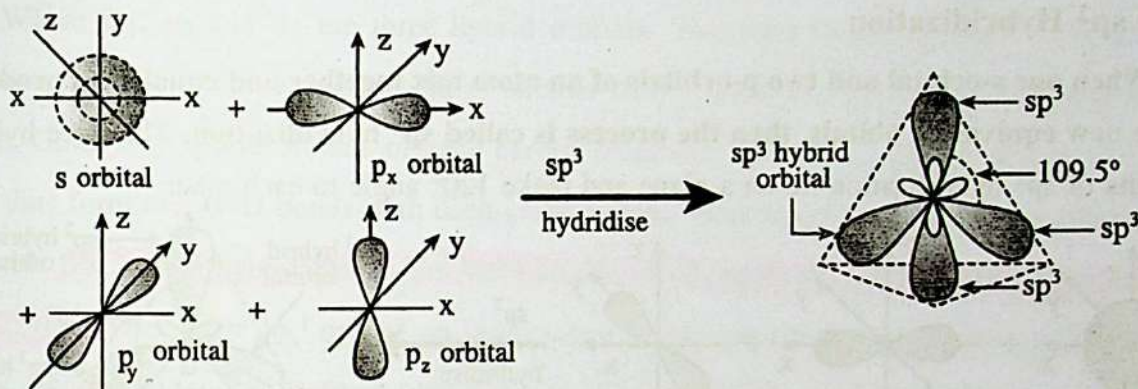
(Ref : General chemistry: by John E. Mc Murry and Robert C. Fay)]

Carbon atoms undergo sp^3 hybridization to form carbon-carbon single bond or sigma bond (C-C), sp^2 hybridization to form carbon-carbon double bond (C=C) and sp hybridization to form carbon-carbon triple bond (C≡C). These three types of orbital hybridization normally shown by main group elements are discussed below :

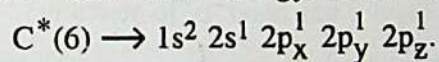
sp^3 Hybridization

The process of formation of four equivalent orbitals by mixing and equalising of one s-orbital and three p-orbitals of an atom is known as sp^3 hybridization.

The four hybrid orbitals of sp^3 hybridization are directed towards the four corners of a regular tetrahedron making angles of $109^\circ 28'$ or 109.5° between them.

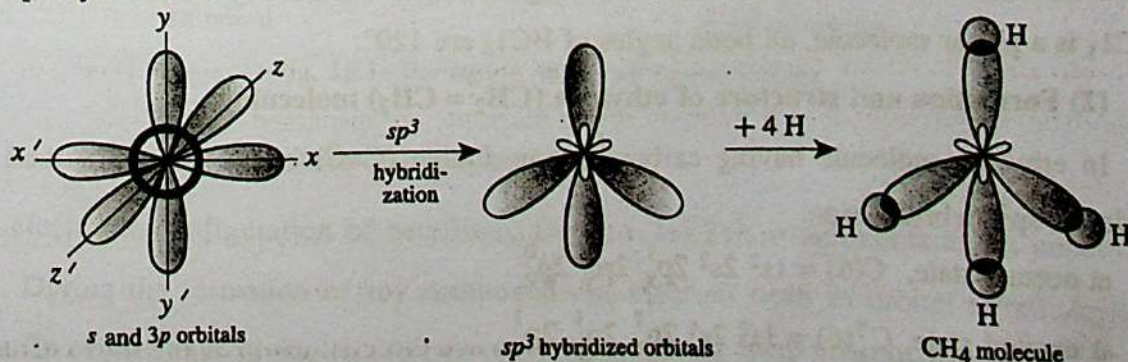
Fig : 3.20 : Four hybrid orbitals formed by sp^3 hybridization**Example : Formation of CH_4 by sp^3 hybridization of C-atom :**

The electronic configuration of carbon atom is $\text{C}(6) = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. It has two unpaired electrons. So from this configuration one would expect that valence of carbon atom is two. But the valency of carbon is 4 in almost all compounds and so it is assumed that one electron from its 2s orbital is transferred to vacant $2p_z$ orbital just before to form bonds with other atom like H-atom. It needs some energy. This is an excited state of carbon atom.



Although this explains the quadrivalence of carbon atom, it cannot explain the equivalence of four bonds of carbon in methane (CH_4) molecule.

So according to hybridization, before the formation of bonds, the 2s orbital and three 2p orbitals of carbon atom mix together and form four equivalent hybrid orbitals, $2\psi_1$ $2\psi_2$ $2\psi_3$ $2\psi_4$ which are elongated towards the four corners of a tetrahedron. Then each of them overlaps with 1s orbital of a hydrogen atom. Thus CH_4 molecule is formed. In this tetrahedral structure of methane (CH_4) molecule all bond angles i. e. $\angle \text{HCH}$ equal to $109^\circ 28'$ or 109.5° . Since the hybridization takes place among one s-orbital and three p-orbitals of C-atom it is called sp^3 hybridization.

Fig 3.21 : Formation of tetrahedral structure of CH_4 molecule through sp^3 hybridization of carbon atom

3.9.2 sp^2 Hybridization

When one s-orbital and two p-orbitals of an atom mix together and equalise to produce three new equivalent orbitals, then the process is called sp^2 hybridization. The three hybrid orbitals of sp^2 hybridization lie on a plane and make 120° angle to each other.

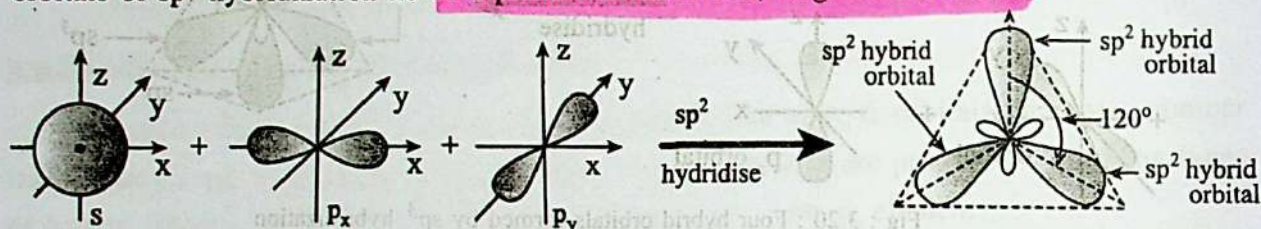


Fig 3.22 : Three hybrid orbital formed by sp^2 hybridization

(1) Formation and Structure of BCl_3 by sp^2 hybridization of B-atom :

The electronic configuration of Boron is $B(5) = 1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$. When one electron of $2s^2$ orbital is transferred to vacant $2p$ orbital, then it has three unpaired electrons. This explains the valency of three for Boron. Then sp^2 hybridization takes place on boron atom.

at normal state, $B(5)$

$$= 1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$$

at excited state, $B^*(5)$

$$= 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$$

after sp^2 hybridization $B^*(5)$

$$= 1s^2 2\psi_1^1 2\psi_2^1 2\psi_3^1 2p_z^0$$

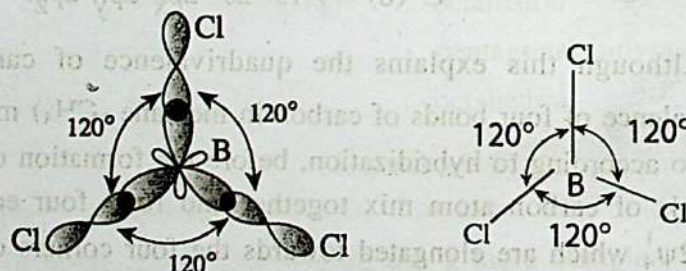


Fig. 3.23 : Formation of planar trigonal BCl_3 molecule

Here ψ_1 , ψ_2 and ψ_3 are three hybrid orbitals. They overlap with three $3p_z$ orbitals of three chlorine atoms and form three B-Cl sigma bonds. Then BCl_3 molecule is formed. **So BCl_3 is a planar molecule, all bond angles of BCl_3 are 120° .**

(2) Formation and structure of ethylene ($CH_2 = CH_2$) molecule :

In ethylene molecule having carbon-carbon double ($C=C$) bond, the two carbon atoms undergo sp^2 hybridization.

$$\text{at normal state, } C(6) = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$$

$$\text{at excited state, } C^*(6) = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$$

$$\text{after } sp^2 \text{ hybridization, } C^*(6) = 1s^2 2\psi_1^1 2\psi_2^1 2\psi_3^1 2p_z^1$$

Where ψ_1 , ψ_2 and ψ_3 are three hybrid orbitals. Then one hybrid orbital of one carbon atom overlaps with one hybrid orbital of another carbon atom and thus forms C–C sigma (σ) bond. Other two hybrid orbitals of each carbon atom overlap with 1s orbital of two H-atoms and thus form two C–H bonds with each carbon atom. Thus the main structure of ethylene is formed. Due to sp^2 hybridization, the bond angles in ethylene are 120° and all the atoms are on a plane. Then each $2p_z$ orbital on two carbon atoms remains perpendicular to the plane. They overlap sidewise to form one pi-bond. Thus a carbon-carbon double bond ($C=C$) consisting of a sigma bond and a pi-bond is formed.

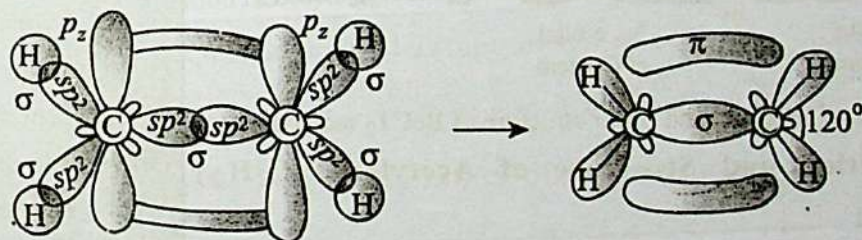


Fig. 3.24 : Formation of σ bond and π bond in ethylene (C_2H_4) molecule

3.9.3 sp -Hybridization

When one s-orbital and one p-orbital of an atom mix together and equalise to produce two new equivalent orbitals, then the process is known as sp -hybridization.

The two hybrid orbitals make 180° angle to each other and lie on a plane.

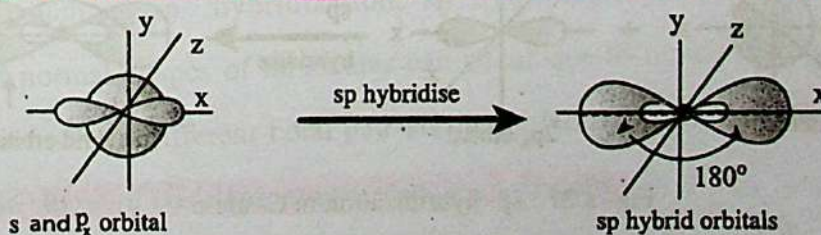


Fig. 3.25 : Formation of two sp hybrid orbitals

(1) Formation and Structure of $BeCl_2$ molecule :

The electronic configuration of beryllium, $Be(4) = 1s^2 2s^2$; which contains no unpaired electron. During the formation of any compound one electron from 2s orbital is transferred to vacant 2p orbital, thus giving rise to two unpaired electrons. This explains the divalency of beryllium. Then 2s and 2p orbitals undergo sp -hybridization to form two hybrid orbitals.

at normal state, $\text{Be}(4) = 1s^2 2s^2$

at excited state, $\text{Be}^*(4) = 1s^2 2s^1 2p^1$

after sp hybridization, $\text{Be}^*(4) = 1s^2 2\psi_1^1 2\psi_2^1$

Then two hybrid orbitals overlap with $3p_z$ orbital of two chlorine atoms [electronic configuration of $\text{Cl}(17) \rightarrow [\text{Ne}(10) = 3s^2 3p_x^2 3p_y^2 3p_z^1]$ and form two Be-Cl sigma bonds.

Due to sp-hybridization $\angle \text{ClBeCl}$ angle is 180° , so **BeCl_2 molecule is linear.**

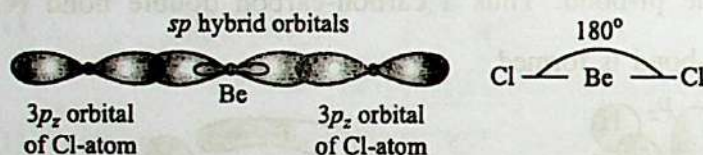


Fig-3.26 : Formation and linear structure of BeCl_2 molecule

(2) Formation and Structure of Acetylene (C_2H_2) molecule :

In acetylene molecule having carbon-carbon triple bond ($\text{C}\equiv\text{C}$), the two carbon atoms undergo sp-hybridization :

at normal state, $\text{C}(6) = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

at excited state, $\text{C}^*(6) = 1s^1 2s^1 2p_x^1 2p_y^1 2p_z^1$

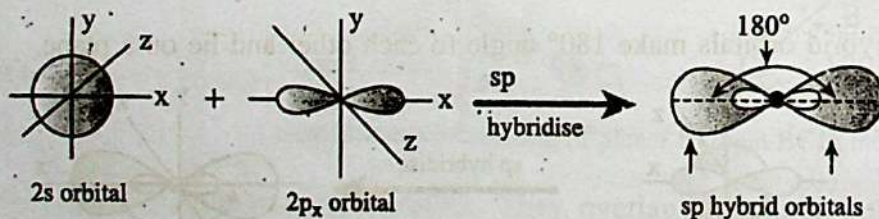


Fig- 3.27 : sp- hybridization in C- atom

Here ψ_1^1 and ψ_2^1 are two sp-hybrid orbitals. One hybrid orbital of a carbon atom overlaps with one hybrid orbital of another carbon atom to form a C-C sigma bond. The second hybrid orbital on each carbon atom overlaps with $1s^1$ orbital of H-atom and forms C-H sigma bond. Thus the main structure of acetylene (C_2H_2) with three σ -bonds is formed.

Now on each carbon atom, there are two unhybridized $2p_y^1$ and $2p_z^1$ orbitals. These orbitals are at right angles to the H-C-C-H-line and are at right angle to each other. Then they can overlap sidewise like p_y-p_y and p_z-p_z orbital of two carbon atoms to form two π

MCQ-3.3 : Characteristics of NH_3 molecule are—

- (i) sp^3 hybridised N-atom
 - (ii) lone-pair electrons present.
 - (iii) tetrahedral structure
- Which is correct?

- (a) i, ii
- (b) ii, iii
- (c) i, iii
- (d) i, ii and iii

bonds. So out of the three bonds in carbon-carbon triple bond ($C \equiv C$), one is sigma bond and other two are pi-bonds. Due to sp-hybridization, each of the two bond angles $\angle HCC$ is 180° and the structure of acetylene ($HC \equiv CH$) molecule is linear.

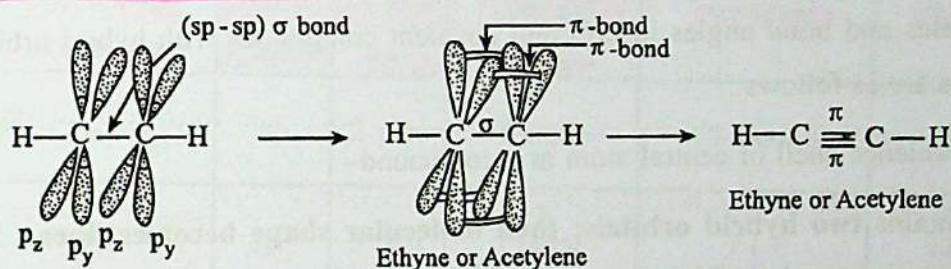


Fig. 3.28 : Formation of ethyne molecule with a sigma bond and two pi (π) bonds.

Student Work -3.12 : Orbital hybridization Based :

Problem - 3.26 : Describe the hybridization of C-atom in formaldehyde molecule formation.

Problem - 3.27 : Describe the hybridization of C-atom in formation of acetylene molecule.

3.10 Relation between Shapes of Covalent Compounds and Hybrid Orbitals

The hybrid orbitals of a central atom in a covalent compound with spatial orientation determines the shape of the compound. So the molecular shapes and bond angles of different covalent compounds are controlled by the natures of hybridization of the central atoms of the compounds, such as sp^3 hybridization, sp^2 hybridization, sp hybridization etc. Again distortion of normal shapes of molecules can occur due to repulsion of different numbers of lone-pair electrons on different bond pair electrons. Normally the number of hybrid orbitals indicates the shape of covalent compounds. For example,

- (i) sp hybridization forming two hybrid orbitals produces linear structure;
- (ii) sp^2 hybridization forming three hybrid orbitals produces trigonal planar structure;
- (iii) sp^3 hybridization forming four hybrid orbitals produces tetrahedral structure;
- (iv) $sp^3 d$ hybridization forming five hybrid orbitals produces trigonal bipyramidal;
- (v) $sp^3 d^2$ and $d^2 sp^3$ hybridization forming six hybrid orbitals produces octahedral;

(vi) sp^3d^3 hybridization forming seven hybrid orbitals produces **pentagonal bipyramidal** structure.

Again lone pair electrons can distort normal structures of molecular structures. The shapes of molecules and bond angles in different covalent compounds with hybrid orbitals and their distortions are as follows :

When valence shell of central atom in a compound—

(i) Contains two hybrid orbitals; then molecular shape becomes linear. For example, $BeCl_2$, $CH \equiv CH$ molecules. Here sp hybridization occurs at central atom. Then bond angle becomes 180° .

(ii) Contains three hybrid orbitals, then molecular shape becomes **triangular planar**. For example, BCl_3 , $CH_2 = CH_2$ molecules. Here sp^2 hybridization occurs at central atom. Then bond angle becomes 120° .

(iii) Contains four hybrid orbitals, then molecular shape becomes **tetrahedral**. For example, CH_4 , NH_4^+ , BH_4^- etc. Here sp^3 hybridization occurs at central atom. Then bond angle becomes 109.5° .

* When the central atom contains one lone pair electrons in sp^3 , then normal tetrahedral structure of the molecule is distorted and becomes **triangular pyramidal**. For example, $\ddot{N}H_3$ molecule; here bond angle becomes 107° .

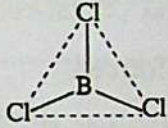
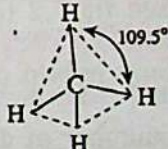
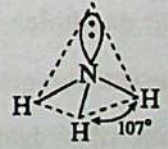
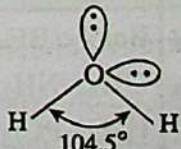
* When the central atom contains two lone pair electrons in sp^3 , then normal tetrahedral structure of the molecule is more distorted and becomes **V-shaped**. For example, $H_2\ddot{O}$ molecule; here bond angle becomes 104.5° .

* When central atom contains five hybrid orbitals, then molecular structure becomes **triangular bipyramidal** (PCl_5).

* If six hybrid orbitals are present on central atom, the molecular shape becomes **octahedral** (SF_6).

* With seven hybrid orbitals, the molecular shape becomes **pentagonal bipyramidal** such as IF_7 molecule.

Table- 3.4 : Different shapes of Covalent Compounds :

Compound Molecule	Electron distribution in Molecule	Orbitals hybridization	Valence electron pair	Molecular shape and name	Molecular structure	Bond angle
BeCl ₂	$\ddot{\text{O}} \times \text{Be} \times \ddot{\text{Cl}}:$	sp	2 pair	Linear	Cl-Be-Cl	180°
BCl ₃	$\begin{array}{c} \ddot{\text{Cl}}: \\ \\ \text{B} \\ \\ \ddot{\text{Cl}}: \end{array} \times \text{B} \times \begin{array}{c} \ddot{\text{Cl}}: \\ \\ \text{B} \\ \\ \ddot{\text{Cl}}: \end{array}$	sp ²	3 pair	Planar Triangular		120°
CH ₄	$\begin{array}{c} \text{H} \\ \times \\ \text{H} \times \text{C} \times \text{H} \\ \times \\ \text{H} \end{array}$	sp ³	4 pair	Tetrahedral		109.5°
NH ₃	$\begin{array}{c} \ddot{\text{N}} \\ \times \\ \text{H} \times \text{N} \times \text{H} \\ \times \\ \text{H} \end{array}$	sp ³	4 pair, one lone pair	Deformed tetrahedral Triangular pyramidal		107°
H ₂ O	$\begin{array}{c} \text{H} \\ \times \\ \text{H} \times \text{O} \end{array}$	sp ³	4 pair, two lone pair	Deformed tetrahedral V-shaped		104.5°

3.10.1 Determination of Hybridization State of Central Atom

It is known already from the electron distribution of the central atom of a compound what type of orbital hybridization can occur with that central atom before the formation of that compound. Now with the following **general formula** we can determine the number of orbitals (H) taken part in orbital hybridization of central atom of a compound or an ion. After that nature of orbital hybridization of central atom can be known. Again molecular structure of the compound or the ion is known from central atom's orbital hybridization. For example,

$$(1) H = \frac{1}{2} \times \boxed{\text{Valence Shell electron number (V)}} + \boxed{\text{Monovalent atom number (X)}} - \boxed{\text{Charge on cation (C)}} + \boxed{\text{Charge on anion (A)}}$$

$$\text{or, } H = \frac{1}{2} \times (V + X - C + A)$$

Value of H \rightarrow	2	3	4	5	6	7
Hybridization \rightarrow	sp	sp ²	sp ³	sp ³ d	sp ³ d ²	sp ³ d ³
Structure of the Molecule or, Ion \rightarrow	Linear structure	Planar triangular	Tetra-hedral structure	Triangular bipyramid	Octahedral structure	Pentahedral bipyramid

* When hybrid orbital contains lone pair electrons, then above general molecular shape will be deformed.

* sp³d³ hybridised XeF₆ molecule has one lone-pair electron. So its shape is pentagonal pyramid [see fig-3.2 (b)].

(2) Central atom's hybrid orbital with lone-pair electrons number, L = H - X - D

(here D = number of divalent atom)

From following examples we can know the state of orbital hybridization of central atom and number of lone-pair electrons on hybrid orbitals in some molecules and ions :

Calculation of nature of hybridization of central atom of different molecules & ions :

Nature of Molecule	Compounds	Calculation of hybridization, Structure in a compound or, ion
(1) Central atom of compound contains only monovalent atom.	BeCl ₂ , BF ₃ , CH ₄ , NH ₃ , H ₂ O, PCl ₃ , PCl ₅ , SF ₄ etc.	<p>➤ Molecule : CH₄, here, $H = \frac{1}{2} (V + X - C + A)$</p> $= \frac{1}{2} (4 + 4 - 0 + 0) = 4$ <p>∴ Central atom's (C) hybridization : sp³, L = 4 - 4 - 0 = 0</p> <p>∴ Central atom's (C), no. of lone-pair electrons = 0</p> <p>∴ Structure of molecule : tetrahedral</p>
(2) Central atom of compound contains only divalent atom.	CO ₂ , CS ₂ , SO ₂ , SO ₃ etc.	<p>➤ Molecule : SO₃, here $H = \frac{1}{2} (V + X - C + A)$</p> $= \frac{1}{2} (6 + 0 - 0 + 0) = 3$ <p>∴ Central atom's (S) hybridization : sp², L = 3 - 0 - 3 = 0</p> <p>∴ Central atom's (S), no. of lone-pair electrons = 0</p> <p>∴ Structure of molecule : triangular planar</p>
(3) Central atom of compound contains monovalent and divalent atoms both.	COCl ₂ , POCl ₃ , H-CHO etc.	<p>➤ Molecule : HCHO, here, $H = \frac{1}{2} (4 + 2 - 0 + 0) = 3$</p> <p>∴ Central atom's (C) hybridization : sp², L = 3 - 2 - 1 = 0</p> <p>∴ Central atom's (C) no. of lone-pair electrons = 0</p> <p>∴ Structure of molecule : triangular planar</p>

(4) For Cation :	NH_4^+ , CH_3^+ , H_3O^+ etc,	\triangleright Compound Cation: NH_4^+ , here, $H = \frac{1}{2} (5 + 4 - 1 + 0) = 4$ \therefore Central atom's (N), hybridization : sp^3 , $L = 4 - 4 - 0 = 0$ \therefore Central atom's (N), no. of lone-pair electrons = 0 \therefore Structure of ion : tetrahedral
(5) For Anion :	BCl_4^- , BF_4^- , CO_3^{2-} , NO_3^- , SO_4^{2-} , PO_4^{3-} etc	\triangleright Anion : BF_4^- , here, $H = \frac{1}{2} (3 + 4 - 0 + 1) = 4$ \therefore Central atom's (B), hybridization, sp^3 , $L = (4 - 4 - 0) = 0$ \therefore Central atom's (B), no. of lone pair electrons = 0 \therefore Structure of ion : tetrahedral

3.11 Affect of Lone pair Electrons on Molecular Shapes

The bond-pair electrons and lone-pair electrons on the valence shell of a central atom of a compound repel among themselves decreasing the degree of bond angle from normal value. Electron pairs, both bond-pair and lone pair, repel mutually and their degree of repulsion depends on electron density of different orbitals of the central atom. Bond-pair (bp) electrons, involved in covalent bond formation, move under the influence of both the nuclei of the related two atoms. On the other hand, lone-pair (lp) electrons move under the influence of nucleus of the central atom only. For this reason, electron cloud density in orbital of lone-pair electrons near the central atom remains more than that of bond pair electron. The magnitude of repulsion between the two sets of electron-pair is directly proportional to the product of each pair of electron cloud density.

As a result, the magnitude of repulsion among the different number of bond pair (bp) and lone pair (lp) of electrons are as follows :

Repulsion between (lone pair electrons–lone pair electrons > lone pair electrons – bond pair electrons) > (bond pair electrons – bond pair electrons);

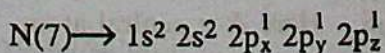
simply, $(lp-lp) > (lp-bp) > (bp-bp)$

On the basis of above relations, the shapes and bond angles of the compounds and ions such as NH_3 , H_2O and NH_4^+ are discussed below :

(A) Impact of Lone Pair Electronics on Bond-angle :

(1) Structure of Ammonia Molecule (NH_3) : By sp^3 Hybridization of N-atom

The electronic configuration of N atom in ammonia, i.e.



Just before the formation of ammonia (NH_3) molecule, the 2s and three 2p orbitals of N atom undergo sp^3 hybridization. Thus four equivalent hybrid orbitals are formed, which may be designated as ψ_1, ψ_2, ψ_3 and ψ_4 ; with electronic configuration $\psi_1^2 \psi_2^1 \psi_3^1 \psi_4^1$. Here last three hybrid orbitals contain one electron each. Then each of them overlaps with $1s^1$ orbital of H-atom to form three N–H bonds. Thus NH_3 molecule is formed. Since the N-atom has undergone sp^3 hybridization, the four hybrid orbitals should be elongated towards the four corners of a tetrahedron. The angle between two hybrid orbitals should be 109.28° .

But the electron cloud density of the lone pair of ψ_1^2 hybrid orbital is greater than the electron cloud density of the bonding pairs ψ_2, ψ_3 and ψ_4 hybrid orbitals. Hence the repulsion between ψ_1^2 and bonding pairs is more than that of any other bonding pairs. Therefore the $\angle \text{H-N-H}$ bond angles in ammonia decrease from 109.28° to 107° .

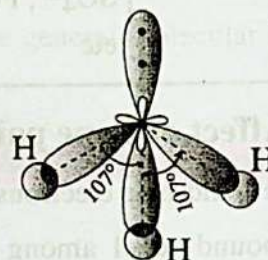


Fig-3.29 : Structure of NH_3 molecule and bond angle.

Thus the structure of ammonia molecule is like a **trigonal pyramid**. Nitrogen atom (N) is situated at the centre of this pyramid and three H-atoms are situated at the three corners of its base.

(2) Structure of Water Molecule (H_2O) : By sp^3 Hybridization of O-atom

The electronic configuration of O atom in water molecule is $\text{O}(8) = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. Just before the formation of water molecule, 2s and three 2p orbitals of oxygen atom undergo sp^3 hybridization and form four hybrid orbitals $\psi_1^2, \psi_2^2, \psi_3^1$ and ψ_4^1 . Of them two hybrid orbitals contain 2 electrons each and hence they do not take part in σ -bond formation.

The other two hybrid orbitals contain one electron each and overlap with $1s^1$ orbital of two H-atoms to form two O–H bonds. Thus water molecule is formed. Since the lone pair exerts more repulsion than the shared bond electron pairs, then the $\angle \text{H-O-H}$ angles decrease from ideal angle value $109^\circ 28'$ to 104.5° .

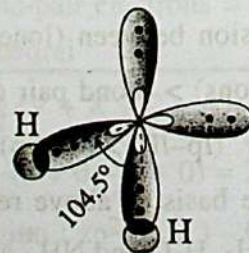


Fig. 3.30 : Structure of H_2O molecule and bond angle

(B) Impact of Lone Pair Electrons & Electronegativity on Bond-angle

Electronegativity also has effect on bond angle in molecules with lone-pair electrons like AB_3L (such as $\ddot{\text{N}}\text{F}_3$, $\ddot{\text{N}}\text{F}_3$, $\ddot{\text{P}}\text{H}_3$ and AB_2L_2 (such as $\text{H}_2\ddot{\text{O}}$, $\text{H}_2\ddot{\text{S}}$). Here A = central atom,

B = bonded atoms and L = lone pair electrons). In every compound with general formula AB_3L and AB_2L_2 , central atom has sp^3 hybridization; so its structure is to be tetrahedral with bond angle $109^\circ 28'$. But central atom has lone pair electrons; so due to repulsion between lp-bp electrons, bond angle becomes less than $109^\circ 28'$. Besides this bond pair-(lp-bp) repulsion may also be more or less due to difference in electronegativity of bonded atoms.

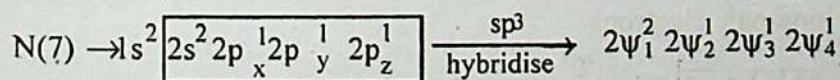
(i) When central atom of a molecule is more electronegative than lateral atom, then bond-pair electrons is more attracted by central atom. As a result repulsion between bp-bp electrons becomes more with increased bond angle.

(ii) When lateral atom of a molecule is more electro-negative than central atom, then bond-pair electrons is more attracted towards lateral atom. As a result repulsion between bp-pb electrons becomes less with less bond angle.

(1) **Bond-angle in NH_3 is 107° ; but bond angle in NF_3 is $102^\circ 29'$, or, 102.5° ;**

explain why.

In both $\ddot{N}H_3$ and $\ddot{N}F_3$ molecules, central N atom has sp^3 hybridization :

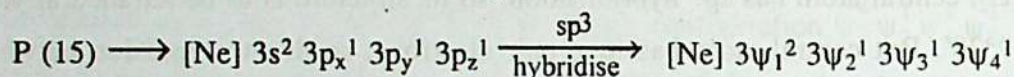
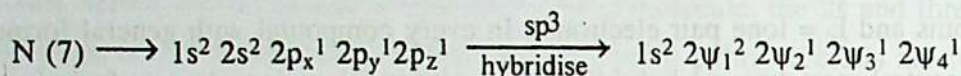


Out of four hybrid orbitals of N atom one hybrid orbital ($2\psi_1^2$) contains lone pair electrons. So in $\ddot{N}H_3$ and $\ddot{N}F_3$ molecules, lone-pair electrons and bond-pair electrons do not remain in tetrahedral structure but get pyramidal triangular shape due to unequal repulsion. Again in each molecule degree of repulsion between bp-bp electrons differs depending on difference in electronegativities of two bonded atoms. For example more electronegative F atom in NF_3 molecule attracts N-F bond pair electrons towards itself. But in NH_3 molecule more electronegative N atom attracts N-H bond pair electrons towards itself. So repulsion between bp-bp bonds is more in NH_3 molecule than NF_3 molecule.

Besides this lone-pair containing hybrid orbital of N atom in NF_3 repels much (lp-bp) than in NH_3 . As a result bond angle in NF_3 decreases still more. Hence bond angle $\angle HNH$ of NH_3 molecule is 107° and bond angle $\angle FNF$ in NF_3 decreases to 102.5° .

(2) **Bond-angle in NH_3 is 107° ; but bond-angle in PH_3 is 94° ; explain why?**

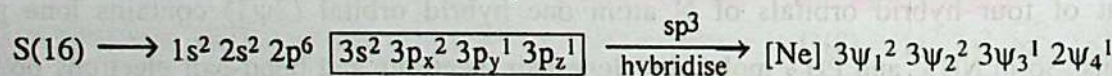
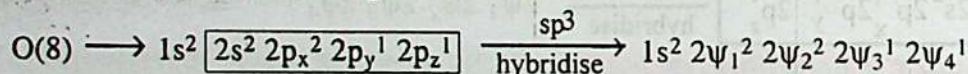
During formation of NH_3 and PH_3 molecules, central atom of each molecule undergoes sp^3 hybridization :



As central atom of NH_3 and PH_3 molecules are in sp^3 hybridization, then structure of each molecule is to be tetrahedral. But in each case central atom N and P has lone pair electron hybrid orbital which repels the bond pair electron. So lp-bp repulsion decreases bond angle $109^\circ 28'$ of tetrahedral structure. Again more electro-negative N atom in NH_3 attracts N-H bond-pair electrons more towards itself and atomic size is smaller than P atom. On the otherhand less electronegative P atom attracts P-H bond electron less than N atom and atomic size of P is bigger than N. So comparatively repulsion between two bonds (bp-bp) in NH_3 is more than that in PH_3 . For this reason the bond angle $\angle \text{HNH}$ in NH_3 molecule is 107° and bond angle $\angle \text{HPH}$ in PH_3 molecule is 94° .

(3) Bond-angle in H_2O is $104^\circ 28'$; but bond-angle in H_2S is 90° ; explain why?

In both $\text{H}_2\ddot{\text{O}}$ and $\text{H}_2\ddot{\text{S}}$ molecules central atom O and S are in sp^3 hybridization and both the molecules contain two lone-pair electrons.



Although central atoms of H_2O and H_2S are being sp^3 hybridised, yet due to repulsion between lone-pair and bond-pair (lp-bp) electrons bond angle in each molecule decreases from $109^\circ 28'$. We know electronegativity of O and S atoms are 3.5 and 2.5 respectively. Moreover O atom of 2nd period element has smaller size than S atom of 3rd period element. Hence bond-angle in compound like AB_2L_2 (central atom 'A' with two lone-pair 'L' electrons) of 2nd period element will be greater than that of 3rd period element.

In H_2O molecule more electronegative O atom attracts bond-pair electrons of O-H bond towards itself more. But in H_2S molecule less electronegative S atom comparatively less attracts bond-pair electrons of S-H bond. Hence repulsion between two bond-pair electrons (bp-bp) is less in H_2S molecule than H_2O . So in H_2O molecule bond angle $\angle \text{HOH}$ is 104.5° and is more than bond angle $\angle \text{HSH}$ in H_2S of 92° .

Change in Molecular Shape & Bond-angle of Compounds with sp^3 Hybridised Central atom due to effect of lone-pair electrons & electronegativity.

Compound molecule	Orbital hybridized	Bond pair electrons	Lone pair electrons	Electro-negativity	Bond angle	Molecular shape
NH ₃	sp ³	3 pair	1 pair	3.0–2.1	107°	triangular pyramid
NF ₃	sp ³	3 pair	1 pair	3.0–4.0	102.5°	triangular pyramid
NH ₃	sp ³	3 pair	1 pair	3.0–2.1	107°	triangular pyramid
PF ₃	sp ³	3 pair	1 pair	2.1–2.1	94°	triangular pyramid
H ₂ O	sp ³	2 pair	2 pair	3.5–2.1	104.5°	V-shaped deformed tetrahedral
H ₂ S	sp ³	2 pair	2 pair	2.5–2.1	92°	V shaped deformed tetrahedral

Student's Work-3.13 : Orbital Hybridization & Molecular Shape Based :

Problem-3.28 (a) : Valence electrons of 'A' and 'B' elements are ns^2np^3 and $ns^2 np^4$

($n = 2$). The orbital hybridizations of 'A' and 'B' in hydrides are same, yet their molecular shapes are different; explain. [Di. B. 2015]

Problem-3.28 (b) : Valence electrons of 'X' and 'Y' elements are ns^2np^2 and ns^2np^4

($n = 2$). The central atoms of hydrides of 'X' and 'Y' have same orbital hybridization; then what will be the shapes and bond angles of both hydride? Explain.

Problem-3.28 (c) : Calculate the nature of orbital hybridization in each of the following compounds and ions and explain what will be its shape; Explain :

(1) H₂O, CO₂, NO₂, SO₂, SO₃, CH₄, CCl₄, C₂H₄, C₂H₂.

(2) BeCl₂, PCl₃, CF₄, PCl₅, SF₄, XeF₂, XeF₄, XeF₆.

(3) NH₄⁺, PH₄⁺, H₃O⁺, CH₃⁺

(4) NO₃⁻, CO₃²⁻, ClO₃⁻, BF₄⁻, SO₄²⁻, PO₄³⁻.

Problem-3.29(a) : Bond angle of NH₃ is 107° but bond-angle of NF₃ is 102.5°; explain it.

Problem-3.29(b) : Bond-angle of NH₃ is 107° but bond-angle of PH₃ is 94°; explain why.

Problem-3.29 (c) ; Bond-angle in H₂O is 104.5° but bond angle in H₂S is 92°; explain why.

Problem-3.30 : Calculate orbital hybridization in each C-atom, number of sigma (σ) bond and pi (π) bond in following compounds :

(a) CH₃-CH₃, (b) CH₃-CH=CH₂, (c) CH₂=C=CH₂, (d) CH₃-CHO.

Problem-3.31 (a) : Describe orbital hybridization in BeCl₂ molecule. [J. B. 2016]

Problem-3.31 (b) : Why do the covalent bonds become direction oriented?

3.12 To Make Molecular Models of Covalent Compounds

Students' Group Based Work : Covalent Bond Based :

1. Get the idea of comparative atomic sizes of C, N and H from Fig-3.7. With that idea select or collect three types of sizes of small, medium and big sizes round potatoes with similarity of those comparative sizes of three types of atoms. Collect match sticks to be used as bonds of atoms. A single match stick will be used as a sigma bond between two atoms, connected with them.

2. Now confirm the maximum valency of each of those atoms from their positions in the periodic table.

3. Then prepare the molecular models of the following compounds with the three types of selected potatoes as atoms and match sticks as covalent bonds on the basis of your knowledge about the shapes and bond angles of covalent compounds earned till now.

(a) Methane molecule, (b) Ethane molecule, (c) BeCl_2 molecule, (d) Ammonia molecule.

4. As an example and to make the idea clear, some atom models and model of covalent compounds formed with them are shown by ball and stick method below.

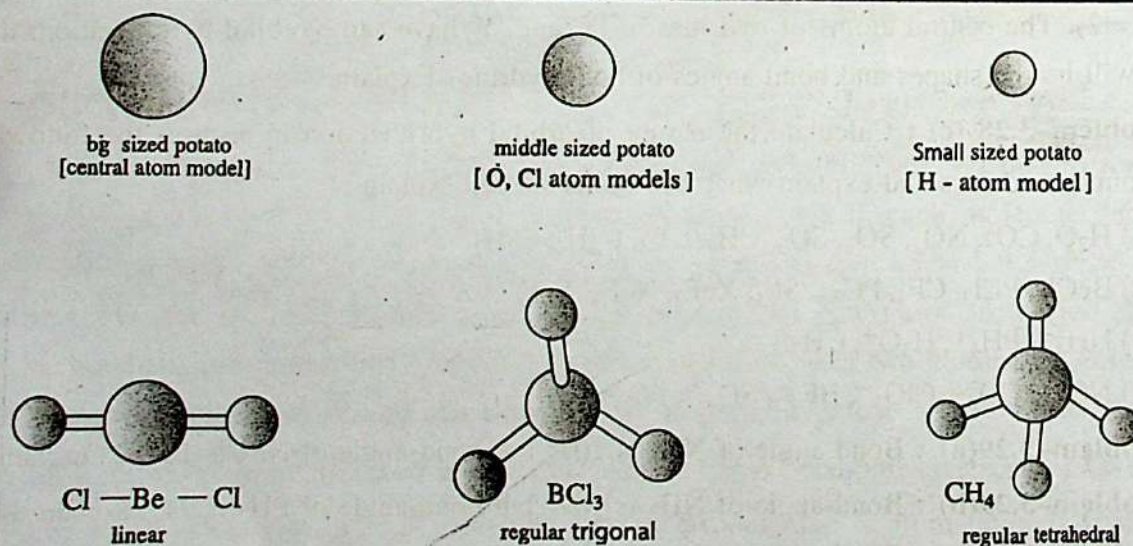


Fig-3.31 : Models of BeCl_2 , BCl_3 and CH_4 molecules.

3.13 Co-ordinate Covalent Bond

In the formation of a covalent bond between two atoms, each atom supplies one electron to form an electron pair which is shared by the related two atoms equally. You can write ammonium ion as NH_4^+ ; this ion is formed from NH_3 molecule and hydrogen ion H^+ .

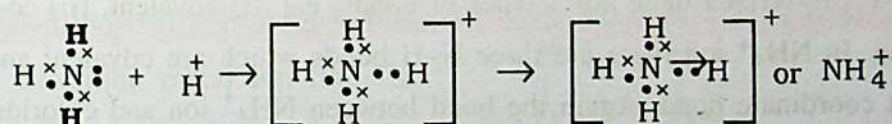
Here hydrogen ion H^+ devoid of any electron, yet can combine with $\ddot{N}H_3$ without supplying any electron but sharing with the lone pair electrons on N atom of NH_3 molecule.

Thus when one atom in a compound contributes one pair of electrons and the other atom without contributing any electron shares this pair with the first atom to form a covalent bond; then the formation of this type of bond is known as co-ordinate covalent bond or simply co-ordinate bond.

The atom supplying the electron pair for bond formation is called 'donor atom' and the atom which does not contribute any electron but shares the electron pair, is called 'acceptor atom'. Covalent bond is denoted by an arrow (\rightarrow) indicating donor and acceptor atoms.

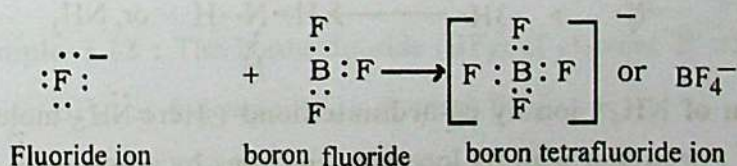
Condition for Co-ordinate Bond : For the formation of co-ordinate bond the donor atom must have at least one lone pair and the acceptor atom must have the capacity to accept it.

Example : Ammonia molecule ($\ddot{N}H_3$) with its lone pair electrons combines with proton or hydrogen ion (H^+) to form ammonium ion (NH_4^+) by co-ordinate bond as follows :



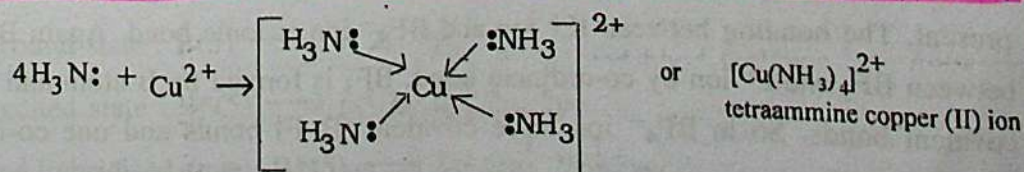
Some more examples of coordinate bond formation are shown below.

(i) Fluoride ion (F^-) with its lone pair electrons combines with boron trifluoride (BF_3) to form boron tetrafluoride ion by coordinate bond as follows :



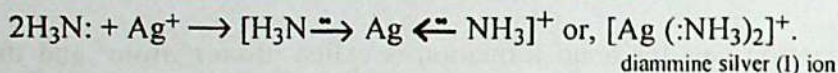
Maximum examples of formation of co-ordinate bonds are found in complex compounds with 3 d-block metal ions which act as acceptor atom-ions. Then the lone-pair electrons donors are known as ligands.

For example (i) Ammonia ($\ddot{N}H_3$) molecule with its lone pair electrons combines with Cu^{2+} ion to form tetra-ammine copper (II) ion, a complex ion by co-ordinate bonds.



Co-ordinate bond formed between d-block metal atom or ion and donor atom is called co-ordination bond and the metal compounds formed are called **complex compounds**. Different ligands, or lone pair electron donors are NH_3 , H_2O and Cl^- ion etc. So the complex compounds are also known as **co-ordination compounds**.

(ii) Similarly, silver ion (Ag^+) and ammonia (NH_3) forms diammine silver (I) ion with co-ordinate bonds.



Note, number of ligand in complex ion is double the charge number of metal ion in each case.

This is a general rule in complex ion formation (with some exceptions).

MCQ-3.4 : $[\text{Cu}(\text{NH}_3)_4]^{2+}$

Contains bonds : (i) ionic, (ii) covalent, (iii) coordinate

What is correct?

(a) i and ii (b) ii and iii

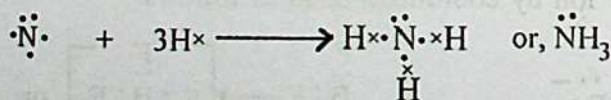
(c) i and iii (d) i, ii and iii

3.13.1 Presence of Different Types of Bonds in a Compound

In many compounds different types of bonds are present. Covalent bond, co-ordinate bond and ionic bond may be present in same molecule of a compound. For example,

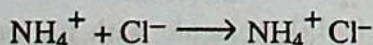
Example-1 : In NH_4Cl there are 3 types of bonds; e.g. (i) covalent, (ii) co-ordinate and (iii) ionic bond. In NH_4^+ ion there are three N-H bonds which are covalent and one N \rightarrow H bond which is coordinate bond. Again the bond between NH_4^+ ion and chloride (Cl^-) ion is an ionic bond.

(i) **Formation of NH_3 by covalent bond :** One N-atom combines with three H-atoms with covalent bond to form NH_3 molecule.



(ii) **Formation of NH_4^+ ion by co-ordinate bond :** Here $\ddot{\text{N}}\text{H}_3$ molecule combines with hydrogen ion (H^+) or proton with its lone pair electrons by co-ordinate bond to form NH_4^+ ion. $\text{H}^+ + \text{:NH}_3 \longrightarrow [\text{H} \leftarrow \text{NH}_3]^+ \text{ or, } \text{NH}_4^+$

(iii) **Formation of NH_4Cl by ionic bond :** Here NH_4^+ ion and Cl^- ion are attracted by electrostatic force to form NH_4Cl .



Similarly, in KBF_4 three types of bonds like (i) ionic, (ii) co-ordinate and (iii) covalent bonds are present. The bonding between K^+ ion and BF_4^- ion is ionic bond. Again BF_4^- ion is formed between BF_3 and F^- ion by co-ordinate bond. BF_3 is formed by B atom and three H atoms by covalent bonds. So in BF_4^- ion three covalent (B-F) bonds and one co-ordinate (B \leftarrow F) bond are present.

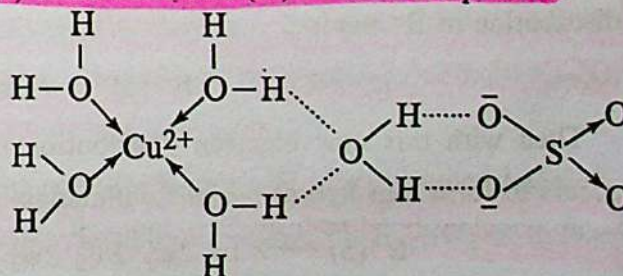
Example-2 : In $(\text{H}_3\text{N} \rightarrow \text{BF}_3)$ compound two types of bonds like covalent bond (like N-H and B-F) and co-ordinate bond (like $\text{N} \rightarrow \text{B}$) are present, On the other hand in KOH molecule there is ionic bond between K^+ ion and OH^- ion, Again in $\text{O}-\text{H}^-$ ion there is covalent bond.

Example-3 : In hexaammine cobalt (III) chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ there are three types of bonds like (i) covalent (ii) co-ordinate and (iii) ionic bond. In NH_3 molecule there are three covalent (N-H) bonds. Again Co^{3+} ion and six NH_3 molecules as ligand, form six co-ordinate bonds to form complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ which finally is bonded with three chloride (Cl^-) ions by ionic bond.

In most of the different complex compounds these three types of bonds are present. The bonding between the ligands and metal ion is co-ordinate, the bonding within ligand molecule (NH_3 , H_2O) is covalent and the bonding between complex ion positive or negative and opposite ion is being ionic bond.

Example-4 : In hydrated copper sulphate or blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 4 types of bond like (i) covalent bond (ii) co-ordinate bond (iii) ionic bond and (iv) H-bond are present.

Here transition metal ion like Cu^{2+} ion forms 4 co-ordinate bonds with 4 H_2O molecules and 5th H_2O molecule is bonded with SO_4^{2-} ion and other part with four H-bonds.

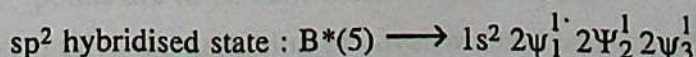
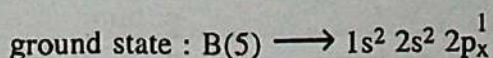


Worked Example-3.12 : The boron fluoride (BF_3) of element 'B' of group-13 or, 3A in period-2 forms anion BF_4^- as follows : $\text{BF}_3 + \text{F}^- \longrightarrow \text{BF}_4^-$ [Ctg. B. 2015]

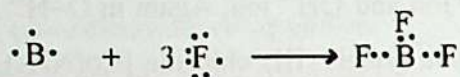
- What type of bond is formed between BF_3 and F^- ion; explain.
- Verify whether change in hybridization occurs in atom 'B' due to given stem reaction.

Solution : (a) **Explanation for bond formation between BF_3 and F^- ion :**

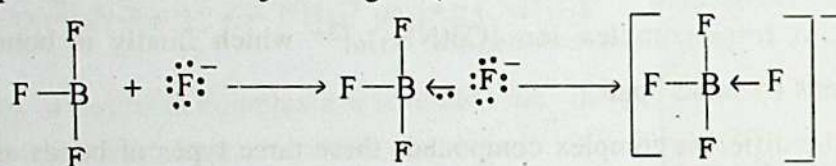
As per stem, the element 'B' is of group-13 or 3A in 2nd period. So the element is boron B (5) and the electron distribution of 'B' is as follows :



With three hybrid orbitals of sp^2 hybridised 'B' atom three fluorine atoms are combined with covalent bonds to form BF_3 . The formation of covalent bond is shown with Lewis symbols below :

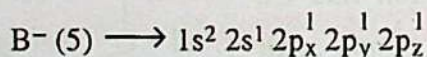


In the product BF_3 molecule octet set is incomplete. So as per given stem fluoride ion (F^-) supplies lone-pair electrons to BF_3 forming BF_4^- ion with co-ordinate bond as follows :

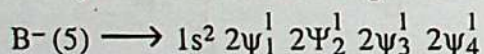


Solution : (b) Explanation whether change in hybridization of 'B' atom occurs or not :

We know during the formation of BF_3 molecule 'B' atom undergoes sp^2 hybridization. As per given stem BF_4^- ion is formed by co-ordination bond between BF_3 molecule and fluoride ion (F^-). Then one electron is added to vacant $2p_z$ orbital of B atom. At this state electron distribution of B^- ion is :



Then with this new electron distribution of B^- ion sp^3 orbital hybridization in B^- ion occurs to form four hybrid orbitals with single electron :



Among the four hybrid orbitals, the fourth F atom gets bonded with covalent bond. So according to given stem reaction, orbital hybridization in atom 'B' is changed from sp^2 state to sp^3 state in BF_4^- ion. Then structure of BF_4^- ion becomes tetrahedral.

Verification : From following general formula the number of orbitals (H) taken part in hybridization of central atom in compound molecule and anion can be calculated and structure also can be determined from nature of orbital hybridization. For example,

$$H = \frac{1}{2} \times \left[\begin{array}{c} \text{valence shell} \\ \text{electron number (V)} \end{array} + \begin{array}{c} \text{Monovalent} \\ \text{atom number (X)} \end{array} - \begin{array}{c} \text{charge on} \\ \text{cation (C)} \end{array} + \begin{array}{c} \text{Charge on} \\ \text{anion (A)} \end{array} \right]$$

$$\text{or, } H = \frac{1}{2} \times [V + X - C + A]$$

\therefore Number of orbitals taken part in hybridization for BF_4^- ion formation :

$$H = \frac{1}{2} \times [3 + 4 - 0 + 1] = 4$$

Here four orbitals like 2s and three 2p orbitals have taken part in hybridization. So in BF_4^- ion formation, sp^3 hybridization in atom 'B' has occurred. Before the reaction of stem, 'B' atom was in sp^2 hybridised in BF_3 molecule and during co-ordination bond formation with F^- ion new sp^3 hybridization has occurred. It is proved.

Student's Work-3.14 : Explanation of Nature of Bond Based :

Problem-3.32 (a) : Explain the nature of bond in NH_4Cl molecule. [D. B. 2015]

Problem-3.32(b) : Valence electrons of the elements 'A' and 'D' are respectively $\text{ns}^2 \text{np}^1$ and $\text{ns}^2 \text{np}^3$. Explain what type of bond is possible between AlCl_3 and DH_3 . [B. B. 2015]

Problem-3.32 (C) : Co-ordinate bond is actually a covalent bond; explain. [Ctg. B. 2017]

Properties of Compounds with Different Bonds :

(1) Many inorganic salts contain ionic bond and covalent bond together. As those compounds have ions of different charges, they show the properties of ionic compounds such as high m.p and b.p, electrical conductivity and individuality of ions etc. (i) If the ions remain unchanged in reaction, then that reaction occurs rapidly. For example, the ions of Na_2SO_4 which contains 3 types of bonds, remain unchanged in solution. So when BaCl_2 solution is mixed with Na_2SO_4 solution, the precipitation occurs rapidly. Similarly, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ solution reacts with AgNO_3 solution rapidly to form ppt. of AgCl .

(ii) On the otherhand, when covalent bond breaks or forms in an ion during reaction, then rate of reaction will be slow. For example, when Na_2SO_4 is reduced to Na_2SO_3 or to Na_2S , then S-O covalent bond is to be broken, In that case the reaction occurs at high temperature and slowly.

(2) Generally, when covalent bond and co-ordinate bonds are present together with ionic bond in a compound, then in that compound properties of ionic bond will predominate. Those compounds are treated as ionic compounds. Examples are K_2SO_4 , NaNO_3 , NH_4Cl etc.

Students' Work :

3.14 : Comparison between Covalent and Co-ordinate Bonds

Key Concept : It is to be proved 'co-ordinate bond is a special type of covalent bond'.

Guide line : For the comparison between covalent bond and co-ordinate bond following points are to be considered. For example;

(1) Give the definition of covalent bond and co-ordinate bond first.

- (2) Write the structures of NH_3 and NH_4^+ ion with Lewis symbols and outermost electron set of central atom 'N'. Then explain the covalent and co-ordinate bond formation with these electron set.
- (3) Now explain, there is no difference between the three N–H bonds in NH_3 molecule and four N–H bonds in NH_4^+ ion.
- (4) Then prove, the bond angle of every covalent bond in NH_4^+ ion such as $\angle \text{HNH} = 109.5$ is being equal to that of an ideal tetrahedron, the electron cloud density in every covalent bond is equal.
- (5) Thus equality of covalent bond and co-ordinate bond is proved.

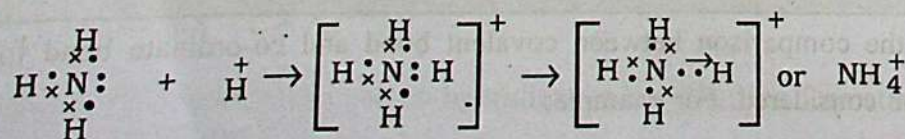
The elaborate explanation on the basis of above key points are the followings :

Formation of covalent bond : Two nonmetal atoms, contributing equal number of electron and forming electron pair, can form bond between them with a set of duplet or octet similar to their nearest inert gas member; this type of bond formation by sharing of electron is known as **covalent bond**.

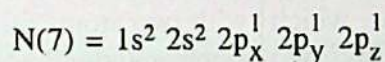
Co-ordinate bond : Again, when one atom in a compound contributes one pair of electrons and the other atom without contributing any electron shares this pair with the first atom to form a covalent bond, then the formation of this type of bond is called **co-ordinate covalent bond or simple co-ordinate bond**.

Similarity between Covalent bond and Co-ordinate bond : Although the sources of electron for the formation of bonds are different, yet co-ordinate bond is a special case of covalent bond. This factor will be clear from comparative study of formation of NH_3 molecule and NH_4^+ ion as follows :

According to Lewis concept, in ammonia (NH_3) molecule there are three single N–H bonds and a lone pair on nitrogen atom. When it reacts with H^+ ion, the lone pair electron is used to form co-ordinate bond between nitrogen (N) atom and H^+ ion. Thus ammonium ion (NH_4^+) is formed. The electrons of N atom have been denoted by dot and those of H atom by cross. So by definition there are three covalent bonds like N–H and one co-ordinate bond like ($\text{N} \rightarrow \text{H}$) in NH_4^+ ion.



Now from **valence bond theory**, let us consider the overlapping of orbitals of N-atom and H-atoms for the formation of ammonium ion. The electronic configuration of N atom is as follows :



Just before the formation of ammonia (NH_3) molecule, N atom undergoes sp^3 hybridization to form four equivalent hybrid orbitals. Of which three contain one electron each and the fourth hybrid orbital contains two electrons. The first three orbitals overlap separately with $1s^1$ orbitals of three hydrogen atoms and thus ammonia molecule (NH_3) is formed. In ammonia the fourth hybrid orbital contains a lone pair, which is used for the formation of ammonium ion. When this hybrid orbital overlaps with the vacant $1s^0$ orbital of hydrogen ion (H^+) then a co-ordinate bond is formed:

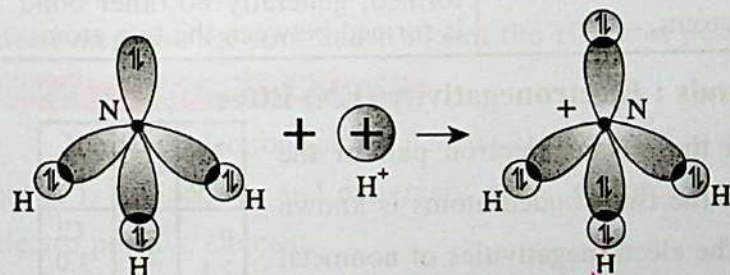


Fig. 3.32 : Formation of co-ordinate bond to form ammonium ion

MCQ-3.5 : NH_4Cl contains following bond : (i) ionic (ii) covalent (iii) co-ordinate bond

Which is correct?

- (a) i, ii (b) ii, iii
(c) i, iii (d) i, ii and iii.

After formation of co-ordinate bond a positive charge is formed on the donor N-atom. One negative charge should be formed on hydrogen ion, but that is neutralised by the positive charge already present. So no difference exists between this new N-H bond and the other three N-H bonds. Because each N-H bond is formed by the overlap of one hybrid orbital of N atom and $1s$ orbital of H atom and all bonds are formed by two electron-orbitals. So each bond is a single bond. In fact the structure of NH_4^+ ion is tetrahedrally similar to that of methane. In NH_4^+ ion all hydrogen atoms are equivalent, all N-H bonds are equivalent and all $\angle\text{H-N-H} = 109^\circ 28'$, which are equal to ideal tetrahedral angles.

From the above discussion, according to molecular orbital theory there are three single covalent bonds and one coordinate bond in NH_4^+ ion which are completely equivalent, So a co-ordinate bond is equivalent to one single covalent bond.

Table-3.5: Comparison between Covalent bond and Co-ordinate bond :

Basic points	Covalent Bond	Co-ordinate bond
1. Lewis Concept :	1. Covalent bond is formed by sharing of two electrons, which are supplied equally by two atoms.	1. Co-ordinate bond is formed with two atoms by sharing of two electrons supplied by one donor atom only.
2. V. Bond Concept :	$A \cdot + \cdot B \rightarrow A : B$ 2. It is formed by overlapping of two orbitals each having one electron.	$A : + B \rightarrow A \rightarrow B$ 2. It is formed by overlapping of two orbitals, one of which contains two electrons and another is vacant.
3. Symbol :	3. The bond is represented by a single short line.	3. The bond is represented by an arrow (\rightarrow).
4. Related atoms :	4. Covalent bond is formed between two non-metal atoms.	4. Co-ordinate bond generally is formed between two molecules or a molecule and an ion.
5. Number of bond :	5. A single double or triple covalent bond may be formed between two atoms.	5. When a co-ordinate bond is formed, generally no other bond is formed between the two atoms.

3.15 Polarity in Covalent Compounds : Electronegativity (EN) Effect

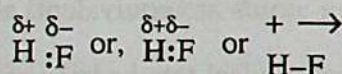
The relative more ability to attract the shared electron pair of the covalent bond towards itself by one of the two bonded atoms is known as the electronegativity of that atom. The electronegativities of nonmetal elements are higher than those of metals. The highest electronegativity value, EN = 4.0 is for fluorine, then for oxygen, chlorine and nitrogen is in fourth position (EN = 3.0).

N 3.0	O 3.5	F 4.0
P 2.1	S 2.5	Cl 3.0
		Br 2.8
		I 2.5

The shared electron cloud is more attracted towards more electronegative elements. hence that atom acquires a partial negative

more electronegative elements

charge (δ^-) and the other atom acquires similarly a partial positive charge (δ^+). The covalent molecule with partial positive and partial negative charges is known as **polar covalent compound** and the two oppositely charged poles created on two ends of the molecule are called **dipoles**. This is shown with HF molecule below :



American chemist Linus Pauling developed the most common scale of relative EN values for the elements. One of the ways in which EN's were first calculated by American physicist R. S. Mulliken in 1934, was by taking the average of the absolute values of E_{ea} and E_i and

setting up a scale with fluorine assigned a value of 4.0. by Pauling. According to Pauling scale, the EN values of some common elements are :

$F = 4.0$, $O = 3.5$, $Cl = 3.0$, $N = 3.0$, $Br = 2.8$, $I = 2.5$, $C = 2.5$, $H = 2.1$

When electronegativity difference (ΔEN) of two atoms in a covalent molecule is more (generally 0.5–1.9), two different partial charges or poles like delta plus (δ^+) and delta minus (δ^-) are developed at two ends of the molecule; then both the poles together is called a **dipole**. The formation of a dipole in a covalent compound molecule having two different poles at two ends of it is called a **polar compound**. The common polar compounds are HF, H_2O , HCl,

HF molecule is the most polar covalent compound molecule; because the electronegativity difference, ΔEN is $(4.0 - 2.1) = 1.9$ which indicates the magnitude of highest polarity of all covalent compounds. Among the halogens, fluorine is the highly electronegative element and it makes the HF most polar. Polarity gradation among hydrogen halides is $HF > HCl > HBr > HI$

The least electronegative element also referred to as the most electropositive is Francium; but it is radioactive and extremely rare : so for all practical purpose, Caesium is the most electro positive element.

Remember, no compound has 100% ionic character and some diatomic elementary molecules, such as Cl_2 (g) have 0% ionic character NaCl has 80% ionic character; that is electron sharing occurs to some extent partial in every bond. An approximate relation between the partial ionic character and electronegativity difference (ΔEN) values of the bonded atoms is shown below :

Electronegativity difference, ΔEN :	0.1	0.2	0.6	0.9	1.1	1.7	2.0	2.1	3.0
Average partial ionic character :	0.5	1.0	10	19	25	50	75	80	90

The covalent compounds express partial ionic characteristics due to formation of partial positive and partial negative charges at the two ends of their molecules. Polar compounds with H-atom can form intermolecular weak bonds known as **hydrogen bond**. Molecules of H-bonded compounds remain associated and show difference in properties with other compounds. For example, partial characteristics of ionic compounds like-physical state, melting point and density etc. are shown by those compounds. The hydrides of oxygen and sulphur of group-6A or 16 are H_2O and H_2S . Here polar H_2O remains as liquid, but nonpolar

H_2S is a gas. Different acids like HCl , HNO_3 , H_2SO_4 molecules are polar. They can produce H^+ ions in aqueous solutions, and show acidic properties. Similar to NaCl aqueous solution the acid solutions can conduct electricity; and are electrolytes. The polar covalent compounds in aqueous solutions react very first like the ionic compounds react between them in aqueous solutions. But pure covalent molecules and nonpolar covalent compounds react slowly in solutions.

3.15.1 Polarization of Ions

When a positively charged cation comes close to a negatively charged anion, then the cation attracts the electron cloud of the anion towards itself. At the same time it repels the nucleus of the anion; then polarisation of ions occur.

Polarization : Due to the electron cloud attraction by the cation and its repulsion of anionic nucleus the shape of the anion is changed and its electron cloud is some what shifted towards the cation. This is called deformation or polarization of the anion by the cation. The power of cation to deform the anion is called the polarizing power of the cation.

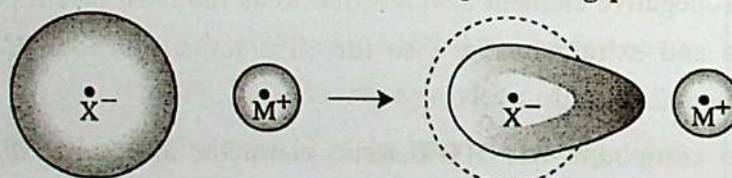


Fig -3.33 : Polarization of Anion (X^-) by Cation (M^+).

Different states of electron clouds in two ions in an ionic compound, the electron cloud deformation in polarized anion, electron cloud in polar covalent compound and pure covalent molecule are shown in following figure fig-3.34 :

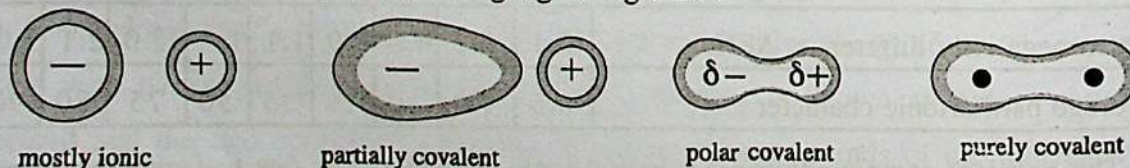


Fig-3.34 : Different states of electron clouds in different molecules.

3.15.2 Covalent Character in Ionic Compounds

Polarization of anions by cations is definitely a deviation from characteristic properties of ionic compounds. For this, with the increase of magnitude of polarization of anions, the different characteristic properties of the ionic compounds such as high melting point, high boiling point, volatility, solubility in water etc. are changed to lower magnitudes and gradually properties of covalent compounds appear. Polarization of anions are primarily

affected by some factors. These polarizing factors are known as Fajan's rules. **Fajan's rules** are as follows :

The magnitude of polarization of anions –

- (i) Increases with the increase of charges on cations and anions : it is a periodic relation.
- (ii) Increases with decrease of sizes of cations and increase of sizes of anions : it is a group relation.
- (iii) Increased by cations with non-inert gas electronic configuration $ns^2 np^6 nd^{1-10}$ than cations with inert gas electronic configuration $ns^2 np^6$.

Explanation of Fajan's rules of Anions Polarization :

Rule-1 : Higher Charge on Cation and Anion :

The polarizing power of a cation depends on the amount of positive charge on the cation.

As the charge on cation increases, the cation can attract the electron cloud of the anion more strongly towards itself and it can deform anion more.

Periodic relation : In a period polarizing power of cations increases from left to right.

For example : In a third period & polarizing power of Al^{3+} ion is more than Mg^{2+} ion, and Mg^{2+} ion has more polarizing power than Na^+ ion. So the increasing covalent character of the compounds of these cations are as follows : $Al^{3+} > Mg^{2+} > Na^+$. Since ionic compounds have high melting points and covalent compounds have low melting points, the increase of covalent character will result in the lowering of their melting points. This is clearly seen in case of chloride salts of these cations :

$NaCl$ (m.p. $801^\circ C$) $>$ $MgCl_2$ (m. p. $714^\circ C$) $>$ $AlCl_3$ (m.p. $190^\circ C$ under pressure)

(a) Cation with variable charge : If a metal atom forms several cations, then cation with lowest charge has least polarizing power and its compound shows less covalent character

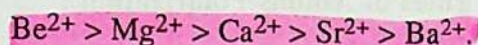
For Example : Iron forms two cations Fe^{2+} ion and Fe^{3+} ion. Here Fe^{3+} ion has higher polarizing power than Fe^{2+} ion. Hence its compounds have more covalent character. So, melting point of anhydrous $FeCl_3$ ($306^\circ C$) is less than that of anhydrous $FeCl_2$ ($670^\circ C$).

(b) High charge on anion : The tendency of the anions to be polarized increases with the increase of amount of negative charge on them. So for example nitride (N^{3-}) ion is much more polarized than oxide (O^{2-}) ion, which is again more polarized than fluoride (F^-) ion.

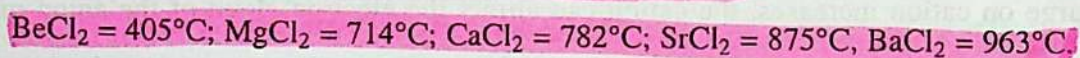
Rule 2 : Size of the Cation and Anion :

(a) **Large size of cation :** When size of cation increases, its charge density decreases and polarizing power decreases. So in a group with increase of atomic sizes, then the polarization due to different cations decreases. So covalent character of the compounds of these cations also decreases. For example the radii of divalent cations of group 2A increase from top to bottom as follows :

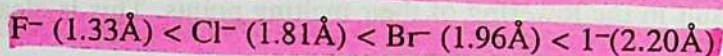
$\text{Be}^{2+} = 0.35\text{\AA}$, $\text{Mg}^{2+} = 0.66\text{\AA}$, $\text{Ca}^{2+} = 0.99\text{\AA}$, $\text{Sr}^{2+} = 1.12\text{\AA}$, $\text{Ba}^{2+} = 1.34\text{\AA}$. Hence their polarizing power decreases in the following order with the increase of their radii



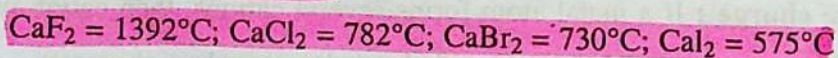
This results to the gradual restoration of ionic character and hence gradual increase of melting points of their anhydrous chloride salts is as follows :



(b) **Large size of anion :** With the increase of sizes of anions, their tendency to be polarized increases. Because as the size of anion increases, the distance between its nucleus and outermost electrons increases and hence the nucleus can attract the electrons less. So the cation can more easily deform the anion. So in any group the tendency of the anion to be polarized increases from top to bottom. For example the radii of the halide ions are as follows and their tendency to be polarized and with covalent character increases more in this order,



This is supported by the gradual decrease of melting points and increase of covalent character of calcium halides :

**Rule-3 : Electronic Configuration of the Cation :**

The polarizing power of cations with non-inert gas electronic configuration ($ns^2 np^6 nd^{1-10}$) is greater than that of cations with inert gas electronic configuration ($ns^2 np^6$). It becomes evident, when we compare the sizes of monovalent group I and II cations and the melting points of their chloride salts. The radii of Na^+ (0.95\AA) and Cu^+ (0.96\AA) are almost equal;

they have same charge (+1). But the melting point of NaCl is 801°C , and that of CuCl or Cu_2Cl_2 is 422°C , which indicates more covalent nature in Cu_2Cl_2

Student's Work-3.15 : Fajan's Rule of Polarization Based :

Problem-3.33 (a) : Melting point of CuCl is lower than that of NaCl; explain why.

[D. B. 2016]

(b) Between CaCl_2 and AlCl_3 which salt is more soluble in water; explain. [Ctg. B. 2016]

(c) Between FeCl_2 and FeCl_3 which salt has lower melting point; explain.

[Ctg. B. 2015; B. B. 2016]

(d) Among BeCO_3 , MgCO_3 and CaCO_3 what will be order of temperature for their dissociation; explain. [D. B. 2016]

(e) AgF is water-soluble but AgCl is insoluble; explain.

(f) AgCl is white but AgI is yellow; explain why.

(g) PbCl_2 is white but PbI_2 is golden yellow; explain why.

3.15.3 Ionic Potential

From Fajan's rules we know that the polarizing power of a cation increases with the increase of charge on it and decreases with its increase of radius. To compare the polarizing power of different cations, a term ionic potential is used; which is defined as :

$$\text{Ionic potential of a cation, } \Phi = \frac{\text{amount of charge on cation}}{\text{radius of cation}}$$

The higher the ionic product of a cation, the more is its polarizing power. With increase of polarizing power of cation, (i) melting point and boiling point of ionic compound decrease; it is explained in Fajan's 1st rule. Besides this, (ii) solubility of salt in water decreases; (iii) compounds become coloured; (iv) metallic carbonates dissociate at lower temperatures etc.

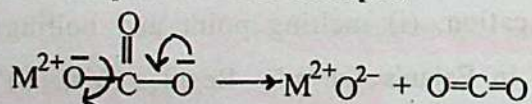
(1) **Solubility in water decreases** : Ionic compounds are soluble in water; but covalent compounds are less soluble in water or insoluble. When anion of ionic compound is more polarized, then covalent property increases in that polarized compound. With increase of size of anion it is polarised more. As a result that compound becomes less soluble in water. For example in four halides like AgF, AgCl, AgBr, AgI, the anion in AgF is less polarised. Because size of F^- ion is smallest. So AgF has more ionic character than remaining 3 halides and AgF is soluble in water; but AgCl, AgBr, AgI are water insoluble, because their anions are more polarised.

(2) **Colour of Compound** : Generally d and f block metal ions with unpaired electron become coloured. Another cause of being coloured of a compound is its more polarised anion. Oxide and sulphide ions are more polarised. So the compounds of these anions with Hg^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} etc, become more polarised and coloured like CuS , PbS , HgS are black and CdS is yellow.

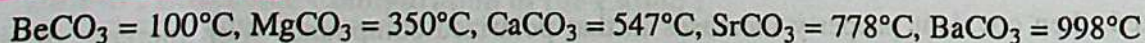
In AgF , AgCl , AgBr and AgI , the polarising power of Ag^+ ion is more. Among halide ions F^- ion and Cl^- ion are less polarised; – hence AgF and AgCl are colourless or white; Br^- ion is more polarised so AgBr is light yellow. Iodide ion (I^-) is most polarised, so AgI is deep yellow.

The cause of colour production in polarised compound is the transitional transfer of electron from anion to vacant orbital of cation. Then required energy is absorbed from visible light and the rest wave-length of visible light produces colour. Again when anion's size is small, then less polarization may occur there and more energy is required for transitional transfer of electron. For this energy with high frequency is absorbed from UV light and that compound becomes colourless. For example, AgCl is white, but AgI is yellow; HgCl_2 is white; but HgI_2 is red; PbCl_2 is white, but PbI_2 is golden yellow.

(3) **Stability of Metal Carbonate** : When ionic potential of cation is much then electron cloud of carbonate anion is more attracted by cation and anion is more polarised. Then thermal stability of that metal carbonate decreases and dissociates to metal oxide and CO_2 gas with less amount of heat at lower temperature. For example,



The ionic potential of group-2 metal ions (M^{2+}) decreases with increase of their sizes in the group downwards; such as, $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. So thermal stability of those metal carbonates increase in same order. So their dissociation temperatures increase gradually. For example,



3.15.4 Diagonal Relationship of the Elements

The properties of the elements of different groups of 2nd period of the periodic table, show more similarities with the properties of right side elements of different groups of 3rd period diagonally. The diagonal similarity in properties of two elements of two groups of 2nd and 3rd periods is known as diagonal relationship of elements.

Group-1 (or. 1A) element Li of 2nd period shows many similarities with group-2 (or, 2A) element Mg of 3rd period. Similarly Be shows similar properties with Al and B shows similar properties with Si. They are related as follows :

Group	: 1	2	3	4
2nd period	: Li	Be	B	C
3rd period	: Na	Mg	Al	Si

Causes of similarities between diagonally related pair of elements : **Li and Mg; Be and Al; B and Si.**

(1) Ionic radius : Each pair of elements have closely equal ionic radii. Example;

$\text{Li}^+ = 0.068 \text{ nm}$ and $\text{Mg}^{2+} = 0.078 \text{ nm}$; $\text{Be}^{2+} = 0.034 \text{ nm}$ and $\text{Al}^{3+} = 0.050 \text{ nm}$.

(2) Ionisation energy : Each pair of elements have closely equal ionisation energy.

Example; I. P. of Li and Mg are 520 kJ mol^{-1} and 738 kJ mol^{-1} ,

Similarly I.P. of Be and Al are 899 kJ mol^{-1} and 578 kJ mol^{-1} respectively.

(3) Electronegativity : Each pair of elements have closely equal electronegativity.

Electronegativity of Li, Mg are 1.0 and 1.2 respectively. That of Be, Al are 1.5 and 1.5.

(4) Polarisation power : Their polarisation power are very close to each other.

(5) Ionic charge density : Their ionic charge density are very near to each other.

Worked Example- 3.13 :

[D. B. 2016]

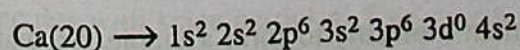
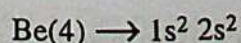
Element \rightarrow	D	E	G	
Valence electron \rightarrow	ns^2	$(n+1)s^2$	$(n+2)s^2$	$n=2$

(a) Of the given stem, ionization energy of G is less than that of D element; explain why.

(b) Which of the compounds DCO_3 , ECO_3 , GCO_3 has lowest dissociation temperature; explain.

Solution : (a) Explanation for lower ionization energy of G than D :

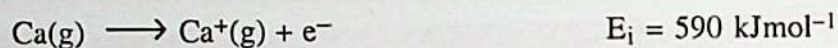
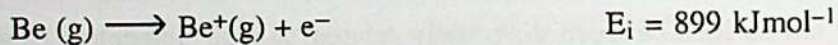
As per stem, 'D' having valence electrons ns^2 or, $2s^2$ is Be(4) atom and 'G' having valence electrons $4s^2$ is Ca (20) atom. Both are group-2 elements. Their electron distributions are :



Be or D is 2nd period element and Ca or G is 4th period element. From group based relation with the increase of atomic number the ionization energy of element decreases.

Here the valence electrons of 2nd period element Be is more attracted by its nucleus. So in gaseous state to convert 1 mole Be atoms into 1 mole Be^+ ion by removal of 1 mole electrons, more energy is required.

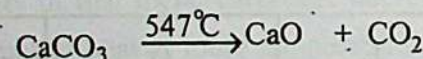
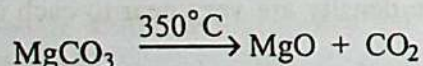
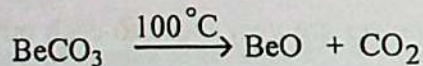
On the otherhand, the valence electron of 4th period element Ca is attracted comparatively less by its nucleus. So in gaseous state to convert 1 mole Ca atoms into 1 mole Ca^+ ion by removal of 1 mole electrons comparatively less energy is required.



Solution : (b) Explanation for thermal dissociation temp. of DCO_3 , ECO_3 , GCO_3 :

As per stem, D is Be (4), E is Mg (12) and G is Ca (20). So the corresponding carbonates are BeCO_3 , MgCO_3 and CaCO_3 . Here Be, Mg, Ca are group-2 elements and the ionic potential of these metal ions decreases downwards in group -2.

Hence ionisation potential is in order $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$. So thermal stability of their carbonates increases in same order; i. e. their stability is $\text{CaCO}_3 > \text{MgCO}_3 > \text{BeCO}_3$. Here dissociation temperature of BeCO_3 is minimum and that of CaCO_3 is maximum.



Practical

Students' Work in the Laboratory

3.16. Name of Expt : To prove the presence of Dipole in Water Molecule

Expt. No. – 12

Date :

Time : 1 Period

Principle : Water is a polar covalent compound molecule. Electronegativity value of oxygen atom is 3.5 and that of hydrogen atom is 2.1; the difference of electronegativities (ΔEN) of two bonded atoms is $\Delta\text{EN} = (3.5 - 2.1) = 1.4$ which is in between the range of 0.5–1.9, the necessary condition for a covalent molecule to form a dipole. So water molecule has a dipole. Hence water molecules are attracted by unlike charged plastic rods and repelled by carboxylate ion like stearate ions of soap water.

Required Substances : (1) One big beaker and one small beaker, (2) Small amount of powdered spice like powdered red pepper or turmeric, (3) Hand wash liquid soap. (4) Two match sticks, (5) water.

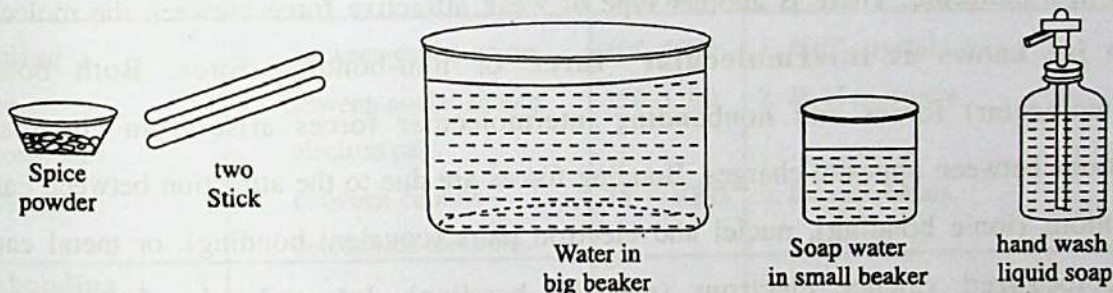


Fig- 3.35 : Experiment to prove the presence of dipole on water molecule

Procedure :

- (1) Pour water into the big beaker as per fig -3.35.
- (2) Scatter or disperse some turmeric or red pepper powder on surface of water taken in big beaker. Note, fine powder of this spices float on the water surface and the heavy particles settle at the bottom in the beaker.
- (3) Now make soap solution in small beaker on adding small amount of hand wash liquid soap in water.
- (4) Take one match stick and dip it into soap water partly to wet. Now dip that wet match stick partly in water layered with spices powder.

Now observe whether any movement of powdered spice layer on water surface occurs.

Observation : (a) As soon as you dip the soap-water wetted stick, you can see the spice-particles are moving apart on the water surface.

(b) Now take the second match stick in left hand and dip directly half of it into spice layered water. Here observe the spice layered does not move apart.

(c) Then keep the second stick deeping as before; Wet the first stick in soap water again and dip it in spice-water. Now observe the spice-layer is moving apart from the soap water wetted stick.

Conclusion : The negative carboxylate stearate ions of the soap repel the negative poles of water molecules with spice particles. This practical observation proves that water is a polar compound, that is water has dipole or partially positive pole and partially negative pole

3.17 Vander Waals Force : Inter Molecular Force

We know chemical bonding forces are **intramolecular forces** i.e. forces between the atoms in a molecule. There is another type of weak attractive force between the molecules, which is known as **intermolecular force** or non-bonding force. Both bonding (intramolecular) forces and nonbonding intermolecular forces arise from electrostatic attractions between opposite charges. Bonding forces are due to the attraction between cations and anions (ionic bonding), nuclei and electron pairs (covalent bonding), or metal cations and delocalized valence electrons (metallic bonding). Intermolecular forces, on the otherhand, are due to the attraction between molecules as a result of partial charges, or the attraction between ions and molecules. The two types of forces differ in magnitude, and Coulomb's law explains why :

- * Bonding forces or intra molecular forces are relatively strong enough because they involve large charge that are closer together.
- * Intermolecular forces are relatively weak enough because they typically involve smaller charges that are farther apart.

Besides bonding forces or intramolecular forces, all types of other forces acting on molecules are generally called **intermolecular forces** which generally refer to interactions among all kinds of particles, including molecules, ions and atoms.

Intermolecular forces as a whole are usually called **Vander Weals forces** after the Dutch scientist Jahannes Vander Waals (1837–1923). Although the attraction between nonpolar gaseous covalent molecules was meant by Vander Waals force at first. Now all types of nonbonding forces are discussed under Vander Waals forces. **Intermolecular forces are of several types such as :**

(1) ion-dipole forces (2) hydrogen bonds, (3) dipole -- dipole forces (4), ion-induced dipole forces, (5) dipole-induced dipole forces, (6) London dispersion forces.

All these intermolecular forces are electrostatic in origin and result from the mutual attraction of unlike charges or the mutual repulsion of like charges. In the table-3.7, the magnitude of different types of bonding attractions and non-bonding attraction are shown with their sources and examples :

Table – 3.7 : Comparison of Bonding and Nonbonding (intermolecular) forces :

Effective forces	Basis of attraction	Energy kJ/mol	Example
Bonding : 1. Ionic : 2. Covalent : 3. Metallic:	1. between cation-anion 2. between nuclei-shared electron pair. 3. between cations–delocalized electrons.	400–4000 150–1100 75 – 1000	1. NaCl crystal. 2. H–H molecule. 3. Fe and metals.
Nonbonding : 1. Ion–dipole :	1. ion charge–dipole charge	10 – 50	$\text{Na}^+ \cdots \delta^- \text{O} \begin{matrix} \delta^+ \text{H} \\ \delta^+ \text{H} \end{matrix}$
2. H-bonds :	2. polar bond to H–dipole charge [high EN of N, O, F]	10– 40	$\delta^+ \text{H} - \delta^- \text{O} \cdots \delta^+ \text{H} - \delta^- \text{O} \delta^+$
3. Dipole – dipole :	3. dipole charges	3 – 4	$\delta^- \text{Cl} - \delta^+ \text{I} \cdots \delta^- \text{Cl} - \delta^+ \text{I}$
4. Ion–induced dipole	4. ion charge-polarizable electron cloud	3 – 15	$2+ \text{Fe} \cdots \text{O}_2$
5. Dipole–induced dipole	5. dipole charge – polarizable e^- cloud	2 – 10	$\delta^+ \text{H} - \delta^- \text{Cl} \cdots \text{Cl} - \text{Cl}$
6. Dispersion force [London force]	6. polarizable e^- cloud	1 – 10	6. $\text{F}-\text{F} \cdots \text{F}-\text{F}$

On the basis of sources, Vander Waals forces are of two types; such as;

(a) Permanent dipole – Induced dipole forces, (b) Dispersion or London forces.

(1) Ion–Dipole Forces

When an ion and a nearby polar liquid molecule (dipole) attract each other, an ion-dipole force results. The most common and important example takes place when an ionic compound like NaCl dissolves in water. The positive and negative ions of NaCl are separated because the attractions between the ions and the oppositely charged poles of the H_2O molecules overcome the attractions between the ions themselves. The magnitude of the interaction energy (E) depends on : (i) the charge on the ion, Z; (ii) on the strength of the dipole as measured by its dipole moment, μ ; and (iii) on the inverse square of the distance, r from the ion to the dipole:

$E \propto \frac{\mu}{r^2}$. Again, dipole moment, $\mu = Q \times r$; here Q = electron charge (1.6×10^{-19} C, r = distance between opposite charges in meter unit); the unit of dipole moment (μ) is debye (D); $1D = 3.336 \times 10^{-30}$ coulomb meters (C.m).

The measure of net molecular polarity is a quantity called the dipole moment (μ , Greek μ), which is defined as the magnitude of the charge Q at either end of the molecular dipole times the distance ' r ' between the charges: $\mu = Q \times r$.

(2) Dipole– Dipole Forces

The partial opposite charges or poles like delta plus ($\delta+$) and delta minus ($\delta-$) developed on two ends of a covalent compound containing highly electronegative elements (F, Cl, O, N), is called **dipole**. Dipoles are of two types; such as **permanent dipole** and **temporary dipole**. The molecules with permanent dipoles are HF, HCl, H_2O , NH_3 etc.

Neutral but polar molecules experience dipole– dipole forces as the result of electrical interactions among dipoles on neighbouring molecules. The forces can be either attractive or repulsive, depending on the orientation of the molecules, and the net force in a large collection of molecules is a summation of many individual interactions of both types. The forces are generally weak, with energies on the order of 3–4 kJ/mol, and are significant only when molecules are in close contact.

The strength of a given dipole–dipole interaction depends on the sizes of the dipole moments involved. The more polar the substance, the greater is the strength of its dipole–dipole interactions. For example, butane is a nonpolar molecule with a molecular mass of 58 amu and a boiling point of -0.5°C , while acetone has the same mass; yet it boils at 57°C ; Which is higher because it is polar. Several substances with similar molecular masses but different higher dipole moments, generally have higher boiling points (table– 3.7)

Table–3.7 : Comparison of molecular masses, dipole moments (D), and boiling points of Compounds.

Substances	Mol. mass (amu)	Dipole moment (D)	B. P. (K)
1. $CH_3CH_2CH_3$ (propane)	44	0.08	231
2. CH_3OCH_3 (methoxy methane)	46	1.30	248
3. CH_3Cl (chloro methane)	50.5	1.90	249

(A) **Vander Waals Force** : The force of attraction among the molecules of non polar covalent compounds is known as Vander Waals force. Vander Waals force is very weak, much weaker than covalent bond and even weaker than dipole–dipole interaction. For example the strength of covalent bond in O_2 molecule is 402 kJ mol^{-1} , while the strength of Vander Waals force in solid oxygen is about 7 kJ mol^{-1} .

Again based on the origin, Van der Waals force is divided into two types – (i) Forces between permanent dipole and induced dipole and (ii) Dispersion force or London forces

(3) **Permanent Dipole–Induced Dipole Forces** : When the positive end of a dipole comes near to a nonpolar molecule it attracts the electron cloud of the nonpolar molecule towards itself. Then at that end a partial negative charge is formed and a partial positive charge at other end. The formation of such induced dipoles is known as **polarization**. The near ends of permanent dipole and the induced dipole, being of opposite charge, then they attract each other.

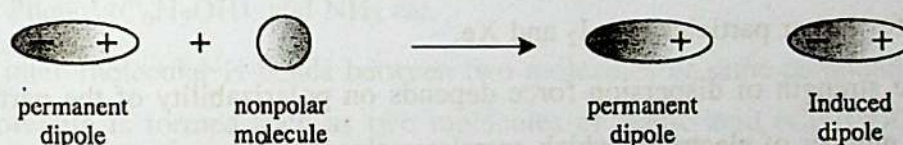


Fig. 3.36 : Permanent dipole and induced dipole forces

(4) **Dispersion force or London force** : Since the electrons are continuously moving in an atom or molecule the dispersion of electron cloud in any atom or molecule cannot be equal at all points at all moments. At some instance the concentration of electron cloud becomes high at one end and then a partial negative charge is developed at this end. So at the other end the concentration of electron cloud becomes low and a partial positive charge is developed at that end. Thus the molecule or atom becomes a dipole, which is transient. Due to this dipole, the adjacent molecules are also induced and they become also dipoles. The positive end of one dipole attracts the negative end of another dipole. This type of attraction is known as **dispersion force** or **London force** named for Fritz London, the physicist who explained the quantum-mechanical basis of attraction.



Fig 3.37 : Origin of dispersion force

For the dispersion force, there is a relation between the molecular mass and boiling point of similar types of substances. As the molecular mass increases, the number of electrons in the molecule also increases and hence the attraction due to dispersion force also increases. Therefore the boiling point also increases. For example, among the halogens the molecular masses increase in the order $F_2 < Cl_2 < Br_2 < I_2$ and their boiling points increase in the same order. Therefore F_2 and Cl_2 are gases at room temperature, but Br_2 is a liquid and I_2 is a solid.

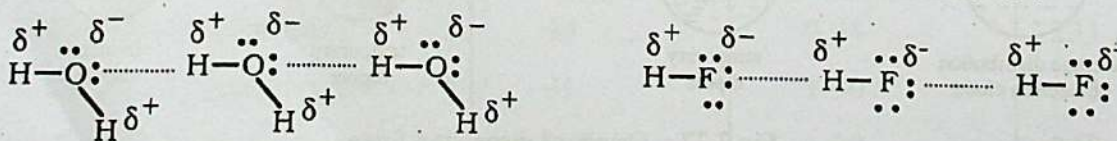
Dispersion force is the dominant intermolecular force. Calculations show, for instance, that 85% of the total energy of attraction between HCl molecules is due to dispersion forces and only 15% is for dipole-dipole forces. Even for water, estimates indicate that 75% of the total energy of attraction comes from the strong H-bonds and nearly 25% from dispersion force. Dispersion forces are very weak for small particles like H_2 , He (helium) molecules but much stronger for larger particles like I_2 and Xe.

The relative strength of dispersion force depends on polarizability of the particle, which depends on the number of electrons, which correlates closely with molar mass.

3.18 Hydrogen Bond

A special type of dipole-dipole force arises between molecules that have an H atom bonded to a small, highly electronegative atom with lone electron pairs. The most important atoms that fit this special type of force are N, O and F. The H-N, H-O, and H-F bonds are very polar, so electron density is withdrawn from H. As a result, the partially positive H of one molecule is attracted to the partially negative lone pair on N, O, F of another molecule, and a hydrogen bond (H-bond) forms.

Definition : A hydrogen bond is defined as an weak attractive force between a partially positive hydrogen atom of H-N, H-O, H-F bond and an unshared electron pair on another highly electronegative small atom (N, O, F). Three examples of H-bonds forming in molecules are NH_3 , H_2O and HF. Here H-bond is shown as dotted line as follows :



Two conditions for H-bonding :

The small sized N, O or F atoms are essential to form H-bonding for two reasons :

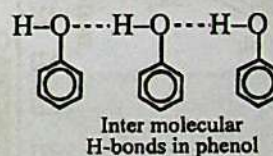
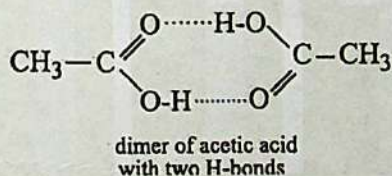
- (★) These electronegative atoms polarise covalently bonded H atom partly positive.
- (★) The lone pair on N, O or F atom can come close to the polar H atom to form H-bond.
- (★) Gradational strength of H bond is $H \cdots F > H \cdots O > H \cdots N$.

(★) One HF molecule can form two H-bonds between two HF molecules. But one H_2O molecule form four H-bonds with adjacent four H_2O molecules. H_2O molecules remain as associated molecules more. So HF has boiling point $19.5^\circ C$, and remains as gas at room temperature ($25^\circ C$). But more associated H_2O molecules require more heat energy to break their H-bonds. Hence boiling point of water is $100^\circ C$ and water remains as liquid at $25^\circ C$.

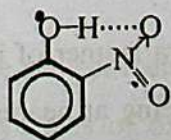
H-bonds are of two types : (i) Inter-molecular H-bond and (ii) Intra molecular H-bond.

(1) Inter-molecular H-bond occurs between two or more molecules like HF, H_2O , alcohol (CH_3OH), Phenol (C_6H_5OH), and NH_3 etc.

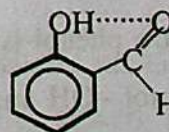
When inter-molecular H-bonds between two molecules of same compound occurs, then a **dimer molecule** is formed such as two molecules of acetic acid (CH_3COOH) can form a dimer by two H-bonds between two $-COOH$ groups.



(2) Again in a single molecule intra molecular H-bond can form between two different functional groups forming a ring also. For example, in ortho nitro phenol and ortho hydroxy benzaldehyde intra-molecular H-bond can form. In ortho nitro phenol H-bond occurs between $-OH$ and $-NO_2$ groups forming a ring with a single H-bond. Again in ortho hydroxy benzaldehyde H-bond occurs between $-OH$ and $-CHO$ groups forming a ring with a single H-bond.



Intra molecular H-bond
in ortho nitro phenol



Intra molecular H-bond
in ortho Hydroxy benzaldehyde

Influence of H-bond on physical property of compounds : There is differential influence of H-bond on physical properties like melting point (m.p) and boiling point (b, p) of hydrides of same group elements. Generally m.p and b.p of hydrides of same group elements increase gradually downwards with the increase of their molecular masses. Because with increase of mass of the molecules, dispersion force or London force increases.

It is supported by the different hydrides of group-14 (4A) elements (fig-3.38) such as $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$. But in group-15(5A), 16 (6A), 17 (7A), there are exceptions for the hydrides of 1st element like NH_3 , H_2O and HF of N, O and F. The cause of differences is the presence of active intermolecular H-bonds which increases inter-molecular attraction. So m.p and b.p of NH_3 , H_2O and HF become more than m.p and b.p of other hydrides of the same group elements. (fig. 3.39)

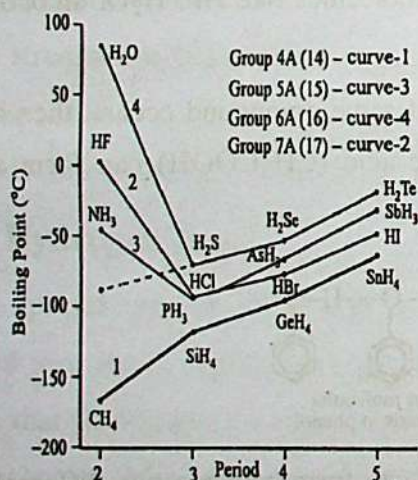


Fig-3.38 : Graph of b.p of hydrides of group-14(4A)-17(7A) Elements Versus Periods.

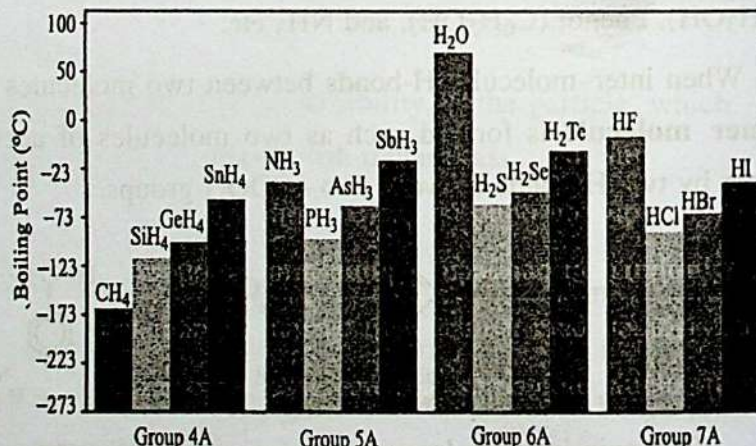


Fig-3.39 : Column graph of b.p of hydrides of group -14 (4A) -17(7A) Elements Versus Groups.

Similarly, due to intra-molecular H-bond a new ring is formed in aromatic organic molecule, it is known as **Chelation** (pronounced as key-lation). As a result, m.p and b.p of ortho-isomers of aromatic organic compounds becomes lower than m.p and b.p of para isomers. For example,

The m.p of ortho-nitro phenol is 45°C, but m.p of para isomer of it is 114°C. The reason is that in ortho-nitrophenol -OH and -NO₂ groups are being at nearest positions in benzene ring like at 1: 2 positions, both the groups are close enough to form intra-molecular H-bond and remain as separate molecules with lower inter molecular force. On the otherhand in para

nitro phenol $-\text{OH}$ and $-\text{NO}_2$ groups are being at far apart in benzene ring like at 1: 4 positions, so intramolecular H-bond is not possible, but can form inter-molecular H-bonds among many molecules and get associated as cluster-molecules. Hence in comparison to ortho- isomer, para-isomer with cluster-molecules, has higher m.p and b.p.

Comparison between H-bond and Covalent bond :

(i) Hydrogen bond is electrostatic in nature and a weak type bond. The magnitude of H-bond remains in between 10–40 kJ/ mol. On the otherhand, the magnitude of covalent bond energies is many times more of the energy of H-bonds. The magnitude of covalent bond remains in between 150–1100 kJ/mol.

(ii) Due to the presence of H-bonds, many changes occur in properties of covalent bonded compounds. So H-bond is important to explain and determine the different properties of covalent compounds.

Comparison between H-bond and Vander Waals forces :

The magnitude of H-bond remains in between 10–40 kJ/mol. On the other hand, the other non-bonding Vander Waals forces such as ion-dipole forces remains in between 10–50 KJ/mol and different types of dipole– induced dipole forces vary in between 2–10 kJ/mol and the magnitude of dispersion forces are 1–10 kJ/mol.

Students' Work :

3.19 Comparison Among Bonds in H_2O , H_2S , H-bond and Vander Waals Force

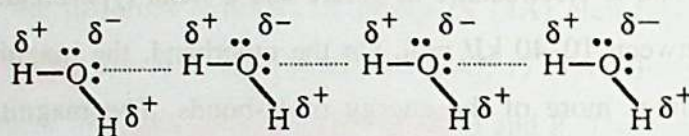
Guide line : The comparison is to be done on the basis of following three points; such as :

- (1) H_2O and H_2S are the hydrides of O and S of Group-16 (6A). So according to group properties relation, both the hydride have similar physical and chemical properties.
- (2) Actually H_2O is a liquid and H_2S is a gas. For the explanation of this difference, the presence and absence of H-bond in them is to be considered.
- (3) Finally explain the affect of H-bond and Vander Waals force on determination of physical states of them.

On the basis of above subject matters, the explanation follows :

H_2O and H_2S are hydrides of oxygen and sulphur of group-16; hence there should be similarities between these two hydrides according to group relation in physical states. But due to difference in electronegativities between these two atoms, H_2O molecule is polar and H_2S is

nonpolar. The difference in electronegativity value of O and H atoms is $(3.5 - 2.1) = 1.4$, which lies in the range of 0.5– 1.7, the necessary condition of electronegativities difference (ΔEN) value for a covalent compound, to be a polar compound. On the otherhand the difference of electronegativities of H and S atoms is $(2.5 - 2.1) = 0.4$, which follows the condition to be a nonpolar covalent compound. Hence polar H_2O molecules can form H-bonds among themselves; but non-polar H_2S molecules can not form H-bonds.



Due to the formation of H-bonds, H_2O molecules become associated and close up to decrease intermolecular distance. Hence water molecules remain in liquid state. On the otherhand, H_2S molecules remain separately as single molecules in gaseous state. Then except H-bond, other Vander Waals forces are present in H_2S gaseous molecules.

Now, comparison between H-bond and Vander Waals force in magnitude will be done. **The magnitude of H-bond is 10–40 kJ/mol.** It is maximum in HF molecules. After HF, the next higher value is for H_2O . On the otherhand, other Vander Waals forces, except H-bond, such as dispersion forces are present in H_2S molecules. The magnitude of dispersion forces lies in between 1– 10 kJ/mol.

Worked Example–3.14 : Identifying Intermolecular Forces based :

Identify the likely kinds of intermolecular forces in the following substances :

- (a) HCl, (b) CH_3CH_3 , (C) CH_3NH_2 , (d) Kr

Strategy : Know the structure of each molecule and then decide what intermolecular forces are present. All molecules have dispersion forces; polar molecules have dipole-dipole forces; and molecules with H-N, H-O, or H-F bonds have H bonds.

Solution : (a) HCl is a polar molecule but cannot form H-bond. It has dipole-dipole forces and dispersion forces.

(b) CH_3CH_3 is a nonpolar molecule and has only dispersion forces.

(c) CH_3NH_2 is a polar molecule that can form H-bonds. It has also dipole forces and dispersion forces.

(d) Kr is nonpolar and has only dispersion forces.

Students' Work - 3.16 : H-bond Based :**Problem-3.34 :** What is H-bond?

[D. B. 2015]

Problem-3.35 : H_2O is liquid; but H_2S is a gas. explain?

[Ctg. B. 2016; J.B. 2016; D. B. 2015]

Problem-3.36 : (a) Physical states of H_2O and CO_2 are different at room temperature; explain why.

[Syl. B. 2015]

Problem-3.36 : (b) Between ortho-nitrophenol and para-nitrophenol which has more melting point; explain?

[C. B. 2015]

Problem-3.36 : (c) At room temp. H_2O is liquid; but HF is gas; explain why. or, Boiling point of HF (19.5°C) is lower than boiling point of water, (100°C); explain why.

[J. B. 2017]

Problem-3.37 : Among the substances Ar , Cl_2 , CCl_4 and HNO_3 , which has :-

- (a) The more dipole-dipole force?
- (b) The more hydrogen bond force?
- (c) The less dispersion force?

Problem-3.36 : Identify the nature of intermolecular forces present in the following molecules, and rank the molecules in order of increasing boiling point.(a) H_2S (34 amu), (b) CH_3OH (amu), (c) C_2H_6 (amu), (d) Ar (40 amu).

3.20 Importance of H-Bonds

Do you know, the hydrogen bond has a profound impact in biological systems and plays an enormous important roles for the existence of life on earth.

They cause water to be a liquid rather than a gas at ordinary temperatures. The H-bond is a principal feature in the structures of the three major biopolymers such as : proteins, nucleic acids, and carbohydrates. Some important roles of H-bonds are pointed out below :

(i) About 70% of our body weight is water. Without liquid water, cellular constitution and their preservation of living beings is not possible at all. Due to the presence of H-bonds in water molecules, the liquid state of water is possible.

(ii) Carbohydrates and proteins are the principal foods which supply energy in our body. The first compounds contain electronegative atom O and the second compounds contain O, N atoms. So in those molecules, H-bonds play an important role.

(iii) Different organs of a living body such as skin, tissue, blood, hair and bones etc. contain proteins in which H-bonds exist to play proper functions in every case. In addition, H-bond is responsible for the action of many enzymes, the tertiary proteins that speed all metabolic reactions.

Students' Work :**The importance of H-bonds :**

Key Concept : Students can explain the importance of H-bonds for the existence of life on earth.

'Existence of Life on earth' means the survival of plant kingdom and animal kingdom. On this consideration, the importances of H-bonds will be discussed including the following topics :

(i) Plant and animal bodies are formed with plant cells and animal cells as their constitutional units respectively.

(ii) For restoration of life, every living body needs essential foods.

(iii) Next to food, every man needs clothes to wear, house to live, medicine for diseases, many other things for education and in every day's life.

With these three points, the importances of H-bonds are discussed as follows :

(1) **Life on Earth :** The origin and existence of life on this earth is fundamentally dependent on 'liquid water' as a constitutional compound. There is no existence of life on those planets which are devoid of water. Hence the maxim, 'water is life' Water molecules are associated with H-bonds. For this reason, water remains in liquid state. With this liquid water, the plant and animal kingdoms were originated and have been continuing their existences from the endless time. So the importance of H-bonds is associated with the chemistry of life on this earth.

(2) **H-bond in Protein Chain :** Body structure of any living being is made of 'unit cell' which is formed of proteins. Proteins are the natural biopolymers made of amide bonds among different amino acids, having general formula $R-CH(NH_2)COOH$. The important H-bonds are present in secondary and tertiary proteins' chains as follows :

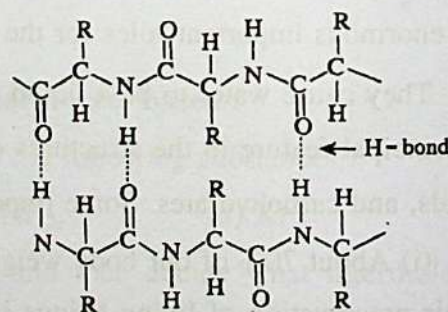


Fig. 3.40 : H-bonds in secondary protein chains.

(3) **H-bonds in Liquid Water :** We know that when any liquid freezes to solid, then its volume decreases and its density increases generally. But in case of water, at lower temperature liquid water freezes to solid ice; here density of ice decreases. Then ice floats on water. Here exists the important role of H-bonds among the water molecules. In the structure of a piece of ice, all the water molecules remain associated with maximum numbers of H-bonds among themselves. Two H-bonds are present in each of the water molecules binding other two water molecules.

Then void space remains in the crystalline structure of ice. Thus the volume of ice increases and its density lowers than that of water from which ice is formed.

At this stage ice floats on water and at lower the ice the residual water remains as liquid. For this reason, in the large cold polar regions of earth, aquatic beings can survive in all lakes, ponds and rivers etc.

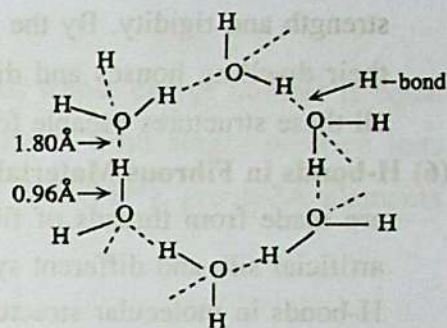


Fig-3.41 : H-bonds in crystalline ice piece

(4) **H-bonds in DNA, RNA** : The nucleus of an animal cell contains genetic components two nucleic acid DNA and RNA; [DNA = deoxyribonucleic acid; RNA = Ribonucleic acid.] Double-helix of two chains of nucleic acids are joined by the H-bonds between base-pair of the two chains. Base-pairs are adenine-thymine (A-T) form two H-bonds and base pairs guanine-cytosine (G-C) form three H-bonds. With these H-bonds, double helix of nucleic acids get their stability.

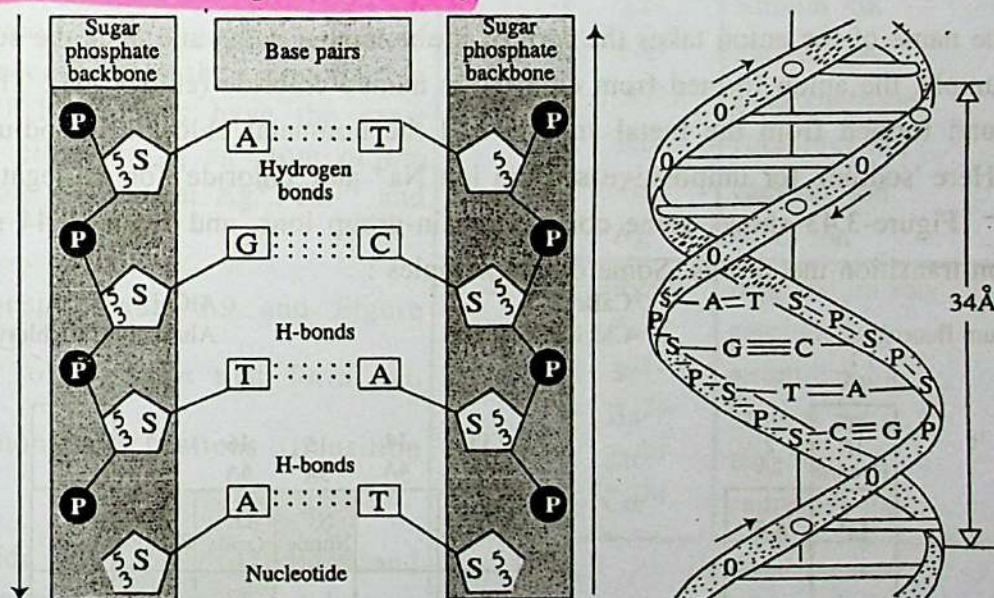


Fig. 3.42 : Chemical symbolic structure of DNA. Double helix model of DNA (with.....H bond)

Two H-bonds between adenine-thymine (A-T) and
three H-bonds between guanine-cytosine (G-C)

Here, S = deoxyribose sugar, P = phosphate, A = adenine, G = guanine T = thymine, C = cytosine

(5) **H-bonds in Glucose Polymers** : Cellulose and starch are polysaccharides of glucose monomer. Cellulose is the body construction material for plants and starch is the major source of energy for plants and animals. In these glucose polymers' chains electronegative oxygen atom forms H-bonds. Due to H-bonds, cellulose fibres get

strength and rigidity By the use of strong and rigid body structure of plant, men prepare their dwelling houses and different useable furnishers. The strength of H-bonds makes all these structures useable for the people living on earth.

- (6) **H-bonds in Fibrous Materials** : The various clothings used by civilized men and women, are made from threads of fibrous natural and synthetic materials such as cotton, wool, artificial silk and different synthetic fibres. The strength of threads is due to presence of H-bonds in molecular structures of the natural polymers.

Thus for the existance of life on earth, presence of H-bonds in all the components related to life play an unparallel and unique role.

3.21 Nomenclature of Inorganic Compounds

(A) Binary Ionic Compounds :

Binary ionic compounds are those compounds of ions of two elements. Ionic compound contains positive ion or cation and negative ion or anion.

* The name of the cation is the same as the name of the metal. Many metal names end in '-ium'.

* The name of the anion takes the root of the nonmetal name and adds the suffix '-ide'. For example, the anion formed from chlorine is named chloride (chlor+ ide). Therefore, the compound formed from the metal sodium and the nonmetal chlorine is sodium chloride, NaCl. Here 'sodium' for unipositive sodium ion Na^+ and 'chloride' for uninegative chloride ion Cl^- . Figure-3.43 shows some common main-group ions, and Figure-3.44 shows some common transition-metal ions. Some other examples :

LiF
Lithium fluoride

CaBr_2
Calcium bromide

AlCl_3
Aluminium trichloride

1 1A							18 8A
Hydride	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	
H^+ H^-				N^{3-} Nitride	O^{2-} Oxide	F^- Fluoride	
Li^+	Be^{2+}	Al^{3+}			S^{2-} Sulfide	Cl^- Chloride	
Na^+	Mg^{2+}	Ga^{3+}			Se^{2-} Selenide	Br^- Bromide	
K^+	Ca^{2+}	In^{3+}	Sn^{2+} Sn^{4+}		Te^{2-} Telluride	I^- Iodide	
Rb^+	Sr^{2+}	Tl^+ Tl^{3+}	Pb^{2+} Pb^{4+}				
Cs^+	Ba^{2+}						

Fig-3.43 : Main group cations and anions. A cation bears the same name as the element it is derived from. An anion name has an '-ide' ending.

(*) Here are some points to note about ion formulas :

- (1) **Main group metals usually form cations or positive ions** whose charge number is equal to the group number. For example, group-1A all elements form singly positive ions (M^+), group 2A elements form doubly charged positive ions (M^{2+}), group-3A elements form triply charged positive ions (M^{3+}).

[Exception in group-4A elements Sn^{2+} , Sn^{4+} , Pb^{2+} , Pb^{4+} .]

- (2) **Main-group non-metals usually form anions** Whose charge number is equal to the group number minus eight. For example S is a group-6A element, so S forms doubly charged negative ion $(6-8) = -2$; so this sulphide or sulfide ion is written as S^{2-} . Similarly group-7A elements form singly charged negative ions $(7-8) = -1$ such as F^- , Cl^- , Br^- , I^- . But group - 8A elements form no anion at all $(8-8) = 0$.

Table -3-8 : Common Monatomic ions.

Charge	Formula	Name
Cations : 1+	H^+	hydrogen ion
	Li^+	lithium ion
	Na^+	sodium ion
	K^+	potassium ion
	Rb^+	rubidium ion
	Cs^+	caesium ion
	Ag^+	silver ion
2+	Mg^{2+}	magnesium ion
	Ca^{2+}	calcium ion
	Sr^{2+}	strontium ion
	Ba^{2+}	barium ion
	Zn^{2+}	zinc ion
	Cd^{2+}	cadmium ion
3+	Al^{3+}	aluminium ion
Anions: 1-	H^-	hydride ion,
	F^-	fluoride ion
	Cl^-	chloride ion,
	Br^-	bromide ion
	I^-	iodide ion

* * Here are some suggestions about how to learn names and formulas :

(1) Memorize the monatomic ions of Table-3.8 according to their positions in Figure-3.30 These ions have the same number of electrons as an atom of the nearest noble gas except Ag^+ , Zn^{2+} and Cd^{2+} ions.

(2) Consult Table-3.9 and Figure - 3.44 for some metals that form two different monatomic cations (transition metal ions).

3. Divide the tables of names and charges into smaller batches, and learn a batch each day. Try flash cards, with the name on one side and the ion formula on the other.

(4) All ionic compound names give the positive ion (cation) first and the negative ion (anion) second.

(5) On writing formula of an ionic compound, the positive charges of the cations must balance the negative charges of the anions; so the compound has zero net charge.

For example, calcium bromide is composed of Ca^{2+} ions and Br^- ions; therefore two Br^- ions balance each Ca^{2+} ion. So its formula is CaBr_2 . In this and all other formulas –

2–	O^{2-} S^{2-}	oxide ion, sulfide ion
3–	N^{3-}	nitride

* The subscript refers to the element preceding it.

(*) The subscript 1 is understood from the presence of the element symbol (that is we donot write $\text{Ca}_1 \text{Br}_1$).

(*) The charge without the sign of one ion becomes the subscript of the other. Again reduce the subscripts to the smallest whole numbers that retain the ratio of ions. Thus, for example, from the ions Ca^{2+} and O^{2-} we have Ca_2O_2 , which we can reduce to the formula CaO

Exception : Compounds of mercury (I) ion such as Hg_2Cl_2 and peroxides of the alkali metals such as Na_2O_2 .

(6) Notice in both Figures 3.43 and 3.44 that some metals form more than one kind of cation. For example, iron forms both the doubly charged Fe^{2+} ion and triply charged Fe^{3+} ion. In naming these ions, in modern IUPAC system, we distinguish between them by using a Roman numeral in parentheses to indicate the number of positive charges.

3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 9B	10 10B	11 11B	12 12B
Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{2+} Cr^{3+}	Mn^{2+}	Fe^{2+} Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^+ Cu^{2+}	Zn^{2+}
Y^{3+}					Ru^{3+}	Rh^{3+}	Pd^{2+}	Ag^+	Cd^{2+}
									Hg^{2+}

Fig-3.44 : Common transition-metal ions that exist in aqueous solutions are shown.

Thus FeCl_2 is named iron (II) chloride and FeCl_3 is iron (III) chloride. In older common name method they are named as ferrous chloride (FeCl_2) and ferric chloride (FeCl_3); here naming is done by using latin name of the element together with the ending '–ous' for the ion with lower charge and '–ic' for the ion with higher charge; (Table-3.9)

Table-3.9 : Transition metal ions in 'systematic name' and older 'common name'.

Ion	Systematic name (IUPAC)	Common name
Cr^{2+}	Chromium (II) ion	Chromous ion
Cr^{3+}	Chromium (III) ion	Chromic ion
Fe^{2+}	Iron (II) ion	Ferrous ion
Fe^{3+}	Iron (III) ion	Ferric ion
Cu^{+}	Copper (I) ion	Cuprous ion
Cu^{2+}	Copper (II) ion	Cupric ion

Worked Example – 3.15 : Naming Binary Ionic Compounds Based :

Give systematic names for the following compounds :

- (a) BaCl_2 (b) CrCl_3 , (c) PbS_2 , (d) Fe_2O_3

Strategy : Calculate the number of positive charges on each cation by counting the number of negative charges on the associated anion(s). Confirm from Figure-3.43 and 3.44, if you are unsure.

Solution :

- (a) BaCl_2 : Barium chloride : (a) No Roman numeral is necessary because Ba, a group-2A element, forms only Ba^{2+} ion.
- (b) CrCl_3 : Chromium (III) Chloride : (b) The Roman numeral III is necessary to specify the + 3 charge on Cr, a transition metal.
- (c) PbS : Lead (II) sulfide : (c) The sulfide ion (S^{2-}) has a double negative charge, so lead cation must be doubly charged positive. Pb shows variable valency.
- (d) Fe_2O_3 : Iron (III) oxide : (d) The 3 oxide anions (O^{2-}) have a total negative charge of '-6', So the two iron cations must have a total charge of '+6', Thus, each is Fe (III).

Worked Example-3.16 : Converting Names into Formulae Based :

Write formulae for the following compounds :

- (a) Magnesium fluoride, (b) Iron (III) sulfide, (c) Tin (IV) oxide

Strategy : For transition-metal compounds, the charge on the cation is indicated by Roman numeral in the name. Knowing the number of positive charges, the number of negative charges for total anions can be calculated.

Solution :

- (a) Magnesium fluoride: MgF_2 : Mg (group-2A) forms only a $2+$ cation, so there must be two fluoride ions (F^-) to balance the charge.
- (b) Iron (III) sulfide, Fe_2S_3 : Iron (III) has a $+3$ charge and sulfide ion a -2 charge (S^{2-}), So there must be two irons and three sulfurs ions.
- (C) Ti (IV) oxide, SnO_2 : Tin (IV) has a $+4$ charge, so there must be two oxide ions (O^{2-}) to balance the charge.

Students' Work : 3.17 : Naming of Compounds Based :

Problem – 3.39 : Write systematic names for the following compounds :

- (a) CsF (b) K_2O (c) CuO (d) BaS

Problem– 3.40 : Write formulae for the following compounds :

- (a) Manganese (IV) oxide (b) Aluminium oxide ,
(c) Copper (II) sulphide (sulfide) (d) Iron (III) chloride.

(B) Compounds with Polyatomic Ions :

Charged and covalently bonded group atoms, is called polyatomic ion. This type of ions are also common. Ammonium ion (NH_4^+), hydroxide ion (OH^-), nitrate ion (NO_3^-) and doubly charged sulphate ion (SO_4^{2-}) are examples.

Memorize the names and formulas of polyatomic ions from Table– 3.10 next and then proceed to name any compound.

Here are some suggestions about how to learn the names and formulas of polyatomic ions with their speciality :

- (1) First note that the names of most polyatomic anions end in '-ite' or '-ate', for example nitrite. (NO_2^-) and nitrate (NO_3^-) ions. Only hydroxide (OH^-), cyanide (CN^-) and peroxide (O_2^{2-}) have the '-ide' ending.
- (2) Second, note that several of the anions form a series of oxoanions (oxygen containing anions), in which an atom of a given element is combined with different numbers of O atoms, When there are only two oxoanions in a series, of the two ions with fewer O atoms takes the '-ite' ending and the ion with more O atom takes the '-ate' ending. example, nitrite (NO_2^-) and nitrate (NO_3^-).
- (3) Third, when there are more than two oxoanions in a series; first they are grouped into '-ite' ions and '-ate' ions and then prefix hypo-(meaning 'less than') is used for that '-ite ion'

with the fewest O atom. Again prefix 'per-' (meaning more than) is used for that '- ate ion' with the most O atoms. For example :

ClO^- ion : its name is hypo chlorite

ClO_2^- ion : its name is (only) chlorite

ClO_3^- ion : its name is (only) chlorate

ClO_4^- ion : its name is perchlorate

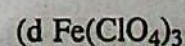
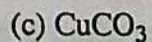
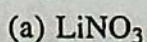
(4) Fourth, produced from same mother acid, oxoanion pair like HCO_3^- , CO_3^{2-} and HSO_4^- , SO_4^{2-} ions are related by the presence or absence of a hydrogen. The hydrogen carbonate anion (HCO_3^-) differs from the carbonate anion (CO_3^{2-}) by the presence of one H^+ ion. The ion that has the additional 'H' is sometimes referred to using the prefix 'bi' – although this usage is now discouraged, for example, NaHCO_3 is sometimes called sodium bicarbonate. For example, CO_3^{2-} is caronate ion, HCO_3^- is hydogen carbonate, SO_4^{2-} is sulphate ion, HSO_4^- is hydrogen sulphate (bisulphate ion)

Table-3.10: Some Common Polyatomic Ions.

Formula	Name	Formula	Name
Cation :		ClO_4^-	: Perchlorate
NH_4^+	: Ammonium	MnO_4^-	: Permanganate
Singly Charged Anions :		CH_3CO_2^-	: Acetate
NO_2^-	: Nitrite	Doubly Charged Anions :	
NO_3^-	: Nitrate	CO_3^{2-}	: Carbonate
OH^-	: Hydroxide	SO_3^{2-}	: Sulphite
CN^-	: Cyanide	SO_4^{2-}	: Sulphate
HCO_3^-	: Hydrogen carbonate	$\text{S}_2\text{O}_3^{2-}$: Thiosulphate
HSO_4^-	: Hydrogen sulphate	HPO_4^{2-}	: Hydrogen phosphate
H_2PO_4^-	: Dihydrogen phosphate	CrO_4^{2-}	: Chromate
ClO^-	: Hypochlorite	$\text{Cr}_2\text{O}_7^{2-}$: Dichromate
ClO_2^-	: Chlorite	O_2^{2-}	: Peroxide
ClO_3^-	: Chlorate	Triply Charged Anion :	
		PO_4^{3-}	: Phosphate

Worked Example– 3.17 : Naming Compounds with Polyatomic Ions Based :

Give systematic names for the following compounds :



Strategy : The names and charges of the common polyatomic ions must be memorized.

Refer to table-3.10, if you need help.

Solution :

- (a) LiNO_3 : Lithium nitrate : Lithium (group-1A) forms only Li^+ ion and does not need a Roman numeral.
- (b) KHSO_4 : Potassium hydrogen sulphate : K (group-1A) forms only the K^+ ion.
- (c) CuCO_3 : Copper (II) Carbonate : The carbonate ion has a -2 charge, so copper must be + 2. A Roman numeral is needed because copper, a transition metal, can form more than one ion.
- (d) $\text{Fe}(\text{ClO}_4)_3$: Iron (III) Perchlorate : There are three perchlorate ions here, each with a - 1 charge, so the iron must have a + 3 charge. So Roman numeral is used.

(c) Oxo-Acids and Their Nomenclature

Oxoacids : The acidic compounds containing hydrogen and oxygen together with a central non-metal or metal atom in their molecular formulae, are called oxo-acids. Generally oxoacids of non-metals are stable such as HNO_3 , H_2SO_4 , H_3PO_4 . But oxoacids of metals are less stable and their salts are stable. For example, aluminic acid HAlO_2 (unstable) and its salt sodium aluminate NaAlO_2 (stable); chromic acid ($\text{H}_2\text{Cr}_2\text{O}_7$) unstable and its salt potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) stable. Generally most of the non-metals have more than one oxoacids. For example chlorine (Cl) has four oxoacids, like HClO , HClO_2 , HClO_3 , HClO_4 together with its hydracid HCl (hydrochloric acid). In naming the oxoacids, oxidation number of central acid is taken as basis. In above said four oxoacids of chlorine, their molecular formulae contain increased number of O atoms one after another. So oxidation number of central Cl atom is also increased by 2 units; such as $\text{H}\overset{+1}{\text{Cl}}\text{O}$, $\text{H}\overset{+3}{\text{Cl}}\text{O}_2$, $\text{H}\overset{+5}{\text{Cl}}\text{O}_3$, $\text{H}\overset{+7}{\text{Cl}}\text{O}_4$

Following rules are used in naming these oxo-acids :

- (1) For naming oxo-acid of 3rd element, a non-metal with its lowest oxidation number (O.N.) is named as hypo-acid : (hypo + 3rd element + ous acid). For example.
 HClO hypochlorous acid, here oxidation no. of Cl = + 1
 HBrO hypobromous acid, here oxidation no. of Br = + 1
 HIO hypoiodous acid, here oxidation no. of I = + 1
 $\text{H}_2\text{N}_2\text{O}_2$ hyponitrous acid, here oxidation no. of N = + 1
- (2) For naming oxo-acid of 3rd element, a non-metal with its lower O.N. but more than hypo-acid is named as ous-acid : (3rd element + ous-acid). For example,

HClO_2 chlorous acid, here oxidation no. of Cl = + 3

HBrO_2 bromous acid, here oxidation no. of Br = + 3

HIO_2 iodous acid, here oxidation no. of I = + 3

H_2SO_3 sulphurous acid, here oxidation no. of S = + 4

(3) For naming oxo-acid of 3rd element, a non-metal with its higher O. N. (more than 'ous'-acid is named as ic-acid : (3rd element + ic acid); For example

HClO_3 chloric acid, here oxidation no. of Cl = + 5

HBrO_3 bromic acid, here oxidation no. of Br = + 5

HIO_3 iodic acid, here oxidation no. of I = + 5

H_2SO_4 sulphuric acid, here oxidation no. of S = + 6

(4) For naming oxo-acid of 3rd element, a non-metal with its highest O.N. (more than ic-acid) is named as per-ic-acid : (per + 3rd element + ic - acid). For example,

HClO_4 perchloric acid, here oxidation no. of Cl = + 7

$\text{H}_2\text{S}_2\text{O}_8$ persulphuric acid, here oxidation no. of S = + 7

As per above rules, the changes in 'suffix' of different oxo-acids of a non-metal with increase in O.N. of central atom, are the followings :

hypo \rightarrow ous \rightarrow ic \rightarrow per

$\text{HClO} \rightarrow \text{HClO}_2 \rightarrow \text{HClO}_3 \rightarrow \text{HClO}_4$

(5) When same acidic oxide of a non-metal reacts with different number of water molecules to form different oxo-acids with same oxidation number, then they are named as follows. The oxo-acid produced from acidic oxide with maximum water molecules, is called ortho-acid; acid formed with minimum water molecules is called 'meta'-acid and acid formed with water molecules in between 'ortho' and 'meta' is called pyro-acid.

$\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4$ ortho-phosphoric acid

$\text{P}_2\text{O}_5 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{P}_2\text{O}_7$ pyro-phosphoric acid

$\text{P}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HPO}_3$ meta-phosphoric acid

(6) **Per-oxo-acid** : When in molecular structure of a oxo-ic acid, a O-atom is replaced with a per-oxide ($-\text{O}-\text{O}-$) group, then that acid is called per-oxo-acid. For example.

(i) Nitric acid (HNO_3) \rightarrow per oxo-nitric acid (HNO_4)

(ii) Sulphuric acid (H_2SO_4) \rightarrow per oxo-sulphuric acid (H_2SO_5)

(iii) Phosphoric acid (H_3PO_4) \longrightarrow per oxo-phosphoric acid (H_3PO_5)

(iv) Ethanoic acid (CH_3COOH) \longrightarrow per oxo-ethanoic acid ($\text{CH}_3\text{COO}_2\text{H}$)

* **Oxo-acids of Halogens** : (F has no oxo-acid).

(1) **Hypo-halous acid** : Hypochlorous acid (HClO), Hypobromous acid (HBrO), Hypoiodous acid (HIO).

(2) **Halous acid** : Chlorous acid (HClO_2), Bromous acid (HBrO_2), Iodous acid (HIO_2).

(3) **Halic acid** : Chloric acid (HClO_3), Bromic acid (HBrO_3), Iodic acid (HIO_3).

(4) **Per halic acid** : Perchloric acid (HClO_4), Perbromic acid (HBrO_4), Periodic acid (HIO_4).

* Perchloric acid (HClO_4) is the most strong acid among oxo-acids.

(7) **Nomenclature of Hydrated Compounds** :

(1) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ \longrightarrow Copper (II) sulphate pentahydrate;

(2) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ \longrightarrow Iron (II) sulphate heptahydrate;

(3) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ \longrightarrow Magnesium sulphate heptahydrate;

(4) $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ \longrightarrow Zinc fluoride tetrahydrate;

(5) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ \longrightarrow Sodium sulphate decahydrate;

(6) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ \longrightarrow Zinc sulphate heptahydrate;

Students' Work : 3.18 : Naming in Systematic System Based.

Problem-3.41 : Give systematic names for the following compounds :

(i) $\text{Ca}(\text{ClO})_2$, (b) $\text{Ag}_2\text{S}_2\text{O}_3$, (c) $\text{Sn}(\text{NO}_3)_2$, (d) $\text{Pb}(\text{CH}_3\text{CO}_2)_2$, (e) NaH_2PO_4 , (f) $(\text{NH}_4)_2\text{SO}_4$

Problem-3.42 : Write formula for the following compounds in systematic name method.

(a) Lithium phosphate

(b) Magnesium hydrogen sulphate

(c) Manganese (II) nitrate

(d) Chromium (III) sulphate

3.21.1 Formulas and Names of Complex or Coordination compounds of Transition metal

There are three important rules for writing the formulas of co-ordination compounds, the first two being the same for writing formulas of any ionic compound :

* (1) The cation is written before anion.

* (2) The charge of the cation(s) is balanced by the charge of the anion (s).

* (3) In the complex ion, neutral ligands are written before anionic ligands, and the formula for the whole ion is placed in brackets.

Other Rules :

(4) The molecules or negative ions that surround the central metal ion in a co-ordination or complex compound with co-ordinate bonds are ligands. For example, neutral ligands are H_2O called 'aqua', NH_3 called 'ammine.' Negative ions or anionic ligands end in '-o', changing anion ending -ide to '-o' and -ate to '-ato'; for example see table-3.11 next.

(5) The whole complex ion may be a cation or anion. When total charge of a complex ion is negative then complex ion becomes anion and we drop the ending of the metal name and add '-ate'.

For example zincate, chromate, ferrate, cuprate, argentate. etc. (see, table-3.11 next). So the name of anion $[\text{Fe}(\text{CN})_6]^{4-}$ is hexacyano ferrate (II) ion. Similarly, $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^{-}$ is amminepentachloro platinate (IV) ion.

* **Charge of Complex ion = Charge of metal ion + total charge of ligands.**

Example, in $\text{K}_2[\text{Co}(\text{NH}_3)_2\text{Cl}_4]$, two K^+ ions counter balance the charge of the complex anion $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^{2-}$, which contains two NH_3 molecules and four Cl^- ions as ligands. The two NH_3 are neutral and the four Cl^- ions have a total charge of 4^- , and the total complex ion has a charge of 2^- , so the central metal ion must be Co^{2+} ion. So for the ion $[\text{Co}(\text{NH}_3)_2\text{Cl}_4]^{2-}$ we can calculate the metal ion charge as follows :

Charge of complex ion = Metal ion charge + total charge of ligands

$$\therefore 2- = \text{Metal ion charge} + [(2 \times 0) + 4 (1-)]$$

$$\therefore \text{Metal ion charge} = (2-) - (4-) = 2+$$

Co-ordination compounds are named systematically through a set of IUPAC rules :

1. The cation is named before the anion.
2. Within the complex ion, the ligands are named in alphabetical order, before the metal ion.
3. A numerical prefix indicates the number of ligands of a particular type.
4. The oxidation state of the central metal ion is given by a Roman numeral (in parentheses) only. For example :

(i) In naming $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, we name the $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ion before the Cl^- ion. Thus the name of it is tetraamminedichlorocobalt (III) chloride

The only space in the name appears between the cation and anion.

(ii) In naming $K[Pt(NH_3)Cl_5]$; note that there is one K^+ counter ion, so the complex anion has a negative charge (1-). The five Cl^- ion ligands have a total charge of 5-, so Pt must be in the + 4 oxidation state. Hence its name is :

Potassium amminepentachloroplatinate (IV),

Table- 3.11 : Some neutral and negative ligands with their names and some metallate anions with names :

Neutral ligand	Ligand's name	Anion ligand	Ligand's name	Metal in complex ion	Anion's name
H_2O	Aqua	F^-	Fluoro	Iron	: Ferrate
NH_3	Ammine	Cl^-	Chloro	Copper	: Cuprate
CO	Carbonyl	Br^-	Bromo	Lead	: Plumbate
NO	Nitrosyl	I^-	Iodo	Silver	: Argentate
		OH^-	Hydroxo	Nickel	: Nickelate
		CN^-	Cyano	Zinc	: Zincate
		CNS^-	Thiocyanato	Platinum	: Platinatate

Students' Work - 3.19 : Name and Formula of Complex Compounds :

Problem-3.43 : Name each of the following compounds :

- $[Cu(NH_3)_4]SO_4$, a deep blue compound obtained when $CuSO_4$ is mixed with excess ammonia solution.
- $Na[Cr(OH)_4]$, the compound formed when $Cr(OH)_3$ is dissolved in an excess of aqueous NaOH.
- $Fe(H_2O)_5(CNS)]^{2+}$, the red complex ion formed in a qualitative analysis test for iron.

Problem-3.44 : Write the formula for each of the followings :

- Tetraamminezinc(II)nitrate, a compound formed with zinc nitrate and excess ammonia.
- Potassium amminetrichloroplatinate(II), a compound that contains a square planar anion.
- Hexaamminecobalt(III)chloride, generally considered to be the first coordination compound.

Recapitulation

* **Alkali Metals** : Group-1 metals react with water to form alkalis; hence they are called so.

* **Alkali Earth Metals** : Group-2 metals form alkalis with water and their compounds are earth's components. So they are called alkaline earth metals.

* **Transition Metals** : The d-block metals which can produce stable ions with partially filled d-orbitals d^{1-9} are called transition metals like, Fe, Cr, Mn etc.

* **Periodic Properties** : The physical and chemical properties of the elements such as m.p, b.p, valency, ionisation energy, electron affinity, electronegativity, metallic and nonmetallic properties based on atomic sizes related with their electron configurations in the periodic table, are called periodic properties of the elements.

* **Orbital Overlapping** : According to quantum mechanics two atoms overlap their two orbitals with opposite spins to form covalent bond. Then the overlapping two atomic orbitals remain under the attraction of two nuclei, which is called molecular orbital.

* **Orbital Hybridization** : Before reaction, the different orbitals of an atom in a same orbit, mix and equalize to form equal number of equivalent orbitals known as hybrid orbitals; and this process is known as-orbital hybridization.

* **Co-ordinate Bond** : The bond formed between two atoms with lone pair electron sharing is called co-ordinate bond. The atom which supplies the lone pair electron to form co-ordinate bond, is called donor atom and the other bonded atom is called the acceptor atom.

* **Polarization** : The displacement of electron cloud of an anion by the attraction of a cation towards itself is called polarization of anion by cation. As a result ionic compound gets somewhat covalent characteristics.

* **Vander Waals Force** : Non-bonding intermolecular attraction or attraction between any charged or uncharged species is known as Vander Waals force. Ion-dipole attraction, H-bond, dipole-dipole attraction, London force etc, are of this type.

* **H-bond** : The covalent bond between H-atom and more electronegative atoms like F, O, N etc. becomes polar. In such polar molecules, a weak attraction between opposite poles of polar molecules exists; this weak bond between polar molecules containing H-atom is called H bond.

* **Importance of H-bond** : The natural polymers such as polysaccharides, proteins, nucleic acids and water contain H-bond. For biological processes, the importance of H-bond plays a unique role.

* **Nomenclature of Inorganic compounds** : Now 'IUPAC system Name' is used for inorganic compounds replacing old 'Common Name'.

Answer to MCQ. : 3.1(a), 3.2(c), 3.3(a), 3.4(b), 3.5(d).