HYDROGEN BONDING

(a) When a hydrogen atom forms a covalent bond with a highly electronegative atom, it can also create a supplementary, relatively weak connection with another electronegative atom, whether within the same molecule or in different molecules. This additional linkage is referred to as a hydrogen bond.

(b) To differentiate it from a standard covalent bond, a hydrogen bond is typically depicted with a dashed or broken line.

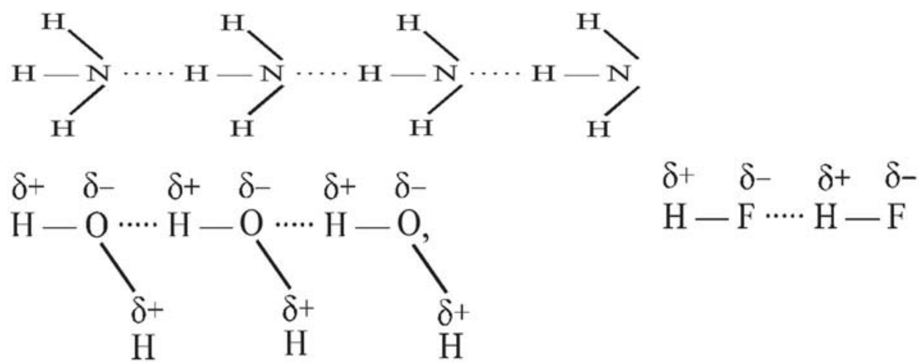
Ex. X – H ... Y where X and Y are two electronegative atoms. The strength of hydrogen bond is quite low about 2-10 kcal mol^{-1} or 8.4-42 kJ mol^{-1}.

(c) Criteria for the occurrence of hydrogen bonding:

(i) The molecule must contain a highly electronegative atom linked to H-atom.
(If E.N. ↑ polarity of bond ↑)

(ii) The size of the electronegative atom should be small.
(size ↓ electrostatic attraction ↑)

Ex.



(d) Strength of H-bond:

H .... F	bond dissociation energy = 41.8 kJ mol^{-1}
H .... O	bond dissociation energy = 29.3 kJ mol^{-1}
H .... N	bond dissociation energy = 12.6 kJ mol^{-1}

(e) Effect of H-bond

(i) It causes the association of many molecules.

(ii) Due to hydrogen bond molecules are associated and show high molecular weight.

(iii) M.P. & B.P. of the molecules increases

(iv) Viscosity & surface tension of the molecules increases.

(v) The compounds which can form H-bond with the covalent molecules are soluble in such solvents.

Ex.: Alcohol & Ammonia are water soluble.

Type Of H-Bonding

Types of Hydrogen Bonding

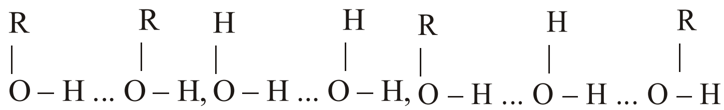
(a) Intermolecular

(b) Intramolecular

(a) Intermolecular H-bond:

(i) This type of H-bonding takes place between two molecules.

Ex. ROH, H_2O, R - OH & H_2O



(ii) In such compounds molecular wt., M.P, & B.P. are high.

(iii) Extent of H-bonding ↑ viscosity & density ↑.

(b) Intramolecular Bond

(i) This refers to intramolecular hydrogen bonding within a compound, often referred to as chelation.

(ii) The solubility in water, as well as the melting and boiling points of these compounds, exhibits a reduction.

(iii) The acidity level of an acid is contingent on the equilibrium between the acid and its conjugate base. If intramolecular hydrogen bonding stabilizes the conjugate base, the acid strength increases. Conversely, if this bonding stabilizes the conjugate acid, the acid strength decreases.

Hydrogen bonding exerts significant effects on the physical properties of substances, as evidenced by the following phenomena:

(i) H_2O remains in a liquid state at room temperature, whereas H_2S, despite its greater molecular weight, exists as a gas at the same temperature.

(ii) Ice, despite being in a solid state, is lighter than water due to the elongation of H-bonds in ice. This results in a cage-like structure formed by six water molecules, creating a porous nature that leads to a smaller mass and larger volume, ultimately reducing density.

(iii) Alcohols exhibit higher boiling points compared to corresponding alkanes with the same molecular mass. This is attributed to the presence of intermolecular H-bonds among R-OH molecules in alcohols. In contrast, ethers and hydrocarbons lack such strong intermolecular forces, resulting in lower boiling points for these substances.

H_2O > R-OH > R-OH → Exceptional

H_2S < R-SH < R-S-R → Normal

H-bond increases ←

H_2O > R-OH > R-O-R

← B.P. increases

R-O-R → no H-bond

H_2O → H-bonds

R-OH → H-bond.

(iv) The miscibility of alcohol and water in any proportion is facilitated by the formation of hydrogen bonds.

(v) Unlike other gases, ammonia exhibits exceptional solubility in water, a phenomenon attributed to the remarkable ability of NH_3 molecules to create four hydrogen bonds.

$NH_3 > RNH_2 > R_2NH$

(vi) Solubility order of different amines and ammonia in water follows the order:

$NH_3 > RNH_2 > R_2NH$.

This can be explained by the capacity of these elements to form H-bonds.

(vii) KHF_2 exists whereas $KHCl_2$, $KHBr_2$, KHI_2 do not because KHF_2 is constituted by 2 ions i.e.

K^+ & HF_2^-

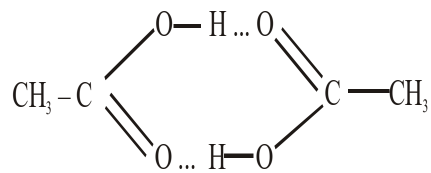
$$[\overset{-}{F} \ldots \overset{\delta+}{H} - \overset{\delta-}{F}]$$

$$[Cl^{-} \ldots H - Cl]$$

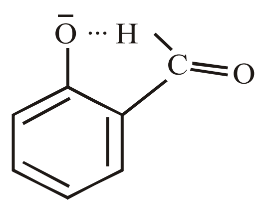
exist does not exist KHF_2 is a red orange coloured solid.

(viii) O-nitrophenol demonstrates higher steam volatility and lower solubility in water compared to its para-isomer. This is attributed to the presence of intramolecular hydrogen bonding within o-nitrophenol, which diminishes its ability to form intermolecular hydrogen bonds with other molecules such as water. Consequently, intermolecular forces among o-nitrophenol molecules are enhanced, leading to increased volatility.

(ix) In benzene, acetic acid exhibits a molecular weight of 60 and demonstrates an exceptionally elevated boiling point, a characteristic attributed to the dimerization of the molecule.

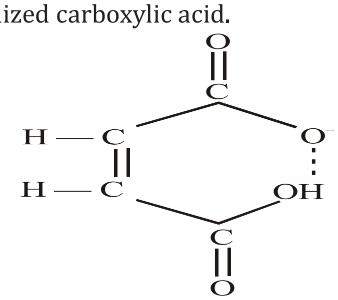


(x) The elevated acidity of salicylic acid results from the chelation of the salicylate ion through hydrogen bonding.

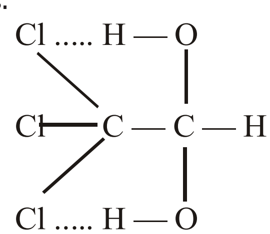


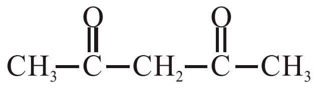
(xi) Chelation refers to the act of capturing nearby atoms as extensively as possible.

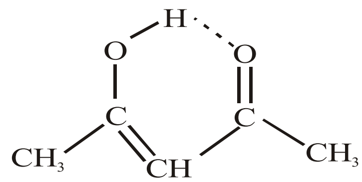
(xii) The increased acidity of maleic acid in comparison to fumaric acid can be elucidated by the chelation of the monooleate anion. This chelation involves a hydrogen bond between the carboxylate anion and the unionized carboxylic acid.



(xiii) Typically, the presence of two hydroxyl groups on the same carbon atom, known as gem diols, renders a molecule unstable. However, "chloral hydrate" defies this trend and remains stable due to the formation of hydrogen bonds.

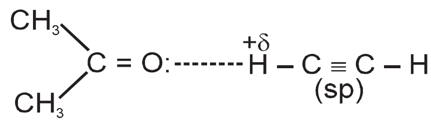


(xiv)  In the above compound, (acetyl acetone) enol form is stable because of the intramolecular H-bond.



Ex. C_2H_2 is not soluble in H_2O but it is highly soluble in acetone.

Sol.

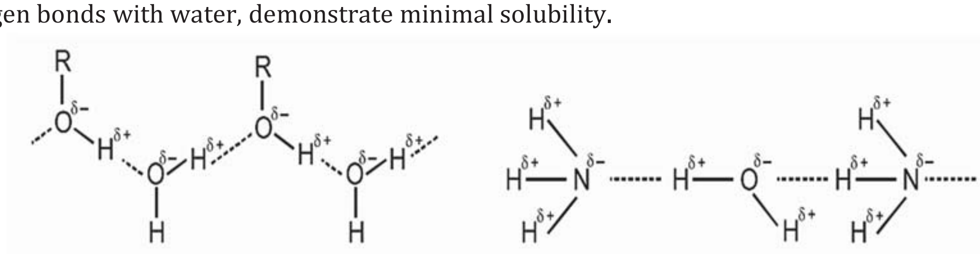


In hybridization as %S character increase, electronegativity increases hence C_2H_2 forms H–bonds with O–atom of acetone and get dissolved. But H_2O molecules are so much associated that it is not possible for C_2H_2 molecules to break that association, hence C_2H_2 is not soluble in H_2O.

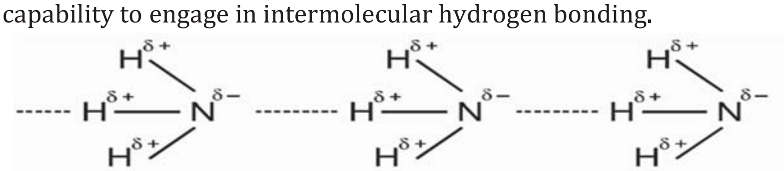
Applications of Hydrogen Bonding

1. **State:** Hydrogen bonding plays a pivotal role in influencing the physical state of a compound. This is exemplified by the contrasting states of HF and HCl at room temperature, with HF existing as a liquid while HCl is in a gaseous state. The distinction is attributed to the presence of intermolecular hydrogen bonding between H-F molecules, absent in HCl. Similarly, the disparate states of H_2O (liquid) and H_2S (gas) further underscore the effect of hydrogen bonding on a compound's state.

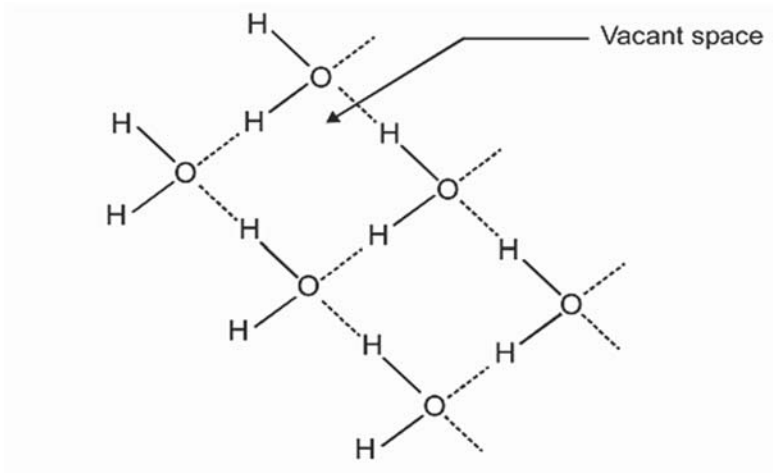
2. **Solubility Characteristics:** Solubility in water is contingent upon the propensity of covalent molecules to engage in intermolecular hydrogen bonding with water molecules. Notably, substances such as alcohols, 1º amines, NH_3, and 2º amines exhibit solubility due to their ability to form hydrogen bonds with water. Conversely, alkyl halides and 3º amines, lacking the ability to form intermolecular hydrogen bonds with water, demonstrate minimal solubility.



3. **Boiling Point Elevation:** The presence of intermolecular hydrogen bonding contributes to an increase in the boiling point of a compound. A striking example is the higher boiling point of NH_3 compared to PH_3, attributed to the presence of intermolecular hydrogen bonding in NH_3 but not in PH_3. Similarly, the higher boiling point of ethyl alcohol in comparison to diethyl ether can be attributed to the former's capability to engage in intermolecular hydrogen bonding.



4. **Density Discrepancy between Ice and Water:** Hydrogen bonding induces a distinctive cage-like structure in ice, where H-O-H molecules are tetrahedrally linked to four other H-O-H molecules. This structure results in the creation of vacant spaces, reducing the density of ice in comparison to liquid water.



Strength of Hydrogen Bonding

Hydrogen bonds, characterized by their relatively weak nature, exhibit a strength that is primarily contingent upon the electronegativity difference between the atoms involved in the bonding.

The bond energies for three illustrative examples underscore this variation:

1. **F – H ---- F:** The bond energy for the hydrogen bond between fluorine atoms is approximately 41.8 kJ/mol, signifying a relatively stronger interaction due to the substantial electronegativity difference between fluorine and hydrogen.
2. **HO – H ---- O:** In the context of the hydrogen bond between oxygen atoms, the bond energy is approximately 29.3 kJ/mol. This intermediate strength is reflective of the electronegativity difference between oxygen and hydrogen, which is less pronounced compared to the F – H case.
3. **H_2N – H ---- N:** The hydrogen bond involving nitrogen atoms exhibits a lower bond energy, approximately 12.6 kJ/mol. This reduced strength is attributed to a smaller electronegativity difference between nitrogen and hydrogen, underscoring the correlation between electronegativity and hydrogen bond strength.