⇒ Covalent bond ?

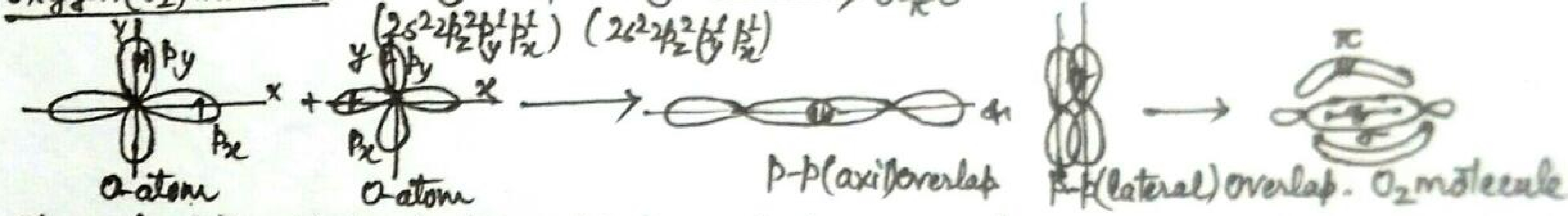
Classical Concept: When two similar or dissimilar atoms combine by sharing of electron(s) in their outermost orbit, the electronic pull (bond) formed between them is called covalent bond. The compound, thus formed is called covalent compound. Covalent bond may be single (–), double (=) or triple (≡) depending upon numbers of electron pair(s) utilised in bond formation.

Modern Concept: When two atomic orbitals (both half filled or one full filled & other vacant) of proper symmetry overlap together, a covalent bond is formed. Formation of a covalent bond is possible only if the approach of atomic orbitals is accompanied by decrease of energy.

Overlapping of atomic orbitals may be axial (along axis) or lateral (side wise). So covalent bond is of two types: (i) Sigma (σ) covalent bond (ii) Pie (π) covalent bond.

For examples: (i) Chlorine (Cl_2) molecule: Cl + Cl ⟶ Cl$\overset{\sigma}{-}$Cl
($3s^2 3p_z^2 p_y^2 p_x^1$) ($3s^2 3p_z^2 p_y^2 p_x^1$)

(ii) Oxygen (O_2) molecule: O + O ⟶ O$\overset{\sigma}{\underset{\pi}{=}}$O
($2s^2 2p_z^2 p_y^1 p_x^1$) ($2s^2 2p_z^2 p_y^1 p_x^1$)



Characteristics of covalent compds: (i) Covalent compounds exist as solids, liquids or gases of low boiling points at ordinary temperature and pressure.

(ii) Their melting and boiling points are relatively low, due to presence of weak Vander waals attraction which can be pull out by supply of small amount of heat energy.

(iii) They are generally soluble in non-polar solvents, e.g. benzene, CCl_4 etc. but insoluble in polar solvents, e.g. water. This based on principle "Like dissolves Like".

(iv) They are generally bad conductor of electricity. However, polar covalent compds. like HCl in aqueous solution can conduct electricity.

(v) They are generally soft, rigid and directional, However, some covalent compds. are crystalline.

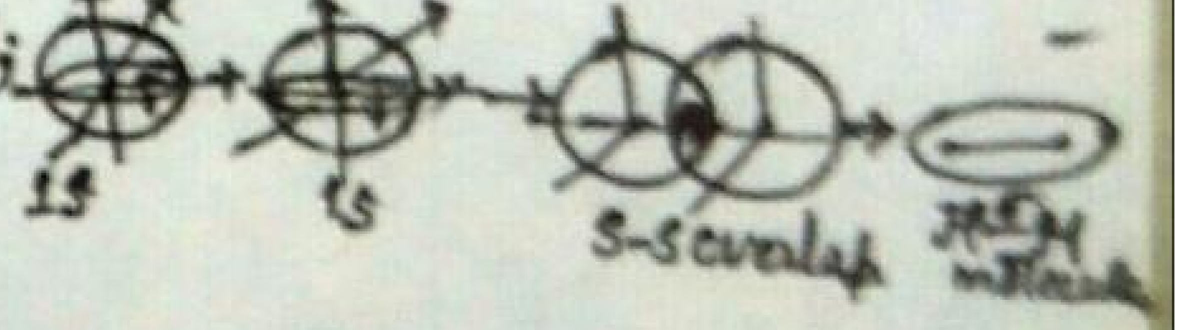
(vi) They exhibit structural and stereoisomerism due to rigid & directional nature.

⇒ Sigma (σ) bond ?

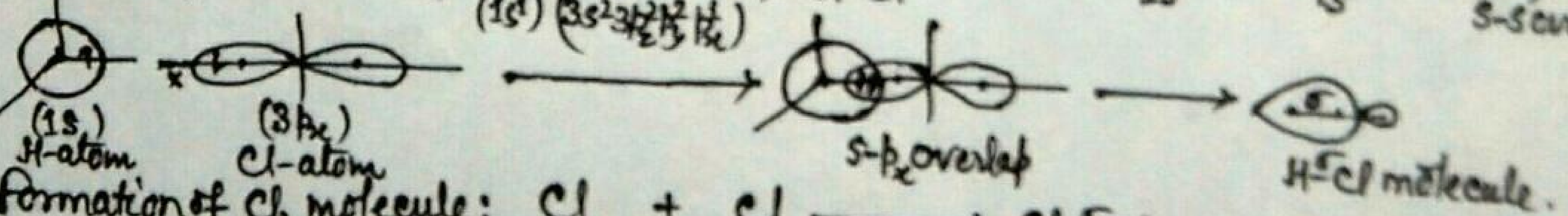
A covalent bond formed between two atoms (same or different) by co-axial overlapping of their atomic orbitals (half filled or full filled & vacant) is called Sigma (σ) bond. In other words, σ-bond is produced by head to head or axial overlap of the two half filled orbitals belonging to the valence shell of two combining atoms.

It is formed by s-s overlap (e.g. H_2 molecule), s-p_x overlap (e.g. HX molecule), p_x-p_x overlap (e.g. X_2 molecule), and also between pure-hybrid or hybrid-hybrid orbitals.

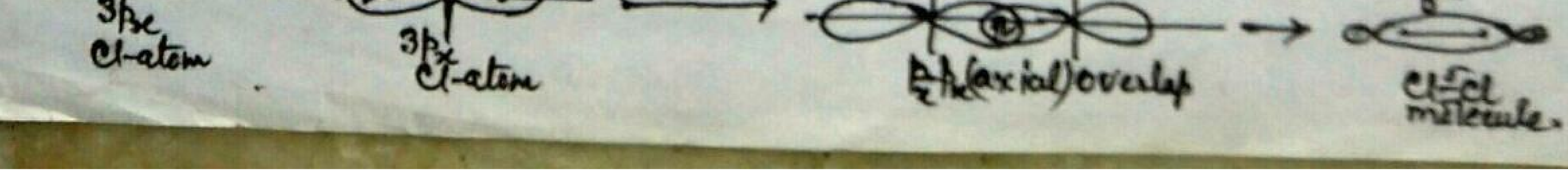
For examples: (i) Formation of H_2 molecule: H + H ⟶ H$\overset{\sigma}{-}$H;
($1s^1$) ($1s^1$)



(ii) Formation of HCl molecule: H + Cl ⟶ H–Cl
($1s^1$) ($3s^2 3p_z^2 p_y^2 p_x^1$)



(iii) Formation of Cl_2 molecule: Cl + Cl ⟶ Cl$\overset{\sigma}{-}$Cl
($3s^2 3p_z^2 p_y^2 p_x^1$) ($3s^2 3p_z^2 p_y^2 p_x^1$)



— Stability of σ-bonds : $\sigma_{s-s} > \sigma_{p-p} > \sigma_{s-p}$ (due to extent of overlap of atomic orbitals: s-s > p-p > s-p)

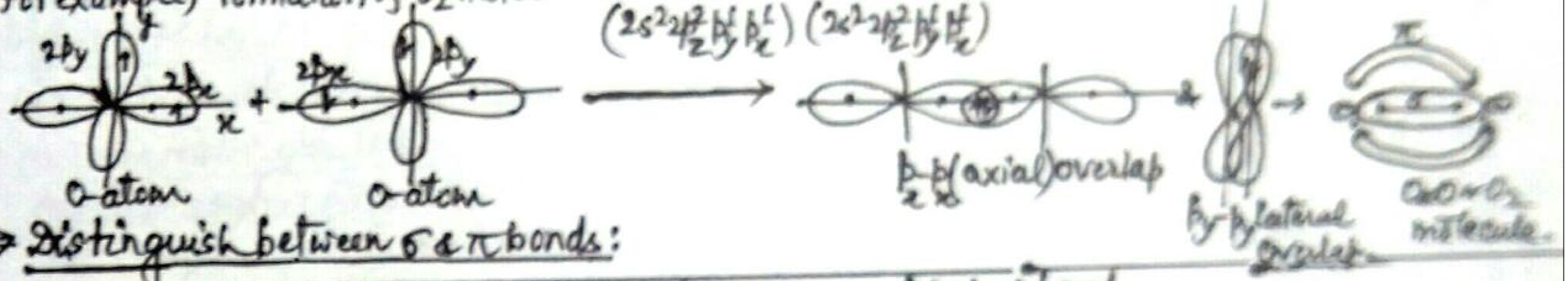
⇒ **Pie(π) bond ?**

A covalent bond formed between two atoms by the overlap of their half filled orbitals along a line perpendicular to the internuclear axis is called pie(π) bond. In other words, "π-bond is produced by the side wise or lateral overlap of the two half filled orbitals belonging to the valence shell of the two combining atoms."

π-bond generally involves the overlapping of p-orbitals (i.e; p_y-p_y or p_z-p_z overlap), but it also involves d-orbitals (i.e; p-d overlap). It's generally formed along with σ-bond, i.e; when a σ-bond already exists. It is weaker bond than σ-bond.

For example, formation of O_2 molecule: O + O ⟶ $O \frac{\sigma}{\pi} O$

$(2s^2 2p_x^2 2p_y^1 2p_z^1)$ $(2s^2 2p_x^2 2p_y^1 2p_z^1)$



⇒ **Distinguish between σ & π bonds:**

Sigma (σ) bond	Pie (π) bond
1. σ-bond is formed by axial or end to end or head to head overlap of two pure or hybrid orbitals.	1. π bond is formed by lateral or side wise overlap of two pure atomic orbitals.
2. It involves s-s, s-p_x, p_x-p_x etc. overlap.	2. It involves p_y-p_y, p_z-p_z, p-d etc. overlap.
3. It is stronger bond, since the overlap of orbitals along the internuclear axis takes place to a greater extent.	3. It is weaker bond, since the overlap of orbitals along a line perpendicular to the internuclear axis is less as σ-bond restricts the distance between the atoms.
4. It is of free existance, i.e; it is formed independently in the molecule.	4. It is not of free existance. It is generally formed when a sigma(σ) bond already exists.
5. There is free rotation of atoms about σ-bond.	5. It restricts rotation of atoms.
6. It is directional nature	6. It is nondirectional nature.

⇒ **Tau or Banana bond ?**

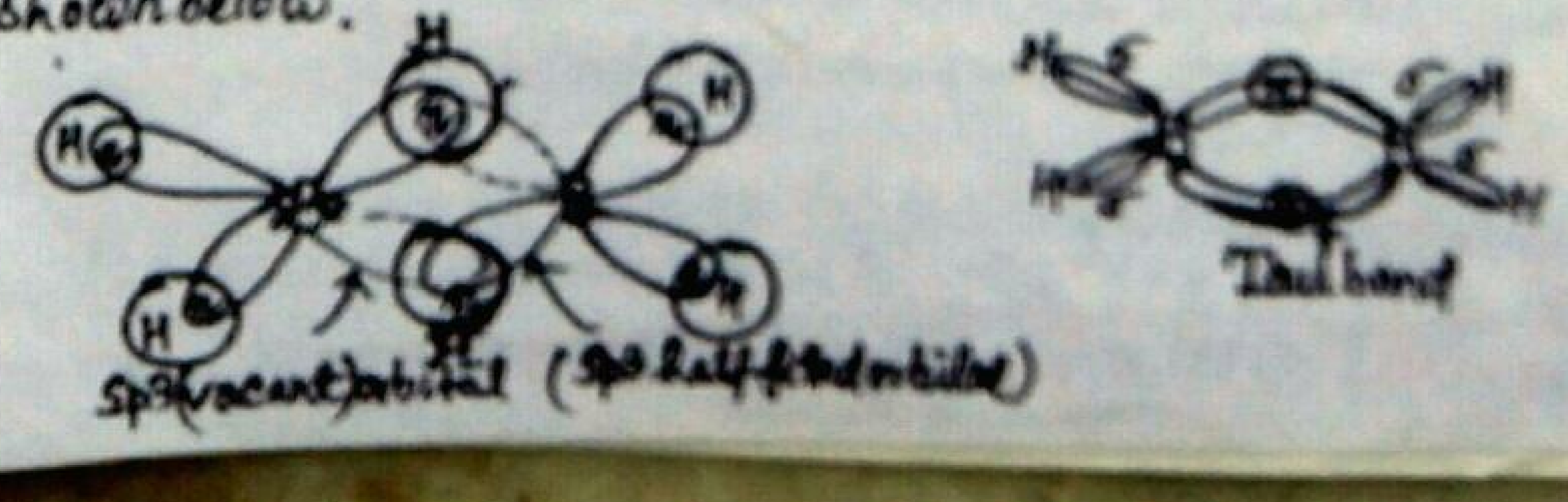
Three centred (atoms) two electron bond is called tau(τ) bond. Since shape of the delocalised electron cloud embracing two orbitals of two atoms of an element and one orbital of another element is just like a 'banana', so this bond is also called banana bond.

This is special type of covalent bond. A typical example of tau bond is diborane (B_2H_6).

B_5 : $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$ or, [1s][2s][2p] (Ground state) ; H_1 : $1s^1$ or [ ]

$1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$ or, [1s][2s][2p] (Excited state)

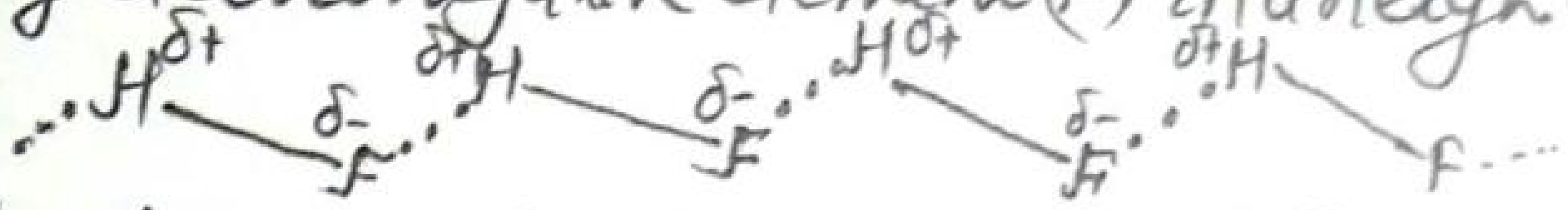
Boron atom in diborane (B_2H_6) is sp^3 hybridised involving 2s & three 2p orbitals including one empty orbital. The two sp^3 hybrid orbitals of B atom overlap with 1s orbital of the two H-atoms to form B–H bonds. Out of the two hybridized orbitals (sp^3) left, one contains an unpaired electron while the other is empty. The hybridised orbital belonging to one B atom and the empty orbital belonging to the other B atom overlap simultaneously with the 1s orbital of H atom on both sides resulting three centred two electron bond, i.e, tau bond. The orbital picture of diborane (B_2H_6) is shown below:



Hydrogen bond?

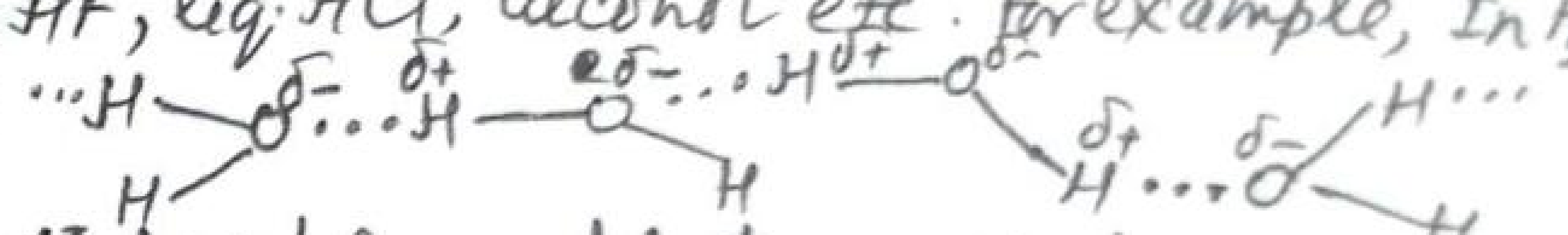
If a covalent compound contains hydrogen atom having partial positive charge ($\delta+$) and a smaller size high electronegative element (viz. F, N, O & Cl) there exists a intermolecular attraction between the H atom and high electronegative element. This type of intermolecular attraction is called hydrogen bond. This is a weaker bond and electrostatic nature. It is denoted by dotted line (···).

For example, in HF (hydrogen fluoride), the partially positive charged H atom of more mol. attracts the strongly electronegative element (F) in a neighbouring molecule resulting hydrogen bond.

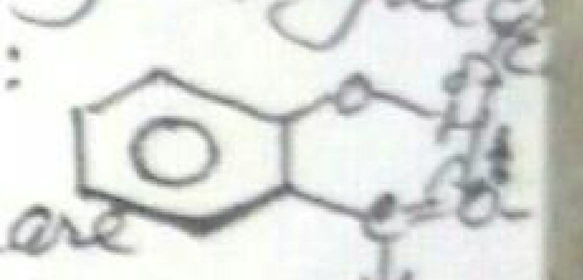


Types of H-bond: There are two types of H-bond (i) Intermolecular hydrogen bond (ii) Intramolecular hydrogen bond.

(i) **Intermolecular H-bond:** H-bond formed between H-atom of one molecule and high electronegative element/atom of other neighbouring molecule is called intermolecular H-bond. The best examples of the covalent compds having this type of H-bond are H_2O, liq. NH_3, anhydrous HF, liq. HCl, alcohol etc. For example, In H_2O intermolecular H-bond shown as:



(ii) **Intramolecular H-bond:** H-bond formed between H-atom and high electronegative element/atom within the same covalent molecule is called intramolecular H-bond. This type of bond is generally formed in organic compds having two atoms (H & X) are closer to each other, i.e; orthopositions in benzene ring. The best suited examples are: o-nitrophenol, salicylic acid, salicyaldehyde etc. For example, in salicyaldehyde intramolecular H-bond shown as:



Consequences of H-bond:

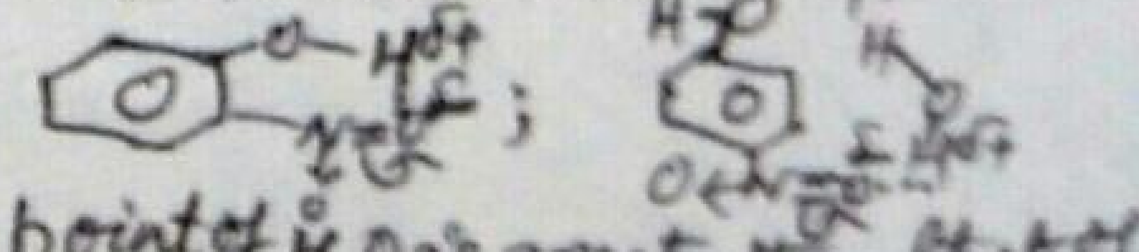
A number of physical properties are affected by H-bond, some are discussed below: (i) Melting & boiling points of NH_3, H_2O & HF are higher than those of next/other members in respective groups. e.g. Boiling point of H_2O is more than H_2S. This is due to intermolecular H-bond in H_2O (since En of O is more than S, H-O bond is more polar than H-S) which increase intermolecular attraction and hence more amount of energy/heat required to evaporate or convert its vapour state.

(ii) Solubility of a compound in a polar solvent (e.g. H_2O, alcohol) is due to H-bond e.g. glucose, ethanol (C_2H_5OH) are soluble in water due to H-bond (intermolecular).

(iii) Water contracts when heated between 0-4°C, or water has density maximum at 4°C due to intermolecular H-bond.

(iv) As a result of hydrogen bond (intermolecular), ice has open porous structure having holes throughout its structure. This makes ice to have a low density, i.e, ice is lighter than water.

(v) p-nitrophenol is steam volatile but o-nitrophenol is not. This is because p-nitrophenol can form intermolecular hydrogen bond with steam/water vapours. On the other hand, o-nitrophenol has intramolecular H-bond, cannot form intermolecular H-bond with steam.



Text Questions:

1. Q. H_2O is liquid while H_2S is gas Or, Boiling point of H_2O is greater than that of H_2S

2. Q. Water has maximum density at 4°C. 3. Q Ice is lighter than water.

Ans → see consequences of H-bond (i), (iii) & (iv) for Q.(1) (2) & (3) respectively.

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