



# Physical properties & POC

## Section (A) : Dipole Moment

Due to difference in electronegativity polarity develops between two adjacent atoms in the molecule. The degree of polarity of a bond is called dipole moment.

(a) Dipole moment is represented by  $\mu$ .

$$\mu = e \times l$$

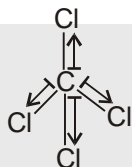
$l$  = internuclear distance between two atoms, i.e., bond length in cm ( $\text{\AA} = 10^{-8} \text{ cm}$ ).

$e$  = magnitude of separated charge in e.s.u. ( $e = 10^{-10} \text{ e.s.u.}$ )

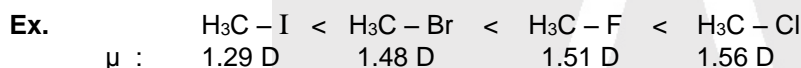
So  $1\text{D} = 1 \times 10^{-18} \text{ esu.cm}$

The Debye (D) is the unit of dipole moment.

(b) The dipole moment is represented by arrow head pointing towards the positive to the negative end.



(c) Charge and distance oppose each other, with the larger halogens having longer bond but weaker electronegativity. The overall result is that the bond dipole moment increase in the order as follows.



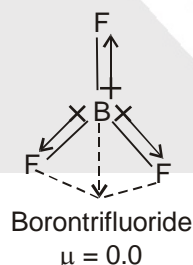
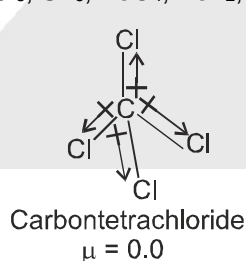
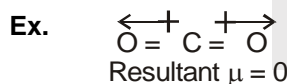
(d) Dipole moment of the compound does not depend only on the **polarity of the bond** but also depends on the **shape of the molecule**.

(e) Dipole moment of symmetrical compound is always zero. ( $\mu = 0$ )

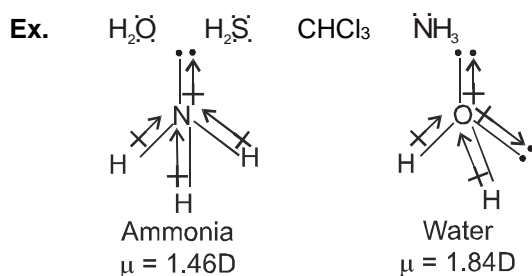
Symmetrical compounds are those compounds which fulfill the following two conditions.

(i) Central atom is bonded with the same atoms or groups.

(ii) Either central atom should not have lone pair of electrons or their dipole must be cancelled out.

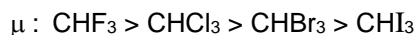


(f) Dipole moment of **unsymmetrical** compound is always greater than zero ( $\mu > 0$ ).

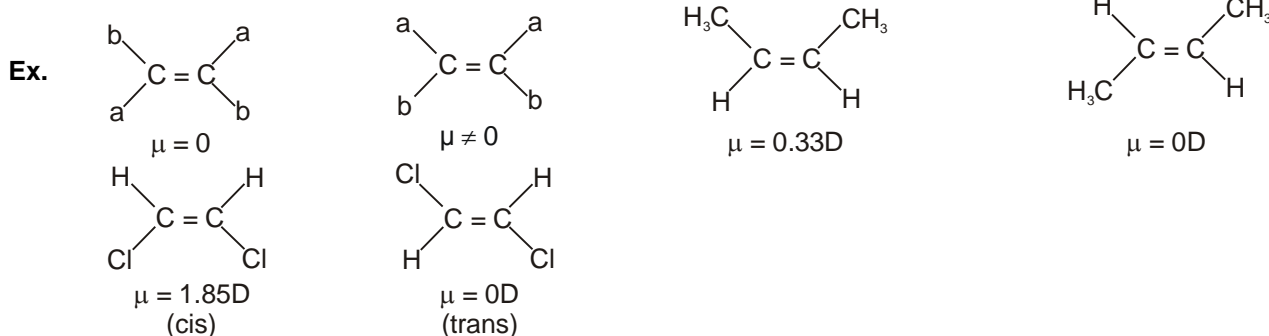




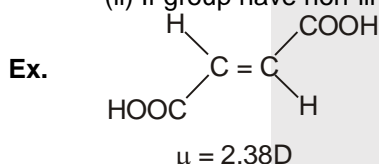
(g)  $\mu \propto$  electronegativity difference between central atom and surrounding atoms present on the central atom of the molecule.



(i) Net dipole moment of the trans derivative of the compound will only be zero if both the atoms attached to carbons are in the form a and b with linear dipole moment.



(ii) If group have non-linear moments, then the dipole moment of the trans isomer will not be zero.



(h) Dipole moment of the compounds like disubstituted benzene are :

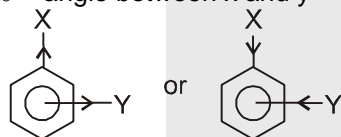
**Case I:-** When both groups x and y are electron donating or both groups are electron withdrawing then:-

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

$\mu_1$  = dipole moment of bond c – x

$\mu_2$  = dipole moment of bond c – y

$\theta$  = angle between x and y

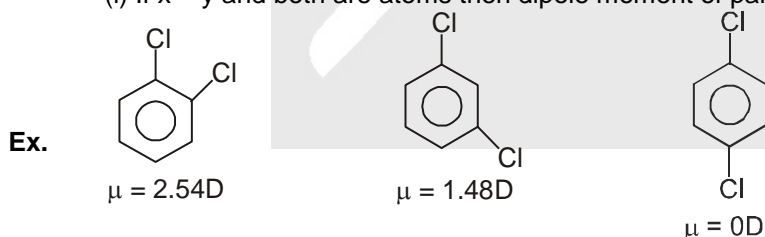


→ If value of  $\theta$  will be more, then  $\cos \theta$  will be less.

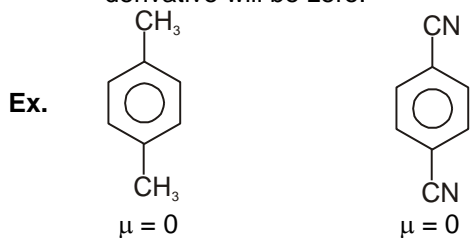
o-derivative > m-derivative > p-derivative

$\mu$  in decreasing order

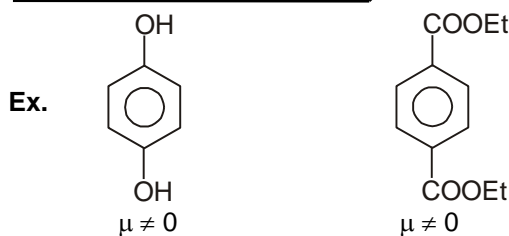
(i) If  $x = y$  and both are atoms then dipole moment of para derivative will be zero.



(ii) If x and y are same groups and group have linear moments then the dipole moment of para derivative will be zero.

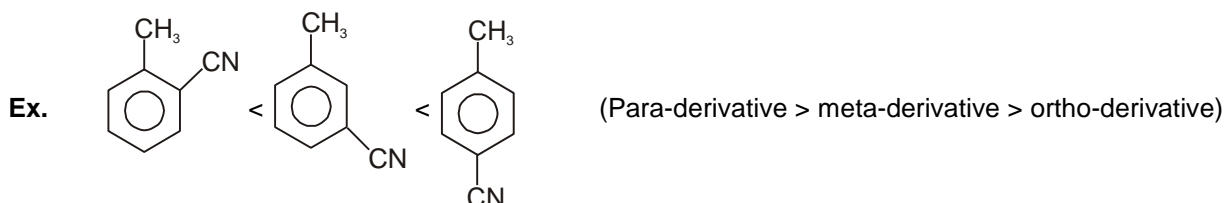


(iii) If x and y are same groups and  $x = y$  and group have non-linear moments then the dipole moment of para derivative will not be zero.



**Case-II:-** When one group is electron withdrawing and the other group is electron donating then:-

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos \theta}$$



### Intermolecular forces:

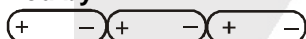
- Attractions between molecules are particularly important in solids and liquids. In these "Condensed" phases, the molecules are continuously in contact with each other. The melting points, boiling points, and solubilities of organic compounds show the effects of these forces. Two major kinds of attractive forces cause molecules to associate into solids and liquids;
  - Dipole-dipole interactions
  - VanderWaals forces

#### (I) Dipole-Dipole interaction :

Dipole-dipole interactions result from the approach of two polar molecules.

- If their positive and negative ends approach, the interaction is an attractive one.
- If two negative ends or two positive ends approach, the interaction is repulsive one.
- In a liquid or a solid the molecules are mostly oriented with the positive and negative ends together and the net forces is attractive.

Symbolized by :



- An especially strong kind of dipole-dipole attraction is hydrogen bonding

### Hydrogen Bonding :

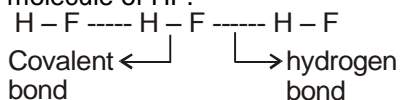
#### (1). Definition :

The hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, N) of another molecule.

**eg:-** Consider the hydrogen fluorine bond in hydrogen fluoride, HF. This bond is a polar covalent bond in which hydrogen is attached to a strongly electronegative element.



The positive charge on hydrogen will be attracted electrostatically by the negative charge on F atom by another molecule of HF.

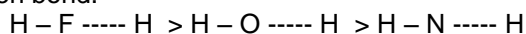


Hydrogen bond is a very weak bond (strength about 2–10 kcal/mol) as compared to normal covalent bond. But stronger than vander Waal's force of attraction.

#### (2). Conditions for hydrogen bonding :

- The molecule must contain a highly electronegative atom linked to hydrogen atom.
  - The size of electronegative atom should be small.
- Only F, O and N atoms form effective hydrogen bonding.

**Example :** Greater the electronegativity and smaller the size of the atom (F, O, N), the stronger is the hydrogen bond.



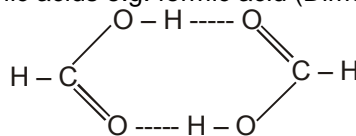


### (3). Types of Hydrogen Bonding :

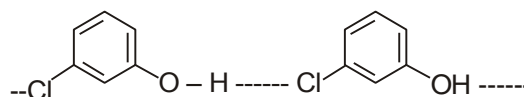
- (a) **Intermolecular hydrogen bonding** : In such type of linkages the two or more than two molecules of the same compound combine together to give a polymeric aggregate. This phenomena is also known as association.

**Example :**

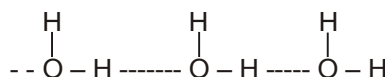
(I) Hydrogen bonding in carboxylic acids e.g. formic acid (Dimerisation)



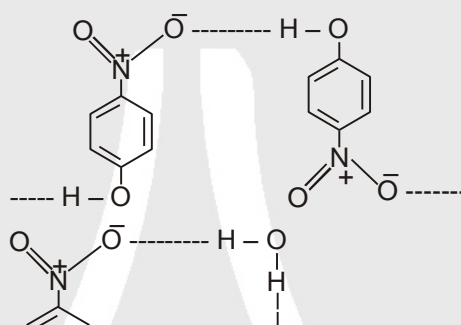
(II) In m-Chlorophenol



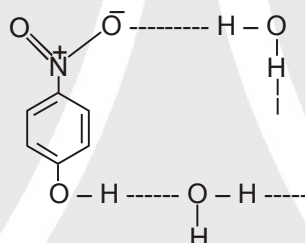
(III) In water



(IV) In p-Nitrophenol

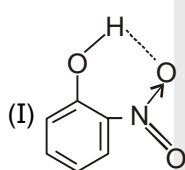


(V) In p-Nitrophenol & water

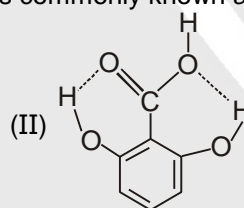


- (b) **Intramolecular hydrogen bonding**:- In this type, hydrogen bonding occurs within two atoms of the same molecule. This type of hydrogen bonding is commonly known as chelation.

Ex.



o-Nitrophenol



2, 6-Dihydroxybenzoic acid

### Conclusion :

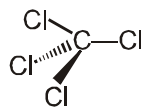
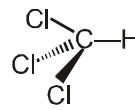
- The chelation between the ortho substituted groups restricts the possibility of intermolecular hydrogen bonding.
- Chelation does not take place in m – & p – isomers because the two groups are far away from each other.

### (II) Vander-Waal forces :

- Vander Waals forces** or **London dispersion force** can be observed in nonpolar molecules such as carbon tetrachloride.
- A small temporary dipole moment is induced when one molecule approaches another molecule in which the electrons are slightly displaced from a symmetrical arrangement.
- The electron in the approaching molecule are displaced slightly so that an attractive dipole-dipole interaction results.
- These temporary dipoles last only a fraction of a second, and they change continuously; yet they are correlated so their net force is attractive.



- This attractive force depends on close surface contact of two molecules, so it is roughly proportional to the molecular surface area.
- Carbon tetrachloride ( $\text{CCl}_4$ ) has zero dipole moment, yet its boiling point is higher than of chloroform ( $\mu = 1.0\text{D}$ ).

 $\mu = 0$ Carbon tetrachloride, bp =  $77^\circ\text{C}$  $\mu = 1.0\text{D}$ chloroform, bp =  $62^\circ\text{C}$ 

- Carbon tetrachloride has a larger surface area than chloroform (a chlorine atom is much larger than a hydrogen atom), so the intermolecular van der Waals attractions between carbon tetrachloride molecules are stronger than they are between chloroform molecules.

## Section (B) : Boiling point

The boiling point (bp) of a compound is the temperature at which the compound's vapor pressure equals the atmospheric pressure. In order for a compound to vaporize, the force that hold the molecules close to each other in the liquid must overcome. This means that the boiling point of a compound depends on the strength of the attractive forces between the individual molecules.

- If the molecules are held together by strong forces, it will take a lot of energy to pull the molecules away from each other and the compound will have a high boiling point.
- If however, the molecule are held together by weak forces, only a small amount of energy will be needed to pull the molecules away from each other and the compound will have a low boiling point.

### Factors affecting boiling point :

#### (1) Hydrogen Bonding :

##### Alcohols :

Alcohols have much higher boiling points than alkanes or ethers of comparable molecular weight because, in addition to van der Waals forces and the dipole-dipole interactions of the carbon-oxygen bond alcohols can form hydrogen bonds.

The successive replacement of hydrogen atom of the  $-\text{OH}$  group of alcohol by alkyl group to form ether blocks the probability of hydrogen bonding reduces and thus B.P. of alcohols are higher than ether.

Ex.	$\begin{array}{c} \text{CH}_2 - \text{OH} \\   \\ \text{CH}_2 - \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2 - \text{OCH}_3 \\   \\ \text{CH}_2 - \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2 - \text{OCH}_3 \\   \\ \text{CH}_2 - \text{OCH}_3 \end{array}$
B.P.	$197^\circ\text{C}$	$125^\circ\text{C}$	$84^\circ\text{C}$

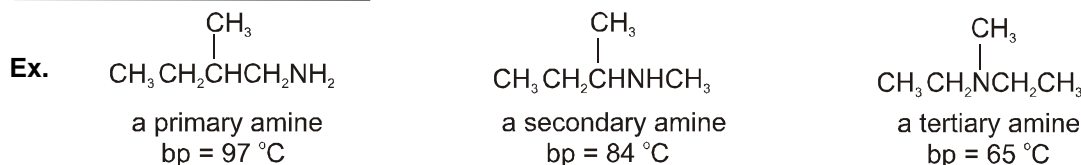
##### Water :

Water has the lowest molecular weight among hydrides of the VI group of periodic table, it has the highest boiling point. Water molecules associate through intermolecular hydrogen bonding and thus require more energy to separate the molecules for vaporization.

Ex.	$\begin{array}{c} \text{H} \\   \\ \text{H} - \text{O} - \cdots - \text{H} - \text{O} - \cdots - \text{H} - \text{O} - \cdots - \text{H} - \text{O} - \end{array}$		
Compound	$\text{H}_2\text{O}$	$\text{H}_2\text{S}$	$\text{H}_2\text{Se}$
B.P.	$100^\circ\text{C}$	$-59.6$	$-42^\circ\text{C}$

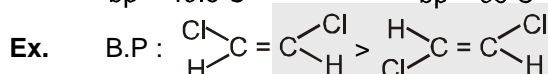
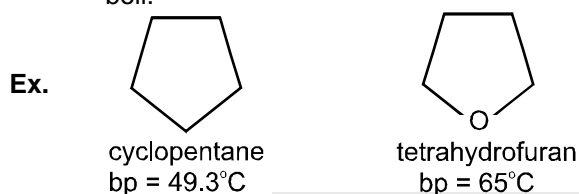
##### Amines :

- Primary and secondary amines also form hydrogen bonds, so these amines have higher boiling points than alkanes with similar molecular weights.
- Nitrogen is not as electronegative as oxygen, however, which means that the hydrogen bonds between amine molecules are weaker than the hydrogen bonds between alcohol molecules.
- Amines, therefore, have lower boiling points than alcohols with similar molecular weights.
- Because primary amines have two  $\text{N}-\text{H}$  bonds, hydrogen bonding is more significant for primary amines than for secondary amines. Tertiary amines cannot form hydrogen bonds with each other because they do not have a hydrogen attached to the nitrogen. Consequently if you compare amines with the same molecular weight and similar structures, primary amines have higher boiling point than secondary amines and secondary amines have higher boiling points than tertiary amines.



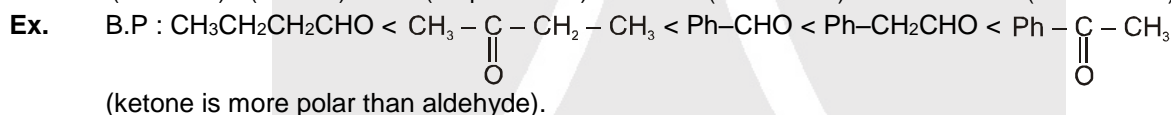
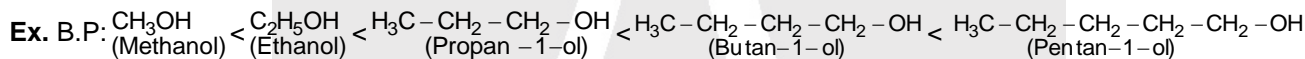
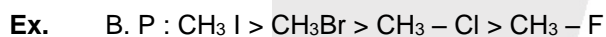
## (2) Dipole - Dipole interactions :

Dipole-dipole interactions, are stronger than van der Waals forces but not as strong as ionic or covalent bonds. Ethers generally have higher boiling points than alkanes of comparable molecular weight because both van der Waals forces and dipole-dipole interactions must be overcome for an ether to boil.



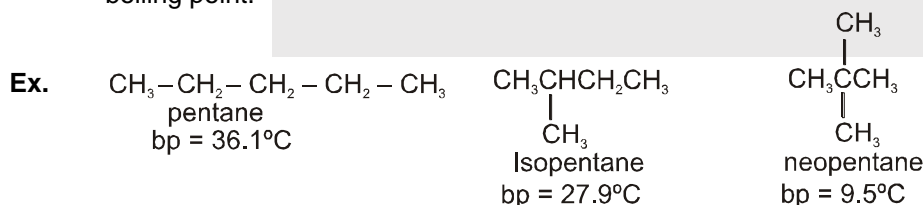
## (3) Molecular weight :

The boiling points for any homologous series of compounds increase as their molecular weights increase because of the increase in van der Waals forces. So the boiling points of a homologous series of ethers, alkyl halides, alcohols, and amines increase with increasing molecular weight.

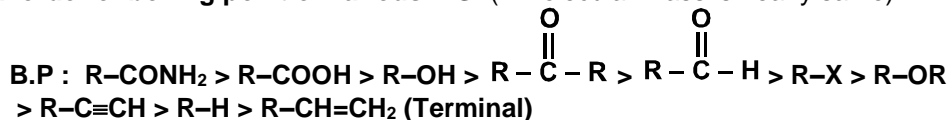


## (4) Vander Waals forces

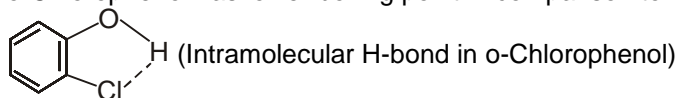
- The molecules of an alkane are held together by these induced dipole-induced dipole interactions known as van der Waals forces or London forces. In order for an alkane to boil, these van der Waals forces must be overcome.
- The homologous series of alkanes boiling points increase as their size increases. This occurs because each additional methylene group increases the area of contact between the molecules.
- Because the strength of van der Waals force depends on the area of contact between molecules, branching in a compound lowers its boiling point because it reduces the area of contact.
- If two alkanes have the same molecular weight, the more highly branched alkane will have a lower boiling point.



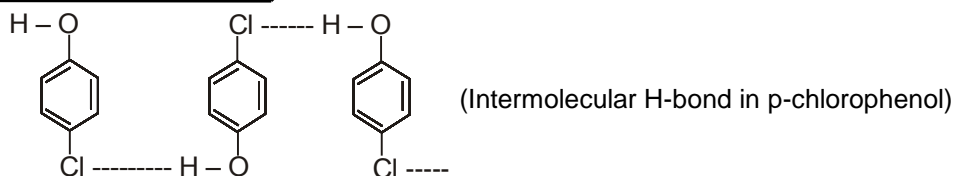
**General order of boiling point of various F.G. (if molecular mass is nearly same)**



Ex. o-Chlorophenol has lower boiling point in comparison to its p-isomer.







## Section (C) : Melting Point

The temperature at which the thermal energy of the particles is great enough to overcome the intracrystalline forces that hold them in position is known as melting point.

- Melting is the change from the highly ordered arrangement of particles in the crystalline lattice to the more random arrangement that characterizes a liquid.

### Factors affecting melting point :

#### (1) Molecular weight :

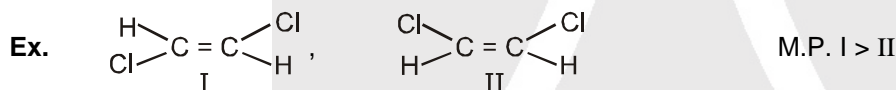
Melting points of alkanes increase in a homologous series as the molecular weight increases.

Ex. **M.P.** :  $\text{CH}_3\text{--CH}_2\text{--CH}_3 < \text{CH}_3\text{CH}_2\text{--CH}_2\text{--CH}_3 < \text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$

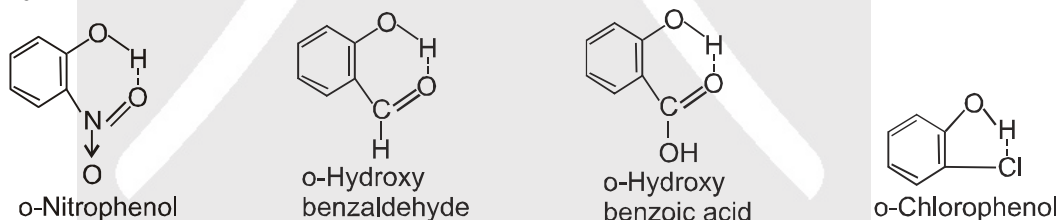
#### (2) Packing :

- Packing is a property that determines how well the individual molecules in a solid fit together in the crystal lattice. The tighter they fit, the more energy required to break the lattice and melt the compound.
- Alkanes with an odd number of carbon atoms pack less tightly than alkanes with an even number of carbon atoms. This decreases the intermolecular forces between alkanes with odd number of carbon atoms, which decreases their melting points.
- In geometrical isomers the trans isomers are more symmetrical than cis isomers ( $C_{ab}=C_{ab}$  type alkenes) so trans form have higher M.P. than cis isomers.

The heavier the molecule and stronger the intermolecular forces, higher will be the M.P. of the compound.



Ex. Ortho - hydroxy, nitro-, carbonyl, carboxylic or chloro compounds have lower melting and boiling points than the respective meta or para isomer due to intramolecular H-bonding in ortho substituted compound.



## Section (D) : Solubility in water

### (1) Solvation of ionic salts by ion dipole interaction :

Intermolecular forces are of primary importance in explaining the solubilities of substances. Dissolution of a solid in a liquid is, in many respect, like the melting of a solid. The orderly crystal structure of the solid is destroyed, and result in the formation of the more disorderly arrangement of the molecules (or ions) in solution. In the process of dissolving, too, the molecules or ions must be separated from each other, and energy must be supplied for both changes. The energy required to overcome lattice energies and intermolecular or interionic attractions comes from the formation of new attractive forces between solute and solvent.

Consider the dissolution of an ionic substance as an example. Hence both the lattice energy and interionic attractions are large. We find that water and only a few other very polar solvents are capable of dissolving ionic compound. These solvents dissolve ionic compounds by hydrating or solvating the ions.

Water molecules, by virtue of their great polarity as well as their very small, compact shape, can very effectively surround the individual ions as they are free from the crystal surface. Positive ions are



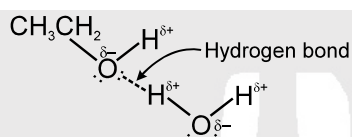
surrounded by water molecules with the negative end of the water dipole pointed toward the positive ion; negative ions are solvated in exactly the opposite way. Because water is highly polar, and because water is capable of forming strong hydrogen bond, the dipole-ion attractive forces are also large. The energy supplied by the formation of these forces is great enough to overcome both the lattice energy and interionic attractions of the crystal.

## (2) Solvation of compounds by dipole-dipole interaction :

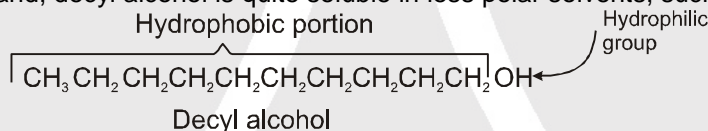
A thumb rule for predicting solubilities is that "like dissolves like." Polar and ionic compound tend to dissolve in polar solvents. Polar liquids are generally miscible with each other. Nonpolar solids are usually soluble in nonpolar solvents. On the other hand nonpolar solids are insoluble in polar solvents. Nonpolar liquids are usually mutually miscible, but nonpolar liquids and polar liquids "like oil and water" do not mix.

## (3) Solvation of compounds by hydrogen bonding :

Methanol and water are miscible in all proportions; so too are mixtures of ethanol and water and mixtures of both propyl alcohols and water. In these cases the alkyl groups of the alcohols are relative small, and the molecules therefore resemble water more than they do an alkane. Another factor in understanding their solubility is that the molecules are capable of forming strong hydrogen bonds to each other.



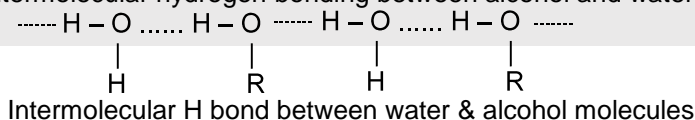
If the carbon chain of an alcohol is long, however, we find that the alcohol is much less soluble in water. Decyl alcohol (see following structures) with a chain of 10 carbon atoms is only very slightly soluble in water. Decyl alcohol resembles an alkane more than it does water. The long carbon chain of decyl alcohol is said to be hydrophobic (hydro, water; phobic, fearing or avoiding – "water avoiding"). Only the OH group, a rather small part of the molecule, is hydrophilic (philic, loving or seeking – "water seeking"). (On the other hand, decyl alcohol is quite soluble in less polar solvents, such as chloroform.)



An explanation for why nonpolar groups such as long alkane chains avoid an aqueous environment, that is, for the so-called hydrophobic effect, is complex. The most important factor seems to involve an unfavorable entropy change in the water. Entropy changes have to do with changes from a relatively ordered state to a more disordered one or the reverse. Changes from order to disorder are favorable, whereas changes from disorder to order are unfavorable. For a nonpolar hydrocarbon chain to be accommodated by water, the water molecules have to form a more ordered structure around the chain, and for this, the entropy change is unfavorable.

## (4) Solubility in water :

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.



But this is true only for the lower alcohols, where the – OH group constitutes a large part of the molecule. As the alkane like alkyl group becomes larger, water solubility decreases. For practical purpose we consider that the borderline between solubility and insolubility in water occurs at about four to five carbon atoms for normal primary alcohols.

Polyhydroxy alcohols provide more than one site per molecule for hydrogen bonding and their solubility is appreciable till seven carbon atoms. Amongst isomers, as branching increases, the surface area of hydrocarbon part (hydrophobic part) decreases so solubility increases.

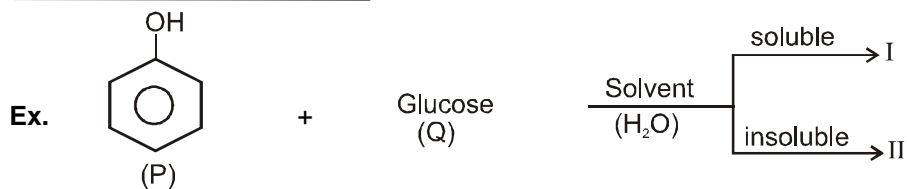
It follows the order :  $3^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 1^\circ \text{ alcohol}$ .





**Table : Solubility of Organic Compounds**

Compounds	H <sub>2</sub> O (cold)	Aq. NaHCO <sub>3</sub>	Aq. NaOH	Aq. HCl
(I) Small aliphatic compound with F.G. (Hydrogen bonding) C <sub>1</sub> to C <sub>2</sub> (a) R-COOH (b) R-OH (c) R-NH <sub>2</sub> (d) R-C-NH <sub>2</sub>    O	Soluble	Soluble	Soluble	Soluble
(II) Small aliphatic compound containing two F.G (Hydrogen bonding) C <sub>1</sub> to C <sub>5</sub> (a) 2(COOH) – diacids (b) 2(-OH) – diols/glycol/ sugar (c) 2(NH <sub>2</sub> ) (d) – COOH + (-OH) (e) (-COOH) + (NH <sub>2</sub> ) (f) –CONH <sub>2</sub> some common compounds are urea, glucose, oxalic acid, succinic acid	Soluble	Soluble	Soluble	Soluble
(III) Aromatic acids (H <sub>2</sub> O insoluble) Benzoic acid & derivative (a) Ar-COOH  (b) Ar-SO <sub>3</sub> H (c) picric acid (d) Ar – C – Cl    O	Insoluble  Insoluble  Insoluble  Insoluble	Soluble ArCOONa Soluble  Soluble  -	soluble ArCOONa Soluble  Soluble  -	Insoluble  Insoluble  Insoluble  Insoluble
(IV) Phenols	Insoluble	Insoluble	soluble Ph-ONa	Insoluble
(V) Aromatic Amines, Anilines (weaker bases) Ar – NH <sub>2</sub>	Insoluble	Insoluble	Insoluble	Soluble ArN <sup>+</sup> H <sub>3</sub> Cl <sup>-</sup>



Identify P, Q.

Sol. I  $\rightarrow$  Q, II  $\rightarrow$  P

Ex. Binary mixtures - (Two components)

