## **UNIT-I: BASICS OF ATOMS AND MOLECULES**

## \* Atom

An atom is called the fundamental unit of matter. It cannot be further divided into smaller parts and is made up of neutrons, electrons, and protons. Chemical reactions take place because of the reactions between atoms. The union of atoms along with each other forms a molecule. Generally, the number of protons and the number of electrons equal each other. Protons and neutrons form the nucleus in an atom. The electrons surround the nucleus and are placed on various levels of orbitals.

## Protons and Neutrons

Protons and neutrons are subatomic particles that make up the centre of the atom, or its atomic nucleus.

- A **proton** is positively charged. The number of protons in the nucleus of an atom is the atomic number for the chemical element. Different elements' atomic numbers are found in the Periodic Table of Elements. For example, sodium has 11 protons, and its atomic number is 11. A proton has a rest mass, denoted m<sub>p</sub>, of approximately 1.673 x 10<sup>-27</sup> kilogram (kg).
- A **neutron** is electrically neutral and has a rest mass, denoted  $m_n$ , of approximately 1.675 x  $10^{-27}$ .
- Electrons are found outside the nucleus in the electron cloud. Electrons, symbolized e<sup>-</sup>, have a negative charge. Electrons are attracted to the positively charged nucleus.

Atoms are electrically neutral and therefore have the same number of electrons as proton.

# The structure of an atom



# \* Molecule

A molecule is described as the merging of two or more same atoms or different atoms that are held together by various chemical bonds. A molecule is considered to be the smallest part of a substance and also it portrays every characteristic of that particular substance. When a molecule is broken down, it shows the features of the elements it is constituted of. Even when a pure substance is divided into its smaller parts, every part contains the characteristics of the main elements.

## **Characteristics of molecules**

1. Molecules can be solid, liquid, or gas.

2. Molecules have a low melting point or high boiling point as compared to ionic compounds.

- 3. Molecules can either have low solubility or high solubility.
- 4. Molecules are poor conductors of heat and electricity.
- 5. In molecules, many solids attach and form a network crystal like a diamond.
- 6. Examples of molecules are  $H_2O$ ,  $N_2$ ,  $O_3$ , CaO etc.



## Difference between an atom and a molecule

	ATOMS	MOLECULES
Definition	Fundamental unit of matter.	Two or more atoms form a molecule.
Structure	The smallest particle that contains the structure of the respective element	It is an amalgamation of two or more atoms of the same or different kinds.
Stability	An atom may or may not be stable.	Molecules are stable in their nature.
Constituent elements	Electrons, neutrons, and protons.	Atoms
Reactivity	Apart from noble elements, they portray reactivity.	The level of reactivity is less in molecules.
Example	O, N, H, Fe, etc.	O <sub>2</sub> , N <sub>2</sub> , HCl, NH <sub>3</sub> , etc.

Hydrogen ions are spontaneously generated in pure water by the dissociation (ionization) of a small percentage of water molecules into equal numbers of hydrogen (H<sup>+</sup>) ions and hydroxide (OH<sup>-</sup>) ions. The hydroxide ions remain in solution because of their hydrogen bonds with other water molecules; the hydrogen ions, consisting of naked protons, are immediately attracted to unionized water molecules and form hydronium ions (H<sub>3</sub>O<sup>+</sup>). By convention, scientists refer to hydrogen ions and their concentration as if they were free in this state in liquid water.

## $2H_2O \rightleftharpoons H_3O^+ + OH^-$

The concentration of hydrogen ions dissociating from pure water is  $1 \times 10^{-7}$  moles per litre of water. The pH is calculated as the negative of the base 10 logarithm of this concentration:

# $pH = -log_{10}[H^+]$

The negative log of  $1 \times 10^{-7}$  is equal to 7.0, which is also known as neutral pH. Human cells and blood each maintain near neutral pH.

#### pH Scale

The pH of a solution indicates its acidity or basicity (alkalinity). The pH scale is an inverse logarithm that ranges from 0 to 14: anything below 7.0 (ranging from 0.0 to 6.9) is acidic, and anything above 7.0 (from 7.1 to 14.0) is basic (or alkaline). Extremes in pH in either direction from 7.0 are usually considered inhospitable to life. The pH in cells (6.8) and the blood (7.4) are both very close to neutral, whereas the environment in the stomach is highly acidic, with a pH of 1 to 2.



The pH scale: The pH scale measures the concentration of hydrogen ions  $(H^+)$  in a solution.

Non-neutral pH readings result from dissolving acids or bases in water. Using the negative logarithm to generate positive integers, high concentrations of hydrogen ions yield a low pH, and low concentrations a high pH.

An acid is a substance that increases the concentration of hydrogen ions  $(H^+)$  in a solution, usually by dissociating one of its hydrogen atoms. A base provides either hydroxide ions (OH<sup>-</sup>) or other negatively-charged ions that react with hydrogen ions in solution, thereby reducing the concentration of H<sup>+</sup> and raising the pH.

#### Strong Acids and Strong Bases

The stronger the acid, the more readily it donates  $H^+$ . For example, hydrochloric acid (HCl) is highly acidic and completely dissociates into hydrogen and chloride ions, whereas the acids in tomato juice or vinegar do not completely dissociate and are considered weak acids; conversely, strong bases readily donate OH<sup>-</sup> and/or react with hydrogen ions. Sodium hydroxide (NaOH) and many household cleaners are highly basic and give up OH<sup>-</sup> rapidly when placed in water; the OH<sup>-</sup> ions react with H<sup>+</sup> in solution, creating new water molecules and lowering the amount of free H<sup>+</sup> in the system, thereby raising the overall pH. An example of a weak basic solution is seawater, which has a pH near 8.0, close enough to neutral that well-adapted marine organisms thrive in this alkaline environment.

#### Buffers

Buffer Solution is a water solvent based solution which consists of a mixture containing a weak acid and the conjugate base of the weak acid, or a weak base and the conjugate acid of the weak base. They resist a change in pH upon dilution or upon the addition of small amounts of acid/alkali to them.

The pH of Buffer Solutions shows minimal change upon the addition of a very small quantity of strong acid or strong base. They are therefore used to keep the pH at a constant value.

The buffer solution is a solution able to maintain its Hydrogen ion concentration (pH) with only minor changes on the dilution or addition of a small amount of either acid or base. Buffer Solutions are used in fermentation, food preservatives, drug delivery, electroplating, printing, the activity of enzymes, blood oxygen carrying capacity need specific hydrogen ion concentration (pH).

#### **Types of Buffer Solution**

The two primary types into which buffer solutions are broadly classified into are acidic and alkaline buffers.

#### **Acidic Buffers**

As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong base. An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.

- 1. pH of these solutions is below seven
- 2. These solutions consist of a weak acid and a salt of a weak acid.

3. An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

## **Alkaline Buffers**

These buffer solutions are used to maintain basic conditions. Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with strong acid. The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.

- 1. The pH of these solutions is above seven
- 2. They contain a weak base and a salt of the weak base.
- 3. An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

# \* Mechanism of Buffering Action

In solution, the salt is completely ionized and the weak acid is partly ionized.

 $CH_3COONa \rightleftharpoons Na^+ + CH_3COO^ CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ 

# **On Addition of Acid and Base**

On addition of acid, the released protons of acid will be removed by the acetate ions to form an acetic acid molecule.

 $H^+ + CH_3COO^-$  (from added acid)  $\rightleftharpoons CH_3COOH$  (from buffer solution)

On addition of the base, the hydroxide released by the base will be removed by the hydrogen ions to form water.

 $OH^- + H^+$  (from added base)  $\rightleftharpoons H_2O$  (from buffer solution)

# \* Solute

A solute is a substance that is dissolved in a solution. The amount of solvent in a fluid solution is greater than the amount of solute. Salt and water are two of the most common examples of solutes in our daily lives. Since salt dissolves in water, it is the solute.

A solute is a substance that can be dissolved into a solution by a solvent. A solute can take many forms. It may be in the form of a gas, a liquid, or a solid. The solvent, or material that dissolves the solute, separates the molecules of the solute and distributes them evenly.

# \* Solvent

The part of a solution that is present in the greatest amount is called a solvent. It's the liquid that the solute is dissolved in. A solvent is usually a liquid. The word "solvent" is derived from the Latin word solv, which means "to loosen or untie."

According to general information on the internet and descriptions given in some books, water is the most powerful solvent among others. It's also known as the "universal solvent" because it can dissolve almost any material better than any other liquid. Also, because of its polarity, water is an excellent solvent.

# **Important Differences between Solute and Solvent**

Some important differences between solute and solvent are tabulated below.

Basis for Comparison	Solute	Solvent
Definition	A solute is a substance that can be dissolved into a solution by a solvent. A solute can take many forms. It may be in the form of a gas, a liquid, or a solid.	The part of a solution that is present in the greatest amount is called a solvent. It's the liquid that the solute is dissolved in. A solvent is usually a liquid.

Phase	The dispersed step of a solution is known as the solute.	The solvent is the solution's medium step, which disperses the solute particles.
Quantity	In a solution, the amount of solute is less than the amount of solvent.	In a solution, the amount of solvent is greater than the amount of solute.
Physical state	The state of a solute may be solid, liquid, or gaseous.	The majority of solvents are liquids, but some solvents can remain in a gaseous state.
State of the solution	The solution may or may not be in the solute's state.	The solution is almost certainly in the solvent state.
Boiling point	The boiling point of the solute is higher than that of the solution.	The boiling point of solvents is lower than that of solutes.
Dependability	Solubility is determined by the solute's properties.	Solubility is determined by the solvent's properties.
Solubility	The solubility of a solute is determined by its properties, such as surface area and molecule size.	Solubility is determined by the solvent's properties, such as polarity.
Heat transfer	Heat is transferred to the solute in a solution.	Heat is moved from the liquid to the solution.
Examples	Examples of solutes include sugar, dissolved carbon dioxide, oxygen, water vapour, carbon dioxide, argon	Examples of the solvent include Water, Ethanol, Methanol, Acetone, tetrachloroethylene, Toluene, Methyl acetate, and Ethyl acetate.

# **\*** Types of Solvents

1. **Hydrocarbon solvents** – Hydrocarbon solvents are organic solvents with only hydrogen and carbon atoms in their molecules. In the refinery of crude oil, hydrocarbon solvents are formed as volatile fractions. The

resulting hydrocarbon solvents have varying proportions of paraffinic, naphthenic, and aromatic constituents.

- 2. **Oxygenated solvents** Solvents of carbon, hydrogen, and oxygen atoms in their chemical structure are known as oxygenated solvents. The oxygen molecule is present in an oxygenated solvent, which has a high solvency and low toxicity. Paints, inks, pharmaceuticals, perfumes, adhesives, cosmetics, detergents, and food processing all use these solvents.
- 3. **Halogenated solvents** Solvents containing a halogen, such as chlorine, bromine, or iodine, are known as halogenated solvents. Many people recognize perchloroethylene as an example a highly effective solvent used in dry cleaning

# **\*** Types of Solutions

## **Define Solution**

A solution is defined as a homogenous mixture which mainly comprises two components namely solute and solvent.

For example, salt and sugar is a good illustration of a solution. A solution can be categorized into several components.

On the basis of physical states of solvent and solute can be categorized as solid, liquid and gaseous solutions.

In solid solutions, solute and solvent are in the solid-state. For example ceramics and polymer blends. In liquid solutions, solid, gas or liquid is mixed in a liquid state. Gaseous solutions are usually homogenous mixtures of gases like air. Depending upon the number of solutions and solutes, it can be classified into dilute and concentrated solutions.

## \* Mixtures

A mixture is composed of two or more substances, but they are not chemically combined. In contrast, the compound contains various elements that are bonded to each other. For instance, consider a mixture of salt that is when salt is dissolved in water it is a mixture but ideally, salts consist of two components namely sodium and chlorine.

Here Sodium and Chlorine are bonded together with the electrostatic force of attraction to form sodium chloride even though there is no chemical bond between water and salt in the mixture. Hence, matter can be classified as mixtures, compounds and elements. Further mixtures can be classified as homogeneous and heterogeneous mixtures.

# Homogenous and Heterogeneous Solutions

Homogeneous solutions are solutions with uniform composition and properties throughout the solution. For example a cup of coffee, perfume, cough syrup, a solution of salt or sugar in water, etc.

Heterogeneous solutions are solutions with non-uniform composition and properties throughout the solution. A solution of oil and water,water and chalk powder and solution of water and sand, etc.

Aerated drinks, Salt-water or Sugar water mixtures, and fruit juices are some examples for solutions. Some solutions are heterogeneous in nature, and they are termed as suspension.

Such suspended particles can be seen quite clearly in the solution. Hence, when light is passed through such solutions, it scatters in different directions. Medicated syrups are one of the finest examples of this.

# Characteristics of Solution

Characteristics of solutions can be stated as Follows:

- 1. A solution is the Homogeneous mixture of two or more substances.
- 2. Once a solution is formed, the solute cannot be separated from the solution with the process of Filtration.
- 3. A beam of light is not allowed to pass through the solution.
- 4. A human eye cannot see the particles of the solute inside the solution.
- 5. A solution is stable and consists of only a single phase.

## **Formation of Solution: A Physical Process**

The combination of Solute and solvent to form a solution is a physical process and not a chemical process. Solute and solvent both can be retrieved back through separation methods in a chemically unchanged form, which can be shown through the following example of solid Zinc nitrate dissolving in water to form the aqueous solution of Zinc nitrate.  $Zn(NO_3)_2(s) + H_2O(l) Zn^{2+}(aq) + 2NO_3(aq)$ 

In the above reaction,  $Zn(NO_3)_2$  can be recovered easily with the help of the evaporation (evaporation of water) process. So, we can say that dissipation of solute in a solvent to form a solution does not include a chemical process.

# Types of Solutions

There are different types of solutions that can be classified on a different basis like the difference in the solute and solvent, number of criteria, etc., which can be shown as follows:-

## **1.** Different types of Solutions on the basis of water as Solvent

Solutions can be classified into two types on the basis of whether the solution is water or not.

## a. Aqueous Solution

The solution in which any state of homogeneous compound completely dissolves in water, in which water acts as a solvent. Examples of this kind of solution are sugar/ salt in water, carbon dioxide in water.

## **b.** Non-Aqueous Solution

These solutions are basically the opposite of the Aqueous solution, as the solvent available in it is not water; it could be anything else like, petrol, benzene, ether, etc. Examples of this kind of solution include phenolphthalein in benzene, sulfur in carbon disulfide, etc.

## 2. Different types of Solutions on the basis of an amount of solute added

Solutions can be classified into three types on the basis of the amount of solute present in the solution.

## a. Saturated Solutions

A solution is said to be saturated only if it reaches its limit to dissolve any more solute in the solvent at a definite temperature.

## b. Unsaturated Solutions

If the solution can still dissolve more solute in solvent, then it is said to be the unsaturated solution.

# c. Supersaturated Solutions

The solution in which solute is present in an excess amount and is dissolved in the solvent forcefully by raising the temperature is called the Supersaturated Solutions. These excess solute particles are later found in the form of crystals with the help of the crystallization process.

# 3. Different types of solutions on the basis of an amount of solvent added

Solutions can be classified into two types on the basis of the amount of solvent present in the solution.

## a. Concentrated Solutions

Large amounts of solute are added to the given solvent to give concentrated solutions.

## **b.** Dilute Solutions

A solution having a small amount of solute in a large amount of solvent is called Dilute Solutions.

# 4. Different types of solutions on the basis of the amount of concentration of solute in two solutions

Solutions can be classified into three types based on the concentration of the solvent in two solvents (in a beaker and a cell in it) in the solution.

## a. Hypertonic Solutions

Hypertonic Solutions are those types of solutions in which the concentration of the solute in solution in which cells are suspended is higher than that of in the cell, so water comes out of the cell, making the cell plasmolyze/ shrink.

# **b. Hypotonic Solutions**

Hypotonic Solutions are those solutions, in which the concentration of solute in which cells are suspended is less as compared to the cell, so the water will move into the cell, causing it to swell and burst afterward.

## c. Isotonic Solutions

These Isotonic Solutions have the same concentration of solute in both beaker and cell, so the water will move around the cell in both directions. Solutions can be distinguished on their ability to conduct electric current, as those solutions which contain molecules are called Non-conductors, while those solutions which contain ions are known as conductors.

The substances which dissolve in water and break into the form of ions are called electrolytes, while those substances which dissolve in water but do not form ions are called Non-electrolytes. These ion-forming substances, which conduct electric current in solutions, known as electrolytes, can be further classified into Strong electrolytes and Weak electrolytes.

## • Strong Electrolyte

Strong electrolytes are available only in the form of ions, as it makes the light bulb glow brilliantly on the conductivity apparatus (which is used to check the electric current in the solution). NaCl is a good example of a Strong electrolyte.

## Weak Electrolyte

The solutions which contain only a few ions are known as weak electrolytes, which makes the light bulb glow dimly on the conductivity apparatus. Weak acids and basis are good examples of weak electrolytes.

## **Examples of solutions**

Some Examples of the Solutions are Listed Below

S. No	Solute	Solvent	<b>Referred Name of the Solution</b>	Formation
1	Gas	Liquid	Foam	Whipped cream
2	Liquid	Liquid	Emulsion	Mayonnaise
3	Liquid	Solid	Gel	Gelation
4	Solid	Solid	Solid Solution	Cranberry Glass
5	Solid	Gas	Solid Aero solution	Smoke

## Redox potential

Redox potential is defined as the specific indicator of the extent to which the oxidizing as well as reducing powers of a substance which has both reducing and oxidizing ingredients, have achieved equilibrium.

Redox potential is used as:

1. An indicator of electrochemical reactivity of substances in environmental conditions

2. for predicting corrosion protection of various substances and systems.

Redox is a shortened form of the term oxidation-reduction. Redox potential, also known as oxidation-reduction potential or ORP, is a way of representing the tendency of a chemical substance to lose electrons to an electrode or to acquire electrons from an electrode. Redox potential of a system can be considered as a measure of the intensity of its oxidizing or reducing power, depending on the electrochemical balance.

Oxidation potential measures the power of a substance or system to add oxygen or to remove hydrogen as well as to lose electrons. Reduction potential indicates the power to add hydrogen, lose oxygen or attract electrons.

As the redox potential increases in value and turns positive, its ability to oxidize is enhanced. When it decreases in value and turns negative, its reducing ability is quantitatively enhanced. It has some resemblance to pH value of a liquid.

Any redox reaction can be analysed as two half-reactions: one half in which a material constituent is oxidized and the other half in which process, another constituent, is reduced.

For the half-reaction such as reduction, the driving power is the negative redox potential. For oxidation, the driving power is the positive redox potential. As corrosion involves both oxidation as well as reduction, redox potential becomes an indicator of the possibility of electrochemical activity likely to lead to corrosion or resistance to corrosion.

## \* Isomers

Chemical compounds that have identical chemical formulae but differ in properties and the arrangement of atoms in the molecule are called **isomers**. Therefore, the compounds that exhibit isomerism are known as isomers.

The word "isomer" is derived from the Greek words "isos" and "meros", which mean "equal parts". This term was coined by the Swedish chemist Jacob Berzelius in the year 1830.

#### **Isomerism Types**

There are two primary types of isomerism, which can be further categorized into different subtypes. These primary types are **Structural Isomerism** and **Stereoisomerism**. The classification of different types of isomers is illustrated below.

#### **1. Structural Isomerism**

Structural isomerism is commonly referred to as constitutional isomerism. The functional groups and the atoms in the molecules of these isomers are linked in different ways. Different structural isomers are assigned different IUPAC names since they may or may not contain the same functional group.

The different types of structural isomerism are discussed in this subsection.

#### a) Chain Isomerism

- It is also known as skeletal isomerism.
- The components of these isomers display differently branched structures.
- Commonly, chain isomers differ in the branching of carbon.
- An example of chain isomerism can be observed in the compound  $C_5H_{12}$ , as illustrated below.

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> Pentane CH<sub>3</sub> | CH<sub>3</sub>-CHCH<sub>2</sub>CH<sub>3</sub> Isopentane (2-Methylbutane)

 $CH_3 - CH_3 CH_3 CH_3$ CH.

Neopentane (2,2-Dimethylpropane)

# b) Position Isomerism

- The positions of the functional groups or substituent atoms are different in position isomers.
- Typically, this isomerism involves the attachment of the functional groups to different carbon atoms in the carbon chain.
- An example of this type of isomerism can be observed in the compounds having the formula C<sub>3</sub>H<sub>7</sub>Cl.



## c) Functional Isomerism

- It is also known as functional group isomerism.
- As the name suggests, it refers to the compounds that have the same chemical formula but different functional groups attached to them.
- An example of functional isomerism can be observed in the compound  $C_3H_6O$ .



## d) Metamerism

- This type of isomerism arises due to the presence of different alkyl chains on each side of the functional group.
- It is a rare type of isomerism and is generally limited to molecules that contain a divalent atom (such as sulphur or oxygen), surrounded by alkyl groups.
- Example:  $C_4H_{10}O$  can be represented as ethoxyethane ( $C_2H_5OC_2H_5$ ) and methoxy-propane ( $CH_3OC_3H_7$ ).

$$\begin{array}{c} CH_3 - CH_2 - O - CH_2 - CH_3 \\ E thoxyethane \end{array} \qquad \begin{array}{c} CH_3 - O - CH_2 - CH_2 - CH_3 \\ 1 - Methoxypropane \end{array}$$

# e) Tautomerism

- A tautomer of a compound refers to the isomer of the compound which only differs in the position of protons and electrons.
- Typically, the tautomers of a compound exist together in equilibrium and easily interchange.
- It occurs via an intramolecular proton transfer.
- An important example of this phenomenon is Keto-enol tautomerism.

# f) Ring-Chain Isomerism

- In ring-chain isomerism, one of the isomers has an open-chain structure whereas the other has a ring structure.
- They generally contain a different number of pi bonds.
- A great example of this type of isomerism can be observed in  $C_3H_6$ . Propene and cyclopropane are the resulting isomers, as illustrated below.

CH<sub>3</sub>CH=CH<sub>2</sub> and Propene



# 2. Stereoisomerism

Stereoisomerism refers to "the isomerism that is caused by the nonsimilar arrangements of atoms or functional groups belonging to an atom in space". These types of isomers have the same constitutions, but different geometric arrangements of atoms. Stereoisomers can be broadly classified into two types, namely enantiomers and diastereomers.

Types of Stereoisomers

Atropisomerism	Atropisomers are stereoisomers resulting from
	hindered rotation about one or more single bonds.
	This is observed in case of many drugs.

Cis-trans isomerism	Cis-trans isomerism shares the same atoms which
	are joined to one another in the same way but
	have a different configuration. This is generally
	observed in the case of alkenes and complexes.
Conformational isomerism	Conformational isomerism is a type of
	stereoisomerism in which isomers can only be
	converted by formally single bond rotations. This
	is observed in single-bonded systems like alkanes.
Diastereomers	Diastereomers are optically active isomers that
	are not enantiomers.
Enantiomers	An enantiomer is one of a pair of optical isomers,
	the structures of which are not superimposable on
	their mirror images. Chirality becomes the criteria
	here.

## 1. Enantiomers

When two isomers are mirror images of each other, the type of isomerism is called enantiomerism and these isomers are referred to as enantiomers.

Enantiomers are stable and isolable compounds that differ in their spatial arrangements in 3-D space.

They generally exist as discrete pairs.

The properties of enantiomers are identical. However, their interaction with a plane of polarized light can vary.

- The direction in which they rotate the plane-polarized light is different, that is, if one rotates in the right direction, the other rotates towards the left. Compounds that exhibit optical isomerism feature similar bonds but different spatial arrangements of atoms forming non-superimposable mirror images.
- These optical isomers are also known as enantiomers.
- Enantiomers differ from each other in their optical activities.
- Dextro enantiomers rotate the plane of polarized light to the right whereas laevo enantiomers rotate it to the left, as illustrated below.

Enantiomers represent non-superimposable mirror images of a molecule. On the other hand, diastereomers represent non-superimposable non-mirror images of a molecule. Given below in a tabular column are the differences between diastereomers and enantiomers.



#### 2. Diastereomers

When two isomers do not behave as mirror images of each other, they are called diastereomers.

A molecule with 'n' number of asymmetric carbon atoms can have up to '2n' diastereomers.

When two diastereomers differ at only one stereocenter, they are referred to as epimers.

# D-glucose and D-galactose are epimeric at carbon-4



These isomers vary in physical properties and chemical reactivity.

An illustration of enantiomers that are mirror images of each other is provided below.



This type of isomerism arises in compounds having the same chemical formula but different orientations of the atoms belonging to the molecule in three-dimensional space. The compounds that exhibit stereoisomerism are often referred to as stereoisomers.

This phenomenon can be further categorized into two subtypes. Both these subtypes are briefly described in this subsection.

# **Geometric Isomerism**

- It is popularly known as cis-trans isomerism.
- These isomers have different spatial arrangements of atoms in threedimensional space.
- An illustration describing the geometric isomerism observed in the acyclic But-2-ene molecule is provided below.



# **Optical Isomerism**

- Compounds that exhibit optical isomerism feature similar bonds but different spatial arrangements of atoms forming non-superimposable mirror images.
- These optical isomers are also known as enantiomers.
- Enantiomers differ from each other in their optical activities.
- Dextro enantiomers rotate the plane of polarized light to the right whereas laevo enantiomers rotate it to the left, as illustrated below.

Enantiomers represent non-superimposable mirror images of a molecule. On the other hand, diastereomers represent non-superimposable non-mirror images of a molecule. Given below in a tabular column are the differences between diastereomers and enantiomers.

## **\*** The Importance of Isomers in Biological Activities

Isomers have the same chemical formula but differ in their chemical structure. The molecule's properties are influenced by its structure. One isomer may have a single bond, whilst another may have double or triple bonding, indicating that the unsaturated isomer is open to bonding with other molecules, whereas the saturated isomer is closed to bonding.

They are crucial in air pollution chemistry because even minor structural variations can result in significant chemical and physical differences.

Because isomers have different pharmacokinetic and pharmacodynamic features, isomerism is important in clinical pharmacology and pharmacotherapeutics. Currently, understanding isomerism has aided in the development of safer and more effective pharmacological alternatives for both new and existing pharmaceuticals. Many existing drugs have gone chiral switch i.e., switching from racemic mixture to one of its isomers. Cetrizine to levocetrizine is one of such examples, where effective and safer drug has been made available.

# SEVERAL NEUROLOGIC DISEASES RESULTS FROM ALTERED PROTEIN CONFORMATION

## **Prions diseases**

Prion diseases are fatal neurodegenerative diseases characterized by spongiform changes, astrocytic gliomas, and neuronal loss resulting from the deposition of insoluble protein aggregates in neural cells. They include Creutzfeldt-Jakob disease in humans, scrapie in sheep, and bovine spongiform encephalopathy in cattle.

## Alzheimer's disease

Refolding or misfolding of protein endogenous to human brain tissue, amyloid beta or Abeta-amyloid, is a prominent feature of Alzheimer's disease. In Alzheimer's disease patients, levels of Abeta-amyloid/amyloid beta or become elevated, and this protein undergoes a conformational transformation from a soluble helix-rich state to a state rich in Abeta or amyloid beta sheet and prone to self-aggregation.

## Chirality

A molecule is referred to as chiral if it is not super imposable to its mirror image. The best example of chirality is our hand. Two hands cannot be superimposed identically, despite the fact that our fingers of each hand are connected in the same way. The term chiral was derived from Greek word "cheir" meaning hand and was applied as a description of left and right handedness of crystal structure resulting from molecular asymmetry. Most optical active drugs are chiral as a result of the presence of asymmetrically tetrahedral carbon atoms.

Optical isomers or enantiomers have same physical and chemical properties like identical melting points, pKa, solubities, etc. Isomerization or enantiomerization is the conversion of one stereo-isomeric form into another (R-ibuprofen to S-ibuprofen).

## Drug isomerism and chirality

Stereoisomers differ in pharmacokinetic and pharmacodynamic properties. Pharmacokinetic differences resulting out of stereoisomerism can be in absorption like L-Methotrexate is better absorbed than D-Methotrexate, Esomeprazole is more bioavailable than racemic omeprazole; in distribution like S-Warfarin is more extensively bound to albumin than R-Warfarin, and hence it has lower volume of distribution. Levocetrizine has smaller volume of distribution than its dextroisomer, d-Propranolol is more extensively bound to proteins than 1-Propranolol; in metabolism like S-Warfarin is more potent and metabolized by ring oxidation while R-Warfarin is 2 hours while it is 54 hours for R-Warfarin.

Isomerism can lead to different therapeutic uses and adverse drug reactions like Quinine has antimalarial activity while quinidine has an antiarrythmic property; D-Ethambutol is antituberculosis drug while Lethambutol has been found to cause blindness; L-dopa, used in treatment for Parkinson's disease has an isomer D-dopa which has never been used because it causes deficiency of white blood cells and thus susceptibility to infections.

Two stereoisomers can compete for binding to same receptors like Smethadone antagonizes respiratory depression action of R-methadone. If the two isomers are of agonist and antagonist type, then racemic mixture acts as partial agonist like picendol and sulfinpyrazone inhibits the metabolism of S-Warfarin significantly but not of R-Warfarin. Many antibiotics have only one enantiomer produced because they are made by fermentation and even the semi-synthetic ones start with the natural fermentation product like quinolones and all penicillins

# Chemical bonds Electrovalent, covalent, coordinate covalent bonds and Noncovalant.

#### **Types of chemical bonds:**

Atoms bind together to form molecules through three different types of chemical bonds:

- 1) Electrovalent
- 2) Covalent
- 3) Co-ordinate covalent
- 4) Noncovalant

#### **\*** Electrovalent bonds:

In forming **electrovalent bonds** electrons are actually transferred from the outer orbit of one atom to the outer orbit of a second atom. In this process both atoms usually obtain completed outer orbits. For example, in sodium chloride the single electron in the outer orbit of the sodium atom is transferred to the outer orbit of the chlorine atom, completing its outer orbit. This leaves both the sodium and the chloride atoms with completed outer orbits. See Fig. 1. In this process the sodium atom becomes sodium Na<sup>+</sup> ion with a +1 charge and the chlorine atom becomes a chlorine Cl<sup>-</sup> ion with a -1 charge. These two ions are bound together into a molecule by the force of electrostatic attraction existing between two opposite charges. Note that the process leaves the sodium atom with the electronic structure of the noble gas neon and the chlorine atom with the electronic structure of argon. See Fig. 1 (c).



Electrovalent bonds of sodium chloride, NaCl



Another example of electrovalent bonding is found in the magnesium bromide  $MgBr_2$  molecule. Here one of the two electrons in the outer orbit of magnesium is transferred to one bromine atom and the other is transferred to the other bromine atom. See. Fig.2. This gives a  $Mg^{++}$  ion and two  $Br^{-}$  ions. The ions are bound together as a molecule by the electrostatic forces existing between dissimilar charges.



Electrovalent bonds in magnesium bromide, MgBr<sub>2</sub>

Fig. 2

#### **\*** Covalent bonds:

In covalent bonds electrons are not transferred from one atom to another as in the electrovalent bond. Instead, two atoms share a pair of electrons with each other. Each of the two atoms contributes one of the electrons of the electron pair. Both electrons in the pair orbit both nuclei. This produces a bond between the two atoms. See Fig. 3 (a) for the covalent bond of hydrogen gas. By this process of sharing pairs of electrons, the atoms involved achieve completed outer orbits which provide them with chemical stability. The bonds of most common gases including hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), fluorine (F<sub>2</sub>), and chlorine (Cl<sub>2</sub>) have covalent bonds. The bonds in water (H<sub>2</sub>O) and ammonia (NH<sub>3</sub>) are of the covalent type. See Figs. 3 (b) and 3 (c).



Covalent bond of the hydrogen gas molecule, H<sub>2</sub>



(Ь)

Covalent bonds in the water molecule, H<sub>2</sub>O



Covalent bonds in ammonia molecule, NH<sub>3</sub>

Fig. 3

## **\*** Coordinate covalent bonds:

A coordinate covalent bond is like a covalent bond with the only difference being that both electrons in the electron pair come from the same atom.

Syn. Coordinate bond, dative covalent bond, dipolar bond.

The sulfur trioxide molecule has both a coordinate covalent bond and a double covalent bond. See Fig. 4.



Coordinate covalent and double covalent bonds of sulfur trioxide, SO1

Fig. 4

## Noncovalent bond

A noncovalent bond is a type of chemical bond that typically bond between macromolecules. They do not involve sharing a pair of electrons. Noncovalent bonds are used to bond large molecules such as proteins and nucleic acids. Noncovalent bonds are weaker than covalent bonds but they are crucial for biochemical processes such as the formation of double helix. There are four commonly mentioned fundamental noncovalent bond types. They include electrostatic interactions, hydrogen bonds, van der Waals interactions, and hydrophobic interactions. Each type differs in geometry, strength, and specificity.

## **Types of Noncovalent bond**

## **Electrostatic interactions:**

A charged group on a molecule can attract an oppositely charged group from another molecule. By contrast, an attractive interaction has a negative energy. The dielectric constant is important for the medium.



#### Hydrogen bonds

A hydrogen bond is the interaction of a hydrogen atom with an electronegative atom. The electronegative atom can be nitrogen, oxygen, fluorine that comes from another chemical group. Hydrogen bonds are responsible for specific base-pair formation in the DNA double helix. The hydrogen atom in a hydrogen bond is shared by two electronegative atoms such as nitrogen or oxygen. A hydrogen-bond donor is the group that includes an electronegative atom where the hydrogen atom is more tightly bound to and a hydrogen-bond acceptor is when an electronegative atom is less tightly bound to the hydrogen atom. The electronegative atom where the hydrogen atom covalently bonds can pull electron density away from the hydrogen atom creating a positive electronegativity charge. The hydrogen atom can also interact with an atom that has negative electronegativity charge.



#### Van der Waals interactions:

Van der Waals interaction is the distribution of electronic charge around an atom that fluctuates with time. It is the sum of the attractive or repulsive forces between molecules. The charge distribution is not perfectly symmetric. The attraction increases as two atoms come closer to each other, until they are separated by the van der Waals contact distance. When the distance of the energy is shorter than the van der Waals contact distance, a very strong repulsive force becomes dominant.



When two atoms come within 5 nanometers of each other, there will be a slight interaction between them, thus causing polarity and a slight attraction.

#### **Hydrophobic interactions:**

Hydrophobic interaction is the physical property of a molecule that is repelled from a mass of water. They are also called hydrophobic exclusions. It is the tendency of hydrocarbons to form intermolecular aggregates in an aqueous medium, and analogous intramolecular interactions. • American chemist Walter Kauzmann discovered that nonpolar substances like fat molecules tend to clump up together rather that distributing itself in a water medium, because this allow the fat molecules to have minimal contact with water.



#### \* Primary Bonds

These are the covalent bonds formed as a result of electron sharing among two or more atoms. They are formed as a result of a chemical reaction that may be reversible or irreversible. Primary bonds are the permanent attractions that are developed among the atoms by the sharing of electrons. The formation of a primary bond either consumes or releases energy and the same energy is needed to break the primary bond.

Primary bonds usually form the primary structure of the biological molecules except the disulfide linkage that serves to maintain the secondary or tertiary structures. The following are the various type of primary bonds found in the biological molecules.

#### **\*** Glycosidic Bond

It is a primary bond or a covalent bond that serves to connect carbohydrates to other groups or molecules. The partner or combining molecule may be carbohydrate or non-carbohydrate in nature.

This bond is formed as a result of a reaction between the carbonyl group of a carbohydrate or its derivate and a hydroxyl group of some other compound. The carbonyl group of carbohydrate may be a part of an aldehydic group or a ketonic group. A molecule of water is released in this process, making it an irreversible reaction.

## Classification

Based on the nature of the molecule linking with a carbohydrate, glycosidic bonds can be of the following types.

# **O-Glycosidic Bond**

It is the most abundant glycosidic bond found in nature. In an O-glycosidic linkage, the carbonyl group of carbohydrates reacts with the hydroxyl group of another compound. This results in a compound in which the sugar or carbohydrate residue is attached to the oxygen of the other compound, thus the name O-glycosidic bond.

The O-glycosidic linkage is found in all oligosaccharides like sucrose, maltose, maltotriose, etc. as well as polysaccharides like cellulose, starch, and glycogen. They are called O-glycosides. It is the primary bond in all types of carbohydrates above the level of monosaccharides.

# **N-Glycosidic Bond**

These are the glycosidic bonds in which a sugar moiety is attached to nitrogen of the non-carbohydrate compound. This bond is formed as a result of a chemical reaction between the carbonyl group of a carbohydrate molecule and amino group (-NH2) of a non-carbohydrate molecule.

This type of linkage is seen in amino sugars and glucosyl amines. Such compounds are called N-glycosides. An example of glucosyl amines is the nucleoside molecule in which the ribose sugar is attached to a nitrogenous base via an N-glycosidic bond.

## **C-Glycosidic Bond**

It is a strange type of glycosidic bond in which the sugar moiety is attached directly to the carbon atom of the other molecule. It is formed as a result of the reaction between the carbonyl group of a sugar molecule and an alkyl compound like methane etc.

These compounds are known as C-glycosides. An example of Cglycosides is Aloin found in aloe vera species. It is a yellowish-brown compound having bitter taste which is formed by modification of the anthraquinone structure by adding a sugar molecule.

## **S-Glycosidic Bond**

In this type of glycosidic bond, the sugar residue is attached to the sulfur group of the non-carbohydrate compound. It is formed when the carbonyl group of sugar reacts with the thiol (-SH) group of the other compound.

The compounds with S-glycosidic bonds are called S-glycosides for example Sinigrin. It is a toxic compound found in some plants like seed of black mustard etc.

## Orientation

Based on the stereochemistry of the anomeric carbon or its orientation in space, a glycosidic bond can either be an alpha-bond or a beta-bond.

## **Alpha-Glycosidic bond**

In an alpha-glycosidic bond, the atoms forming the bond are directed in the same plane i.e. they are identical in stereochemistry. The glycosidic bonds among the glucose molecules in starch are examples of the alpha-glycosidic bonds.

## **Beta-Glycosidic bond**

In beta-glycosidic bonds, the two bond-forming atoms are directed in opposite plane having different stereochemistry. The glycosidic bonds among the glucose residues in cellulose are beta-glycosidic.

## Degradation

Glycosidic bond undergoes degradation in a process called glycolysis. It is a hydrolytic process in which a water molecule is used to break the glycosidic bond and release the carbohydrate and other residues.

Enzymes required to break different types of glycosidic bonds are present in different animals. For example, the enzyme to break the beta-O-glycosidic bond between the glucose molecules in cellulose is present in the GIT of herbivores but not present in humans.

## Peptide Bond

It is the second most abundant bond found in biological molecules. A peptide bond is the one that links amino acids to form polypeptide chains.

It is a covalent bond formed as a result of a chemical reaction between the amino group of one amino acid and the carboxylic group of another amino acid.

## **Synthesis**

It is formed when the amino group and the carboxylic groups of amino acids react and release a water molecule. It is only formed when both the carboxylic group and the amino group are non-side chain groups. It means that in order to form a peptide bond, both the groups much be attached to the alpha carbon and must not be a component of the side chains of amino acids.

In the process of making a peptide bond, the carboxylic group loses hydrogen and oxygen atoms while the amino group only loses its hydrogen.

The resultant compound is called a dipeptide. This dipeptide can also form additional peptide bonds because of the presence of free amino group and carboxylic group at its N-terminal and C-terminal, respectively.

## **Properties**

It has the characteristics of a partial dual bond. Although it is a single bond, it is shorter than the traditional single covalent bonds. Recall that shorter the bond length, the stronger is the bond. Thus, this short bond length imparts rigidity to the peptide bond making it rigid and planar to the extent that the groups attached to it cannot be rotated freely. However, it must be kept in mind that the groups attached to the a-carbon, a-amino and a-carboxylic groups of these amino acids can be rotated freely.

Peptide bond is a polar bond that participates in making hydrogen bonds when the polypeptide chains are organized into higher structural levels. However, the -C=O and the -NH groups in the peptide bond carry no charge and are electrically neutral. Peptide bond is found in proteins, peptones, polypeptides, and dipeptides, etc.

## Degradation

Peptide bonds are broken down during the process of protein degradation. It is also a hydrolytic process as a water molecule is utilized to break the bond between two amino acids.

In living organisms, the hydrolysis of the peptide bond is catalysed by enzymes during the digestion of proteins in GIT as well as the normal turnover of proteins within the cell.

#### **\*** Ester Bond

It is a covalent bond that is essential in various types of lipids. An ester bond or ester linkage is formed between an acid and an alcohol.

#### **Synthesis**

An ester bond is formed when a molecule having the carboxylic group reacts with another molecule having a hydroxyl group. The carboxylic group loses its hydrogen and oxygen while the alcohol loses hydrogen of its hydroxyl group. As a result, a water molecule is released, and the two carbons are linked via an oxygen bridge forming a -COC- linkage.

## Example

The bonds between the glycerol and the fatty acids in a triglyceride are the examples of ester bonds.



#### Thioester bond

It is a modified form of ester linkage in which the oxygen bridge is used to connect a carbon atom with a sulfur atom. It is formed as a result of the reaction between the carboxylic group of one molecule and the thiol group (-SH) of another molecule. The carboxylic group loses the oxygen and hydrogen while the thiol group loses its hydrogen and a thioester bond is formed.



#### Degradation

The ester linkage is a very high-energy bond releasing a tremendous amount of energy upon hydrolysis. Like the rest of the bonds discussed earlier, it is also broken down by incorporating a water molecule. The hydrolysis of the ester linkage yields 9 Kcal/g energy.

#### Phosphodiester Bond

It is the primary covalent bond that joins different nucleotides in a polynucleotide or nucleic acids. It is also a type of ester bond but involves two ester linkages.

#### Degradation

A phosphodiester bond is a double ester linkage formed when the phosphate group at the 5' end of one nucleotide reacts with the free hydroxyl group at the 3' end of another nucleotide. A molecule of water is released, and two ester linkages are formed. In these linkages, the oxygen bridge is used to connect a carbon atom with a phosphate group. The two ester linkages are as follows;

One ester linkage attaches the phosphate group with the 5' carbon of one nucleotide. The second ester linkage attaches the same phosphate to the 3' carbon of the other nucleotide

The compound thus formed is called a dinucleotide. It can form additional phosphodiester bonds at both ends because of having a free hydroxyl group at the 3' end and a free phosphate group at the 5' end.

## **Examples**

Phosphodiester bonds are used to attach nucleotides in DNA and RNA. They are also present in dinucleotides like NAD and NADP. Polynucleotide that don't fall in the category of nucleic acids also have phosphodiester bond linking the individual nucleotides.



## Degradation

The degradation of phosphodiester bonds also requires the use of a water molecule and is thus a hydrolytic process. In living organisms, the degradation of the phosphodiester bond is catalyzed by specific enzymes called nucleases. They are of two types;

Exonucleases, they break the phosphodiester bond beginning from one end of the chain.

Endonucleases, they can break the phosphodiester bond even from within the chain of nucleotides.