CHAPTER-1

STRUCTURES AND PHYSICAL PROPERTIES

Bond Polarity

• Polarity in organic chemistry refers to a separation of charge and can describe a bond or an entire molecule.

• A bond is said to be a polar bond, if it has partial positive charge at positive pole and partial negative charge at negative pole of two different atoms separated by a covalent bond.

• Polarity of bond depends on electronegativity.

• The ability of an atom to attract an electron towards itself is called as electronegativity.

• If electronegativity is more than polarity is also more. For eg; F > O > Cl > N > Br > C > H.

• so F has more electronegativity than other atoms.

\[
\text{H}^+ + \text{Cl}^- \rightarrow \text{H}^+ \cdot \text{Cl}^-
\]

hydrogen and chlorine atoms   hydrogen chloride molecule
• The polarity of bond can lead to polarity of molecules, and thus profoundly affect melting point and boiling point and solubility.

**Molecular Polarity**

• The polarity of the molecule is the sum of all of the bond polarities in the molecule.

• A molecule is said to be a polar if the center of negative charge does not coincide with the center of positive charge. Such a molecule consists of a DIPOLE.

• DIPOLE means two equal and opposite charges separated in a space.

• The molecule possess a dipole moment which is equal to the magnitude of the charge multiplied by the distance between the centers of charge.

• Water is a bent molecule with polar O-H bonds. The bond dipole moments add to give a resultant dipole (m = 1.85 D) directed toward the more electronegative oxygen.
• If we compare the molecular dipole moments of formaldehyde and carbon dioxide, both containing a polar carbonyl (C=O) group, we find that formaldehyde is highly polar while carbon dioxide is nonpolar. Since CO2 is a linear molecule, the dipoles cancel each other.

\[ \mu = 2.2 \text{ D} \quad \mu = 0 \text{ D} \]

• The polarity of other molecules like H2, O2, N2, Cl2 is 0.
• The polarity of chloromethanes reveals the importance of symmetry. All of these compounds contain polar C-Cl bonds but the tetrahedral symmetry of CCl4 causes the bond dipoles to cancel giving a nonpolar molecule.

In CCl4 polarity is 0.

But in ammonia dipole moment is 1.46D.
Melting point:

• For the physical processes that takes place at the melting point, see Melting, Freezing and Crystallization.

• The melting point of a solid is the temperature at which it changes state from solid to liquid.

• At the melting point the solid and liquid phase exist in equilibrium. The melting point of a substance depends (usually slightly) on pressure and is usually specified at standard pressure.

• Melting occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the intracrystalline forces that hold them in position.

• An ionic compounds forms crystals in which the structural units are ions.

• For eg:Sodium chloride has a melting point of 8010C. This is due to the powerful interionic forces.
• An Non-ionic compounds forms crystals in which the structural units are molecules.

• for eg; Methane melts at the temperature of -1830C.

BOILING POINT

• The boiling point of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid and the liquid changes into a vapor.

• A liquid in a vacuum has a lower boiling point than when that liquid is at atmospheric pressure. A liquid at high-pressure has a higher boiling point than when that liquid is at atmospheric pressure.

• In other words, the boiling point of a liquid varies depending upon the surrounding environmental pressure. For a given pressure, different liquids boil at different temperatures.

• The normal boiling point (also called the atmospheric boiling point or the atmospheric pressure boiling point) of a liquid is the special case in which the vapor pressure of the liquid equals the defined atmospheric pressure at sea level, 1 atmosphere. At that temperature, the vapor pressure of the liquid becomes sufficient to overcome atmospheric pressure and allow bubbles of vapor to form inside the bulk of the liquid.
• The standard boiling point is now defined by IUPAC as the temperature at which boiling occurs under a pressure of 1 bar.

• Liquids may change to a vapor at temperatures below their boiling points through the process of evaporation.

• Evaporation is a surface phenomenon in which molecules located near the liquid's edge, not contained by enough liquid pressure on that side, escape into the surroundings as vapor. On the other hand, boiling is a process in which molecules anywhere in the liquid escape, resulting in the formation of vapor bubbles within the liquid.

• Depending on the polar and non-polar compounds also the boiling point varies. For eg; Non-polar Methane boils at -161.50°C and even polar Hydrogen chloride boils at only -850°C.

**Acid & Base**

**ACID:**

• A substance which when added to water produces hydrogen ions [H⁺].

**BASE:**

• A substance which when added to water produces hydroxide ions [OH⁻].
**Bronsted-Lowry Theory**

**Bronsted-Lowry Acid:**

- Any substance that acts as a proton donor is known as brønsted-lowry acid.
- A Bronsted-Lowry acid must have hydrogen somewhere in its formula.
- When an electron is removed from a hydrogen atom...
- A hydrogen ion is produced - a proton.

**Bronsted-Lowry Base:**

- Any substance that acts as a proton Acceptor is known as brønsted-lowry base.
- Most negative ions can acts as Bronsted-Lowry bases.
- The acid/base definitions are broadened because no specific ion must be formed, although hydrogen is the only source of protons.
• The hydronium ion is formed by combining a hydrogen ion and a water molecule.

\[ \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+ \]

• A conjugate base is the particle that remains after an acid gives up a proton.

• A conjugate acid is the particle formed when a base accepts a proton.

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \]

• HCl donates a proton, it is the Bronsted-Lowry acid.

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \]

• H\text{H}_2\text{O} accepts a proton, it is the Bronsted-Lowry base.

**Lewis Acid – Base Theory**

**Lewis Acid:**

• Any substance that acts as an electron-pair acceptor.
Lewis Base:

• Any substance that acts as an electron-pair donor.

The Lewis Theory

• This theory is the broadest of all.

• Any reaction that involves the exchange of electrons will have a Lewis acid and Lewis base.

• In an equation, the Lewis acid gets MORE NEGATIVE from the left side to the right side - it gains e⁻.

• In an equation, the Lewis base gets MORE POSITIVE from the left side to the right side - it loses e⁻.

\[ \text{Cl}_2 + I^- \rightarrow \text{Cl}^- + I_2 \]

• \( \text{Cl}_2 \) gets more negative from the left side to the right, it is the Lewis acid.
ISOMERISM:
The existence of two or more compounds with same molecular formula but different properties is known as isomerism; and the compounds themselves are called isomers.

The difference in properties of two isomers is due to the difference in the arrangement of atoms within their molecules. Isomerism may be of two types:

- Structural isomerism.
- Stereo isomerism.

STRUCTURAL ISOMERISM:
Chain (or) nuclear isomerism:

This type of isomerism is due to the difference in the nature of the carbon chain (i.e. straight or branched) which forms the nucleus of the molecule

e.g.

(i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \) and \( \text{CH}_3\text{CH}==\text{CH}_2 \)  
(ii) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \) and \( \text{CH}_3\text{C}==\text{CH}_2 \)

(iii) \( \text{CH}_2\text{CH}_2\text{C}==\text{C} \) and \( \text{H}_2\text{C}==\text{C}==\text{CH}_2 \)  
(iv) \( \text{CH}_3\text{CH}_2\text{C}==\text{C}==\text{CH}_2 \) and \( \text{CH}_3\text{CH}==\text{CH}==\text{CH}_3 \)
(ii) **Position isomerism:**
It is due to the difference in the position of the substituent atom or group or an unsaturated linkage in the same carbon chain.

**E.g.**
(i) \( \text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2 \text{ and } \text{CH}_3\text{CH} = \text{CH}_3 \)  
(ii) \( \text{CH}_3\text{C} \equiv \text{CH} \text{ and } \text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \)

(iii) Functional isomerism:
This type of isomerism is due to difference in the nature of functional group present in the isomers.

**E.g.**
\( \text{C}_2\text{H}_6\text{O}: \)
- \( \text{CH}_3 - \text{CH}_2\text{OH} \) (note the alcoholic group)
- \( \text{CH}_3 - \text{O} - \text{CH}_3 \) (note the ether group)

\( \text{C}_3\text{H}_6\text{O}: \)
- \( \text{CH}_3\text{CH}_2\text{CHO} \) (propanal)
- \( \text{CH}_3\text{CO.CH}_3 \) (acetone)
- \( \text{CH}_2=\text{CH} - \text{CH}_2\text{OH} \) (allyl alcohol)

\( \text{C}_3\text{H}_2\text{O}_2: \)
- \( \text{CH}_3\text{CH}_2\text{COOH} \) (propanoic acid)
- \( \text{CH}_3\text{COOCH}_3 \) (methyl acetate)

\( \text{C}_5\text{H}_9\text{N}: \)
- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \) (n-propylamine)
- \( \text{CH}_3 - \text{NH} - \text{C}_2\text{H}_5 \) (methyl ethyl amine)
- \( \text{CH}_3 - \text{N} - \text{CH}_3 \) (trimethylamine)

\( \text{C}_2\text{H}_6: \)
- alkyn (note the alkyne)
- \( \text{CH}_3\text{CH} = \text{CH}_2 \) (note the alkadiene)
- \( \text{C} = \text{C} - \text{C} \) (cyclo alkene)

\( \text{C}_2\text{H}_8: \)
- alkene (note the alkene)
- \( \text{CH}_3\text{C} = \text{CH}_2 \) (note the cyclo alkane)
- \( \text{C} = \text{C} - \text{C} \) (note the cyclo alkane)
(iv) **Metamerism:**

It is due to the difference in nature of alkyl groups attached to the same functional group. This type of isomerism is shown by compounds of the same homologous series.

**E.g.**

<table>
<thead>
<tr>
<th>(i)</th>
<th>CH₃CH₂NH–C₂H₅</th>
<th>CH₃–NH–CH₂CH₂CH₃</th>
<th>CH₃–NH–CH–CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methyl propyl ether</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii)</th>
<th>CH₃CH₂–O–C₂H₅</th>
<th>CH₃–O–CH₂CH₃CH₃</th>
<th>CH₃–O–CH–CH₃</th>
</tr>
</thead>
</table>

|-------|-----------|-----------|--------------|

**Stereo isomerism:**

When isomers have the same structural formula but differ in relative arrangement of atoms or groups in space within the molecule, these are known as stereoisomers and the phenomenon as stereoisomerism.

Stereoisomerism is of two types

- Geometrical isomerism
- Optical isomerism

**Geometrical isomerism:**
The isomers which possess the same structural formula but differ in the spatial arrangement of the groups around the double bond are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

**Cis-isomerism:** When similar groups lie on the same side, it is the cis-isomer.

**Trans-isomerism:** While when the similar groups lie on opposite sides, the isomer is trans-isomer.

\[
\begin{align*}
(a) & \quad \text{Maleic acid (cis)} \\
& \quad \text{Fumaric acid (trans)} \\
& \quad \text{Citraconic acid (cis-isomer)} \\
& \quad \text{Mesaconic acid (trans-isomer)} \\
(b) & \quad \text{cis-1, 2-Dichloroethylene} \\
& \quad \text{trans-1, 2-Dichloroethylene} \\
& \quad \text{cis-Butene-2} \\
& \quad \text{trans-Butene-2}
\end{align*}
\]

**Optical isomerism:**

This type of isomerism arises from different arrangements of atoms or groups in three dimensional space resulting in two isomers which are mirror image of each other.

The isomer which rotates the plane polarised light to left is known as laevo (l)

while that which rotates the plane polarised light to the right is known as dextro (d).
(a) $\text{CH}_3$ \[\text{H} - \text{C} - \text{OH} \quad \text{HO} - \text{C} - \text{H}\] $\text{COOH}$ $\text{COOH}$

$d$-Lactic acid $l$-Lactic acid

(b) $\text{CH}_3$ \[\text{H} - \text{C} - \text{OH} \quad \text{HO} - \text{C} - \text{H}\] $\text{COOH}$ $\text{COOH}$

$d$-Mandelic acid $l$-Mandelic acid

(c) $\text{CH}_3$ \[\text{H} - \text{C} - \text{NH}_2 \quad \text{H}_2\text{N} - \text{C} - \text{H}\] $\text{COOH}$ $\text{COOH}$

$d$-Alanine $l$-Alanine

(d) $\text{CH}_3$ \[\text{H} - \text{C} - \text{OH} \quad \text{HO} - \text{C} - \text{H}\] $\text{CH}_2\text{COOH}$ $\text{CH}_2\text{COOH}$

$d$-Malic acid $l$-Malic acid