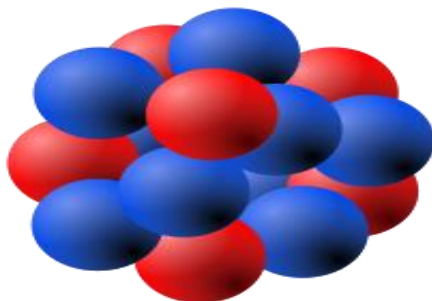


**Unit I**

Radiochemistry or nuclear chemistry is the analysis of radiation from an atomic and molecular perspective, along with elemental transformation and response outcomes, along with bodily, properly being and medical properties.

**Atomic nucleus**



A model of the atomic nucleus showing it as a compact bundle of the two types of nucleons: protons (red) and neutrons (blue). In this diagram, protons and neutrons look like little balls stuck together, but an actual nucleus (as understood by modern nuclear physics) cannot be explained like this, but only by using quantum mechanics. In a nucleus which occupies a certain energy level (for example, the ground state), each nucleon can be said to occupy a range of locations.


The **atomic nucleus** is the small, dense region consisting of protons and neutrons at the center of an atom, discovered in 1911 by Ernest Rutherford based on the 1909 Geiger–Marsden gold foil experiment. After the discovery of the neutron in 1932, models for a nucleus composed of protons and neutrons were quickly developed and Werner Heisenberg. An atom is composed of a positively-charged nucleus, with a cloud of negatively-charged electrons surrounding it, bound together by electrostatic force. Almost all of the mass of an atom is located in the nucleus, with a very small contribution from the electron cloud. Protons and neutrons are bound together to form a nucleus by the nuclear force.

Protons and neutrons are fermions, with different values of the strong isospin quantum number, so two protons and two neutrons can share the same space wave function since they are not identical quantum entities. They are sometimes viewed as two different quantum states of the same particle, the *nucleon*. Two fermions, such as two protons, or two neutrons, or a proton + neutron (the deuteron) can exhibit bosonic behavior when they become loosely bound in pairs, which have integer spin.

In the rare case of a hypernucleus, a third baryon called a hyperon, containing one or more strange quarks and/or other unusual quark(s), can also share the wave function. However, this type of nucleus is extremely unstable and not found on Earth except in high energy physics experiments.

The neutron has a positively charged core of radius  $\approx 0.3$  fm surrounded by a compensating negative charge of radius between 0.3 fm and 2 fm. The proton has an approximately exponentially decaying positive charge distribution with a mean square radius of about 0.8 fm.


Nuclei can be spherical, rugby ball-shaped (prolate deformation), discus-shaped (oblate deformation), triaxial (a combination of oblate and prolate deformation) or pear-shaped.



**ISOTOPES** – nuclides with identical Z  
**ISOBARS** – nuclides with identical A  
**ISOTONES** – nuclides with identical N  
**ISOMERS** – two nuclei of the same species but different energy states, of which at least one is metastable  
**MIRROR NUCLEI** – proton (neutron) number of one is the neutron (proton) number of the other

Which are isotopes, isobars, isotones, mirror nuclei?

$^{12}\text{B}_5$ ,  $^{14}\text{C}_6$ ,  $^{14}\text{N}_7$ ,  $^{14}\text{O}_8$ ,  $^{16}\text{O}_8$



### What are Isotopes?

Isotopes are atoms with the same number of protons, but differing numbers of neutrons. A number of protons in the atom is the atomic number of that atom. A particular chemical element has a fixed number of protons. Hence, the atomic number of the atoms of the same chemical element is similar to each other. Therefore, isotopes are atoms of the same chemical element. The total number of protons and neutrons is known as the atomic mass. Isotopes have different atomic masses.

An isotope is named using the name of the chemical element and the atomic mass of the isotope. For example, the two isotopes of Helium are noted as “helium-2” and “helium-

## What are Isobars?

Isobars are atoms of different chemical elements having equal values for atomic mass. Atomic mass is the sum of protons and neutrons in the nucleus of an atom. A proton or a neutron is known as a **nucleon**. Therefore, isobars have the same number of nucleons.

The atomic numbers of these isobars are different from each other because different chemical elements have different atomic numbers. The Mattauch isobar rule states that if two adjacent elements on the [periodic table](#) have isotopes of the same mass number (isobars), one of these isotopes must be radioactive. If there are isobars of three sequential elements exist, first and last isobars are stable, and the middle one may undergo radioactive decay. An isobar series is a collection of different isotopes that have the same atomic mass.

Isobar Series	Members of the series
40	$^{40}\text{S}$ , $^{40}\text{Cl}$ , $^{40}\text{Ar}$ , $^{40}\text{K}$ , and $^{40}\text{Ca}$
58	$^{58}\text{Fe}$ and $^{58}\text{Ni}$
76	$^{76}\text{Ce}$ and $^{76}\text{Se}$

## What are Isotones?

Isotones are atoms of different elements having an equal number of neutrons in the atomic nucleus. Isotones have different atomic numbers (number of protons in the nucleus is different from each other) as well as different atomic masses. It can be expressed as below;

Atomic number =  $Z$

Atomic mass =  $A$

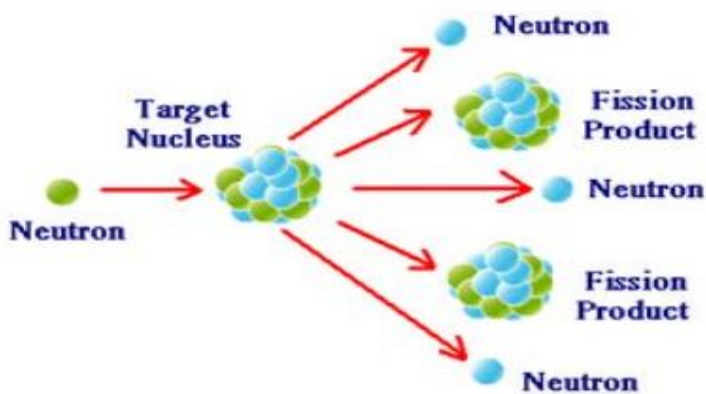
Number of neutron =  $N$

For all isotones in one series,  $A \neq Z$  but  $(A-Z)=N$  ( $N$  is equal for all the isotones in one series). Some examples for isotones are given below.

Isotone Series	Members of the series
20	$^{36}\text{S}$ , $^{37}\text{Cl}$ , $^{38}\text{Ar}$ , $^{39}\text{K}$ , and $^{40}\text{Ca}$
50	$^{86}\text{Kr}$ , $^{88}\text{Sr}$ , $^{89}\text{Y}$ , $^{90}\text{Zr}$ and $^{92}\text{Mo}$
82	$^{138}\text{Ba}$ , $^{139}\text{La}$ , $^{140}\text{Ce}$ , $^{141}\text{Pr}$ , $^{142}\text{Nd}$ and $^{144}\text{Sm}$

### Comparison between Chemical and Nuclear Reaction:

	Chemical Reaction	Nuclear Reaction
Definition	Elements rearrange themselves to form a new element.	Structure of nucleus is changed with release of energy.
Reaction	Electrons are responsible for the reaction.	It takes place in the nucleus of atom.
Position	It takes place outside the nucleus.	It takes place inside the nucleus.
Nature	Involves loss, gain and sharing of electrons.	Involves the decomposition of nucleus.
Energy	Low energy change.	High energy change.
Isotopes	They react the same	They react differently.
Chemical combinations	It is depended.	It does not depend.
Mass	Reactants and products have equal mass.	There is mass change.



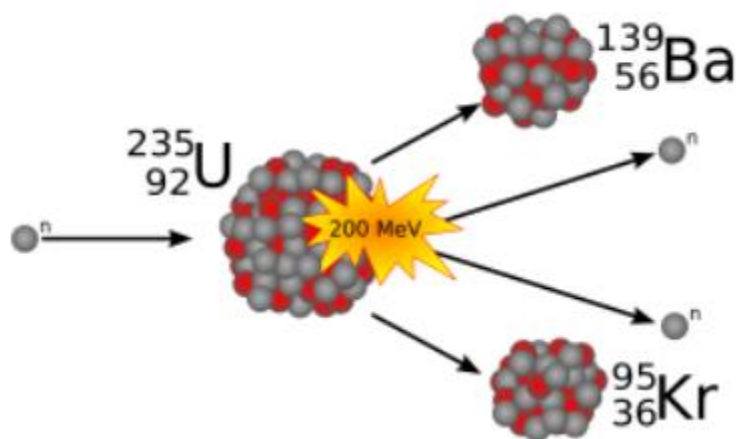
## Nuclear Fission:

Neutron bombardment of Uranium-235 and radioactive decay in unstable isotopes are examples of nuclear fission. Nuclear Fusion: Nuclear fusion reactions are most commonly found as the fusion between Deuterium and Tritium

### What is Nuclear Fission?

When the nucleus of an atom splits into lighter nuclei through a nuclear reaction the process is termed as nuclear fission. This decay can be natural spontaneous splitting by radioactive decay, or can actually be simulated in a lab by achieving necessary conditions (bombarding with neutrinos). The resulting fragments tend to have a combined mass which is less than the original. The missing mass is what is converted into nuclear energy in the above reaction. Therefore, nuclear fission is defined as:

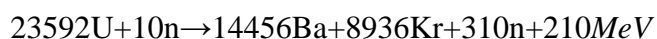
The process in nuclear physics in which the nucleus of an atom splits into two daughter nuclei.



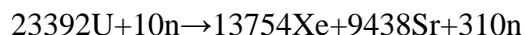
When Uranium-235 atom is bombarded with a neutron, it splits into two lighter nuclei Barium and Krypton.

### Examples of Nuclear Fission

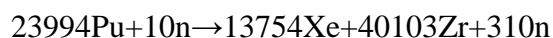
1. An example of nuclear fission is the splitting of Uranium-235. The equation of the reaction has been given below:



2. The other example of nuclear fission is the splitting of Uranium-233. The equation of the reaction has been given below:



3. The splitting of Plutonium-239 is the other example of nuclear fission is given below:



### **Fission in Nuclear Power Plants**

We have discussed the basics of nuclear fission reactions, now let us understand what real-world applications these reactions have. One of the major applications of a fission reaction is the production of electricity via nuclear power plants. Nuclear fission is an advantageous method for producing power for several reasons.

We use nuclear reactors to generate electricity making use of the nuclear fission reaction. The heat from the nuclear fission is passed to a working fluid, which in turn runs through steam turbines. These either drive a ship's propellers or turn electrical generators' shafts.

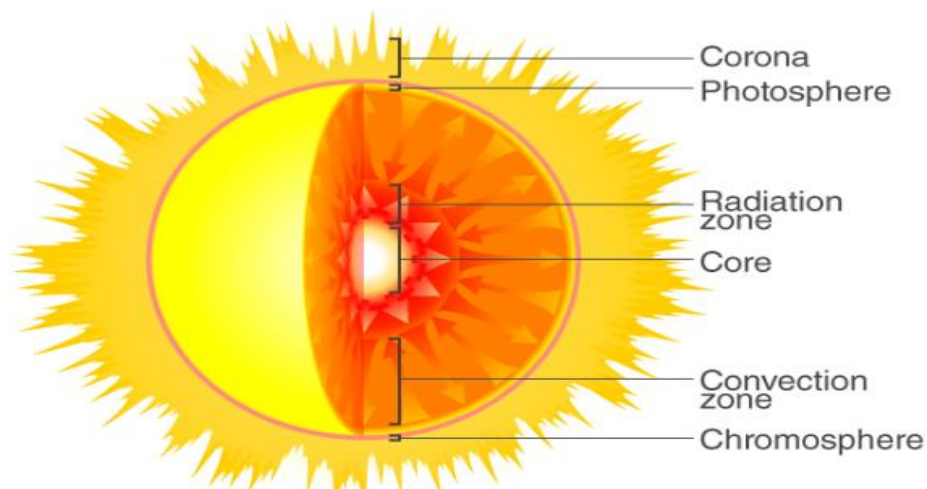
## **Nuclear Fusion**

What is Nuclear Fusion?

Nuclear fusion is a reaction through which two or more light nuclei collide into each other to form a heavier nucleus. This reaction takes place with elements which have a low atomic number, such as Hydrogen. It is the opposite of nuclear fission reaction in which heavy elements diffuse and form lighter elements. Both nuclear fusion and fission produce a massive amount of energy.

### **Nuclear Fusion in the Universe**

Every star in the universe, including the Sun, is alive due to nuclear fusion. It is through this process that they produce such a mind-boggling amount of heat and energy. The pressure at the core of any star is tremendously high and that is where the nuclear fusion reaction takes place.



### Difference between Nuclear Fission and Nuclear Fusion

These two are the major nuclear reactions that take place. The basic differences between Nuclear Fission and Nuclear Fusion are:

Nuclear Fission	Nuclear Fusion
Breaks a heavy atom into two or more smaller ones.	Brings two or more small atoms together to form one large atom.
Does not happen naturally.	The universe is full of instances of nuclear fusion reactions. Every star uses it to produce energy.
Produces a great deal more energy than chemical reactions but still not as much as fusion.	Produces many times more amount of energy than fission.
Does not require a lot of energy to split an atom into two.	Requires a lot of heat and pressure for the process to happen.

### Radioactive series,

Any of four independent sets of unstable heavy atomic nuclei that decay through a sequence of alpha and beta decays until a stable nucleus is achieved.

Radioactive Disintegration Series. "A series of regular disintegration starting from an unstable nucleus and ending at a stable nucleus, is known as radioactive disintegration series". Types of Disintegration Series- There are four disintegration series.

Radioactive decay has a huge benefit beyond the esoteric uses of scientists (such as dating rocks). It is thought that half of the heat present in the body of the Earth is due to radioactive decay.

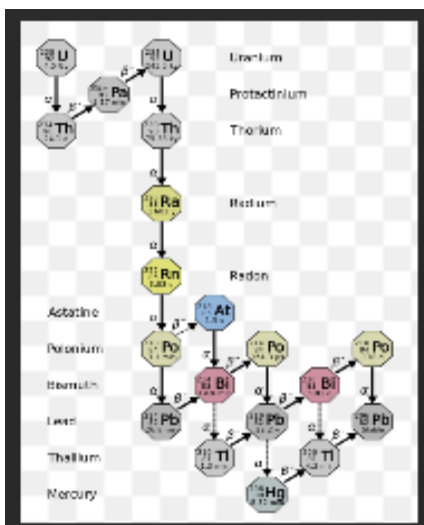
### How does radioactive decay produce new elements?

A neutron converts to a proton and an electron, so the decay product has 43 protons and 56 neutrons. Any atom with 43 protons is technetium, so the decay has formed a new element. Alpha decay ejects alpha particles, which contain 2 protons and 2 neutrons. Uranium-238 decays mostly in this way

Large, heavy elements, such as uranium and thorium, tend to undergo alpha emission. This decay mode relieves the nucleus of two units of positive charge (two protons) and four units of mass (two protons + two neutrons). Each time an alpha particle is emitted, four units of mass are lost.

### What are the half lives of radioactive elements?

For example, calcium-47 has a half life of 'A half life is the time required for half the original sample of matter to decay. 'A radioactive element's half-life is an important factor in how dangerous the radiation can be to humans, plants, and animals. 'HALF LIVES. 4 ½ days.



### Metallic bond.

Metallic bonds are found in metals like zinc. A metallic bond is the sharing of many detached electrons between many positive ions, where the electrons act as a "glue" giving the substance a definite structure. It is unlike covalent or ionic bonding.



## Examples of Metallic Bond.

The examples of metallic bond are iron, cobalt, calcium and magnesium, silver, gold, barium, platinum, chromium, copper, zinc, sodium, lithium and francium are some of the examples of metallic bonds. Covalent Bond. Metallic Bond.

## Electron gas theory

Free-electron theory of metals. The treatment of a metal as containing a gas of electrons completely free to move within it. The theory was originally proposed in 1900 to describe and correlate the electrical and thermal properties of metals.

Given its simplicity, it is surprisingly successful in explaining many experimental phenomena, especially

- the Wiedemann–Franz law which relates electrical conductivity and thermal conductivity;
  - the temperature dependence of the electron heat capacity;
  - the shape of the electronic density of states;
  - the range of binding energy values;
  - electrical conductivities;
  - the Seebeck coefficient of the thermoelectric effect;
  - thermal electron emission and field electron emission from bulk metals
- 
- Free electron approximation: The interaction between the ions and the valence electrons is mostly neglected, except in boundary conditions. The ions only keep the charge neutrality in the metal. Unlike in the Drude model, the ions are not necessarily the source of collisions.
  - Independent electron approximation: The interactions between electrons are ignored. The electrostatic fields in metals are weak because of the screening effect.
  - Relaxation-time approximation: There is some unknown scattering mechanism such that the electron probability of collision is inversely proportional to the relaxation time, which represents the average time between collisions. The collisions do not depend on the electronic configuration.
  - Pauli exclusion principle: Each quantum state of the system can only be occupied by a single electron. This restriction of available electron states is taken into account by Fermi–Dirac statistics (see also Fermi gas). Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi–Dirac occupancy for energies around the Fermi level.

The name of the model comes from the first two assumptions, as each electron can be treated as free particle with a respective quadratic relation between energy and momentum.

## PAULING THEORY

The nature of the chemical bond led to his introduction of the concept of orbital hybridization. While it is normal to think of the electrons in an atom as being described by orbitals of types such as  $s$  and  $p$ , it turns out that in describing the bonding in molecules, it is better to construct functions that partake of some of the properties of each. Thus the one  $2s$  and three  $2p$  orbitals in a carbon atom can be (mathematically) 'mixed' or combined to make four equivalent orbitals (called  $sp^3$  hybrid orbitals), which would be the appropriate orbitals to describe carbon compounds such as methane, or the  $2s$  orbital may be combined with two of the  $2p$  orbitals to make three equivalent orbitals (called  $sp^2$  hybrid orbitals), with the remaining  $2p$  orbital unhybridized, which would be the appropriate orbitals to describe certain unsaturated carbon compounds such as ethylene. Other hybridization schemes are also found in other types of molecules. Another area which he explored was the relationship between ionic bonding, where electrons are transferred between atoms, and covalent bonding, where electrons are shared between atoms on an equal basis. Pauling showed that these were merely extremes, and that for most actual cases of bonding, the quantum-mechanical wave function for a polar molecule  $AB$  is a combination of wave functions for covalent and ionic molecules. Here Pauling's electro negativity concept is particularly useful; the electro negativity difference between a pair of atoms will be the surest predictor of the degree of ionicity of the bond.

### The Band theory

These bands and band gaps by examining the allowed quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. Band theory has been successfully used to explain many physical properties of solids, such as electrical resistivity and optical absorption, and forms the foundation of the understanding of all solid-state devices (transistors, solar cells, etc.). nature of the chemical bond" was the accounting of the structure of aromatic hydrocarbons,

### Assumptions and limits of band structure theory

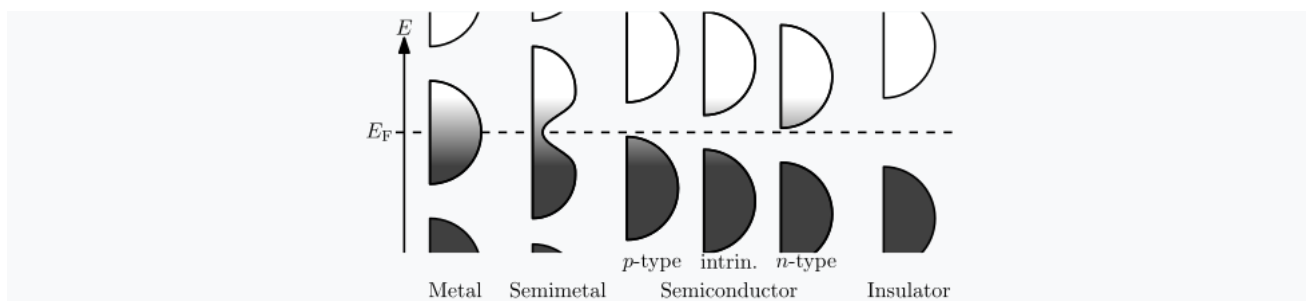
Band theory is only an approximation to the quantum state of a solid, which applies to solids consisting of many identical atoms or molecules bonded together. These are the assumptions necessary for band theory to be valid:

- *Infinite-size system*: For the bands to be continuous, the piece of material must consist of a large number of atoms. Since a macroscopic piece of material contains on the order of  $10^{22}$  atoms, this is not a serious restriction; band theory even applies to microscopic-sized transistors in integrated circuits. With modifications, the concept of band structure can also be extended to systems which are only "large" along some dimensions, such as two-dimensional electron systems.
- *Homogeneous system*: Band structure is an intrinsic property of a material, which assumes that the material is homogeneous. Practically, this means that the chemical makeup of the material must be uniform throughout the piece.
- *Non-interactivity*: The band structure describes "single electron states". The existence of these states assumes that the electrons travel in a static potential without dynamically interacting with lattice vibrations, other electrons, photons, etc.

Energy band gaps can be classified using the wavevectors of the states surrounding the band gap:

- Direct band gap: the lowest-energy state above the band gap has the same  $\mathbf{k}$  as the highest-energy state beneath the band gap.
- Indirect band gap: the closest states above and beneath the band gap do not have the same  $\mathbf{k}$  value.

### Filling of bands



Filling of the electronic states in various types of materials at equilibrium. Here, height is energy while width is the density of available states for a certain energy in the material listed. The shade follows the Fermi–Dirac distribution (black = all states filled, white = no state filled). In metals and semimetals the Fermi level  $E_F$  lies inside at least one band. In insulators and semiconductors the Fermi level is inside a band gap; however, in semiconductors the bands are near enough to the Fermi level to be thermally populated with electrons or holes.

At thermodynamic equilibrium, the likelihood of a state of energy  $E$  being filled with an electron is given by the Fermi–Dirac distribution, a thermodynamic distribution that takes into account the Pauli exclusion principle:

$$f(E) = \frac{1}{1 + e^{(E-\mu)/k_B T}}$$

where:

- $k_B T$  is the product of Boltzmann's constant and temperature, and
- $\mu$  is the total chemical potential of electrons, or *Fermi level* (in semiconductor physics, this quantity is more often denoted  $E_F$ ). The Fermi level of a solid is directly related to the voltage on that solid, as measured with a voltmeter
- The density of electrons in the material is simply the integral of the Fermi–Dirac distribution times the density of states:

$$N/V = \int_{-\infty}^{\infty} g(E) f(E) dE$$

- Although there are an infinite number of bands and thus an infinite number of states, there are only a finite number of electrons to place in these bands. The preferred value for the number of electrons is a consequence of electrostatics: even though the surface of a material can be charged, the internal bulk of a material prefers to be charge neutral. The condition of charge neutrality means that  $N/V$  must match the density of protons in the material. For this to occur, the material electrostatically adjusts itself, shifting its band structure up or down in energy (thereby shifting  $g(E)$ ), until it is at the correct equilibrium with respect to the Fermi level.

## Semiconductor

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A semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. Its resistance falls as its temperature rises; metals are the opposite. Its conducting properties may be altered in useful ways by introducing impurities ("doping") into the crystal structure. Where two differently-doped regions exist in the same crystal, a semiconductor junction is created. The behavior of charge carriers which include electrons, ions and electron holes at these junctions is the basis of diodes, transistors and all modern electronics. Some examples of semiconductors are silicon, germanium, gallium arsenide, and elements near the so-called "metalloid staircase" on the periodic table. After silicon, gallium arsenide is the second most common semiconductor and is used in laser diodes, solar cells, microwave-frequency integrated circuits and others. Silicon is a critical element for fabricating most electronic circuits.

Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping, or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion.

The conductivity of silicon is increased by adding a small amount (of the order of 1 in  $10^8$ ) of pentavalent (antimony, phosphorus, or arsenic) or trivalent (boron, gallium, indium) atoms. This process is known as doping and resulting semiconductors are known as doped or extrinsic semiconductors. Apart from doping, the conductivity of a semiconductor can equally be improved by increasing its temperature. This is contrary to the behaviour of a metal in which conductivity decreases with increase in temperature.

The modern understanding of the properties of a semiconductor relies on quantum physics to explain the movement of charge carriers in a crystal lattice. Doping greatly increases the number of charge carriers within the crystal. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type". The semiconductor materials used in electronic devices are doped under precise conditions to control the concentration and regions of p- and n-type dopants. A single semiconductor crystal can have many p- and n-type regions; the p–n junctions between these regions are responsible for the useful electronic behavior.

Some of the properties of semiconductor materials were observed throughout the mid 19th and first decades of the 20th century. The first practical application of semiconductors in electronics was the 1904 development of the cat's-whisker detector, a primitive semiconductor diode used in early radio receivers. Developments in quantum physics in turn led to the development of the transistor in 1947, the integrated circuit in 1958, and the MOSFET (metal–oxide–semiconductor field-effect transistor) in 1959.

#### **What is semiconductor used for?**

Semiconductors are used extensively in electronic circuits. As its name implies, a semiconductor is a material that conducts current, but only partly. ... Semiconductors are made out of such crystals, usually silicon crystals. Here, each circle represents a silicon atom, and the lines between the atoms represent the shared electrons.

#### **What are some examples of semiconductors?**

Semiconductors can conduct electricity at a certain level without being damaged. Also, the conductivity of a semiconductor increases with increase in temperature. Examples of semiconductors: Silicon (Si) and Germanium (Ge) are two most common examples of semiconductors.

A semiconductor material has an electrical conductivity value falling between that of a conductor, such as metallic copper, and an insulator, such as glass. Its resistance falls as its temperature rises; metals are the opposite.

Silicon (Si) and gallium arsenide (GaAs) are the two most common semiconductor materials used in electronic and electro-optic devices. In some cases other elements, such as aluminum (Al), indium (In) and phosphorus (P), are added to the base semiconductor material to modify the semiconductor properties.

Semiconductors are used extensively in electronic circuits. As its name implies, a semiconductor is a material that conducts current, but only partly. The conductivity of a semiconductor is somewhere between that of an insulator, which has almost no conductivity, and a conductor, which has almost full conductivity.

### **Types of Semiconductor**

There are two basic types of semiconductors; the intrinsic and the extrinsic. The material comprising an intrinsic semiconductor is in a generally pure state. The extrinsic semiconductor can be further categorized as either n-type or p-type. This is one to which impurities have been added to produce a desired state. N-type and p-type semiconductors are extrinsic semiconductors to which different impurities have been added, and consequently have different conductive properties.

A semiconductor is usually a crystalline solid in which conductivity due to electron flow is between that of a metal and an insulator. Intrinsic semiconductors are such materials with little or no impurity, silicon being the most widely used. The atomic lattice structure of silicon crystals is made up of perfect covalent bonds, which means there are few free electrons to move around. The crystal is almost an insulator. As temperatures rise above absolute zero, the likelihood of inducing electron flow in the material increases.

This effect can be greatly increased by introducing impurities into the lattice structure that make a greater number of free electrons available. The process of adding certain impurities to semiconductors is referred to as doping. The impurity added is termed the dopant. The amount of dopant added to an intrinsic semiconductor proportionally changes its level of conductivity. Extrinsic semiconductors are the products of the doping process.

### N-type semiconductors

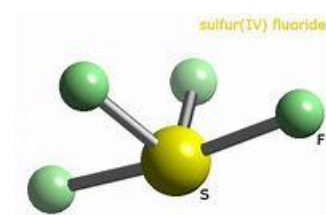
N-type semi conductors are extrinsic semiconductors in which donor dopants have been used. An increase in negative electron charge carriers results. Negative charge carriers are called the majority carrier in the n-type, while positive charge carriers are called the minority.

### P-type semiconductors

P-Type semi conductor are the result of using acceptor dopants. As the covalent bonds of the lattice reform, holes are left in the valence bands of the surrounding material. The increase in holes increases the concentration of positive charge carriers. The majority carrier for the p-type would be positive and the minority negative.

By doping, semiconductors can be produced with different and complementary conductive properties. An important application of this is the p-n junction, where p-type and n-type semiconductors are brought into close contact. One effect of the junction is to permit the holes and the electrons to combine, producing light. This is a light emitting diode (LED). The p-n junction also forms a diode where electricity can flow in one direction through the junction but not in the other, a requirement for digital electronics.

## Sulfur compounds



Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide), and stibnite (antimony sulfide); and the sulfate minerals, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate),...

### Sulfur: compounds information

- Hydrides. The term hydride is used to indicate compounds of the type  $M_x H_y$  and not necessarily to indicate that any compounds listed behave as hydrides chemically.
- Fluorides.
- Chlorides.
- Bromides.
- Iodides.

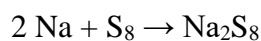
Pure sulfur is a tasteless, odourless, brittle solid that is pale yellow in colour, a poor conductor of electricity, and insoluble in water. It reacts with all metals except gold and platinum, forming sulfides ; it also forms compounds with several nonmetallic elements.

Treatment of sulfur with hydrogen gives hydrogen sulfide. When dissolved in water, hydrogen sulfide is mildly acidic:

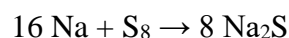


Hydrogen sulfide gas and the hydrosulfide anion are extremely toxic to mammals, due to their inhibition of the oxygen-carrying capacity of hemoglobin and certain cytochromes in a manner analogous to cyanide and azide (see below, under *precautions*).

Reduction of elemental sulfur gives polysulfides, which consist of chains of sulfur atoms terminated with  $S^-$  centers:



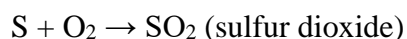
This reaction highlights a distinctive property of sulfur: its ability to catenate (bind to itself by formation of chains). Protonation of these polysulfide anions produces the polysulfanes,  $H_2S_x$  where  $x= 2, 3,$  and  $4$ .<sup>[27]</sup> Ultimately, reduction of sulfur produces sulfide salts:



The interconversion of these species is exploited in the sodium-sulfur battery.

### Oxides, oxoacids, and oxoanions

The principal sulfur oxides are obtained by burning sulfur:



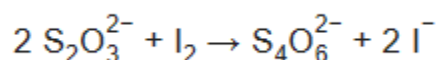
### COMPOUNDS OF SODIUM THIO SULPHATE

Sodium thiosulfate (sodium thiosulphate) is an inorganic compound with the formula  $Na_2S_2O_3 \cdot xH_2O$ . Typically it is available as the white or colorless pentahydrate,  $Na_2S_2O_3 \cdot 5H_2O$ . The solid is an efflorescent (loses water readily) crystalline substance that dissolves well in water.

Sodium thiosulfate is used in gold mining, water treatment, analytical chemistry, the development of silver-based photographic film and prints, and medicine. The medical uses of sodium thiosulfate include treatment of cyanide poisoning and pityriasis. It is on the World Health Organization's List of Essential Medicines, the safest and most effective medicines needed in a health system

Sodium thiosulfate is used in the treatment of cyanide poisoning. Other uses include topical treatment of ringworm and tinea versicolor, and treating some side effects of hemodialysis and chemotherapy

In analytical chemistry, the most important use comes because the thiosulfate anion reacts stoichiometrically with iodine in aqueous solution, reducing it to iodide as the thiosulfate is oxidized to tetrathionate:

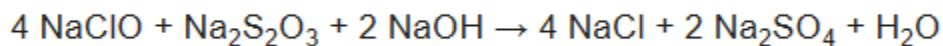


## Photographic processing

Silver halides, e.g., AgBr, typical components of photographic emulsions, dissolve upon treatment with aqueous thiosulfate:

This application as a photographic fixer was discovered by John Herschel. It is used for both film and photographic paper processing; the sodium thiosulfate is known as a photographic fixer, and is often referred to as 'hypo', from the original chemical name, hyposulphite of soda. Ammonium thiosulfate is typically preferred to sodium thiosulfate for this application.

In pH testing of bleach substances, sodium thiosulfate neutralizes the color-removing effects of bleach and allows one to test the pH of bleach solutions with liquid indicators. The relevant reaction is akin to the iodine reaction: thiosulfate reduces the hypochlorite (active ingredient in bleach) and in so doing becomes oxidized to sulfate. The complete reaction is:





## UNIT II

### CARBOHYDRATE, AMINO ACID AND PROTEIN

#### Carbohydrate

A carbohydrate is a biomolecule consisting of carbon, hydrogen and oxygen atoms, usually with a hydrogen–oxygen atom ratio of 2:1 and thus with the empirical formula  $C_m(H_2O)_n$ . This formula holds true for monosaccharides. Some exceptions exist; for example, deoxyribose, a sugar component of DNA, has the empirical formula  $C_5H_{10}O_4$ . The carbohydrates are technically hydrates of carbon; structurally it is more accurate to view them as aldoses and ketoses.

- Sugars. Carbohydrates can be simple or complex.
- Starch. Starches and fiber are complex carbohydrates.
- Fiber. Fiber is a carbohydrate type far different from simple and complex carbohydrates.
- Dietary Recommendations. You need carbohydrates to promote digestive regularity,

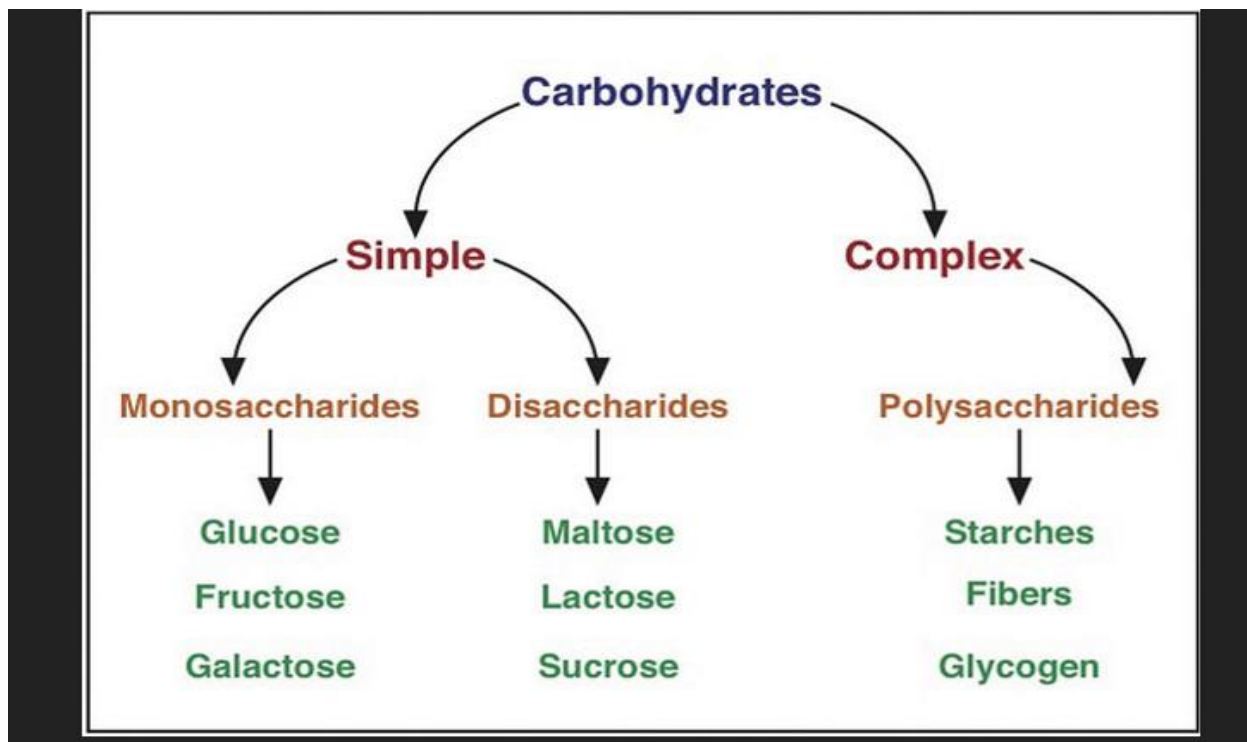
Carbohydrates are essential for two distinct functions in your body -- energy and digestion. Most types of carbohydrates, such as starch and sugar, break down into glucose, which is the simplest form of carbohydrate and your body's primary source of energy.

#### **4 essential functions of carbohydrates**

1. As a source of Energy.
2. Protein sparing Action.
3. Regulation of fat Metabolism.
4. Role in gastro-intestinal function.

#### **flowchart of Classification of Carbohydrates:**

1. Monosaccharides.
2. Oligosaccharides.



Carbohydrates are polyhydroxy aldehydes, ketones, alcohols, acids, their simple derivatives and their polymers having linkages of the acetal type. They may be classified according to their degree of polymerization, and may be divided initially into three principal groups, namely sugars, oligosaccharides and polysaccharides

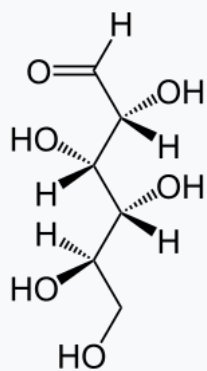
The major dietary carbohydrates		
Class (DP*)	Subgroup	Components
Sugars (1–2)	Monosaccharides	Glucose, galactose, fructose, xylose
	Disaccharides	Sucrose, lactose, maltose, trehalose
	Polyols	Sorbitol, mannitol
Oligosaccharides (3–)	Malto-oligosaccharides	Maltodextrins

9)	Other oligosaccharides	Raffinose, stachyose, fructo-oligosaccharides
Polysaccharides (>9)	Starch	Amylose, amylopectin, modified starches
	Non-starch polysaccharides	Glycogen, Cellulose, Hemicellulose, Pectins, Hydrocolloids

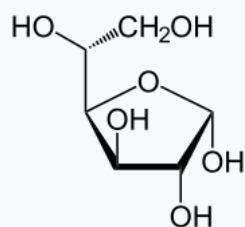
## Glucose

### Different forms and projections of D-Glucose in comparison

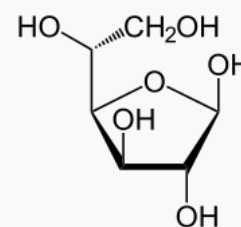
#### Natta projection



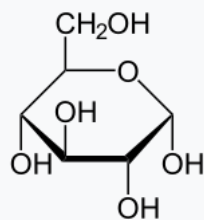
#### Haworth projection



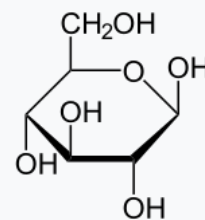
$\alpha$ -D-glucopyranose



$\beta$ -D-glucopyranose

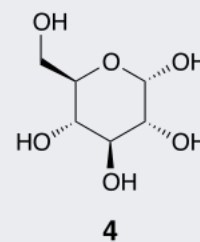
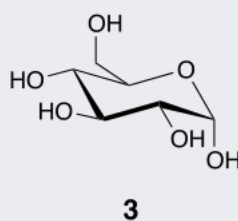
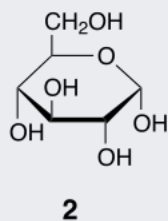
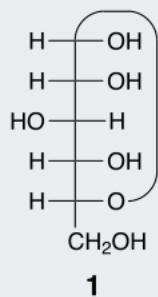


$\alpha$ -D-glucopyranose

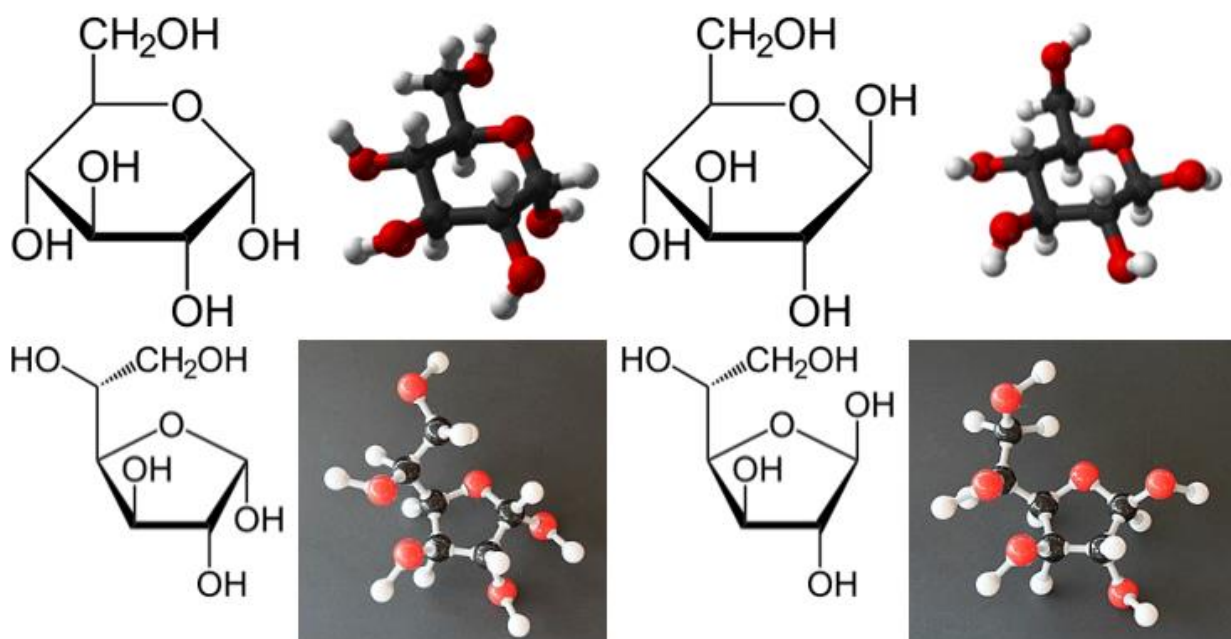


$\beta$ -D-glucopyranose

**$\alpha$ -D-Glucopyranose in (1) Tollens/Fischer- (2) Haworth-projection (3) chair conformation (4) stereochemical view**



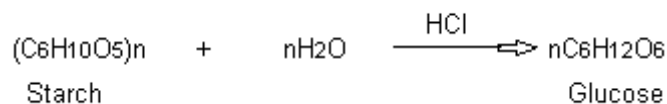
## Cyclic forms of glucose



From left to right: Haworth projections and ball-and-stick structures of the  $\alpha$ - and  $\beta$ - anomers of D-glucopyranose (top row) and D-glucofuranose (bottom row)

### Preparation of glucose.

**Glucose** is produced commercially by the hydrolysis of starch with dilute hydrochloric acid at high temperature under pressure.



An aqueous suspension of starch obtained from corn is acidified with hydrochloric acid, It is then heated with high-pressure steam in an autoclave. When the hydrolysis is complete, the liquid is neutralized with sodium carbonate to a pH of 4-5. The resulting solution is concentrated under reduced pressure to get the crystals of glucose.

## Uses of glucose.

### Glucose is used.

1. As a sweetening agent in syrups and confectionery.
2. As food for infants.
3. As a reducing agent in the silvering of mirrors and to convert indigo blue to indigo white in vat dyeing.
4. As a raw material for wine and alcohol manufacture.

### Structure of glucose.

The **structure of glucose** may be discussed under the following heads.

1. Open Chain formula.
2. Configuration.
3. Cyclic structure.
4. Haworth representation.

### Open-chain Formula.

The **open-chain formula of glucose** is constructed from the following facts:

#### (1) Molecular Formula.

Elemental analysis and molecular weight determination have established that glucose has the molecular formula  $C_6H_{12}O_6$ .

#### (2) Presence of 6-carbon unbranched chain.

The complete reduction of glucose with concentrated hydrogen iodide and red phosphorus gives *n*-hexane. This proves that a glucose molecule is made of an unbranched six-carbon chain.

#### (3) Presence of 5 OH group.

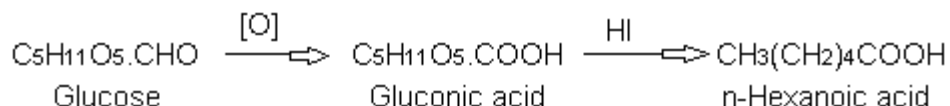
Glucose reacts with acetic anhydride to form the pentadactyl derivative. This shows the presence of five hydroxy groups. Since glucose is a stable compound, no two OH groups are attached to the same carbon. In other words, the five OH groups are on different carbons.

#### (4) Presence of the C=O group.

Glucose reacts with hydroxylamine to form an oxime. It suggests the presence of a carbonyl group.

#### (5) Presence of terminal CHO function.

On mild oxidation with bromine water, glucose is converted to gluconic acid which when reduced with an excess of HI yields *n*-hexanoic acid.



This shows that glucose contains a six carbon straight chain with CHO at one end, which has been oxidised to COOH.

### (6) Construction of open-chain formula.

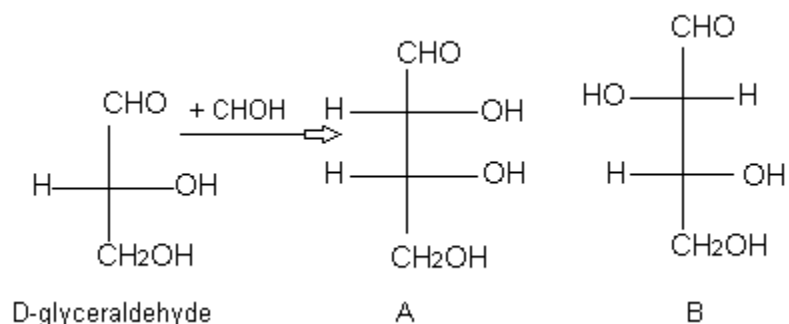
Knowing that glucose has a straight 6-carbon chain with a terminal CHO, the five OH groups can be placed one each on the remaining five carbons. Supplying hydrogen atoms to these carbons to satisfy their tetravalency, the open-chain structure of glucose can be written as

### Configuration of D-Glucose.

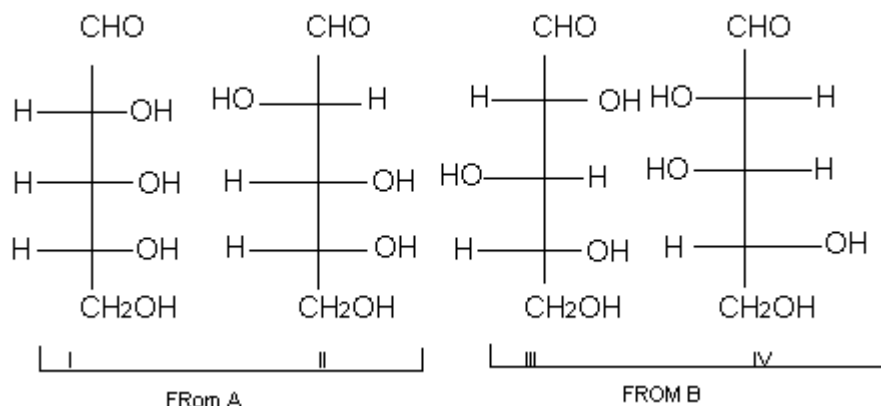
The configuration of D-glucose was proved by Emil Fischer by arguments similar to the ones stated below.

#### (1) Construction of four possible D-pentoses.

Taking the configuration of D-glyceraldehyde as the standard, two possible D-aldotetroses (A and B) may be constructed by adding a CHOH just below CHO, placing OH to the right and then to the left.



Similarly, each of the two D-tetroses (A and B) gives two D-aldopentoses. Thus four possible D-aldopentoses are :

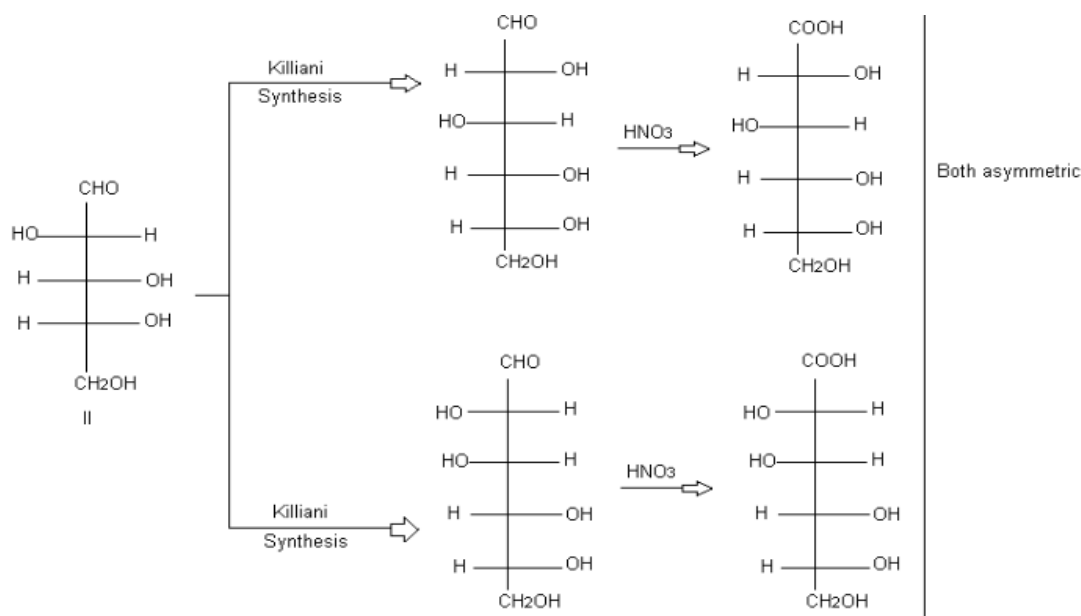


#### (2) D-Arabinose has configuration II or IV.

Oxidation of D-arabinose with nitric acid oxidises the terminal CHO and CH<sub>2</sub>OH groups yielding two optically active (asymmetric) dicarboxylic acids. The forms II and IV can form two optically active (asymmetric) diacids, while I and III can give meso acids only that has a plane of symmetry. Therefore, D-arabinose is either II or IV.

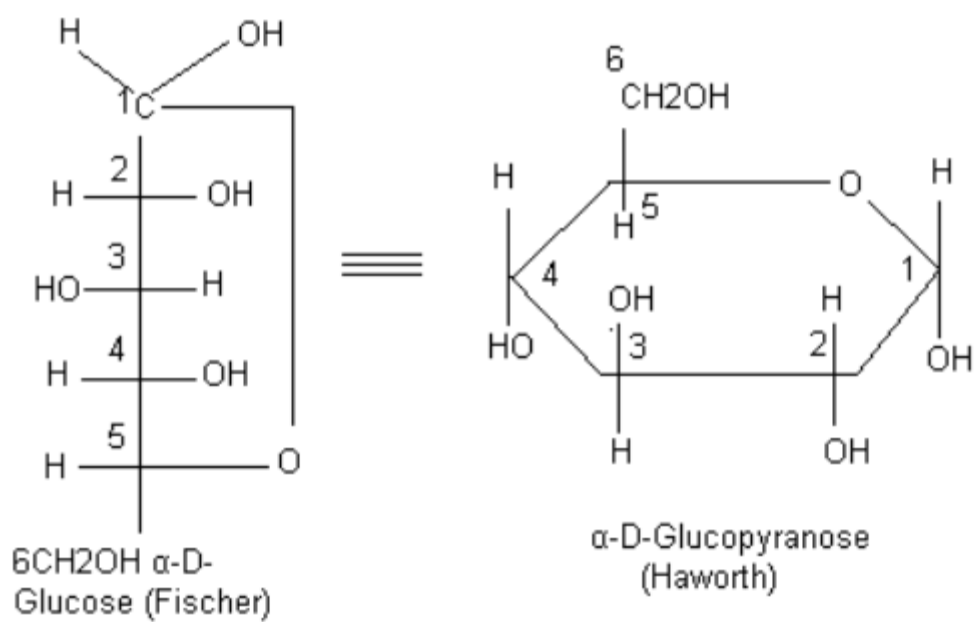
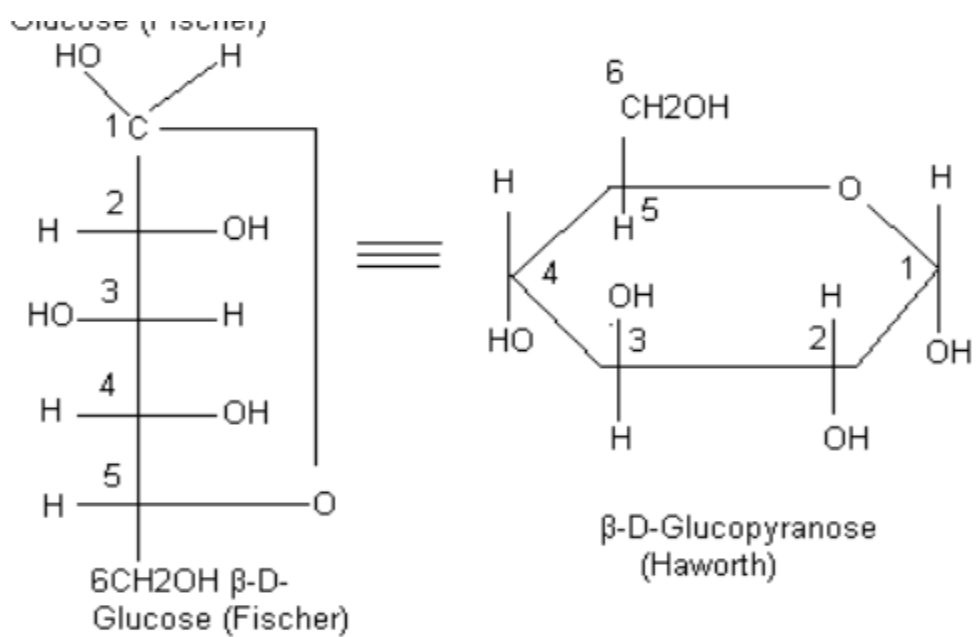
### (3) Configuration II confirmed for D-arabinose.

D-arabinose by Killiani -Fischer synthesis yields two epimeric aldohexoses, D-glucose and D-mannose. These on oxidation with nitric acid form two optically active (asymmetric) dicarboxylic acids. This is theoretically possible only if D-arabinose has the configuration II and not IV.



### The Haworth Representation.

So far we have used Fischer projection formulas for representing the cyclic forms of D-glucose. Haworth thought that these structures were awkward. He introduced the hexagonal representations resembling the heterocycle pyran which contain five carbon and one oxygen in the ring. Thus, he claimed the names  $\alpha$ -D-glucopyranose and  $\beta$ -D-glucopyranose for the hexagonal structures of  $\alpha$ -D-glucose and  $\beta$ -D-glucose.





It may be noted that in hawaoth formula, all the OH groups on the right in Fischer formula are directed below the plane of the ring, while those on the left go above the plane. The terminal CH<sub>2</sub>OH projects above the plane of the ring.

### **Physical properties of glucose.**

Glucose is a white crystalline solid, mp 146°C. When crystallised from cold water, it forms glucose monohydrate (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.H<sub>2</sub>O), mp 86°C. It is extremely soluble in water, only sparingly so in ethanol, and insoluble in ether. It is about three-fourths as sweet as cane sugar (sucrose). It is optically active, and the ordinary naturally occurring form is (+)-glucose.

### **Chemical properties of glucose.**

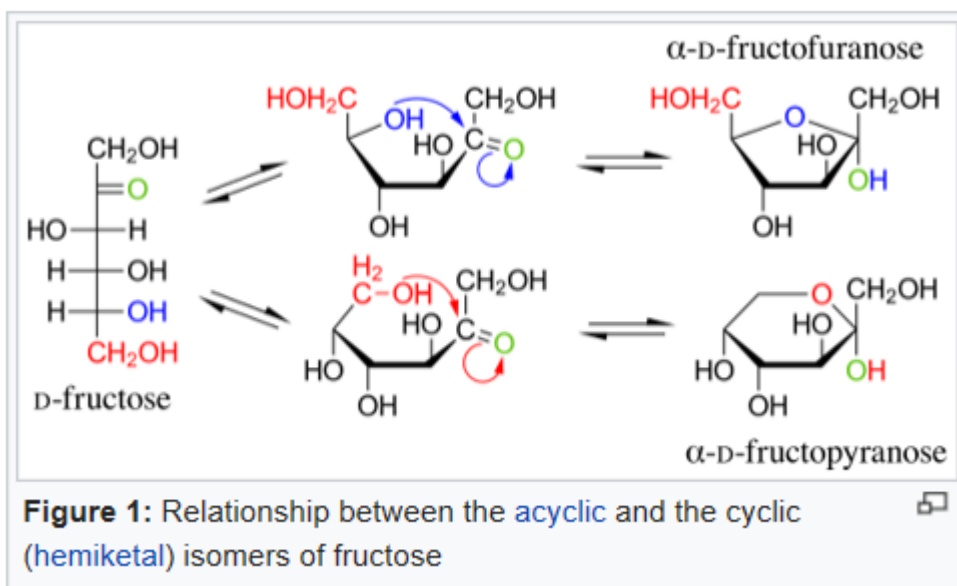
We have seen that D-glucose is an equilibrium mixture of a straight-chain form and a cyclic hemiacetal form.

## Fructose

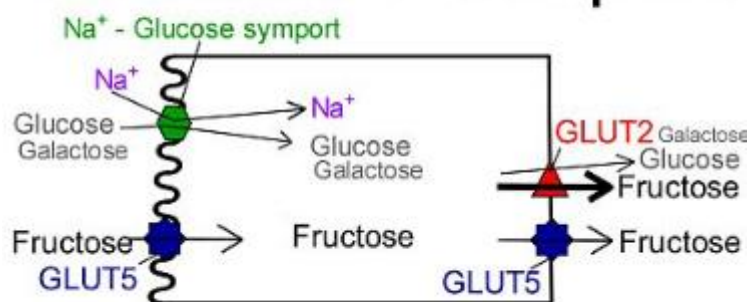
Fructose, or fruit sugar, is a simple ketonic monosaccharide found in many plants, where it is often bonded to glucose to form the disaccharide sucrose. It is one of the three dietary monosaccharides, along with glucose and galactose, that are absorbed directly into blood during digestion. Fructose was discovered by French chemist Augustin-Pierre Dubrunfaut in 1847. The name "fructose" was coined in 1857 by the English chemist William Allen Miller. Pure, dry fructose is a sweet, white, odorless, crystalline solid, and is the most water-soluble of all the sugars. Fructose is found in honey, tree and vine fruits, flowers, berries, and most root vegetables.

### Chemical properties

Fructose is a 6-carbon polyhydroxyketone. Crystalline fructose adopts a cyclic six-membered structure owing to the stability of its hemiketal and internal hydrogen-bonding. This form is formally called D-fructopyranose. In water solution, fructose exists as an equilibrium mixture of 70% fructopyranose and about 22% fructofuranose, as well as small amounts of three other forms, including the acyclic structure.



## Fructose Transport



Amino acids and proteins

### Amino acid

a simple organic compound containing both a carboxyl ( $\text{—COOH}$ ) and an amino ( $\text{—NH}_2$ ) group.  
 "the amino acid sequence of a protein"

Amino acids are organic compounds that combine to form proteins. Amino acids and proteins are the building blocks of life.

When proteins are digested or broken down, amino acids are left. The human body uses amino acids to make proteins to help the body:

- Break down food
- Grow
- Repair body tissue
- Perform many other body functions

Amino acids can also be used as a source of energy by the body.

Amino acids are classified into three groups:

- Essential amino acids
- Nonessential amino acids
- Conditional amino acids

#### ESSENTIAL AMINO ACIDS

- Essential amino acids cannot be made by the body. As a result, they must come from food.
- The 9 essential amino acids are: histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine.

#### NONESSENTIAL AMINO ACIDS

Nonessential means that our bodies produce an amino acid, even if we do not get it from the food we eat. Nonessential amino acids include: alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, proline, serine, and tyrosine.

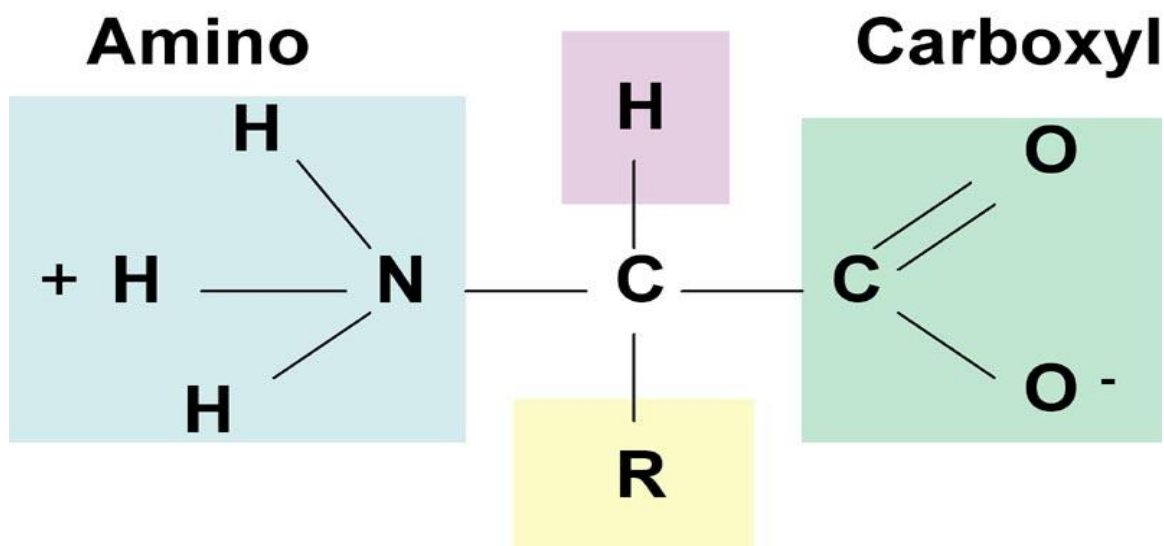
#### CONDITIONAL AMINO ACIDS

- Conditional amino acids are usually not essential, except in times of illness and stress.
- Conditional amino acids include: arginine, cysteine, glutamine, tyrosine, glycine, ornithine, proline, and serine.

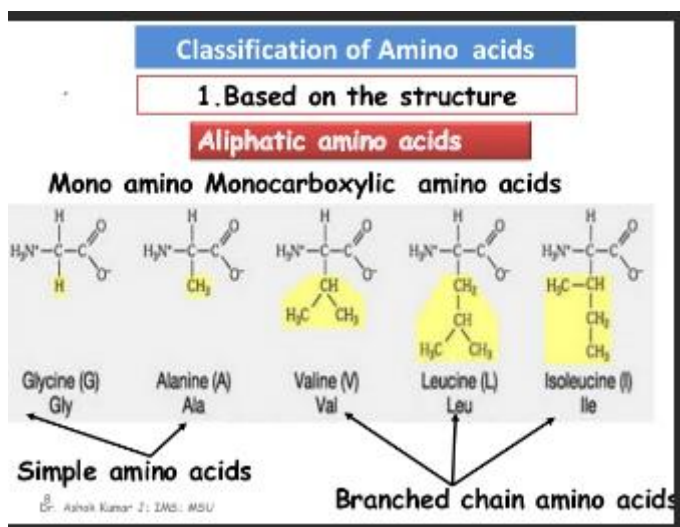
You do not need to eat essential and nonessential amino acids at every meal, but getting a balance of them over the whole day is important. A diet based on a single plant item will not be adequate, but we no longer worry about pairing proteins (such as beans with rice) at a single meal. Instead we look at the adequacy of the diet overall throughout the day.

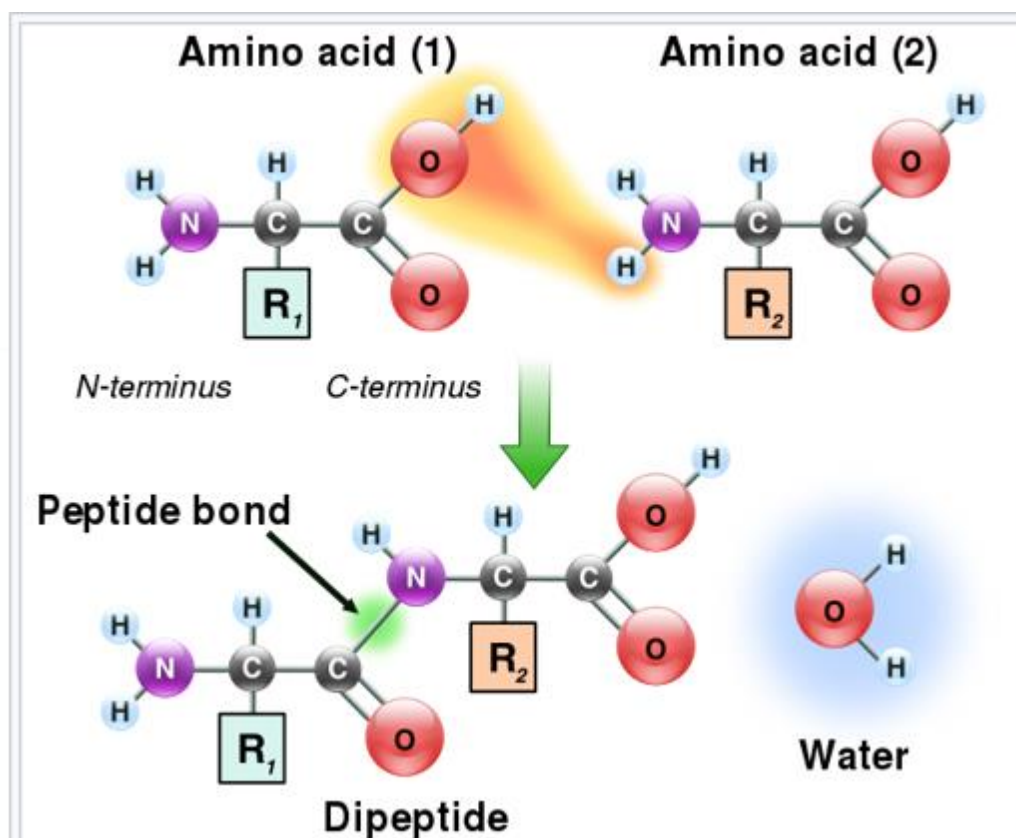
# Amino Acid Structure

Hydrogen



**R-group**  
(variant)



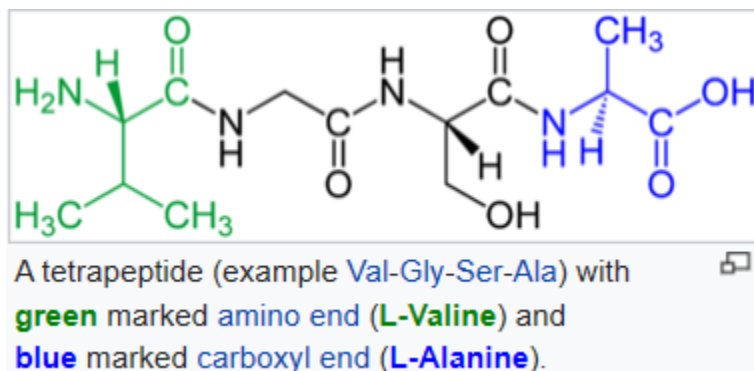


## Peptide

Peptides are short chains of amino acids linked by peptide (amide) bonds. The simplest peptides are dipeptides, followed by tripeptides, tetrapeptides, etc. A polypeptide is a long, continuous, and unbranched peptide chain. Hence, peptides fall under the broad chemical classes of biological oligomers and polymers, alongside nucleic acids, oligosaccharides, polysaccharides, and others.

Peptides are distinguished from proteins on the basis of size, and as an arbitrary benchmark can be understood to contain approximately 50 or fewer amino acids. Proteins consist of one or more polypeptides arranged in a biologically functional way, often bound to ligands such as coenzymes and cofactors, or to another protein or other macromolecule (DNA, RNA, etc.), or to complex macromolecular assemblies. Finally, while aspects of the lab techniques applied to peptides versus polypeptides and proteins differ (*e.g.*, the specifics of electrophoresis, chromatography, etc.), the size boundaries that distinguish peptides from polypeptides and proteins are not absolute: long peptides such as amyloid beta have been referred to as proteins, and smaller proteins like insulin have been considered peptides.

Amino acids that have been incorporated into peptides are termed "residues". A water molecule is released during formation of each amide bond. All peptides except cyclic peptides have an N-terminal (amine group) and C-terminal (carboxyl group) residue at the end of the peptide (as shown for the tetrapeptide in the image).



## Function

- A neuropeptide is a peptide that is active in association with neural tissue.
- A lipopeptide is a peptide that has a lipid connected to it, and pepducins are lipopeptides that interact with GPCRs.
- A peptide hormone is a peptide that acts as a hormone.
- A proteose is a mixture of peptides produced by the hydrolysis of proteins. The term is somewhat archaic.
- A peptidergic agent (or drug) is a chemical which functions to directly modulate the peptide systems in the body or brain. An example is opioidergics, which are neuropeptidergics.

## Protein

Proteins are large biomolecules, or macromolecules, consisting of one or more long chains of amino acid residues. Proteins perform a vast array of functions within organisms, including catalysing metabolic reactions, DNA replication, responding to stimuli, providing structure to cells, and organisms, and transporting molecules from one location to another. Proteins differ from one another primarily in their sequence of amino acids, which is dictated by the nucleotide sequence of their genes, and which usually results in protein folding into a specific three-dimensional structure that determines its activity.

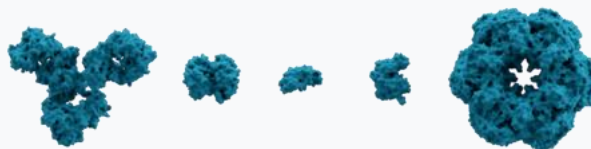
Proteins may be purified from other cellular components using a variety of techniques such as ultracentrifugation, precipitation, electrophoresis, and chromatography; the advent of genetic engineering has made possible a number of methods to facilitate purification. Methods commonly used to study protein structure and function include immunohistochemistry, site-directed mutagenesis, X-ray crystallography, nuclear magnetic resonance and mass spectrometry.

## Structure

Most proteins fold into unique 3-dimensional structures. The shape into which a protein naturally folds is known as its native conformation. Although many proteins can fold unassisted, simply through the chemical properties of their amino acids, others require the aid of molecular chaperones to fold into their native states. Biochemists often refer to four distinct aspects of a protein's structure:

- Primary structure: the amino acid sequence. A protein is a polyamide.
- Secondary structure: regularly repeating local structures stabilized by hydrogen bonds. The most common examples are the  $\alpha$ -helix,  $\beta$ -sheet and turns. Because secondary structures are local, many regions of different secondary structure can be present in the same protein molecule.
- Tertiary structure: the overall shape of a single protein molecule; the spatial relationship of the secondary structures to one another. Tertiary structure is generally stabilized by nonlocal interactions, most commonly the formation of a hydrophobic core, but also through salt bridges, hydrogen bonds, disulfide bonds, and even posttranslational modifications. The term "tertiary structure" is often used as synonymous with the term fold. The tertiary structure is what controls the basic function of the protein.
- Quaternary structure: the structure formed by several protein molecules (polypeptide chains), usually called protein subunits in this context, which function as a single protein complex.
- Quinary structure: the signatures of protein surface that organize the crowded cellular interior. Quinary structure is dependent on transient, yet essential, macromolecular interactions that occur inside living cells.

Proteins are not entirely rigid molecules. In addition to these levels of structure, proteins may shift between several related structures while they perform their functions. In the context of these functional rearrangements, these tertiary or quaternary structures are usually referred to as "conformations", and transitions between them are called conformational changes. Such changes are often induced by the binding of a substrate molecule to an enzyme's active site, or the physical region of the protein that participates in chemical catalysis. In solution proteins also undergo variation in structure through thermal vibration and the collision with other molecules.



Molecular surface of several proteins showing their comparative sizes. From left to right are: immunoglobulin G (IgG, an antibody), hemoglobin, insulin (a hormone), adenylate kinase (an enzyme), and glutamine synthetase (an enzyme).

Proteins can be informally divided into three main classes, which correlate with typical tertiary structures: globular proteins, fibrous proteins, and membrane proteins. Almost all globular proteins are soluble and many are enzymes. Fibrous proteins are often structural, such as collagen, the major component of connective tissue, or keratin, the protein component of hair and nails. Membrane proteins often serve as receptors or provide channels for polar or charged molecules to pass through the cell membrane.

A special case of intramolecular hydrogen bonds within proteins, poorly shielded from water attack and hence promoting their own dehydration, are called dehydrons.

## **Structural proteins**

Structural proteins confer stiffness and rigidity to otherwise-fluid biological components. Most structural proteins are fibrous proteins; for example, collagen and elastin are critical components of connective tissue such as cartilage, and keratin is found in hard or filamentous structures such as hair, nails, feathers, hooves, and some animal shells. Some globular proteins can also play structural functions, for example, actin and tubulin are globular and soluble as monomers, but polymerize to form long, stiff fibers that make up the cytoskeleton, which allows the cell to maintain its shape and size.

Other proteins that serve structural functions are motor proteins such as myosin, kinesin, and dynein, which are capable of generating mechanical forces. These proteins are crucial for cellular motility of single celled organisms and the sperm of many multicellular organisms which reproduce sexually. They also generate the forces exerted by contracting muscles and play essential roles in intracellular transport.



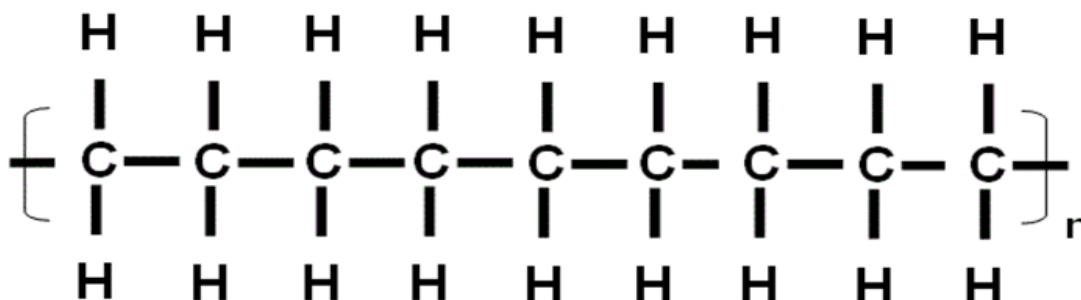
## UNIT III

### POLYMERS, HETEROCYCLIC COMPOUND AND STEREOISOMERISM

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Due to their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass, relative to small molecule compounds, produces unique physical properties including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

**Polymer Uses.** Polyurethane a polymer of ethylene glycol and ethylene di-isocyanate is used in the manufacture of paints and heat insulators. Polythene is used to prepare pipes, toys bags, wire insulators, bottles etc. The polyvinyl chloride is used to prepare sheet, water pipes, hand bags etc.

#### POLYETHYLENE



#### Types Of Polythene

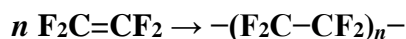
Polythene is the most common plastic used broadly in the packaging industry. Based on the density, polythene can be classified into two types:

- **Low-density polythene:** It has a density range of 0.910–0.940 g/cm<sup>3</sup> and is prepared by the free-radical polymerization of ethane. The reaction is carried out at a temperature of 350 K to 570 K under the pressure of 1000 to 2000 atmospheres in the presence of a catalyst, dioxygen (in traces) or a peroxide initiator. The highly branched structure of LDP gives it a unique flow property in the molten state. It is a poor conductor of electricity and is chemically inert. The LDPs are used for making plastic bags and film wrap.

- **High-density polythene:** It has a density greater than or equal to  $0.941 \text{ g/cm}^3$  and has a low degree of branching. It is obtained when addition polymerization of ethene takes place in a hydrocarbon solvent. The reaction is carried out under a pressure of 6 to 7 atmospheres and at a temperature of 333 K to 343 K in the presence of Ziegler-Natta catalysts or metallocene catalysts. HDPs are chemically inert as well and are used in making bottles, butter tubs, milk jugs, water pipes and garbage containers..

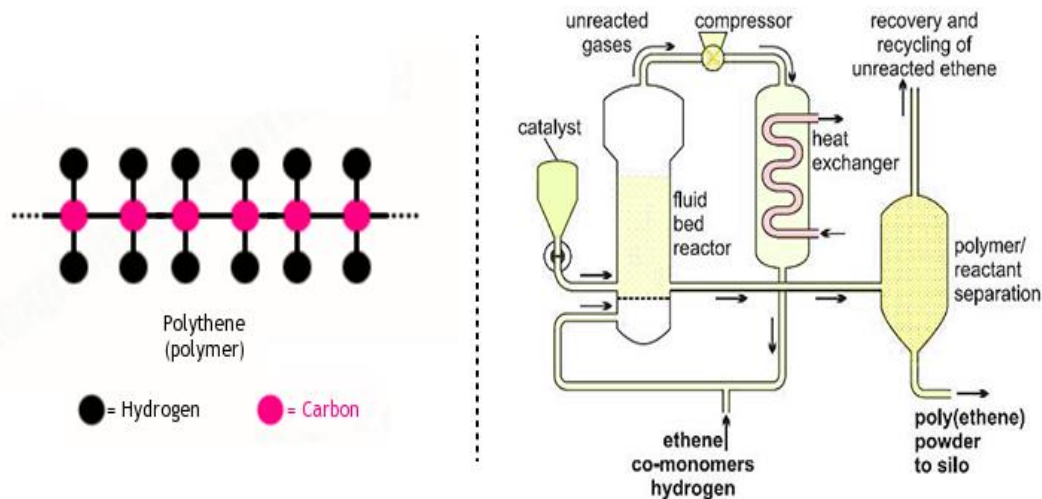
### Polytetrafluoroethylene (Teflon)

Teflon is manufactured by free-radical polymerization of tetrafluoroethylene. The catalyst used is persulphate at high pressures. The reaction is given as:



Teflon is hydrophobic and is inert in nature. It is used in making a non-stick coating for cookware and also as a lubricant in machinery to reduce friction.

Epoxy resins



Epoxy resins

Epoxy refers to any of the basic components or cured end products of epoxy resins, as well as a colloquial name for the epoxide functional group. Epoxy resins, also known as polyepoxides, are a class of reactive prepolymers and polymers which contain epoxide groups.

### Epoxy uses fall into a few core categories:

- **Coating:** Applying one or more thin coats of epoxy to seal the a surface or prepare the surface for varnish or reinforcing layers like fiberglass or carbon fiber
- **Bonding:** Applying the epoxy as a glue, generally with some filler to allow it to fill gaps between the surfaces, or to attach hardware to a surface.

- Laminating: Multiple layers of wood or other materials are laid up to create a thicker solid structure.
- Fairing: Thickened resin is used to fill holes and depressions so that the surface can be sanded and smoothed.

### **5 Best Uses for an Epoxy Adhesive**

1. Fiberglass Repairs. Epoxy adhesives can be used to repair the bodies...
2. Carpentry and Woodworking. In a pinch, epoxy can substitute for wood glue when building furniture...
3. Wood and Metal Fillers. Epoxy adhesives can be used to repair wood rot or rust.
4. Reinforce Bolts. Epoxy adhesives are used to reinforcement

### **Polyester Resin.**

When higher strength, bond and water resistance is required (such as keel, rudder repair, or out-board transom replacement) use LBI's 302 Isothalic Polyester Resin. To achieve the highest bond strength and water resistance use LBI's 901 Vinylester Resin. Vinylester is essentially a styrene modified epoxy resin.

#### **Polyester resin offers the following advantages:**

1. Adequate resistance to water and variety of chemicals.
2. Adequate resistance to weathering and ageing.
3. Low cost.
4. Polyesters can withstand a temperature up to 80 °C.
5. Polyesters have good wetting to glass fibres.
6. Relatively low shrinkage at between 4–8% during curing.
7. Linear thermal expansion ranges from  $100\text{--}200 \times 10^{-6} \text{ K}^{-1}$

#### **Polyester resin has the following disadvantages:**

1. Strong styrene odor
2. More difficult to mix than other resins, such as a two-part epoxy
3. The toxic nature of its fumes, and especially of its catalyst, MEKP, pose a safety risk if proper protection isn't used
4. Not appropriate for bonding many substrates
5. The finished cure is most likely weaker than an equal amount of an epoxy resin

## **HETROCYCLIC COMPOUNDS**

### **Furan**

Furan is a heterocyclic organic compound, consisting of a five-membered aromatic ring with four carbon atoms and one oxygen. Chemical compounds containing such rings are also referred to as furans.

Furan is a colorless, flammable, highly volatile liquid with a boiling point close to room temperature. It is soluble in common organic solvents, including alcohol, ether, and acetone, and is slightly soluble in water. Its odor is "strong, ethereal; chloroform-like". It is toxic and may be carcinogenic in humans. Furan is used as a starting point to other speciality chemicals.

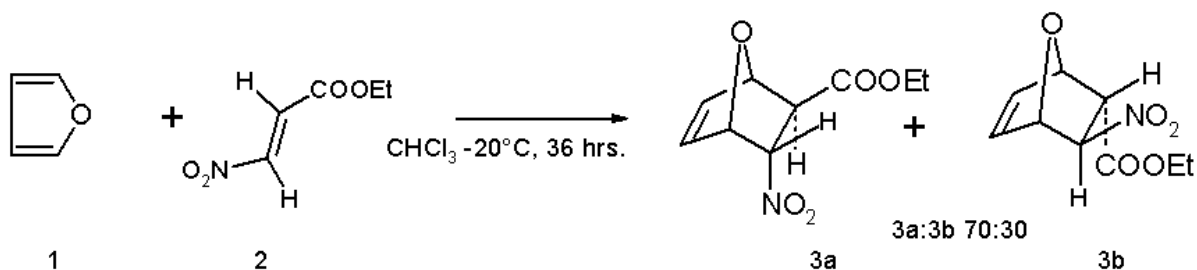
## Production

Industrially, furan is manufactured by the palladium-catalyzed decarbonylation of furfural, or by the copper-catalyzed oxidation of 1,3-butadiene:

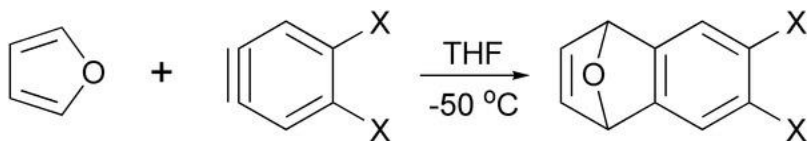


In the laboratory, furan can be obtained from furfural by oxidation to 2-furoic acid, followed by decarboxylation. It can also be prepared directly by thermal decomposition of pentose-containing materials, and cellulosic solids, especially pine wood

- Furan serves as a diene in Diels–Alder reactions with electron-deficient dienophiles such as ethyl (*E*)-3-nitroacrylate. The reaction product is a mixture of isomers with preference for the endo isomer:



Diels-Alder reaction of furan with arynes provides corresponding derivatives of dihydronaphthalenes, which are useful intermediates in synthesis of other polycyclic aromatic compounds.

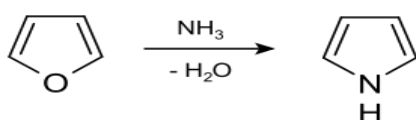


- Hydrogenation of furans sequentially affords dihydrofurans and tetrahydrofurans.
- In the Achmatowicz reaction, furans are converted to dihydropyran compounds.
- Pyrrole can be prepared industrially by reacting furan and ammonia in the presence of solid acid catalysts, such as  $\text{SiO}_2$

Pyrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula  $C_4H_4NH$ . It is a colorless volatile liquid that darkens readily upon exposure to air. Substituted derivatives are also called pyrroles, e.g., *N*-methylpyrrole,  $C_4H_4NCH_3$ . Porphobilinogen, a trisubstituted pyrrole, is the biosynthetic precursor to many natural products such as heme.

## Synthesis

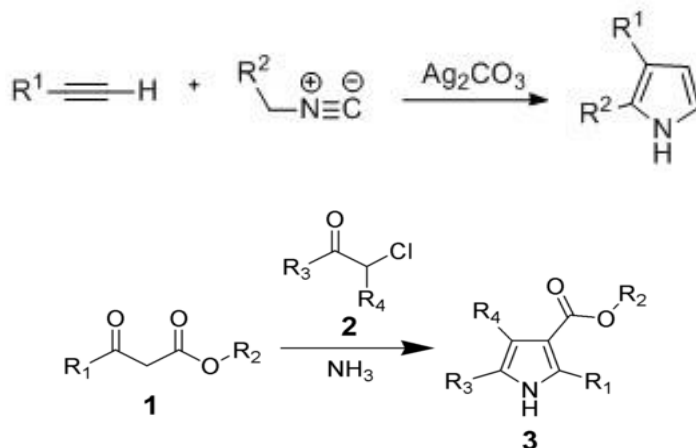
Pyrrole is prepared industrially by treatment of furan with ammonia in the presence of solid acid catalysts, like  $SiO_2$  and  $Al_2O_3$ .



### Hantzsch pyrrole synthesis

The Hantzsch pyrrole synthesis is the reaction of  $\beta$ -ketoesters (**1**) with ammonia (or primary amines) and  $\alpha$ -haloketones (**2**) to give substituted pyrroles (**3**).

pyrroles can be prepared by silver-catalyzed cyclization of alkynes with isonitriles, where  $R^2$  is an electron-withdrawing group, and  $R^1$  is an alkane, aryl group, or ester. Examples of disubstituted alkynes have also been seen to form the desired pyrrole in considerable yield. The reaction is proposed to proceed via a silver acetylide intermediate. This method is analogous to the azide–alkyne click chemistry used to form azoles.

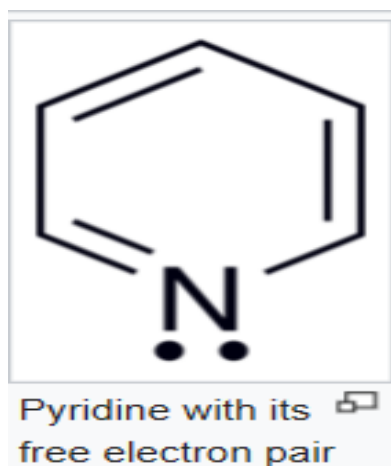


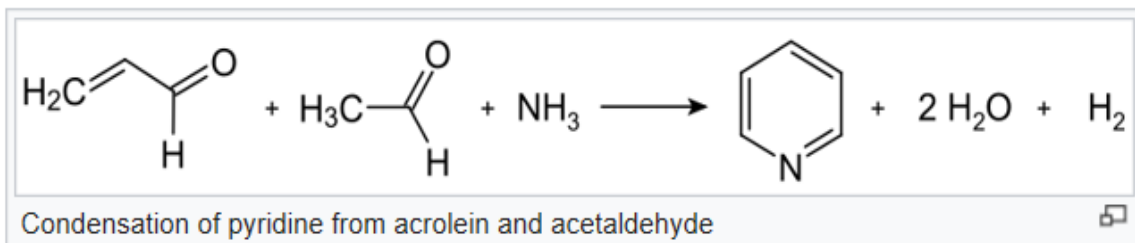
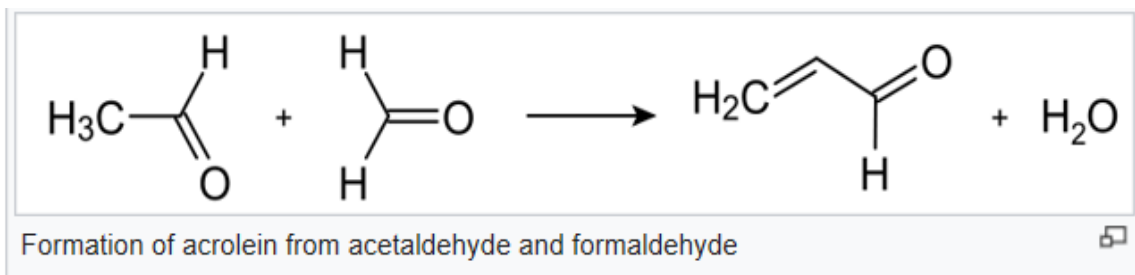
## Pyridine

Pyridine is a basic heterocyclic organic compound with the chemical formula  $C_5H_5N$ . It is structurally related to benzene, with one methine group ( $=CH-$ ) replaced by a nitrogen atom. It is a highly flammable, weakly alkaline, water-miscible liquid with a distinctive, unpleasant fish-like smell. Pyridine is colorless, but older or impure samples can appear yellow. The pyridine ring occurs in many important compounds, including agrochemicals, pharmaceuticals, and vitamins. Historically, pyridine was produced from coal tar. Today it is synthesized on the scale of about 20,000 tonnes per year worldwide.

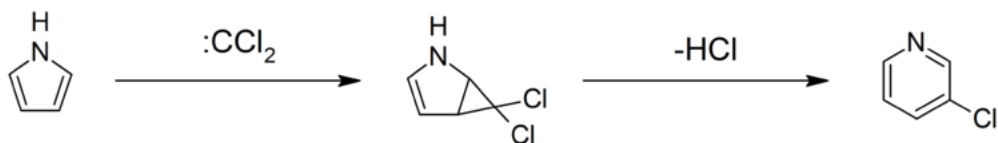
Pyridine has a conjugated system of six  $\pi$  electrons that are delocalized over the ring. The molecule is planar and, thus, follows the Hückel criteria for aromatic systems. In contrast to benzene, the electron density is not evenly distributed over the ring, reflecting the negative inductive effect of the nitrogen atom. For this reason, pyridine has a dipole moment and a weaker resonant stabilization than benzene (resonance energy  $117 \text{ kJ}\cdot\text{mol}^{-1}$  in pyridine vs.  $150 \text{ kJ}\cdot\text{mol}^{-1}$  in benzene).

The ring atoms in the pyridine molecule are  $sp^2$ -hybridized. The nitrogen is involved in the  $\pi$ -bonding aromatic system using its unhybridized p orbital. The lone pair is in an  $sp^2$  orbital, projecting outward from the ring in the same plane as the  $\sigma$  bonds. As a result, the lone pair does not contribute to the aromatic system but importantly influences the chemical properties of pyridine, as it easily supports bond formation via an electrophilic attack. However, because of the separation of the lone pair from the aromatic ring system, the nitrogen atom cannot exhibit a positive mesomeric effect.





The **Ciamician–Dennstedt rearrangement** entails the ring-expansion of pyrrole with dichlorocarbene to 3-chloropyridine.



In the **Gattermann–Skita synthesis**, a malonate ester salt reacts with dichloromethylamine.

### compare the basicity of pyrrole and pyridine

Both pyridine and pyrrole are both aromatic molecules. Basicity is compared on the basis of how easily and effectively a compound can share its lone pair. In Pyridine, as the lone pair of Nitrogen is not involved in the aromatization of the ring, it is available for donation.

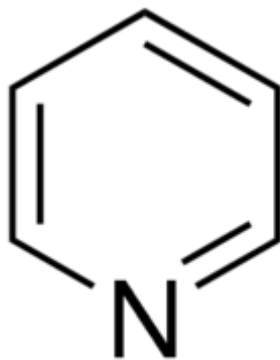
In pyrrole, the lone pair electrons of the nitrogen atom is actively involved with the two carbon-carbon double bonds in the 5-member ring to form a conjugated system of pi electrons, leading to greater stability of the molecule.

Pyridine, on the other hand, already has a stable conjugated system of 3 double bonds in the aromatic hexagonal ring, like benzene. Hence the lone pair electrons on the N atom in pyridine can be easily donated to a H<sup>+</sup> ion or a Lewis acid.

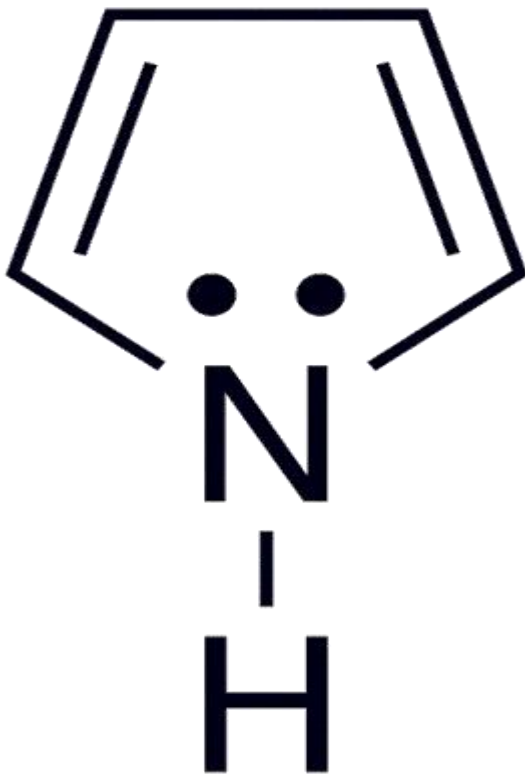
Therefore, pyridine is a stronger base than pyrrole.

Both pyridine and pyrrole are both aromatic molecules. Basicity is compared on the basis of how easily and effectively a compound can share its lone pair.

In Pyridine, as the lone pair of Nitrogen is **not** involved in the aromatization of the ring, it is available for donation.



In Pyrrole, the lone pair of Nitrogen is already involved in the cyclic conjugation and is completely delocalized over 6 atoms, making it unavailable for donation.



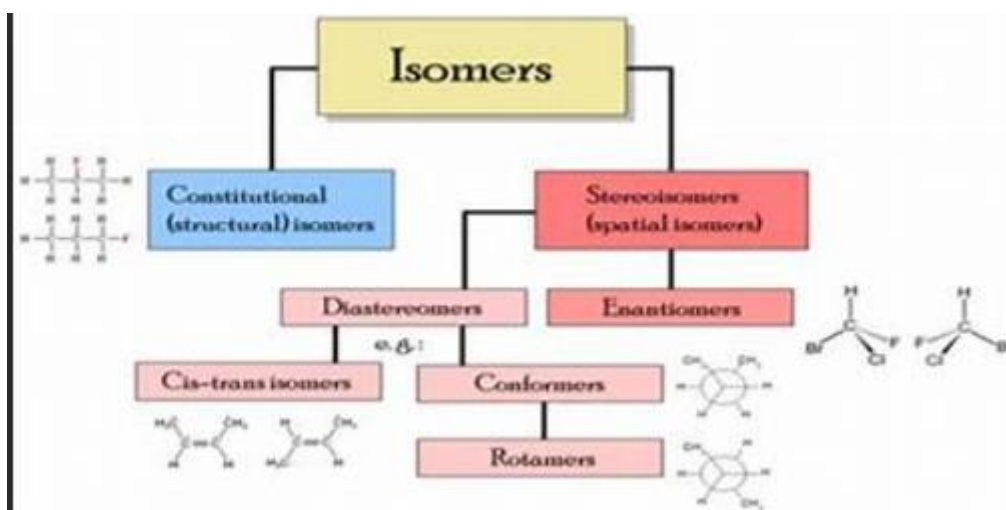


# Stereoisomerism

In stereochemistry, stereoisomerism, or spatial isomerism, is a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space. This contrasts with structural isomers, which share the same molecular formula, but the bond connections or their order differs. By definition, molecules that are stereoisomers of each other represent the same structural isomer.

Explanation: The two main types of stereoisomerism are: Diastereomerism (including 'cis-trans isomerism') Optical Isomerism (also known as 'enantiomerism' and 'chirality'). Cis-trans isomerism occurs when a double bond is present, because the pi bond involved prevents that bond from being "twisted" the same way...

The main difference between diastereomers and enantiomers is that **enantiomers are mirror images of each other whereas diastereomers are not mirror images of each other.**



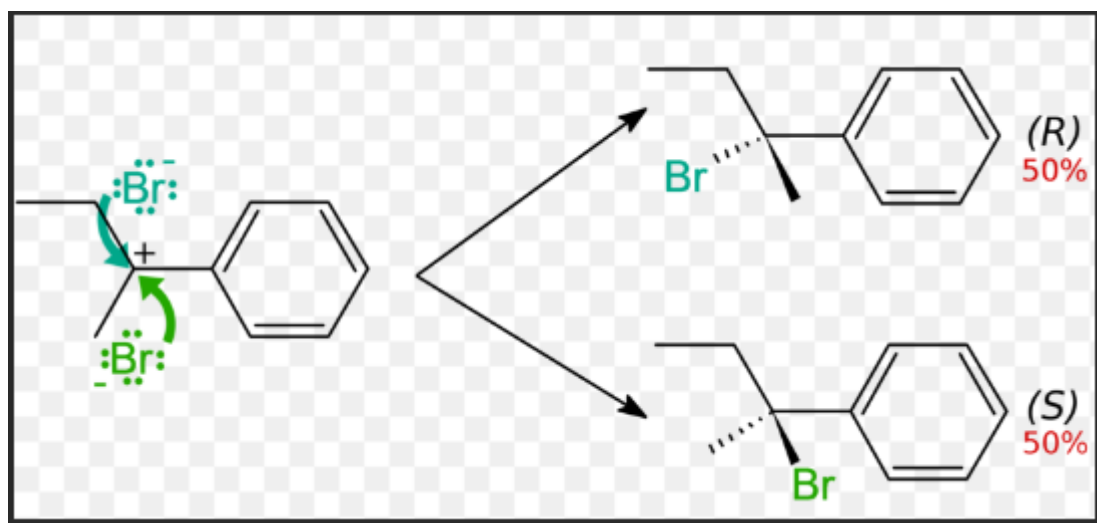
Simple substances which show **optical** isomerism exist as two isomers known as enantiomers. A solution of one enantiomer rotates the plane of polarisation in a clockwise direction. This enantiomer is known as the (+) form. For example, one of the optical isomers (enantiomers) of the amino acid alanine is known as (+)alanine.

## Racemic Mixture

In chemistry, a racemic mixture, or racemate (/reɪˈsiːmeɪt, rə-, ˈræsɪmeɪt/), is one that has equal amounts of left- and right-handed enantiomers of a chiral molecule. The first known racemic mixture was racemic acid, which Louis Pasteur found to be a mixture of the two enantiomeric isomers of tartaric acid. A sample with only a single enantiomer is an enantiomerically pure or enantiopure compound.

The separation of a racemate into its components, the pure enantiomers, is called a chiral resolution. There are various methods, including crystallization, chromatography, and the use of enzymes. The first successful resolution of a racemate was performed by Louis Pasteur, who manually separated the crystals of a conglomerate.

The two terms racemic mixture and meso compound are used in organic chemistry to describe different organic compounds. A racemic mixture is also known as a racemate. It is a mixture of equal amounts of left and right-handed enantiomers. Enantiomers are optical isomers that are non-superimposable mirror images of each other.

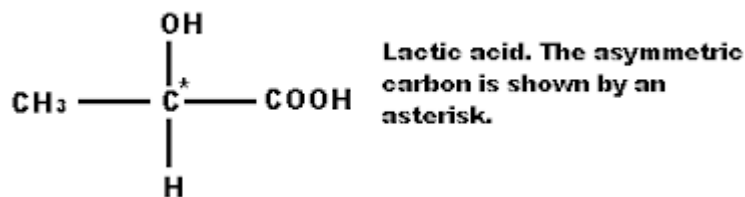


## Optical isomerism of lactic acid

December 13, 2018 Organic chemistry

### Defined Optical Isomerism Of Lactic Acid.

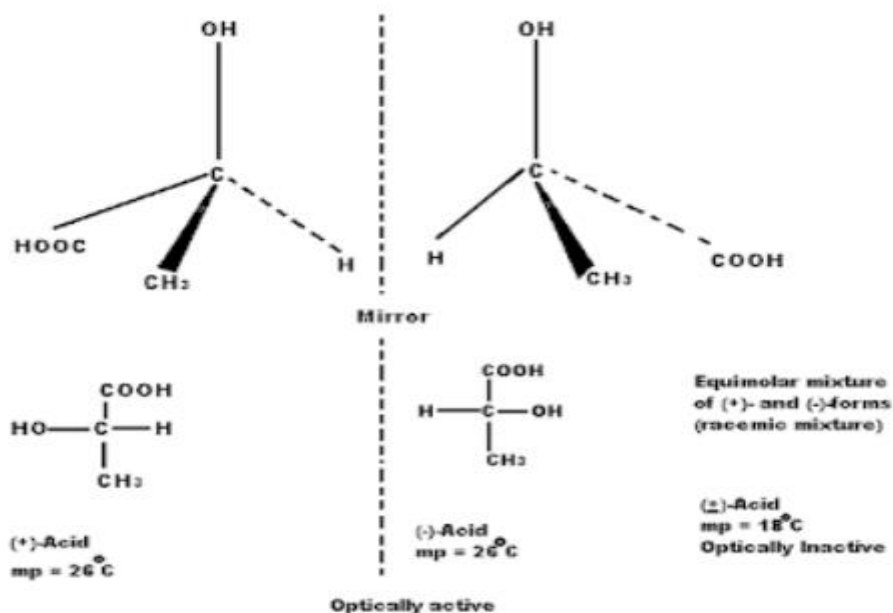
Lactic acid (2-Hydroxypropanoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.



Two 3 dimensional structures are possible for Lactic acid.

These components are not identical because they cannot be superimposed on each other. One is the mirror image of the other. Such nonsuperimposable mirror-image forms are optical isomers and are called enantiomers. Thus, three forms of lactic acid are known. Two are optically active and the third is optically inactive.

1. **(+)-Lactic Acid.** It rotates the plane of polarised light to the right (clockwise direction) and is called dextrorotatory.
2. **(-)-Lactic Acid.** It rotates the plane of polarised light to the left (anticlockwise direction) and is called laevorotatory. (-)-Lactic acid is the mirror image of (+)-Lactic acid and vice versa.
3. **(±)- Lactic Acid.** It does not rotate the plane of polarised light. That is, it is optically inactive. It is an equimolar mixture of (+)-and (-)-forms (racemic mixture).



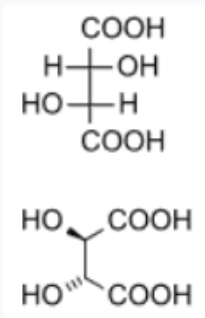
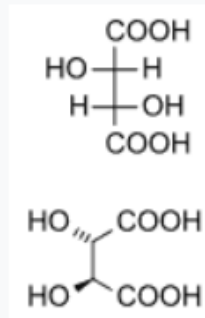
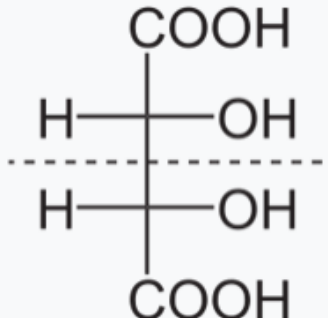
Isomers of Lactic acid. In the upper line, two three-dimensional structures are shown. In the lower line, a commonly used Fischer projection is given. The vertical lines represent bonds going away from the observer/reader and horizontal lines represent bonds coming toward the observer.

## Tartaric acid

Naturally occurring tartaric acid is chiral, and is a useful raw material in organic chemical synthesis. The naturally occurring form of the acid is **dextrotartaric acid** or **L-(+)-tartaric acid** (obsolete name *d*-tartaric acid). Because it is available naturally, it is slightly cheaper than its enantiomer and the meso isomer. The *dextro* and *levo* prefixes are archaic terms.<sup>[14]</sup> Modern textbooks refer to the natural form as (2*R*,3*R*)-tartaric acid (**L-(+)-tartaric acid**), and its enantiomer as (2*S*,3*S*)-tartaric acid (**D-(-)-tartaric acid**). The *meso* diastereomer is (2*R*,3*S*)-tartaric acid (which is identical with '(2*S*,3*R*)-tartaric acid').

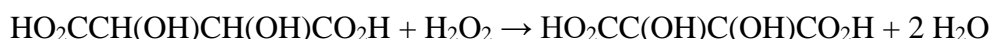
Whereas the two chiral stereoisomers rotate plane polarized light in opposite directions, solutions of meso-tartaric acid do not rotate plane-polarized light. The absence of optical activity is due to a mirror plane in the molecule [segmented line in picture below].

Tartaric acid in Fehling's solution binds to copper(II) ions, preventing the formation of insoluble hydroxide salts.

DL-tartaric acid ( <b>racemic acid</b> ) (when in 1:1 ratio)		mesotartaric acid
dextrotartaric acid (L-(+)-tartaric acid)	levotartaric acid (D-(-)-tartaric acid)	
		

## Reactivity

L-(+)-tartaric acid, can participate in several reactions. As shown the reaction scheme below, dihydroxymaleic acid is produced upon treatment of L-(+)-tartaric acid with hydrogen peroxide in the presence of a ferrous salt.



Dihydroxymaleic acid can then be oxidized to tartronic acid with nitric acid.

## Geometric isomers

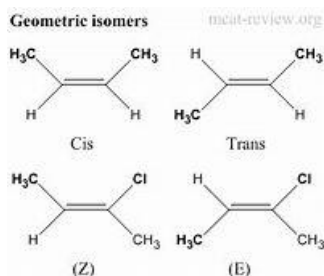
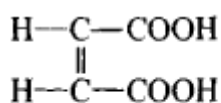


Image: mcat-review.org

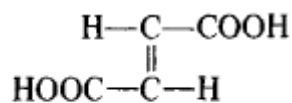
Geometric Isomer Definition. Geometric isomers are chemical species with the same type and quantity of atoms as another species, yet having a different geometric structure. Atoms or groups exhibit different spatial arrangements on either side of a chemical bond or ring structure. Geometric isomerism is also called configurational isomerism...

## Maleic and Fumaric Acids

The geometrical isomerism of ethylene compounds has been studied in great detail using the example of maleic and fumaric acids. Both acids are colorless crystals. Maleic acid, the *cis* isomer (I), has a melting point of 130°C and a boiling point of 160°C; fumaric acid, the *trans* isomer (II), has a melting point of 286°C and a boiling point of 290°C.



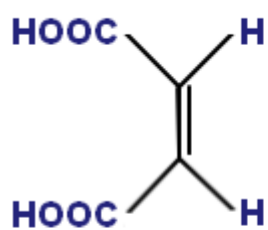
I



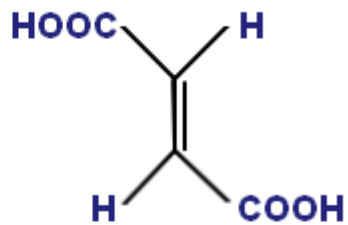
II

Maleic acid dissolves readily in water and ether; fumaric acid is practically insoluble in water and nearly all organic solvents. Maleic acid is stronger than fumaric acid but less stable. It is readily converted to fumaric acid under exposure to light or upon heating to temperatures above 200°C. Fumaric acid is converted to maleic acid upon exposure to ultraviolet irradiation.

Fumaric acid is found in certain species of fungus, lichen, and other plants, including *Fumaria officinalis*. Maleic acid is not found in nature. Both acids can be obtained by heating malic acid. Maleic anhydride (colorless crystals; melting point, 52.8°C; boiling point, 199.9°C) is prepared by oxidizing benzene or furfural over  $\text{V}_2\text{O}_5$  and is used primarily for industrial purposes (for example, in the manufacture of unsaturated polyesters and alkyds).



**cis-butenedioic  
(maleic acid)**

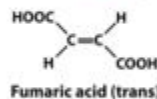
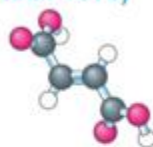
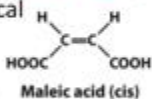
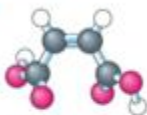


**trans-butenedioic acid  
(fumaric acid)**

### Cis-Trans isomers (geometrical isomers)

- Geometric Isomers

- have **different** physical and chemical properties
- differ in the arrangement about a double bond
- An enzyme binding site that fits maleic acid will not fit fumaric acid and vice versa



Many drugs that contain amines are provided as the maleate acid salt, e.g. carfenazine, chlorpheniramine, pyrilamine, methylergonovine, and thiethylperazine.

## UNIT IV

### SURFACE CHEMISTRY AND PHOTOCHEMISTRY

#### Emulsion

An emulsion is a mixture of two or more liquids that are normally immiscible (unmixable or unblendable). Emulsions are part of a more general class of two-phase systems of matter called colloids. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion should be used when both phases, dispersed and continuous, are liquids. In an emulsion, one liquid (the dispersed phase) is dispersed in the other (the continuous phase). Examples of emulsions include vinaigrettes, homogenized milk, and some cutting fluids for metal working.

Examples of food emulsifiers are:

- Egg yolk – in which the main emulsifying agent is lecithin. In fact, *lecithos* is the Greek word for egg yolk.
- Mustard – where a variety of chemicals in the mucilage surrounding the seed hull act as emulsifiers
- Soy lecithin is another emulsifier and thickener
- Pickering stabilization – uses particles under certain circumstances
- Sodium phosphates
- Mono- and diglycerides - a common emulsifier found in many food products (coffee creamers, ice-creams, spreads, breads, cakes)
- Sodium stearoyl lactylate
- DATEM (diacetyl tartaric acid esters of mono- and diglycerides) – an emulsifier used primarily in baking
- Simple cellulose – a particulate emulsifier derived from plant material using only water

A number of different chemical and physical processes and mechanisms can be involved in the process of emulsification

#### Mechanisms of emulsification

- Surface tension theory – according to this theory, emulsification takes place by reduction of interfacial tension between two phases
- Repulsion theory – the emulsifying agent creates a film over one phase that forms globules, which repel each other. This repulsive force causes them to remain suspended in the dispersion medium
- Viscosity modification – emulgents like acacia and tragacanth, which are hydrocolloids, as well as PEG (or polyethylene glycol), glycerine, and other polymers like CMC (carboxymethyl cellulose), all increase the viscosity of the medium, which helps create and maintain the suspension of globules of dispersed phase.

Oil-in-water emulsions are common in food products:

- Crema (foam) in espresso – coffee oil in water (brewed coffee), unstable emulsion
- Mayonnaise and Hollandaise sauces – these are oil-in-water emulsions stabilized with egg yolk lecithin, or with other types of food additives, such as sodium stearoyl lactylate
- Homogenized milk – an emulsion of milk fat in water, with milk proteins as the emulsifier
- Vinaigrette – an emulsion of vegetable oil in vinegar, if this is prepared using only oil and vinegar (i.e., without an emulsifier), an unstable emulsion results

Water-in-oil emulsions are less common in food, but still exist:

Butter – an emulsion of water in butterfat

- Margarine

Other foods can be turned into products similar to emulsions, for example meat emulsion is a suspension of meat in liquid that is similar to true emulsions.

## Gel

A gel is a solid that can have properties ranging from soft and weak to hard and tough. Gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state. By weight, gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the crosslinking within the fluid that gives a gel its structure (hardness) and contributes to the adhesive stick (tack). In this way, gels are a dispersion of molecules of a liquid within a solid medium. The word gel was coined by 19th-century Scottish chemist Thomas Graham by clipping from gelatine.

## Composition

Gels consist of a solid three-dimensional network that spans the volume of a liquid medium and ensnares it through surface tension effects. This internal network structure may result from physical bonds (physical gels) or chemical bonds (chemical gels), as well as crystallites or other junctions that remain intact within the extending fluid. Virtually any fluid can be used as an extender including water (hydrogels), oil, and air (aerogel). Both by weight and volume, gels are mostly fluid in composition and thus exhibit densities similar to those of their constituent liquids. Edible jelly is a common example of a hydrogel and has approximately the density of water.

## Applications

Many substances can form gels when a suitable thickener or gelling agent is added to their formula. This approach is common in manufacture of wide range of products, from foods to paints and adhesives.

In fiber optics communications, a soft gel resembling hair gel in viscosity is used to fill the plastic tubes containing the fibers. The main purpose of the gel is to prevent water intrusion if the buffer tube is breached, but the gel also buffers the fibers against mechanical damage when the tube is bent around corners during installation, or flexed. Additionally, the gel acts as a processing aid when the cable is being constructed, keeping the fibers central whilst the tube material is extruded around it.



## Chromatography

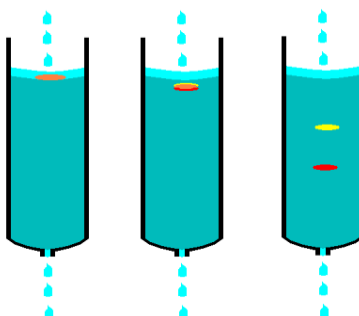
Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the stationary phase. The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus affect the separation.

The basic principle of chromatography is that different chemicals have different degrees of dissolving power in a liquid, and different powers of sticking to a solid surface. Thus, chromatography can identify chemical components in a mixture, and separate them by making them visible on a surface.

Jump to search



Column chromatography is a chromatography technique used to separate mixture of chemical substances into its individual compounds. Column chromatography is a widely used method for the purification or separation of chemical compound mixture in lab.



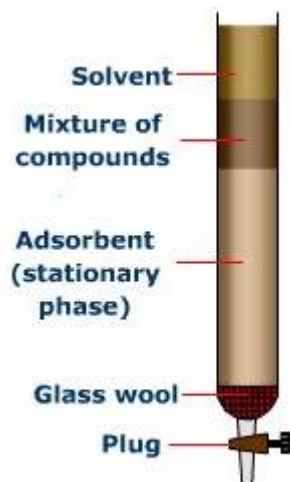
## Principles of column chromatography

Column Chromatography consists of two phases: one mobile phase and one contiguous stationary phase. The stationary phase is solid and the mobile phase is liquid. The compound mixture moves along with the mobile phase through stationary phase and separates depending on the different degree of adhesion (to the silica) of each component in the sample or the compound mixture

## Explanation

The stationary phase

A glass tube with a circle large inlet and a small outlet with a plug or tap, named as column is used for this column chromatography. The column is placed vertically with a stand where the outlet is downward.



A piece of cotton wool is entered into the outlet and placed over the plug if there are no glass wool present to stop escaping the stationary phase from the column. There are two procedure to prepare the column by packing with silica or alumina:

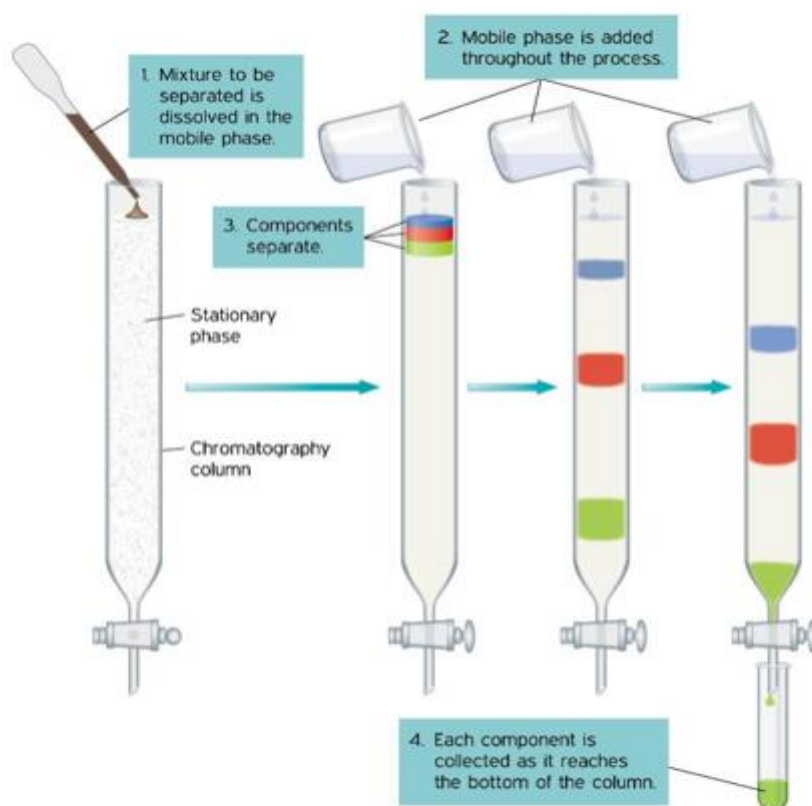
**Dry method:** In dry method at first the column is filled with dry powdered silica. Then the mobile phase, a suitable solvent is flushed through it until all the silica are wet and settled. From this point till the end always the column need to keep wet with solvent.

**Wet method:** In wet method firstly a slurry of silica and solvent is prepared and then poured onto the column using a funnel. More solvent must be used until the silica is settled into it.

## Process

### Column chromatography works in few steps:

**Step 1:** The mobile phase or eluent is either solvent or solvent mixture. The upper level of mobile phase should be same as the stationary phase. That means the stationary phase should be wet with the solvent. On this stage the compound mixture what need to be separated, are added from the top of the column in such a way that the top level of it is not disturbed. By turning on the tap below it is allowed to adsorbed on the surface of the silica.



**Step 2:** Then the solvent or a suitable solvent mixture is added at first touching the side of the glass column slowly and carefully so that the top level of the stationary phase is not disturbed. The solvent is repeatedly added as many times as needed throughout the process.

**Step 3:** When the tap, is on the compounds in the compound mixture move along with the eluent depending on the polarity of the sample molecule. The non polar components travel faster than the polar component.

Suppose if any compound mixture contains three compounds blue, red and green. According to polarity the order of these compounds are blue>red>green. That means blue is the most polar compound and thus will have less tendency to move along with the mobile phase.

**Step 4:** The green colored compound will travel first as it is less polar that other two. When it is near end of the column a clean test tube is taken to collect the green sample. After this the red and at last the most polar blue compound is collected, all in separate test tubes.

Thus a compound mixture is separated or purified by using column chromatography.

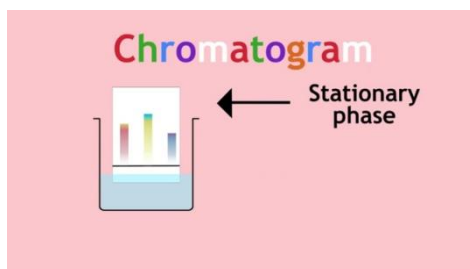
## Summary

- Column layer chromatography is an chromatography technique used to separate mixture of chemical substances into its individual compounds.
- Chromatography consists of two phases: one mobile phase and one contiguous stationery phase.
- Column is prepared my mixing the silica with suitable solvent and poured in into a glass column.
- A suitable solvent (mobile phase) is moved along with compound mixture through the column according to the polarity.

# Paper chromatography

## Introduction to paper chromatography

Paper chromatography is a chromatography technique used to separate mixture of chemical substances into its individual compounds. Paper chromatography is used to teach TLC or other chromatography as it is very similar to TLC.



## Principles of paper chromatography

All chromatography follow the same principle. Paper Chromatography consists of two phases: one mobile phase and one contiguous stationery phase. The stationery phase a paper and the mobile gas is solvent. The compound mixture moves along with the mobile phase through stationery phase and separates depending on the different degree of adhesion (on the paper) of each component in the sample or the compound mixture.

### Explanation The stationery phase :

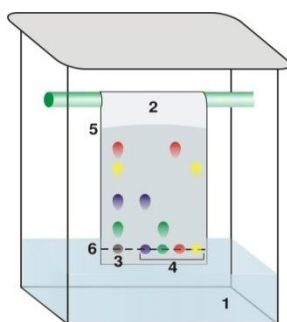
The paper chromatography is very similar to Thin layer chromatography. Difference is, instead of using a thin layer of silica on metal, it uses a special type of chromatography paper as stationery phase. This paper is made of cellulose. Cellulose is a polymer of simple sugar, glucose.

Cellulose contains -OH group similar to the silica or alumina on the TLC plate. The surface of cellulose is thus very polar. So the compounds can form hydrogen bond or can interact by van der waals dispersion forces and dipole dipole forces.

### Process

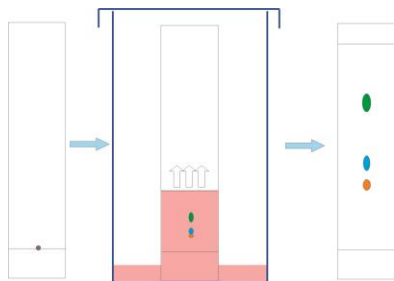
Paper chromatography works in few steps:

**Step 1:** A horizontal line is drawn near one end (about 1.5 cm from the bottom edge) of the paper. In figure below 6 is the horizontal line.



**Step 2:** The sample needs to be separated is placed as a small drop or line on to the paper using capillary tube. Labelling the drop by a pencil with an alphabet or number help to identify the compound later. In figure above 3 and 4 are the drops labelled. The drops are then soaked on the paper and dried.

**Step 3:** The paper is then placed into a sealed container with a swallow layer of suitable solvent. The solvent level must be lower than the pencil line or drop on it. The container need to be covered to stop the solvent to evaporate.



**Step 4:** The solvent rises up the paper chromatography taking each component of the sample with it. The components travel with the solvent depends on three things:

- The polarity of the sample molecule. The non polar components travel faster than the polar component.
- The attraction between the sample molecule and the solvent or solvent mixture.
- The attraction between the sample and the silica.

Suppose any sample compound mixture contains three colored molecules green, blue and red. According to their polarity, the order of these compounds is green<blue<red. Thus the most non polar green will travel first along with the mobile phase. Then blue and at last most polar compound the red one.

**Step 5:** When the solvent rises near the end of the paper then the paper should be taken out from sealed container and air dried. The paper with separated bands of components are then observed under UV-light.

$R_f$  value

The compounds in the sample travels along with solvent to give separate bands on the paper. The distance travelled by same compound with respect to the solvent is always constant. Thus the ratio of the distance that the compound travelled and the distance that the solvent travelled is denoted as  $R_f$ . And mathematically expressed as:

$$R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$$

## Summary

- Paper chromatography is an chromatography technique used to separate mixture of chemical substances into its individual compounds.
- Paper chromatography consists of two phases: one mobile phase and one contiguous stationery phase.
- Paper used in paper chromatography is made of cellulose.
- A suitable solvent (mobile phase) is moved along with a compound mixture through the paper according to the polarity and the degree of adhesion of each component on the stationery phase.
- The ratio of the distance that the compound travelled and the distance that the solvent travelled is denoted as  $R_f$ .

## Thin Layer Chromatography

Thin Layer Chromatography is a technique used to isolate non-volatile mixtures. The experiment is conducted on a sheet of aluminium foil, plastic, or glass which is coated with a thin layer of adsorbent material. The material usually used is aluminium oxide, cellulose, or silica gel.

On completion of the separation, each component appears as spots separated vertically. Each spot has a retention factor ( $R_f$ ) expressed as:

$$R_f = \frac{\text{dist. travelled by sample}}{\text{dist. travelled by solvent}}$$

The factors affecting retardation factor are the solvent system, amount of material spotted, adsorbent and temperature. TLC is one of the fastest, least expensive, simplest and easiest chromatography technique.

### Thin Layer Chromatography Principle

Like other chromatographic techniques, thin layer chromatography (TLC) depends on the separation principle. The separation relies on the relative affinity of compounds towards both the phases. The compounds in the mobile phase move over the surface of the stationary phase. The movement occurs in such a way that the compounds which have a higher affinity to the stationary phase move slowly while the other compounds travel fast. Therefore, the separation of the mixture is attained. On completion of the separation process, the individual components from the mixture appear as spots at respective levels on the plates. Their character and nature are identified by suitable detection techniques.

### Thin Layer Chromatography Diagram

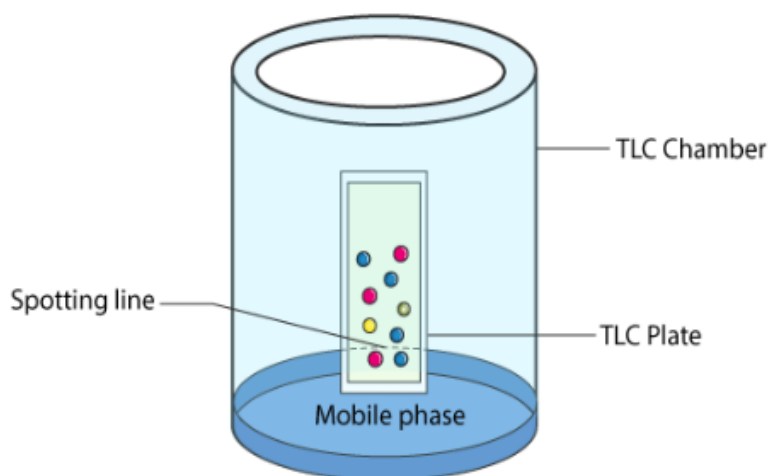


Diagram of Thin Layer Chromatography

## Thin Layer Chromatography Procedure

Before starting with the Thin Layer Chromatography Experiment let us understand the different components required to conduct the procedure along with the phases involved.

1. Thin Layer Chromatography Plates – ready-made plates are used which are chemically inert and stable. The stationary phase is applied on its surface in the form of a thin layer. The stationary phase on the plate has a fine particle size and also has a uniform thickness.
2. Thin Layer Chromatography Chamber – Chamber is used to develop plates. It is responsible to keep a steady environment inside which will help in developing spots. Also, it prevents the solvent evaporation and keeps the entire process dust-free.
3. Thin Layer Chromatography Mobile phase – Mobile phase is the one that moves and consists of a solvent mixture or a solvent. This phase should be particulate-free. The higher the quality of purity the development of spots is better.
4. Thin Layer Chromatography Filter Paper – It has to be placed inside the chamber. It is moistened in the mobile phase.

## Thin Layer Chromatography Experiment

The stationary phase that is applied to the plate is made to dry and stabilize.

- To apply sample spots, thin marks are made at the bottom of the plate with the help of a pencil.
- Apply sample solutions to the marked spots.
- Pour the mobile phase into the TLC chamber and to maintain equal humidity, place a moistened filter paper in the mobile phase.
- Place the plate in the TLC chamber and close it with a lid. It is kept in such a way that the sample faces the mobile phase.
- Immerse the plate for development. Remember to keep the sample spots well above the level of the mobile phase. Do not immerse it in the solvent.
- Wait till the development of spots. Once the spots are developed, take out the plates and dry them. The sample spots can be observed under a UV light chamber.

## Thin Layer Chromatography Applications

- The qualitative testing of Various medicines such as sedatives, local anaesthetics, anticonvulsant tranquilisers, analgesics, antihistamines, steroids, hypnotics is done by TLC.
- TLC is extremely useful in Biochemical analysis such as separation or isolation of biochemical metabolites from its blood plasma, urine, body fluids, serum, etc.
- Thin layer chromatography can be used to identify natural products like essential oils or volatile oil, fixed oil, glycosides, waxes, alkaloids, etc
- It is widely used in separating multicomponent pharmaceutical formulations.
- It is used to purify of any sample and direct comparison is done between the sample and the authentic sample



- It is used in the food industry, to separate and identify colours, sweetening agent, and preservatives
- It is used in the cosmetic industry.
- It is used to study if a reaction is complete.

#### Disadvantages Of Thin Layer Chromatography:

1. Thin Layer Chromatography plates do not have longer stationary phase.
2. When compared to other chromatographic techniques the length of separation is limited.
3. The results generated from TLC are difficult to reproduce.
4. Since TLC operates as an open system, some factors such as humidity and temperature can be consequences to the final outcome of the chromatogram.
5. The detection limit is high and therefore if you want a lower detection limit, you cannot use TLC.
6. It is only a qualitative analysis technique and not quantitative

#### Photochemistry

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).

#### Examples of photochemical reactions[[edit](#)]

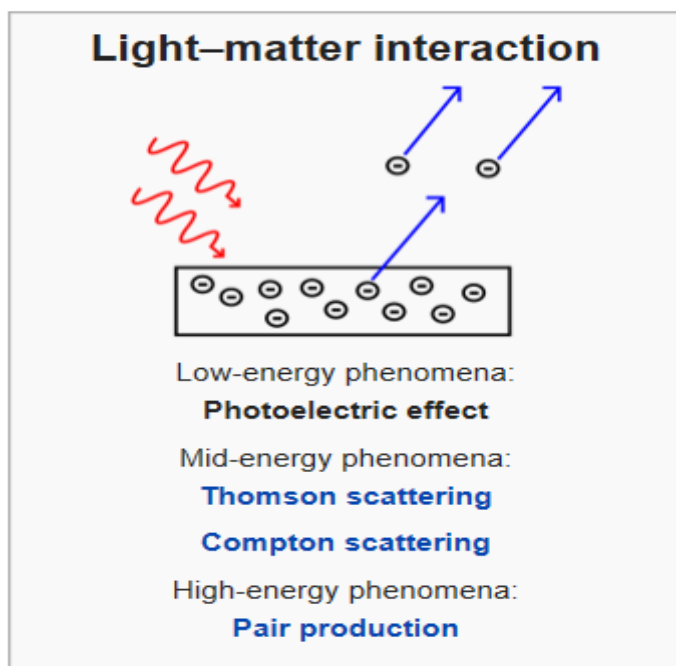
- **Photosynthesis:** plants use solar energy to convert carbon dioxide and water into glucose and oxygen.
- Human formation of vitamin D by exposure to sunlight.
- **Bioluminescence:** *e.g.* In fireflies, an enzyme in the abdomen catalyzes a reaction that produced light.<sup>[8]</sup>
- Polymerizations started by photoinitiators, which decompose upon absorbing light to produce the free radicals for radical polymerization.
- Photodegradation of many substances, *e.g.* polyvinyl chloride and Fp. Medicine bottles are often made with darkened glass to prevent the drugs from photodegradation.
- **Photodynamic therapy:** light is used to destroy tumors by the action of singlet oxygen generated by photosensitized reactions of triplet oxygen. Typical photosensitizers include tetraphenylporphyrin and methylene blue. The resulting singlet oxygen is an aggressive oxidant, capable of converting C-H bonds into C-OH groups.
- Photoresist technology, used in the production of microelectronic components.
- Vision is initiated by a photochemical reaction of rhodopsin.<sup>[9]</sup>
- Toray photochemical production of  $\epsilon$ -caprolactame.<sup>[10]</sup>
- Photochemical production of artemisinin, anti-malaria drug.<sup>[11][12]</sup>
- Photoalkylation, used for the light-induced addition of alkyl groups to molecules.

## Photoelectric effect

The photoelectric effect is the emission of electrons or other *free carriers* when electromagnetic radiation, like light, hits a material. Electrons emitted in this manner can be called *photoelectrons*. This phenomenon is commonly studied in electronic physics and in fields of chemistry such as quantum chemistry and electrochemistry.

Because a low-frequency beam at a high intensity could not build up the energy required to produce photoelectrons like it would have if light's energy was continuous like a wave, Einstein proposed that a beam of light is not a wave propagating through space, but rather a collection of discrete wave packets (photons).

Emission of conduction electrons from typical metals usually requires a few electron-volts, corresponding to short-wavelength visible or ultraviolet light. Emissions can be induced with photons with energies approaching zero (in the case of negative electron affinity) to over 1 MeV for core electrons in elements with a high atomic number. Study of the photoelectric effect led to important steps in understanding the quantum nature of light and electrons and influenced the formation of the concept of wave-particle duality.<sup>[1]</sup> Other phenomena where light affects the movement of electric charges include the photoconductive effect (also known as photoconductivity or photoresistivity), the photovoltaic effect, and the photoelectrochemical effect.



## Uses and effects

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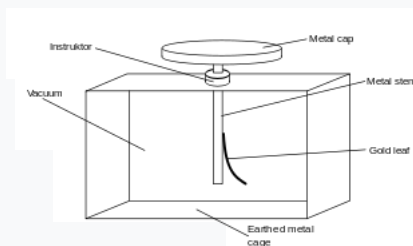
### Photomultipliers

These are extremely light-sensitive vacuum tubes with a photocathode coated onto part (an end or side) of the inside of the envelope. The photo cathode contains combinations of materials such as cesium, rubidium, and antimony specially selected to provide a low work function, so when illuminated even by very low levels of light, the photocathode readily releases electrons. By means of a series of electrodes (dynodes) at ever-higher potentials, these electrons are accelerated and substantially increased in number through secondary emission to provide a readily detectable output current. Photomultipliers are still commonly used wherever low levels of light must be detected.

### Image sensors

Video camera tubes in the early days of television used the photoelectric effect, for example, Philo Farnsworth's "Image dissector" used a screen charged by the photoelectric effect to transform an optical image into a scanned electronic signal.

### Gold-leaf electroscope



The gold leaf electroscope

Gold-leaf electroscopes are designed to detect static electricity. Charge placed on the metal cap spreads to the stem and the gold leaf of the electroscope. Because they then have the same charge, the stem and leaf repel each other. This will cause the leaf to bend away from the stem.

An electroscope is an important tool in illustrating the photoelectric effect. For example, if the electroscope is negatively charged throughout, there is an excess of electrons and the leaf is separated from the stem. If high-frequency light shines on the cap, the electroscope discharges, and the leaf will fall limp. This is because the frequency of the light shining on the cap is above the cap's threshold frequency. The photons in the light have enough energy to liberate electrons from the cap, reducing its negative charge. This will discharge a negatively charged electroscope and further charge a positive electroscope. However, if the electromagnetic radiation hitting the metal cap does not have a high enough frequency (its frequency is below the threshold value for the cap), then the leaf will never discharge, no matter how long one shines the low-frequency light at the cap.

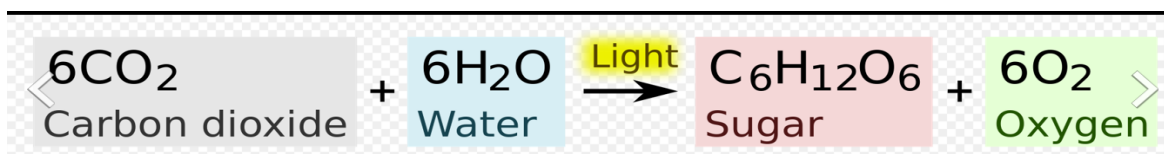
# Photosynthesis

**Photosynthesis** is a process used by plants and other organisms to convert light energy into chemical energy that can later be released to fuel the organisms' activities. This chemical energy is stored in carbohydrate molecules, such as sugars, which are synthesized from carbon dioxide and water – hence the name *photosynthesis*, from the Greek  $\phi\acute{o}\varsigma$ , *phōs*, "light", and *synthesis*, "putting together". In most cases, oxygen is also released as a waste product. Most plants, most algae, and cyanobacteria perform photosynthesis; such organisms are called photoautotrophs. Photosynthesis is largely responsible for producing and maintaining the oxygen content of the Earth's atmosphere, and supplies all of the organic compounds and most of the energy necessary for life on Earth.

Although photosynthesis is performed differently by different species, the process always begins when energy from light is absorbed by proteins called reaction centres that contain green chlorophyll pigments. In plants, these proteins are held inside organelles called chloroplasts, which are most abundant in leaf cells, while in bacteria they are embedded in the plasma membrane. In these light-dependent reactions, some energy is used

to strip electrons from suitable substances, such as water, producing oxygen gas. The hydrogen freed by the splitting of water is used in the creation of two further compounds that serve as short-term stores of energy, enabling its transfer to drive other reactions: these compounds are reduced nicotinamide adenine dinucleotide phosphate (NADPH) and adenosine triphosphate (ATP), the "energy currency" of cells.

o strip from suitable substances, such as water, producing oxygen gas. The hydrogen freed by the splitting of water is used in the creation of two further compounds that serve as short-term stores of energy, enabling its transfer to drive other reactions: these compounds are reduced (NADPH) and (ATP), the "energy currency" of cells.



first law of photochemistry

The first law of photochemistry, known as the Grotthuss–Draper law (for chemists Theodor Grotthuss and John W. Draper ), states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place. According to the second law of photochemistry,...

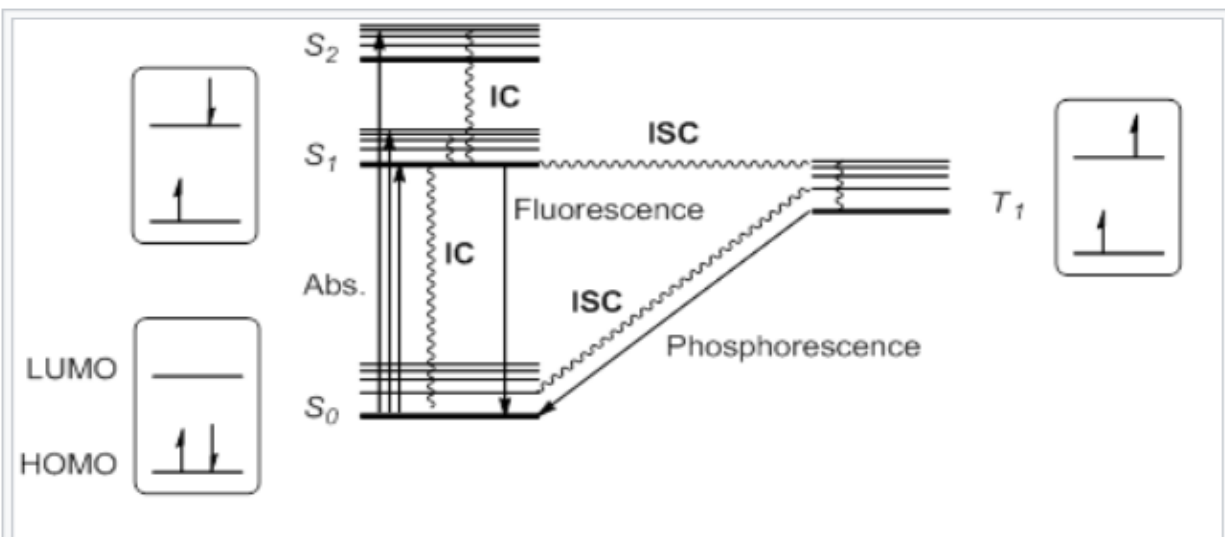
## Grotthuss–Draper law and Stark-Einstein law

Photoexcitation is the first step in a photochemical process where the reactant is elevated to a state of higher energy, an excited state. The first law of photochemistry, known as the Grotthuss–Draper law (for chemists Theodor Grotthuss and John W. Draper), states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place. According to the second law of photochemistry, known as the Stark-Einstein law (for physicists Johannes Stark and Albert Einstein), for each photon of light absorbed by a chemical system, no more than one molecule is activated for a photochemical reaction, as defined by the quantum yield.

## Fluorescence and phosphorescence

When a molecule or atom in the ground state ( $S_0$ ) absorbs light, one electron is excited to a higher orbital level. This electron maintains its spin according to the spin selection rule; other transitions would violate the law of conservation of angular momentum. The excitation to a higher singlet state can be from HOMO to LUMO or to a higher orbital, so that singlet excitation states  $S_1$ ,  $S_2$ ,  $S_3\dots$  at different energies are possible.

Kasha's rule stipulates that higher singlet states would quickly relax by radiationless decay or internal conversion (IC) to  $S_1$ . Thus,  $S_1$  is usually, but not always, the only relevant singlet excited state. This excited state  $S_1$  can further relax to  $S_0$  by IC, but also by an allowed radiative transition from  $S_1$  to  $S_0$  that emits a photon; this process is called fluorescence.



**Jablonski diagram.** Radiative paths are represented by straight arrows and non-radiative paths by curly lines.

## UNIT V

### ELECTROCHEMISTRY AND BUFFER

#### Conductivity

Conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to conduct electricity. The SI unit of conductivity is Siemens per meter (S/m). Conductivity measurements are used routinely in many industrial and environmental applications as a fast, inexpensive and reliable way of measuring the ionic content in a solution. For example, the measurement of product conductivity is a typical way to monitor and continuously trend the performance of water purification systems.

#### Equivalent conductance

Equivalent conductance is defined as the conductance of an electrolyte solution containing one gram equivalent of the electrolyte. It is equal to the product of specific conductance ( $k$ ) of the solution and the volume ( $V$ ) of the solution that contains one gram equivalent of the electrolyte.  $\lambda = k \times V$ .

#### Specific Conductivity

Specific conductivity is another step necessary for describing exactly the way a system carries energy. The measurement is used most often in reference to the way electricity moves through aqueous solutions. Conductivity tests of electricity through various liquid substances are done by placing electrodes at either end of a tank of the solution. Specific conductivity takes the area of the electrodes into account to make sure that the measurement of the current conducted is as accurate as possible.

#### Effect of dilution on conductivity

##### **Effect of Dilution are as follows:**

- (i) The conductivity of solution increases on dilution.
- (ii) The specific conductivity decreases on dilution (as number of ions decreases w.r.t. to volume).
- (iii) The equivalent and molar conductivities increase with dilution.
- (iv) The equivalent and molar conductivities tend to acquire maximum value with increasing dilution. [Maximum at  $\infty$  dilution]
- (v) Variation of molar conductance with concentration: For a strong electrolyte it is shown by Debye-Huckel Sagar equation as follows:

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

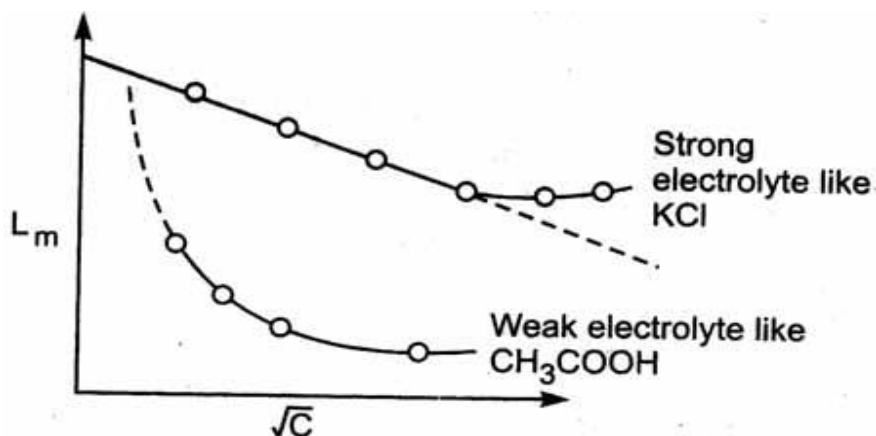
In place of  $\Lambda^0$  we can also use  $\Lambda^\infty$

Here,  $\Lambda_M^0$  = molar conductance at infinite.

dilution (Limiting molar conductance)

$\Lambda_m$  = Molar conductance at V-dilution

b = It is a constant which depends upon nature of solvent and temperature



c = concentration

Effect of dilution

- $\Lambda M$  increases on dilution as inter-ionic attraction also decreases along with dilution.

At higher concentration these attractions are stronger so less deviations are observed in the value of  $\Lambda M$  with dilution.

In case of weak electrolytes  $\Lambda M$  increases as dissociation takes place on dilution. In case of strong electrolyte  $\Lambda^\infty$  can be observed by extrapolating concentration to zero. However in case of weak electrolytes it is possible.

### Determination of specific conductivity

The cell is connected to resistance box, R on one side and thin uniform wire AB of meter bridge on the other secondary of induction coil is connected to the ends of the V bridge while the primary is connected to a battery. The headphone, G is connected to a sliding key, P and the binding screw in between the cell and resistance box.

The sliding key, P is placed near the middle. When the circuit is complete, a buzzing sound is heard in the headphone. Plugs are taken out from the resistance box. The sliding key is moved along the wire until the sound in the headphone is reduced to a minimum. Thus point H is recorded. The observed conductivity of solution is then calculated by applying the following formula:

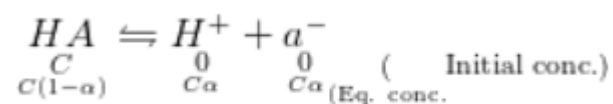
$$\text{or Resistance of solution} = \frac{BH}{AH} \times \text{Resistance, } R$$

$$\text{or } \frac{1}{\text{Obs. Conductivity}} = \frac{BH}{AH} \times \text{resistance}$$

Thus AH and BH are measured on graduated scale and R in ohms from resistance box.

### Ostwald's Dilution Law

Ostwald's dilution law is the application of the law of mass action to weak electrolytes in solution. Suppose an acid HA is dissolved in water, it will ionise as under:



Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\therefore K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Where  $K_a$  is the dissociation (or ionisation) constant of the acid HA and  $\alpha$  is its degree of dissociation.

This equation is known as Ostwald's dilution law equation. If  $\alpha \ll 1$  then the above equation may be written as:

$$K_a = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}}$$

$$\text{As } C \propto \frac{1}{V}$$

$$\text{So } K_a = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2}{V}$$

$$K_a \cdot V = \alpha^2$$

$$\alpha = \sqrt{K_a V}$$

$$\alpha \propto \sqrt{V} \quad \text{At constant temperature}$$



Thus at constant temperature degree of dissociation of weak electrolyte is directly proportional to square root of its dilution. The value of  $\alpha$  can be calculated by measuring conductance of the solution as:

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}}$$

Where  $\lambda_v$  is the equivalent conductance at a particular dilution and  $\lambda_{\infty}$  is equivalent conductance at infinite dilution.

With the help of this equation;  $[H^+]$  or  $p^H$  of the acid solution may be calculated.

If we know the value of  $\alpha$  and C for any acid then  $K_a$  may be calculated. For example, the value of  $\alpha$  for 0.05 N acetic acid is 0.03.

Therefore the value of  $K_a$  for acetic acid will be,

$$K_a = \frac{0.05 \times 0.03 \times 0.03}{1 - 0.02}$$

$$4.64 \times 10^{-5}$$

Weak electrolytes obey Ostwald's dilution law fairly well, but strong electrolytes do not obey this law; because these electrolytes almost completely ionise at every concentration i. e. ,  $\alpha = 1$  or  $\lambda_v = \lambda_{\infty}$ , but in practice it is not so. thus  $\alpha = \lambda_v/\lambda_{\infty}$  is not applicable for strong electrolytes. It is observed that  $\lambda_v < \lambda_{\infty}$  even though  $\alpha = 1$ .

This is due to the following two main effects:

1. **The relaxation effect:** According to this effect, each cation is surrounded by a number of anions and vice versa in solution; which is called ionic atmosphere of the oppositely charged ions. On applying e.m.f., the ion moves towards oppositely charged electrode leaving behind the ionic atmosphere. To form a new ionic atmosphere some time is taken which is called **relaxation time** and this effect of the ionic atmosphere is called **relaxation effect**. Due to this effect the value of  $\lambda_v$ , is not limiting.

2. **The electrophoretic effect:** Since solvent molecules attached to the ionic atmosphere moving in the opposite direction produce friction hence reduce the motion of central ion.

## Kohlrausch law

Kohlrausch law helps us in the determination of limiting molar conductivities for any electrolyte. Weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations.

Kohlrausch's law states that the equivalent conductivity of an electrolyte at infinite dilution is equal to the sum of the conductances of the anions and cations.

The molar conductivity of a solution at a given concentration is the conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. The molar conductivity of a solution increases with the decrease in concentration. This increase in molar conductivity is because of the increase in the total volume containing one mole of the electrolyte. When the concentration of the electrolyte approaches zero, the molar conductivity is known as limiting molar conductivity,  $\Lambda_m^\circ$ .

Kohlrausch observed certain regularities while comparing the values of limiting molar conductivities of some strong electrolytes. On the basis of his observations, Kohlrausch proposed "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte". This law is popularly known as Kohlrausch law of independent migration of ions. For example, limiting molar conductivity,  $\Lambda_m^\circ$  of sodium chloride can be determined with the knowledge of limiting molar conductivities of sodium ion and chloride ion. Some important applications of Kohlrausch law of independent migration of ions are:

1. Kohlrausch law helps us in the determination of limiting molar conductivities for any electrolyte. Weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations. The graph plotted between molar conductivity and  $c^{1/2}$  (where  $c$  is the concentration) is not a straight line for weak electrolytes. The molar conductivity of weak electrolyte increases steeply at lower concentrations. Therefore, limiting molar conductivity,  $\Lambda_m^\circ$  cannot be obtained by extrapolation of molar conductivity to zero concentration. Hence, we use the Kohlrausch law of independent migration of ions for the determination of limiting molar conductivity,  $\Lambda_m^\circ$  for weak electrolytes.
2. Kohlrausch law also helps us in determining the value of dissociation constant from the value of molar conductivity and limiting molar conductivity for a weak electrolyte at a given concentration.

$$\alpha = \frac{\Lambda}{\Lambda_m^\circ}$$

$\Lambda$  = molar conductivity

$\Lambda_m^\circ$  = limiting molar conductivity

### Uses of Kohlrausch's law

- Calculation of Degree of dissociation
- Calculation of solubility of sparingly soluble salt
- Calculation of Dissociation Constant for weak electrolytes
- Calculation of Molar Conductivity for weak electrolytes at infinite dilution

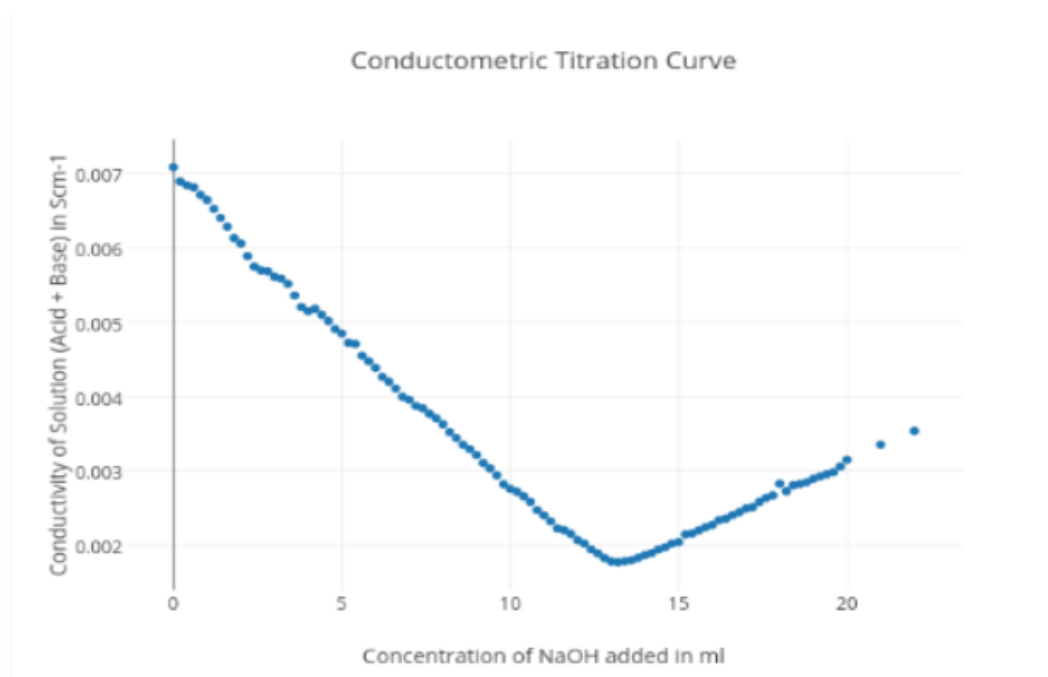
## Conductometric Titration

Conductometric titration is a laboratory method of quantitative analysis used to identify the concentration of a given analyte in a mixture. Conductometric titration involves the continuous addition of a reactant to a reaction mixture and the documentation of the corresponding change in the electrolytic conductivity of the reaction mixture. It can be noted that the electrical conductivity of an electrolytic solution is dependant on the number of free ions in the solution and the charge corresponding to each of these ions.

In this type of titration, upon the continuous addition of the titrant (and the continuous recording of the corresponding change in electrolytic conductivity), a sudden change in the conductivity implies that the stoichiometric point has been reached. The increase or decrease in the electrolytic conductivity in the conductometric titration process is linked to the change in the concentration of the hydroxyl and hydrogen ions (which are the two most conducting ions).

The strength of an acid can be determined via conductometric titration with a standard solution of a base. An example of a curve plotted for such a titration process is given below.

The method of conductometric titration is very useful in the titration of homogeneous suspensions or coloured solutions as these titrations cannot be done with the use of normal chemical indicators.



The method of conductometric titration is very useful in the titration of homogeneous suspensions or coloured solutions as these titrations cannot be done with the use of normal chemical indicators.

## Principle

The principle of the conductometric titration process can be stated as follows – During a titration process, one ion is replaced with another and the difference in the ionic conductivities of these ions directly impacts the overall electrolytic conductivity of the solution.

It can also be observed that the ionic conductance values vary between cations and anions. Finally, the conductivity is also dependant upon the occurrence of a chemical reaction in the electrolytic solution.

## Theory

The theory behind this type of titration states that the end-point corresponding to the titration process can be determined by means of conductivity measurement. For a neutralization reaction between an acid and a base, the addition of the base would lower conductivity of the solution initially. This is because the  $H^+$  ions would be replaced by the cationic part of the base.

After the equivalence point is reached, the concentration of the ionic entities will increase. This, in turn, increases the conductance of the solution. Therefore, two straight lines with opposite slopes will be obtained when the conductance values are plotted graphically. The point where these two lines intersect is the equivalence point.

## Process

For the conductometric titration of an acid with a base, the general process is as follows:

- 10 ml of the acid must be diluted with approximately 100 ml of distilled water (so that the changes in the conductance brought on by the addition of the base become small).
- A burette must now be filled with the base and the initial volume must be noted.
- In this step, a conductivity cell must be inserted into the diluted acid solution in a way that both the electrodes are completely immersed.
- Now, the conductivity cell can be connected to a digital conductometer in order to obtain an initial reading.
- The base must now be added dropwise into the acid solution. The volume of base added must be noted along with the corresponding change in the conductance.
- A sharp increase in the conductance of the solution implies that the endpoint has been reached. However, a few more readings must be taken after the endpoint of the titration.
- These observed values must now be plotted graphically. The equivalence point can be obtained from the point of intersection between the two lines.

The strength of the acid can now be calculated via the formula  $S_2 = (V_1S_1)/10$ ; where  $S_2$  is the strength of the acid,  $V_1$  is the volume of base added (as per the equivalence point on the conductometric titration graph), and  $S_1$  is the strength of the base (already known). Here, the volume of the acid ( $V_2$ ) is equal to 10 ml.

## Advantages and Disadvantages of Conductometric Titration

Some advantages of the conductometric titration process are listed below.

- This process is very useful in the titrations of very dilute solutions and weak acids.
- The end-point of this method of titration is very sharp and accurate when compared to a few other titration processes.
- This type of titration is applicable for solutions that are coloured or turbid, and for which the endpoint of the titration with normal indicators cannot be observed easily by the human eye.
- Conductometric titration has numerous applications in acid-base titrations, redox titrations, precipitation titrations, and complex titrations.

The two major disadvantages of this type of titration include:

1. Only a few specific redox titrations can be done with the help of this process. This is because the conductivity of the solution is masked by relatively high hydronium ion concentration.
2. The accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making the titration process unsatisfactory.

## Buffer Solutions

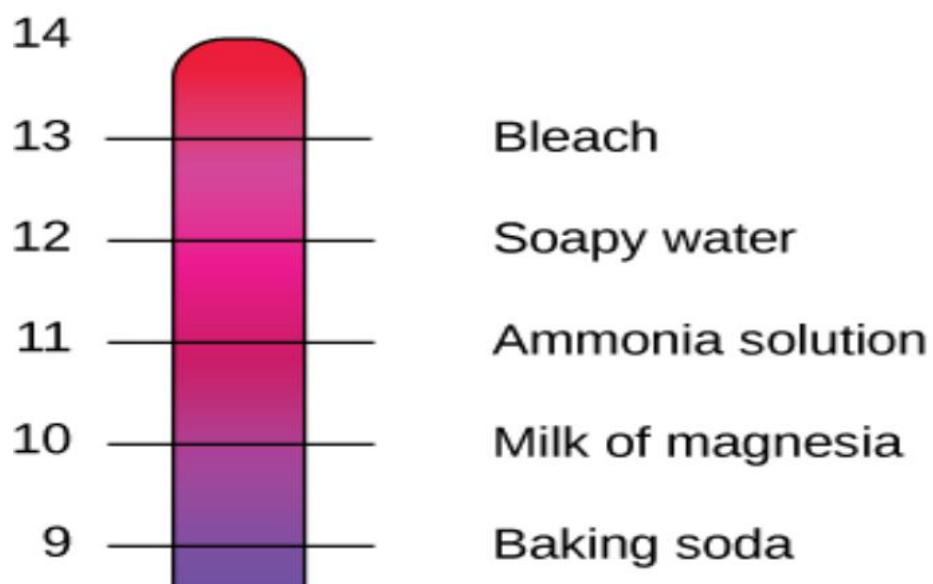
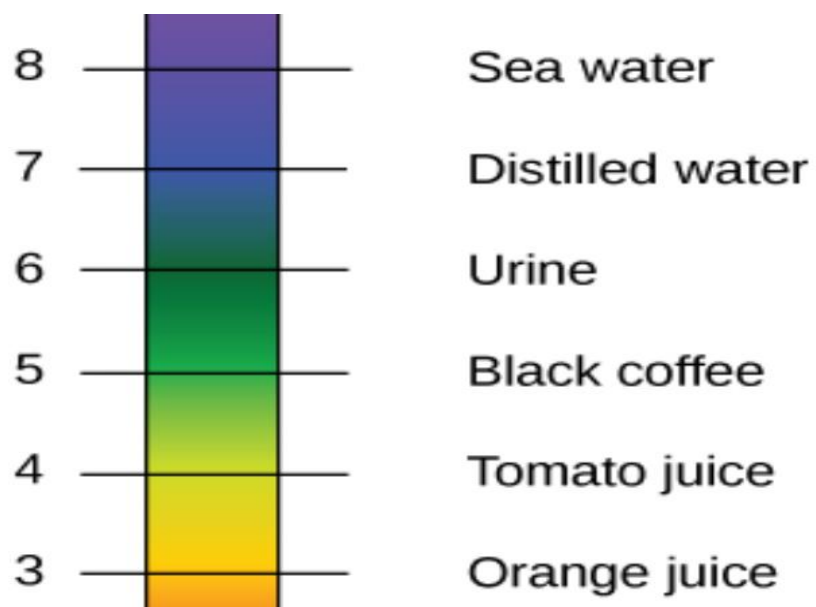
Buffers are solutions that resist a change in pH on dilution or on addition of small amounts of acids or alkali.

A lot of biological and chemical reactions need a constant pH for the reaction to proceed. Buffers are extremely useful in these systems to maintain the pH at a constant value. This does not mean that the pH of buffers does not change. It only means that the change in pH is not as much as it would be with a solution that is not a buffer.

## Types of Buffer Solutions

Buffers are broadly divided into two types – acidic and alkaline buffer solutions. Acidic buffers are solutions that have a pH below 7 and contain a weak acid and one of its salts. For example, a mixture of acetic acid and sodium acetate acts as a buffer solution with a pH of about 4.75.

Alkaline buffers, on the other hand, have a pH above 7 and contain a weak base and one of its salts. For example, a mixture of ammonium chloride and ammonium hydroxide acts as a buffer solution with a pH of about 9.25. Buffer solutions help maintain the pH of many different things.



## Colorimetric analysis

Colorimetric analysis is a method of determining the concentration of a chemical element or chemical compound in a solution with the aid of a color reagent. It is applicable to both organic compounds and inorganic compounds and may be used with or without an enzymatic stage. The method is widely used in medical laboratories and for industrial purposes, e.g. the analysis of water samples in connection with industrial water treatment.

### Examples[edit]

#### Calcium

Calcium + o-cresolphthalein complexone ----> colored complex<sup>[2]</sup>

#### Copper

Copper + bathocuproin disulfonate ----> colored complex<sup>[3]</sup>

#### Creatinine

Creatinine + picrate ----> colored complex

#### Iron

Iron + bathophenanthroline disulfonate ---> colored complex

#### Phosphate (inorganic)

Phosphate + ammonium molybdate + ammonium metavanadate ----> colored complex

### Examples

#### Cholesterol (CHOD-PAP method)

1. Cholesterol + oxygen --(enzyme cholesterol oxidase)--> cholestenone + hydrogen peroxide
2. Hydrogen peroxide + 4-aminophenazone + phenol --(enzyme peroxidase)--> colored complex + water<sup>[7]</sup>

#### Glucose (GOD-Perid method)

1. Glucose + oxygen + water --(enzyme glucose oxidase)--> gluconate + hydrogen peroxide
2. Hydrogen peroxide + ABTS --(enzyme peroxidase)--> colored complex<sup>[8]</sup>

In this case, both stages of the reaction are catalyzed by enzymes.

### **Triglycerides (GPO-PAP method)**

1. Triglycerides + water --(enzyme esterase)--> glycerol + carboxylic acid
2. Glycerol + ATP --(enzyme glycerol kinase)--> glycerol-3-phosphate + ADP
3. Glycerol-3-phosphate + oxygen --(enzyme glycerol-3-phosphate oxidase) --> dihydroxyacetone phosphate + hydrogen peroxide
4. Hydrogen peroxide + 4-aminophenazone + 4-chlorophenol --(enzyme peroxidase)--> colored complex

### **Urea**

1. Urea + water --(enzyme urease)--> ammonium carbonate
2. Ammonium carbonate + phenol + hypochlorite ----> colored complex

### **Electrometric determination**

pH Determination by Electrometric Method The pH indicator of any solution can be determined using an indicator solution or indicator paper, but the obtained results are not accurate since  $\pm 1$  is the built error of pH. For precise measurement, a pH meter is used.

Several indicator electrodes are available for determining pH, Glass electrodes are widely used electrodes and many types of glass are used to make sensitive glass bulbs. Lithia Glass is appropriate on the whole range of pH 0 to 14. The standard buffer is recommended to calibrate the pH meter. (pH 07.00, pH 04.00 and pH 9.20). i.e., determine the asymmetric potential. Then the pH can be read directly from the panel of pH meter of the unknown solution. The pH meter includes of a glass and a reference electrode, LCD/LED display and a temperature compensated.

**Glass electrode:** The sensor electrode is a special glass bulb in which HCL has a certain concentration and has a buffering chloride solution in contact with an inner reference electrode.

### **pH Meter Principle and Applications**

The pH measurement is the most common requirement of today's laboratory which is engaged in soil analysis, water, and wastewater analysis, industrial water, environmental analysis, food processing, agrochemical manufacturing, electroplating, pharmaceutical manufacturing and in bulk drug manufacturing necessitate to check the pH at different level of processes in different aspects like quality control, process monitoring, pollution control and finalize the product etc. Generally, on the scale of 0 to 14 pH units, pH is measured, but with the growth of technology and increasing needs of different industries and study, the pH measurement range is increased from pH 2.0 to pH 20.00.



The measurement of the pH of every aqueous solution provides the degree of alkalinity or acidity of the solution. Generally, pH is defined as the logarithm of the hydrogen ion concentration. The pH electrode measures a solution potentiometrically as the pH electrode is deep in the solution, the electrical signal develops in the sensing membrane of the electrode. The output of the electrode fluctuates with the change in pH value with the linear relationship of 59.16 mV / pH unit value.

Electrode slope varies in temperature, therefore the requirement of temperature compensation; this slope can be compensated automatically or manually with modern pH meter. For accurate pH measurement, automatic temperature compensation with the different sensor is required. pH calibrates auto with measurement buffers, detection with ATC to read the PH value at 25 degrees. It scans, stores, prints and preserves data as per the GLP concept.