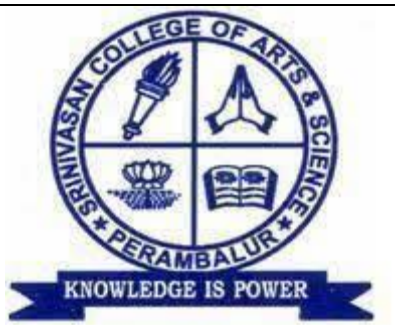

SRINVASAN COLLEGE OF ARTS AND SCIENCE
(Affiliated to Bharathidasan University Trichy)
PERAMBALUR – 62121

DEPARTMENT OF CHEMISTRY

COURSE MATERIAL

I B.Sc., Mathematics, Physics

ALLIED CHEMISTRY II

Subject Code : 16SACCH2

Prepared & Compiled

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UNIT-I

Nuclear chemistry

ISOTOPES-: Isotopes are atom have same atomic number but different mass number or atomic mass.

Ex- hydrogen has 3 isotopes as protiumdutrium and tritium having same atomic number 1 with different mass number 1,2,3.

ISOBARS-: Isobars are atoms of different elements which have same mass number but different atomic number.

Ex- argon and calcium have same mass number 40 but different atomic number 18,20.

ISOTONES-: Isotone are the atom of different element which contain same number of neutron with different mass number and atomic number.

Ex- silicon and phosphorous have same number of neutron 16

Six differences between nuclear reaction and chemical reaction

- Nuclear reactions involve a change in an atom's nucleus, usually producing a different element ,along with the emission of radiations like α,βandγetc rays. Chemical reactions, on the other hand, involve only a rearrangement of electrons and do not involve changes in the nuclei. **So nuclear reaction is nuclear phenomenon and chemical reaction is extra-nuclear phenomenon.**
- Different isotopes of an element normally behave similarly in chemical reactions as their extra-nuclear electronic configurations are same. The nuclear chemistry of different isotopes vary greatly from each other.
- Rates of chemical reactions are influenced by external effect like temperature,pressure and catalysts. Rates of nuclear reactions are spontaneous and are unaffected by such factors.
- Nuclear reactions are independent of the chemical form of the element.This means both in elemental and in compound state same amount of radio-element shows similar radioactivity.
- Energy changes accompanying nuclear reactions are much larger. This energy comes from destruction of mass.
- In a nuclear reaction, mass is not strictly conserved. Some of the mass is converted into energy,according to the equation E = mc2 and the order of energy evolved during a nuclear reaction is much higher than that of a chemical reaction.

	Chemical reactions		Nuclear reactions
1.	These reaction involve some loss, gain or overlap of outer orbital electrons of the reactant atoms.	1.	Nuclear reactions involve emission of alpha, beta and gamma particles from the nucleus.
2.	A chemical reaction is balanced in terms of mass only	2.	Nuclear reaction is balanced in terms of both mass and energy.
3.	The energy changes in any chemical reaction is very much less when compared with nuclear reaction.	3.	The energy changes are far exceed than the energy changes in chemical reactions.
4.	In chemical reactions, the energy is expressed in terms of kilojoules per mole.	4.	In nuclear reactions, the energy involved is expressed in MeV (Million electron volts) per individual nucleus.
5.	No new element is produced since nucleus is unaffected.	5.	New element / isotope may be produced during the nuclear reaction.

Radioactive Series

Radioactive series (known also as a radioactive cascades) are **three naturally occurring** radioactive decay chains and **one artificial radioactive decay chain** of unstable heavy atomic nuclei that decay through a sequence of alpha and beta decays until a stable nucleus is achieved. Most radioisotopes **do not decay directly** to a stable state and all isotopes **within the series** decay in the same way. In physics of nuclear decays, the disintegrating nucleus is usually referred to as the **parent** or classical series. The fourth set, the neptunium series, is headed by neptunium-237. Its members are produced artificially by nuclear reactions and do not occur naturally.

- **the thorium series (4n series),**
- **the uranium series (4n+2 series),**
- **the actinium series (4n+3 series),**
- **the neptunium series (4n+1 series).**

The classical series are headed by primordial unstable nuclei. Primordial nuclides are nuclides found on the Earth that have existed in their current form since before Earth was formed. The previous four series consist of the radioisotopes, that are the descendants of four heavy nuclei with long and very long half-lives:

- the thorium series with thorium-232 (with a half-life of 14.0 billion years),
- the uranium series with uranium-238 (which lives for 4.47 billion years),
- the actinium series with uranium-235 (with a half-life of 0.7 billion years).
- the neptunium series with neptunium-237 (with a half-life of 2 million years).

The half-lives of all the daughter nuclei are all extremely variable, and it is difficult to represent a range of timescales going from individual seconds to billions of years. Since daughter radioisotopes have different half-lives then secular equilibrium is reached after some time. In the long decay chain for a naturally radioactive element, such as uranium-238, where all of the elements in the chain are in secular equilibrium, each of the descendants has built up to an equilibrium amount and all decay at the rate set by the original parent. If and when equilibrium is achieved, each successive daughter isotope is present in direct proportion to its half-life. Since its activity is inversely proportional to its half-life, each nuclide in the decay chain finally contributes as many individual transformations as the head of the chain.

As can be seen from figures, branching occurs in all four of the radioactive series. That means the decay of a given species may occur in more than one way. For example, in the thorium series, bismuth-212 decays partially by negative beta emission to polonium-212 and partially by alpha emission to thallium-206.

Fission

Fission occurs when a neutron slams into a larger atom, forcing it to excite and spilt into two smaller atoms—also known as fission products. Additional neutrons are also released that can initiate a chain reaction.

When each atom splits, a tremendous amount of energy is released.

Uranium and plutonium are most commonly used for fission reactions in nuclear power reactors because they are easy to initiate and control.

The energy released by fission in these reactors heats water into steam. The steam is used to spin a turbine to produce carbon-free electricity.

Fusion

Fusion occurs when two atoms slam together to form a heavier atom, like when two hydrogen atoms fuse to form one helium atom.

This is the same process that powers the sun and creates huge amounts of energy—several times greater than fission. It also doesn't produce highly radioactive fission products.

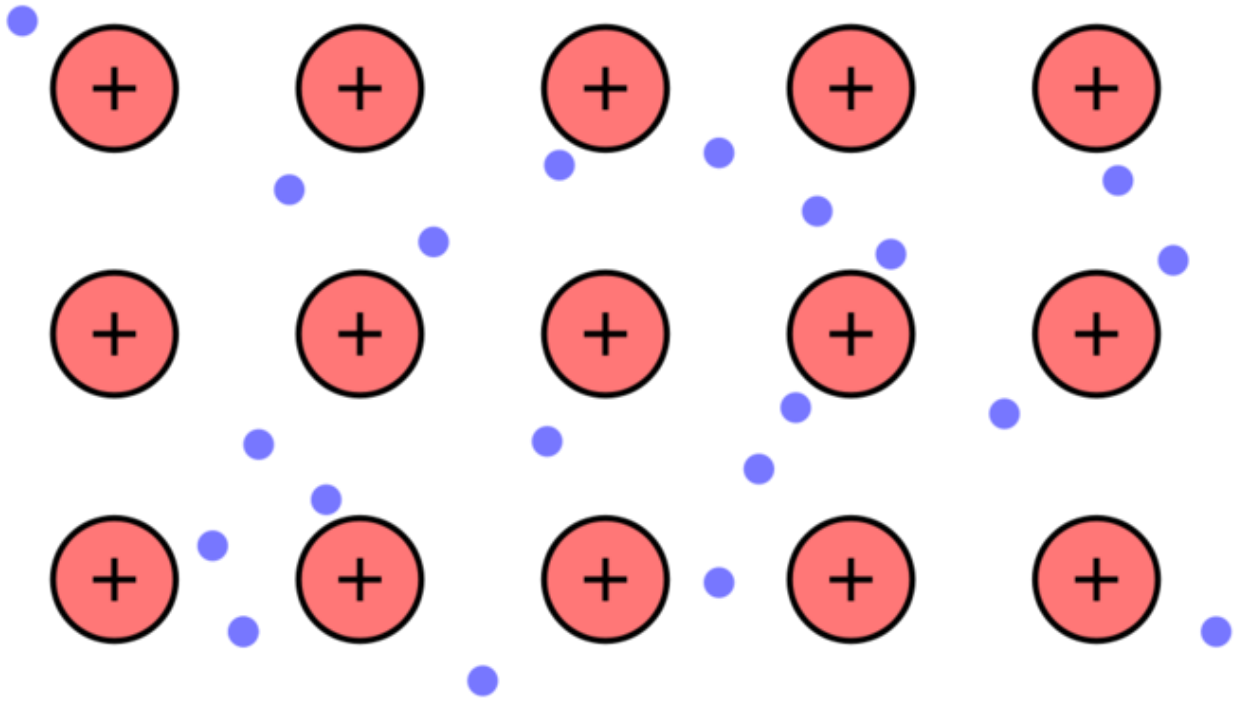
Fusion reactions are being studied by scientists, but are difficult to sustain for long periods of time because of the tremendous amount of pressure and temperature needed to join the nuclei together.

1.2 METALIC BOND

Metallic Bonding

Metallic bonding may be described as the sharing of free electrons among a lattice of positively charged metal ions. The structure of metallic bonds is very different from that of covalent and ionic bonds. While ionic bonds join metals to nonmetals, and covalent bonds join nonmetals to nonmetals, metallic bonds are responsible for the bonding between metal atoms.

In metallic bonds, the valence electrons from the s and p orbitals of the interacting metal atoms delocalize. That is to say, instead of orbiting their respective metal atoms, they form a "sea" of electrons that surrounds the positively charged atomic nuclei of the interacting metal ions. The electrons then move freely throughout the space between the atomic nuclei.



Metallic Bonding: The Electron Sea Model: Positive atomic nuclei surrounded by a sea of delocalized electrons (the blue dots).

The characteristics of metallic bonds explain a number of the unique properties of metals:

- Metals are good conductors of electricity because the electrons in the electron sea are free to flow and carry electric current.
- Metals are ductile and malleable because local bonds can be easily broken and reformed.

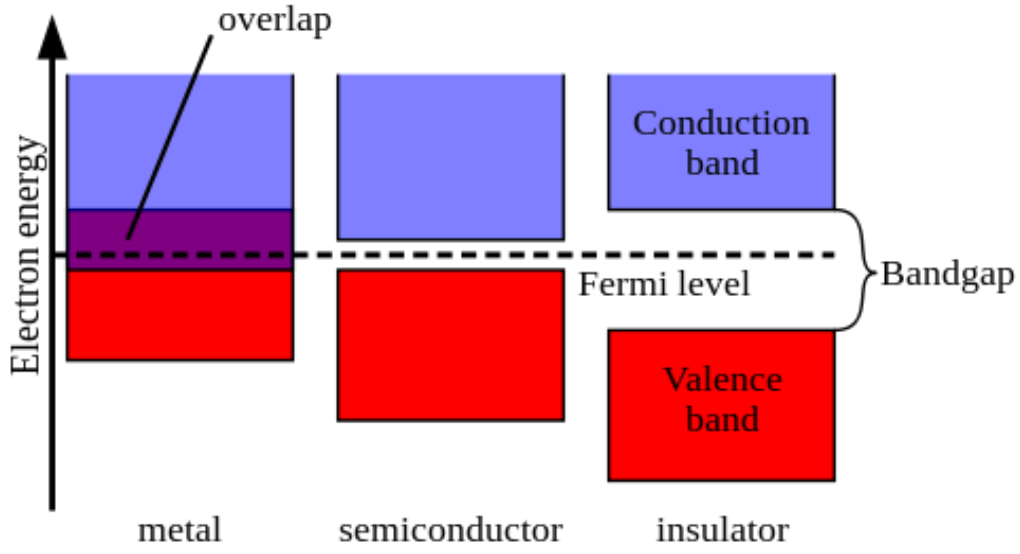
- Metals are shiny. Light cannot penetrate their surface; the photons simply reflect off the metal surface. However, there is an upper limit to the frequency of light at which the photons are reflected.

Energy Bands in Solids

Electrons in free atoms have discrete energy values. In contrast, the energy states available to the free electrons in a metal sample form a continuum of "energy bands." In the atomic lattice of a substance, there is a set of filled atomic energy "bands" with a full complement of electrons, and a set of higher energy unfilled "bands" which have no electrons. The highest energy band contains valence electrons available for chemical reactions. The *conduction band* is the band above the valence band. Electrons in the conduction band are free to move about in the lattice and can conduct current. In order for a substance to conduct electricity, its valence electrons must cross the band gap, which is the energy gap between the valence band and conduction band.

Band Structure: The gap between the valence and conduction bands determines whether a substance will conduct electricity.

If the gap between the valence and conduction bands is large, then the substance does not conduct electricity easily (it is an insulator). On the other hand, these bands overlap in metallic samples, which make these samples excellent conductors of electricity. In the case of semiconductors, the gap is small enough for electrons to jump to the conduction band due to thermal or some other excitation.



Energy Bands in Solids: The overlap or size of the gap between the valence and conduction bands determines the electrical conductivity of a substance.

Because the band gap is so small for semiconductors, doping with small amounts of impurities can dramatically increase the conductivity of the material. Doping, therefore, allows scientists to

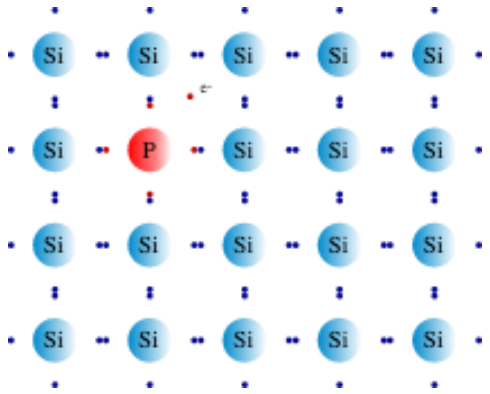
exploit the properties of sets of elements referred to as “dopants” in order to modulate the conductivity of a semiconductor.

Semiconductor Doping

There are two types of dopants, n-type (“n” for negative), and p-type (“p” for positive) dopants. n-type dopants act as electron donors and have extra valence electrons with energies very close to the conduction band. When incorporated into the atomic lattice of a semiconductor, the valence electrons of n-type dopants can be easily excited to the conduction band. p-type dopants assist in conduction by accepting electrons. When a p-type dopant is incorporated into the atomic lattice of a semiconductor, it is able to host electrons from the conduction band, allowing the easy formation of positive holes.

Generating an n-Type Semiconductor

When doping a semiconductor, such as the group IV element silicon (Si), with arsenic (As), a pentavalent n-type dopant from group V in the periodic table (which has one more valence electron than the semiconductor), the dopant behaves as an electron donor. When this occurs, an atom of dopant replaces an atom of silicon in the lattice, and therefore an extra valence electron is introduced into the structure. The fifth valence electron of As creates a *surplus* of electrons. When just a few atoms of the dopant replace silicon atoms in the lattice, an *n-type semiconductor* is created. The newly created semiconductor is better able to conduct current than the pure semiconductor.

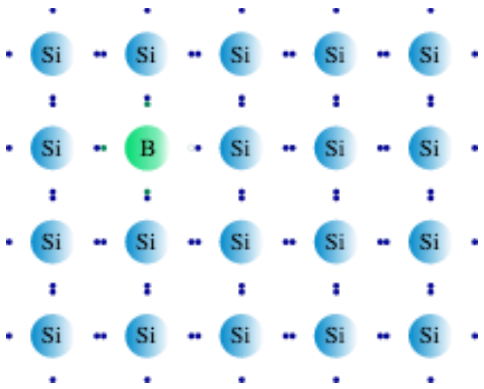


Doping a Silicon Crystal with the n-Type Dopant Arsenic: Doping a pure silicon semiconductor with the group V dopant arsenic creates a surplus of conductive electrons.

Generating a p-Type Semiconductor

When a group IV semiconductor is doped with a p-type trivalent group III dopant (such as boron, B), which has one less valence electron than the semiconductor, the dopant acts as an electron acceptor. When a few atoms of trivalent dopant replace silicon atoms in the lattice, a vacant state (or electron “hole”) is created and can act as electron carrier through the structure, which creates a *p-type semiconductor*. p-type semiconductors are characterized by a deficit of electrons and positive holes, which have the same effect as a surplus of positive charge. These

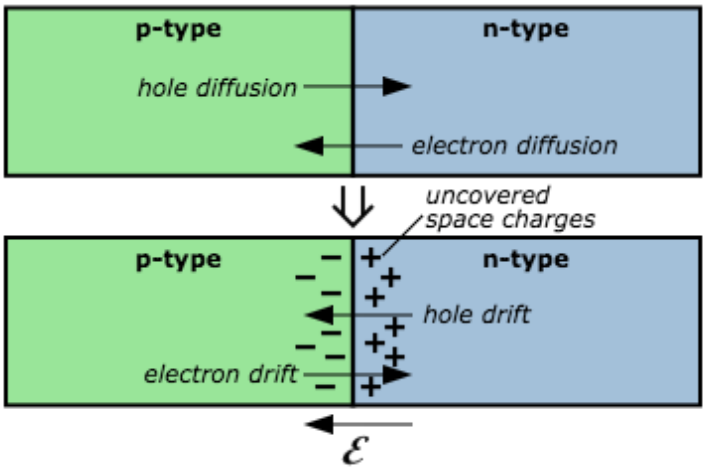
positive holes accept electrons, rendering the semiconductor more effective at conducting current.



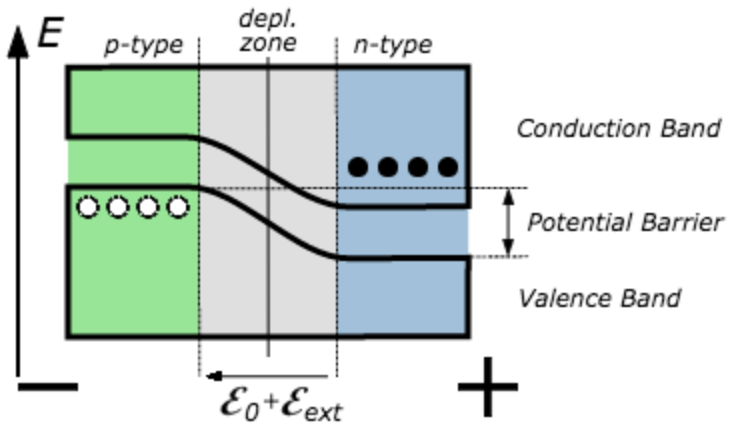
Doping a Silicon Crystal with the p-Type Dopant Boron: Doping a pure silicon semiconductor with the group III dopant boron results in a deficit of conductive electrons and creates a positive hole.

The p-n Junction

When we place p-type and n-type semiconductors in contact with one another, a p-n junction is formed. p-n junctions are basic components of most common electrical devices. While semiconductors doped with either n-type dopants or p-type dopants are better conductors than intrinsic semiconductors, interesting properties emerge when p- and n-type semiconductors are combined to form a p-n junction.

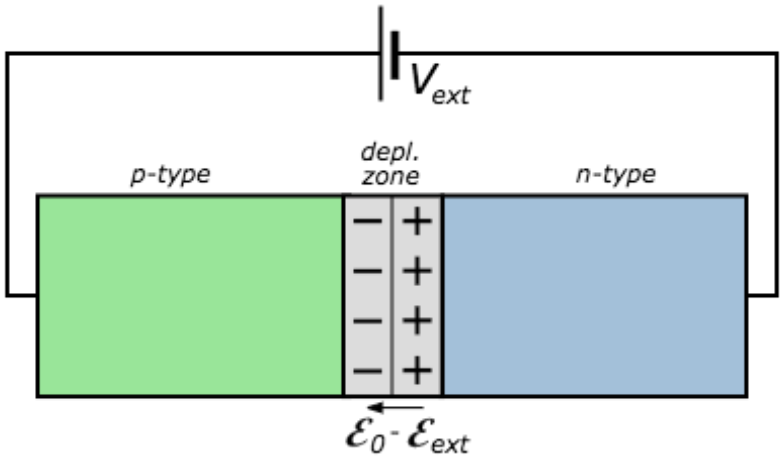


P-n junction diffusion and drift: Diagram of the diffusion across a p-n junction, with the resultant uncovered space charges, the electric field and the drift currents.

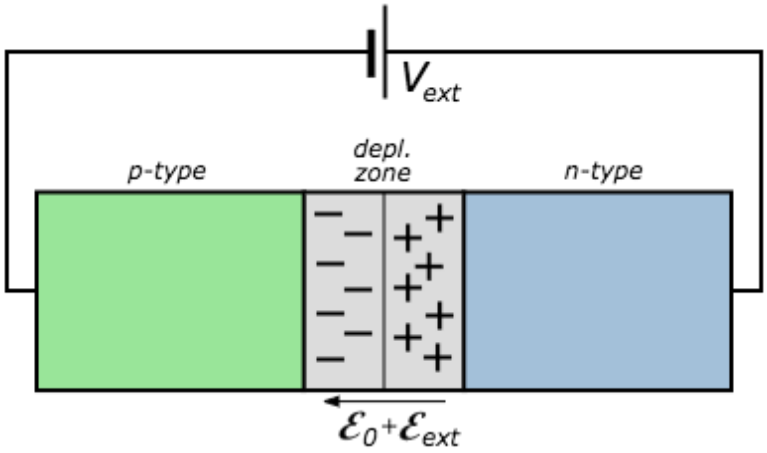


Reverse-biased p-n junction bands: Diagram of a p-n junction under reverse bias, showing conduction and valence bands, the depletion zone, the potential barrier, the resultant electric field, E0+Eextand the types of semiconductor. The p-n junction forms between juxtaposed p- and n-type semiconductors. The free electrons from the n-type semiconductor combine with the holes in the p-type semiconductor near the junction. There is a small potential difference across the junction. The area near the junction is called the depletion band because there are few positive holes and few free electrons in this region.

If no electricity is being passed through the system, then no current passes through the junction between n- and p-type semiconductors. In this scenario, the surplus of electrons from the n-type semiconductor and the deficiency in electrons from the p-type semiconductor combine to create a depletion region. In this state, the system is said to be at equilibrium. However, if the cathode of a battery is connected to the p-type semiconductor, and the anode is connected to the n-type semiconductor, the system is said to be "forward biased." In this scenario, electrons flow from the anode toward the cathode pole and charge flows across the junction. If the connectivity is reversed, with the battery anode connected to the p-type semiconductor and the cathode connected to the n-type semiconductor, the system is said to be "reverse biased" and negligible charge flows across the junction. Combining n-type and p-type semiconductors creates a system which has useful applications in modern electronics.



Forward Biased p-n Junction: If the cathode of a battery is connected to the p-type semiconductor while the anode is connected to the n-type semiconductor, the system is said to be forward biased and current flows through the junction.



Reverse Biased p-n Junction: If the battery anode is connected to the p-type semiconductor and the cathode connected to the n-type semiconductor, the system is said to be reverse biased and negligible current passes.

Electronic devices and instruments, such as digital alarm clocks, mp3 players, computer processors, and the electronics in cell phones, all take advantage of semiconductor technology. Doping provides a way to modulate the properties of semiconductors that have broad applications in daily life.

1.3 COMPONENTS OF SULFER AND SODIUM THIOSULFATE

Sulfur: isolation

Isolation: it is not normally necessary to make sulphur in the laboratory as it is so readily available. It is found as the native element in nature and extracted by the Frasch process. This is an interesting process since it means that sulphur can be extracted from underground without mining it. In the Frasch process underground deposits of sulphur are forced to the surface using superheated water and steam (160°C, 16 atmospheres, to melt the sulphur) and compressed air (25 atmospheres). This gives molten sulphur which is allowed to cool in large basins. Purity can reach 99.5%.

The process in energy intensive. Commercial success for this operation depends upon suitable geological conditions as well as access to cheap water and energy.

Hydrogen sulphide, H_2S, is an important impurrity in natural gas which must be removed before the gas is used. This is done by an absorption and regeneration process to concentrate the H_2S, followed by a catalytic oxidation (Claus process) using porous catalysts such as Al_2O_3 or Fe_2O_3.

$$8H_2S + 4O_2 \rightarrow S_8 + 8H_2O$$

Over the years the Claus process has been improved and a modified process can yield 98% recovery.

In the laboratory, sulphur can be purified by recrystallisation from solutions in carbon disulphide, CS_2. However the resulting crystals are contaminated with solvent, H_2S, and SO_2. One good way to purify sulphur is to use a quartz heater (700°C) immersed in liquid sulphur. Carbon impurities decompose to form volatile materials of solid carbon, which coat the heater. After a week or so, finishing with a distillation under vacuum, the result is sulphur with a carbon content of about 0.0009%.

Sodium Thiosulphate - Preparation, Properties and Uses

Method of prepration of sodium thiosulphate - definition

On an industrial scale, sodium thiosulfate is produced chiefly from liquid waste products of sodium sulphide or sulfur dye manufacture. In the laboratory, this salt can be prepared by heating an aqueous solution of sodium sulphite with sulphur or by boiling aqueous NaOH and sulfur according to this equation:

6 NaOH + 4 S 2 Na2S + Na2S2O3 + 3 H2O.

Properties and uses of sodium thiosulphate - definition

It is used as antidote in cyanide poisoning, used as medicine in end stage kidney diseases.Used in iodometry titration, Gold extraction etc.

Chemical formula Na2S2O3

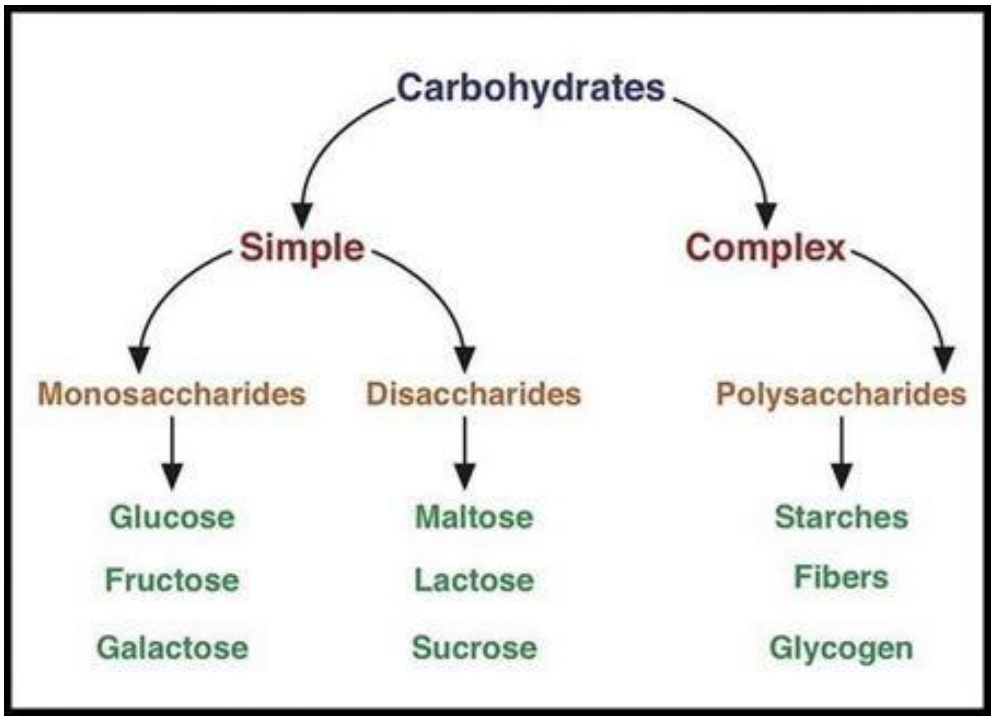
Molar mass	158.11 g/mol (anhydrous) 248.18 g/mol (pentahydrate)
Appearance	White crystals
Odor	Odorless

Unit-II

CARBOHYDRATES

The main classification of carbohydrate is done on the basis of hydrolysis. This classification is as follow:

1. *Monosaccharides*: These are the simplest form of carbohydrate that cannot be hydrolyzed any further. They have the general formula of $(CH_2O)_n$. Some common examples are glucose, Ribose etc.
2. *Oligosaccharides*: Carbohydrates that on hydrolysis yield two to ten smaller units or monosaccharides are oligosaccharides. They are a large category and further divides into various subcategories.
3. *Disaccharides*: A further classification of oligosaccharides, these give two units of the same or different monosaccharides on hydrolysis. For example, sucrose on hydrolysis gives one molecule of glucose and fructose each. Whereas maltose on hydrolysis gives two molecules of only glucose,
4. *Trisaccharides*: Carbohydrates that on hydrolysis gives three molecules of monosaccharides, whether same or different. An example is Raffinose.
5. *Tetrasaccharides*: And as the name suggests this carbohydrate on hydrolysis give four molecules of monosaccharides. Stachyose is an example.
6. *Polysaccharides*: The final category of carbohydrates. These give a large number of monosaccharides when they undergo hydrolysis, These carbohydrates are not sweet in taste and are also known as non-sugars. Some common examples are starch, glycogen etc.



Types of Carbohydrates

Types of Carbohydrates – Monosaccharides, Disaccharides & polysaccharides

The different types of carbohydrates can be classified on the basis of their behavior on hydrolysis. They are mainly classified into three groups:

1. ***Monosaccharides***
2. ***Disaccharides***
3. ***Polysaccharides***

1. Monosaccharides

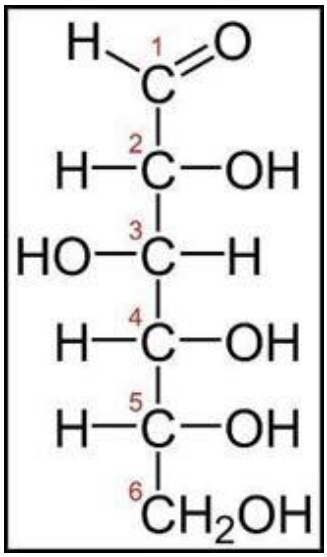
Monosaccharide carbohydrates are those carbohydrates that cannot be hydrolyzed further to give simpler units of polyhydroxyaldehyde or ketone. If a monosaccharide contains an aldehyde group then it is called aldose and on the other hand, if it contains a keto group then it is called a ketose.

Structure of Carbohydrates – Glucose

One of the most important monosaccharides is glucose. The two commonly used methods for the preparation of glucose are

- **From Sucrose:** If sucrose is boiled with dilute acid in an alcoholic solution then we obtain glucose and fructose.
- **From Starch:** We can obtain glucose by hydrolysis of starch and by boiling it with dilute H_2SO_4 at 393K under elevated pressure.

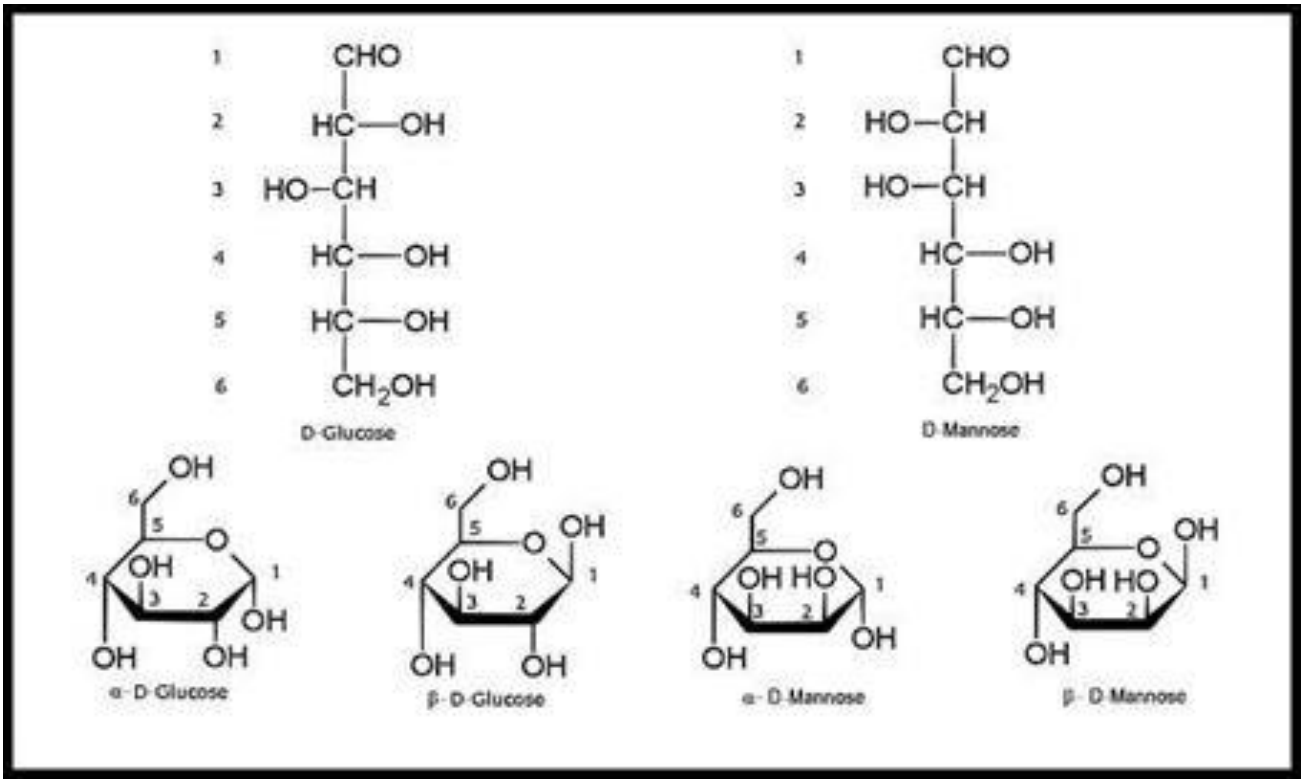
Glucose is also called aldohexose and dextrose and is abundant on earth.



Simple Carbohydrate – Glucose

- Glucose is named as D (+)-glucose, D represents the configuration whereas (+) represents the ***dextrorotatory*** nature of the molecule.
- The ring structure of glucose can explain many properties of glucose which cannot be figured by open-chain structure.
- The two cyclic structures differ in the configuration of the hydroxyl group at C1 called anomeric carbon. Such isomers i.e. α and β form are known as anomers.
- The cyclic structure is also called pyranose structure due to its analogy with pyran.

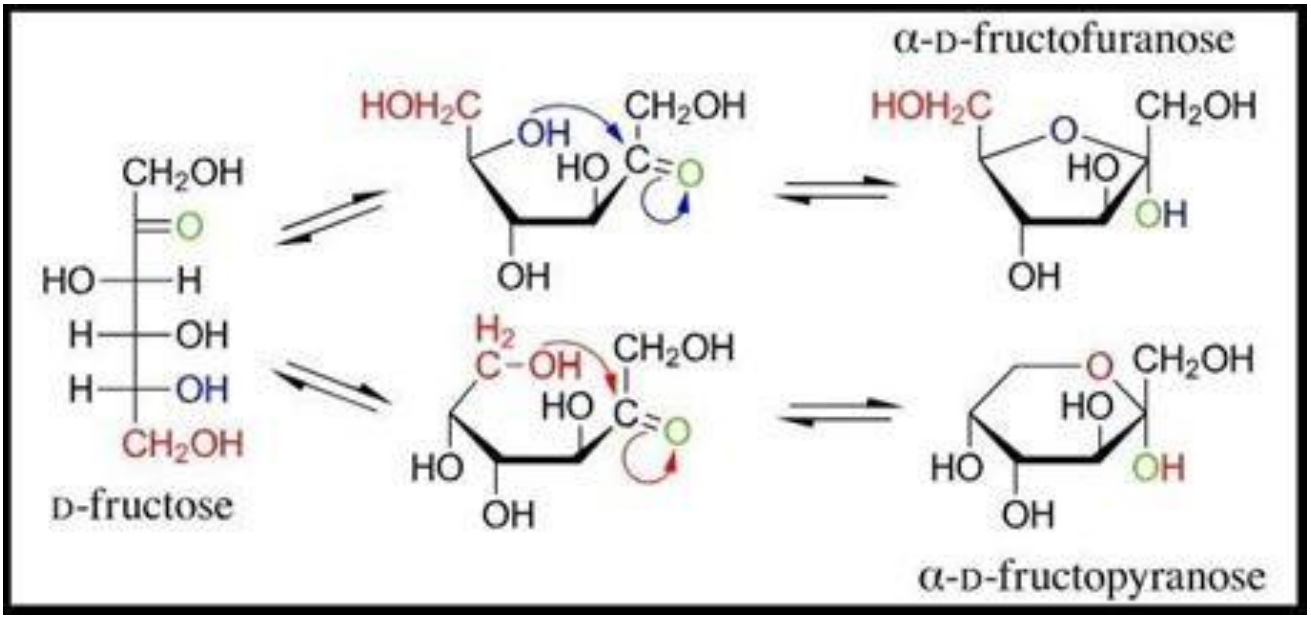
The cyclic structure of glucose is given below:



Cyclic Structure of Carbohydrates – Glucose

Structure of Carbohydrates – Fructose

It is an important ketohexose. The ***molecular formula of fructose is $C_6H_{12}O_6$ and contains ketonic<u>functional group</u> at carbon number 2 and has six carbon atoms in a straight chain.***
The ring member of fructose is in analogy to the compound Furan and is named as furanose. The cyclic structure of fructose is shown below:



Carbohydrate Classification – Fructose

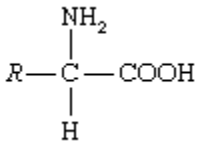
Examples of Carbohydrates

Here are a few examples of where you'll find the most carbs:

- **Dairy Products –** Yogurt, Milk, Ice cream
- **Fruits –** Fruit juice or Whole fruit
- **Grains –** Cereal, Bread, Wheat, Rice
- **Legumes –** Plant-based proteins, Beans
- **Starchy Vegetables –** Corn, Potatoes

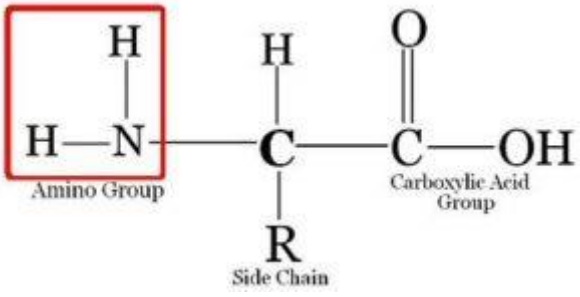
Amino acids

Amino acid, any of a group of organic molecules that consist of a basic amino group (—NH_2), an acidic carboxyl group (—COOH), and an organic *R* group (or side chain) that is unique to each amino acid. The term *amino acid* is short for *α-amino [alpha-amino] carboxylic acid*. Each molecule contains a central carbon (C) atom, called the α-carbon, to which both an amino and a carboxyl group are attached. The remaining two bonds of the α-carbon atom are generally satisfied by a hydrogen (H) atom and the *R* group. The formula of a general amino acid is:



The amino acids differ from each other in the particular chemical structure of the *R* group.

Structure of Amino Acids



(Source: Wikibooks)

There are actually thousands of amino acids occurring in nature. But only about 20 amino acids form a part of the proteins in the human body. These twenty acids will be our focus here. Although all these have varied structures, the basic structure of amino acid remains uniform.

- All amino acids contain a carbon atom in the middle of the molecule, the alpha-carbon
- This atom is surrounded by three chemical groups.
- One is an amine group -NH_2
- The second one is a carboxyl group -OOOH
- The third group is denoted by R. This is the variable radical group and is different for every amino acid. This R group makes the amino acid unique

Classification of Amino Acids

Amino Acid can be classified ***based on their structure*** and the structure of their side chains i.e. the R chains. Now two basic subcategories are

1] Non-Polar Amino Acids

These are also known as Hydrophobic. The R group can be either of Alkyl groups (with an alkyl chain) or Aromatic groups. The acids falling in this group are stated below. Numbers one to seven are Alkyl and the last two are aromatic

i. Glycine (H)
ii. Alanine (CH3)
iii. Valine (CH (CH3)2)
iv. Methionine (CH2CH2SCH3)
v. Leucine (CH2CH(CH3)2)
vi. Isoleucine (-CH(CH3)CH2CH3)
vii. Proline (special structure)
viii. Phenylalanine
ix. Tryptophan

2] Polar Amino Acids

If the side chains of amino acid contain different polar groups like amines, alcohols or acids they are polar in nature. These are also known as Hydrophilic Acids. These are further divided into three further categories.

a) Acidic: If the side chain contains an extra element of carboxylic acid component these are acid-polar amino acids. They tend to donate their hydrogen atom. These are:

i. Aspartic Acid (CH2COOH)
ii. Glutamic Acid (CH2CH2COOH)

b) Basic: These have an extra nitrogen group that tends to attract a hydrogen atom. The three basic polar amino acids are

i. Histidine
ii. Lysine (CH2(CH2)2NH2)
iii. Arginine

c) Neutral: These are neither acidic nor basic. They have an equal number of amino and carboxyl groups. Also, they have at least one hydrogen component connected to electronegative atoms. Some of these neutral acids are

i. Serine (CH2OH)
ii. Threonine (CH(OH)CH3)
iii. Asparagine (CH2OHNH2)
iv. Glutamine (CH2CH2CONH2)
v. Cysteine (CH2SH)
vi. Tyrosine

Amino acid can also be classified on the basis of their need to the human body and their ***availability in the human body***

1] Essential Amino Acids

These are the acids that cannot be synthesized in our bodies. We must rely on food sources to obtain these amino acids. They are

- Leucine
- Isoleucine
- Lysine
- Theorine
- Methionine
- Phenylalanine
- Valine
- Tryptophan
- Histidine (conditionally essential)

2] Non-Essential

These acids are synthesized in our bodies itself and we need not rely on outside sources for them. They are either produced in our bodies or obtained from protein breakdowns.

Properties of Amino Acids

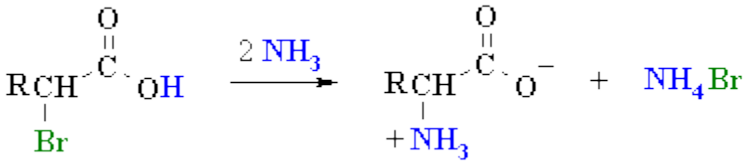
Now that we have seen the structure and types of amino acids. Now from this information, we can arrive at the properties of amino acids.

- Each amino acid has both an acidic and basic group as you can see from its structure. This is the reason they behave like salts.
- Any amino acid in the dry state is in crystalline form. They exist as a dipolar ion. The COOH group exists as an anion. And the NH2 group exists as a cation. This dipolar ion has a special name *"Zwitter ions'.*
- In aqueous solution, alpha amino acids exist in equilibrium between a cationic form, an anionic form and dipolar ion.
- The Isoelectric point is the pH point at which the concentration of zwitter ions is the highest ad the concentration of cationic and anionic form is equal. This point is definite for every α-amino acid.
- They are generally water soluble and also have high melting points.

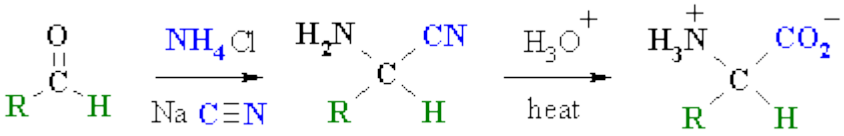
Synthesis of Amino Acids

There are several ways in which α-amino acids can be synthesised using reactions we have already encountered:

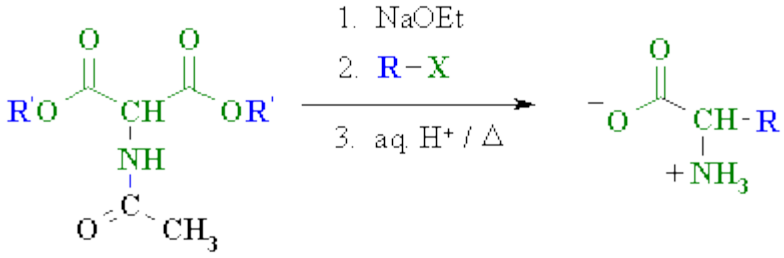
- Nucleophilic substitution of α-halocarboxylic acids



- Strecker synthesis



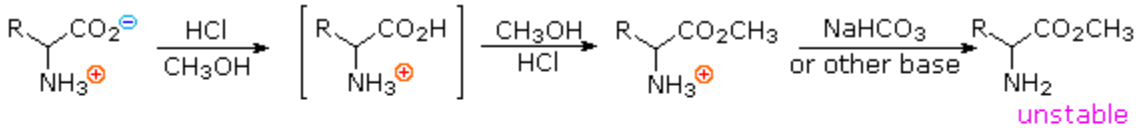
- Alkylation of an acetamidomalonate

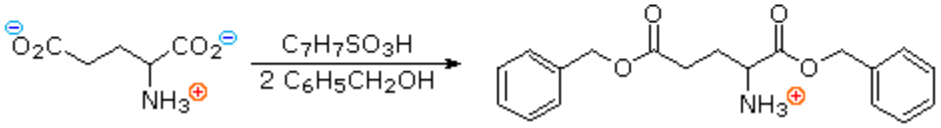


Reactions of α-Amino Acids

1. Carboxylic Acid Esterification

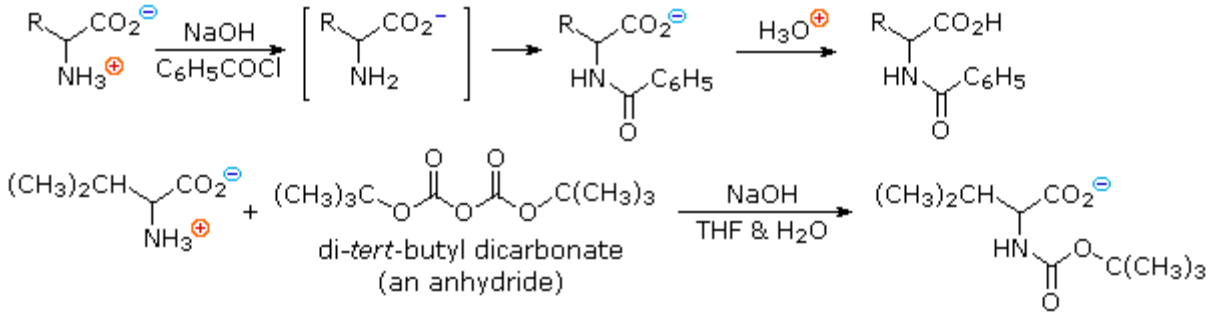
Amino acids undergo most of the chemical reactions characteristic of each function, assuming the pH is adjusted to an appropriate value. Esterification of the carboxylic acid is usually conducted under acidic conditions, as shown in the two equations written below. Under such conditions, amine functions are converted to their ammonium salts and carboxyic acids are not dissociated. The first equation is a typical Fischer esterification involving methanol. The initial product is a stable ammonium salt. The amino ester formed by neutralization of this salt is unstable, due to acylation of the amine by the ester function. The second reaction illustrates benzylation of the two carboxylic acid functions of aspartic acid, using p-toluenesulfonic acid as an acid catalyst. Once the carboxyl function is esterified, zwitterionic species are no longer possible and the product behaves like any 1°-amine.





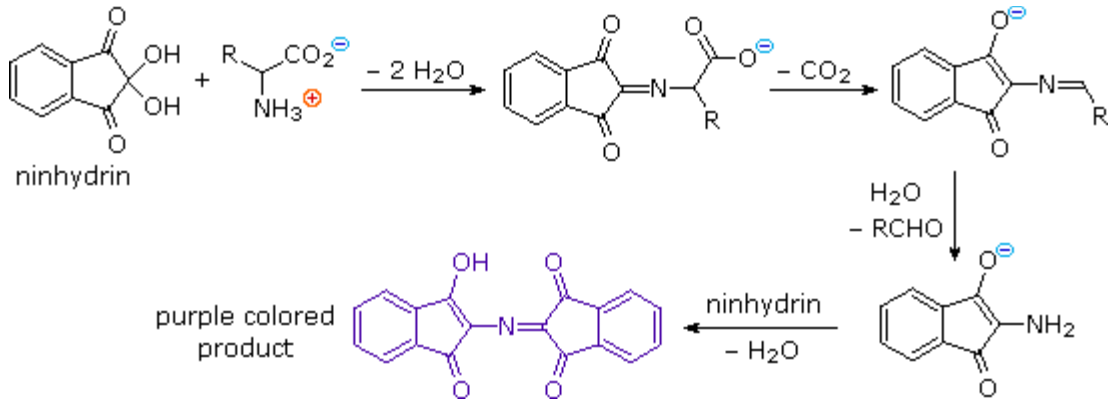
2. Amine Acylation

In order to convert the amine function of an amino acid into an amide, the pH of the solution must be raised to 10 or higher so that free amine nucleophiles are present in the reaction system. Carboxylic acids are all converted to carboxylate anions at such a high pH, and do not interfere with amine acylation reactions. The following two reactions are illustrative. In the first, an acid chloride serves as the acylating reagent. This is a good example of the superior nucleophilicity of nitrogen in acylation reactions, since water and hydroxide anion are also present as competing nucleophiles. A similar selectivity favoring amines was observed in the Hinsberg test. The second reaction employs an anhydride-like reagent for the acylation. This is a particularly useful procedure in peptide synthesis, thanks to the ease with which the t-butylcarbonyl (**t-BOC**) group can be removed at a later stage. Since amides are only weakly basic (pK_a~ -1), the resulting amino acid derivatives do not display zwitterionic character, and may be converted to a variety of carboxylic acid derivatives.



3. The Ninhydrin Reaction

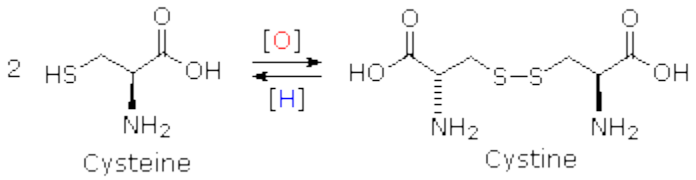
In addition to these common reactions of amines and carboxylic acids, common alpha-amino acids, except proline, undergo a unique reaction with the triketohydrindene hydrate known as ninhydrin. Among the products of this unusual reaction (shown on the left below) is a purple colored imino derivative, which provides as a useful color test for these amino acids, most of which are colorless. A common application of the ninhydrin test is the visualization of amino acids in **paper chromatography**. As shown in the graphic on the right, samples of amino acids or mixtures thereof are applied along a line near the bottom of a rectangular sheet of paper (the baseline). The bottom edge of the paper is immersed in an aqueous buffer, and this liquid climbs slowly toward the top edge. As the solvent front passes the sample spots, the compounds in each sample are carried along at a rate which is characteristic of their functionality, size and interaction with the cellulose matrix of the paper. Some compounds move rapidly up the paper, while others may scarcely move at all. The ratio of the distance a compound moves from the baseline to the distance of the solvent front from the baseline is defined as the retardation (or retention) factor $\mathbf{R_f}$. Different amino acids usually have different R_f's under suitable conditions. In the example on the right, the three sample compounds (1, 2 & 3) have respective R_f values of 0.54, 0.36 & 0.78. To animate this diagram Click on It.



4. Oxidative Coupling

The mild oxidant iodine reacts selectively with certain amino acid side groups. These include the phenolic ring in tyrosine, and the heterocyclic rings in tryptophan and histidine, which all yield products of electrophilic iodination. In addition, the sulfur groups in cysteine and methionine are also oxidized by iodine. Quantitative measurement of iodine consumption has been used to determine the number of such residues in peptides. The basic functions in lysine and arginine are oniumcations at pH less than 8, and are unreactive in that state. Cysteine is a thiol, and like most thiols it is oxidativelydimerized to a disulfide, which is sometimes listed as a distinct amino acid under the name **cystine**. Disulfide bonds of this kind are found in many peptides and proteins. For example, the two peptide chains that constitute insulin are held together by two disulfide links. Our hair consists of a fibrous protein called keratin, which contains an unusually large proportion of cysteine. In the manipulation called "permanent waving", disulfide bonds are first broken and then created after the hair has been reshaped. Treatment with dilute aqueous iodine oxidizes the methionine sulfur atom to a sulfoxide.

Cysteine-CystineInterconversion



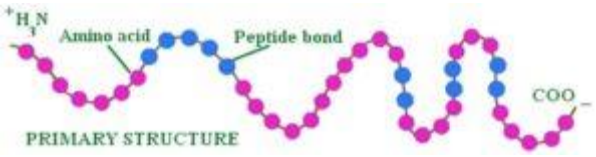
The use of amino acids as fuel varies greatly by organism

- About 90% of energy needs of carnivores can be met by amino acids immediately after a meal
- Microorganisms scavenge amino acids from their environment for fuel when needed
- Only a small fraction of energy needs of herbivores are met by amino acids
- Plants do not use amino acids as a fuel source, but can degrade amino acids to form other metabolites

Structure of Proteins

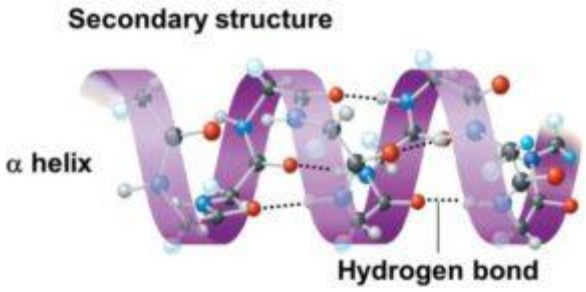
Due to different rearrangement of amino acids, the structure of proteins divides into four types:

- Primary- the covalent linkages of the proteins



(Source: Wikipedia)

- Secondary- the linear peptide chains fold either into an alpha-helical structure(coiled) or a beta-pleated structure(sheets) which contain hydrogen bonds.



(Source: Wikipedia)

- Tertiary- The arrangement and interconnection of proteins into specific loops and bends forms the tertiary structures. This structure contains hydrogen, ionic and disulfide bonds.
- Quarternary- this structure is proteins containing more than one peptide chain.

Proteins are made up of smaller units known as amino acids and the bond linking them is known as a *peptide bond.* This bond is formed when the carboxyl group (-COOH) of one amino acid bonds with the amino group ($– NH_2$) of another amino acid releasing a molecule of water (H2O). A peptide may be dipeptide, tripeptide, and polypeptide.

Classification of Proteins

Classification of proteins is done on the basis of the following:

- Shape
- Constitution
- Nature of molecules

On the basis of shape

- **Fibrous protein(Scleroprotein):** We can find these proteins in animals and are insoluble in water. Fibrous proteins are resistant to proteolyticenzymes and are coiled and exist in threadlike structures to form fibres. e.g. collagen, actin, and myosin, keratin in hair, claws, feathers, etc.
- **Globular proteins:** These proteins, unlike fibrous proteins are soluble in water. They are made up of polypeptides that are coiled about themselves to form oval or spherical molecules e.g. albumin, insulin, and hormones like oxytocin, etc.

On the basis of Constitution

- **Simple proteins:** These proteins are made up of amino acids only. e.g. albumins, globulins, prolamins, etc.
- **Conjugated proteins:** These are complex proteins that are combined with the characteristic of non–amino acid substance called as a prosthetic group. These are of following types:–
    - Nucleoproteins: Combination of protein and nucleic acid

    - Mucoproteins: Combination of proteins and carbohydrates (>4%)
    - Glycoproteins: Combination of proteins and carbohydrates(<4%)
    - Chromoproteins: Combination of proteins and coloured pigments.
    - Lipoproteins: Combination of proteins and lipids.
    - Metalloprotein: Combination of proteins and metal ions.
    - Phosphoprotein: Combination of proteins and phosphate group.
- **Derived proteins:** When proteins are hydrolyzed by acids, alkalies or enzymes, the degradation products obtained from them are called derived proteins.

On the basis of nature of Molecules

- **Acidic proteins:** They exist as anion and contain acidic amino acids. e.g. blood groups.
- **Basic proteins:** They exist as cations and are rich in basic amino acids e.g. lysine, arginine etc.

Functions of Proteins

- **Structural functions:** Proteins are called as the building blocks of the body. They are an essential component of various structures in the cell and tissues. We also find these proteins in the outer membrane of all cells in the human body. We can also find structural proteins in hair, skin, and muscles. Proteins often act to strengthen these structures. Proteins working together can allow movement within the body, such as contraction of muscles and movement of food through the digestive system etc. They are needed for the growth, development, healing, and repair of tissues.
- **Protective:** Proteins are the main constituent of antibodies that protect our body against antigens and pathogens thus preventing infections.
- **Hormonal regulation:** Hormones are majorly composed of proteins. Hormones play a vital role in regulating muscle mass, sex hormones, and growth and development.
- **Enzymes:** Proteins are called as biological buffers because they, as enzymes, regulate many different biochemical reactions that are occurring in the body.

UNIT-III

POLYMER

FORMATION OF POLYTETRAFLUROETHYLENE or TEFLON or PTFE:
It is formed when chloroform is treated with the hydrofluoric acid and antimony trifluoride.

$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl\ (b.pt.\ -76^oC)]{800^oC} CF_2 = CF_2$$

when polymerusedtetrafluoroethylene forms a material which plasic like on appearance and is called *Teflon.*

$$nCF_2 = CF_2 \longrightarrow (-CF_2 - CF_2 -)_n$$
(Tetrafluoroethylene) (Teflon)

PROPERTIES OF TEFLON OR (PTFE):
• Teflon is one of the chemically inert substance. And It is not affected by strong acids which are chemically harmfull and even after by boiling aqua- regia.

- it has the property to be stable at high temperatures

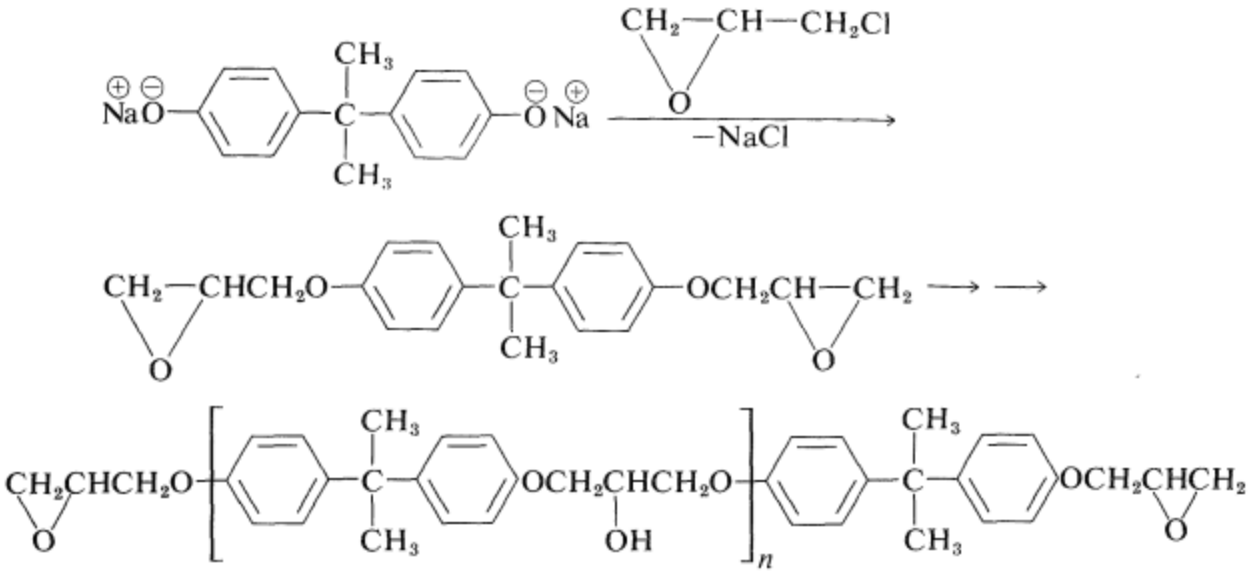
• It is a thermoplastic polymer, that appears as a white solid at room temperature, having a density of about 2200 kg/m3. It has a melting point of 600 K (327 °C; 620 °F).
• It bears mechanical properties such at the degrade gradually at temperatures above 194 K (−79 °C; −110°F).
• PTFE mainly consist of carrbon-fluorine bonds and it also gains the properties from the bonds created only. alkali metals and most highly reactive fluorinating agents are the only chemicals that can affect its property.
• It has a coefficient of friction that is 0.05 to 0.10 which is the third-lowest of any known solid material. It has one of the profecientdielectric properties.

APPLICATIONS AND ITS USES:
• PTFE is usually used to coat in the non-stick frying pans as it has the ability to resist high temperatures.
• IT is mostly used as a film interface patch for sports and medical applications, having a pressure-sensitive adhesive backing. It is installed in one of the high friction areas of footwear, in soles, ankle-foot orthosis.

- It is widely used in medical synthesis,test and many more medicines.

Epoxy Resins

A very useful group of adhesives and plastics is based on condensation polymers of bisphenol A and chloromethyloxacyclopropane (epichlorohydrin). The first step in the formation of epoxy resins is to form a prepolymer by condensation polymerization of the sodium salt of bisphenol A with the epoxide:



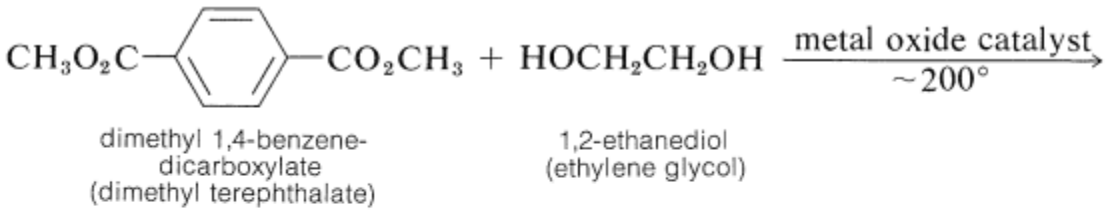
Multiple uses of Epoxy resins

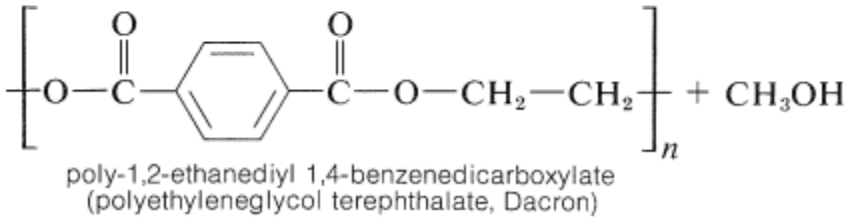
Epoxy is a wonderful chemical known for its versatile nature. Being highly useful chemical compounds, epoxy resins have carved their niche in a number of industrial applications. Below mentioned are some common uses of epoxy resins –

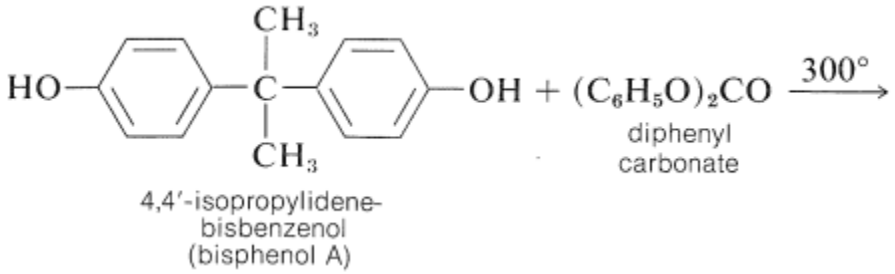
- Epoxies are used in paint industry as it dries quickly and provides protective layers that are highly tough
- Epoxies are used as structural or engineering adhesives used in the construction of aircrafts, automobiles, boats and other such applications
- These are an integral part of the electronic industry and used in overmolding transistors, integrated circuits, PCB's, and hybrid circuits
- As an imperative part of aerospace industry, epoxies are used as structural matrix material
- In a highly technical application, epoxy resin is used for embedding samples for their use under electron microscope
- Not limited just to technical applications, artists have also used epoxies as a painting medium by mixing it with pigments to obtain colors
- As brilliant composites, epoxies are used in the manufacturing of various casts and molds, laminates, plastic toolings, and similar other fixture

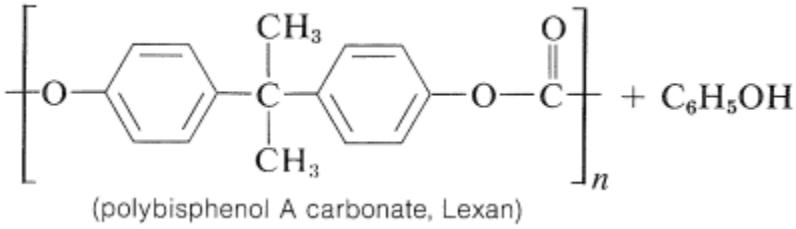
Polyesters

A variety of polyester-condensation polymers are made commercially. Ester interchange appears to be the most useful reaction for preparation of linear polymers:









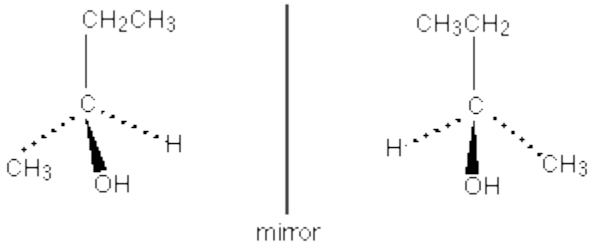
USES OF POLY ESTER RESINS

- **Fire resistant polyester resin**
- ***Electrical resistant polyester resin***
- **Low styrene emission polyester resin**

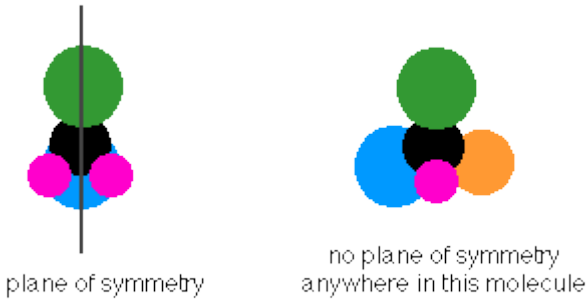
OPTICAL ISOMERISM

Optical isomerism occurs when substances have the same molecular formula and structural formula, but one cannot be superimposed on the other. Put simply, they are mirror images of each other.

Or



Chiral and achiral molecules



A molecule which has no plane of symmetry is described as ***chiral***. The carbon atom with the four different groups attached which causes this lack of symmetry is described as a ***chiral centre*** or as an ***asymmetric carbon atom***.

The molecule on the left above (with a plane of symmetry) is described as ***achiral***.

Only chiral molecules have optical isomers.

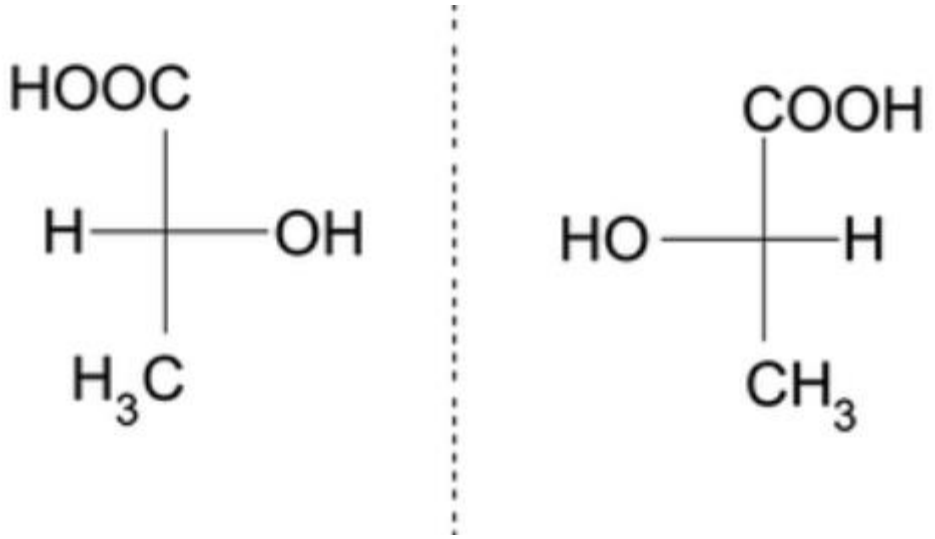
Optical activity of lactic acid

Optical activity of lactice acid. In lactic acid molecule there is an asymmetric chiral carbon atom with four different groups which lead to two spatial configurations (d-lactic acid l-lactic acid) which are super imposable mirror images of each other.

The structures of two enantiomers of lactic acid are as follows:
When a plane polarized light is passed through a lactic acid solution the plane of polarized light gas rotated through a certain angle. This property of rotating the phane of polarized light towards right (clockwise) or towards (left)(anticlockwise) is called optical activity.

d-lactic acid rotates the plane of polarized light towards right whereas l-lactic acid rotates the plane of polarized light towards left, which can be detected by polarimeter. In above structure (I) is representing the (+) isomeric form or dextro rotatory form of lactic acid, while structure (II) is representing (−) isomeric form or laevo rotatory for of lactic acid.

The structures of two enantiomers of lactic acid are shown in image



Optical activity of tartaric acid

Explanation:

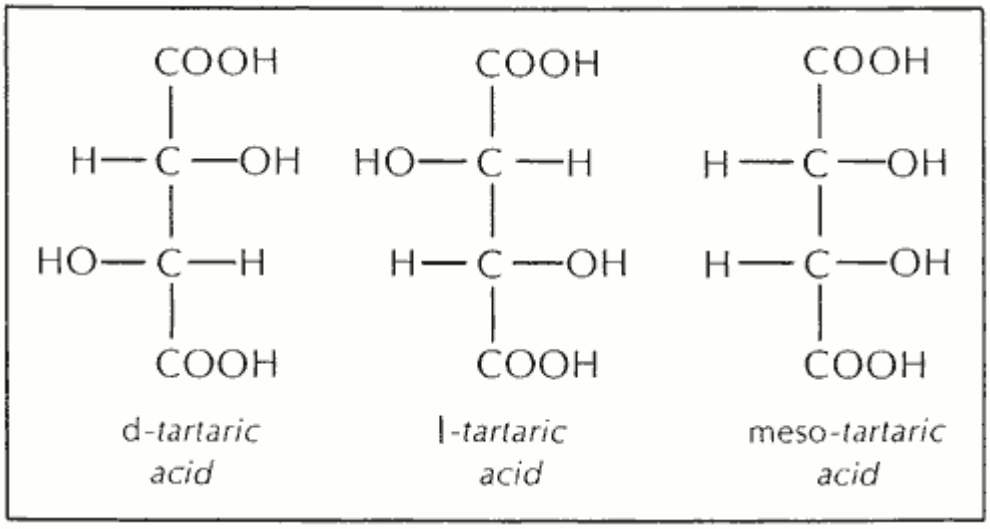
Optical isomerism is arising in the organic molecules which contains a 'carbon atom' attached to a four different 'atoms or groups'.

A carbon with four different groups or atoms attached is called a chiral centre.

If a molecule has a chiral centre in their structure then it forms two mirror images. They are non- super impossible "mirror images" of one other. They are called optical isomers.

Optical isomers are useful in the rotating of "plane polarised light" in opposite directions. One rotates clock wise direction called L- form and another one rotates anti clock wise direction called D- form.

The optical isomer of tartaric acid is as follows and attached below



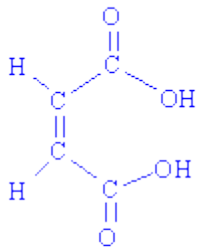
Geometric Isomer Definition

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 or cis-trans isomerism. Note cis-trans isomerism is a different description of geometry than E-Z isomerism.

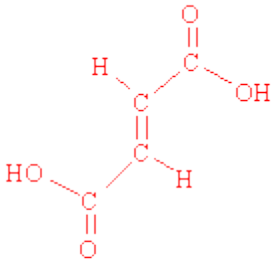
Maleic acid

is otherwise known as ***cis*-butenedioic acid**, which has a double bond that is flanked by two carboxylic acid groups. Maleic acid, a geometric isomer, is thus a diastereomer and therefore a stereoisomer.

An important distinction to make here is that maleic acid is the *cis* isomer, whereas fumaric acid is the *trans* isomer!



cis Butenedioic acid
("Maleic acid")



trans Butenedioic acid
("Fumaric acid")

UNIT –IV

SURFACE CHEMISTRY

Methods of emulsion preparation

There are two methods of preparing a primary emulsion:

1-Dry gum method:-

Emulsifier (acacia) is mixed with oil before water addition.

•The quantities of oil, water and gum for primary emulsion are calculated. The acacia and the oil are placed in a dry porcelain mortar. When the acacia is thoroughly distributed throughout the oil, Water is added, all at once. The mixture is triturated continuously but lightly in one direction until the mixture thickens under the pestle.
•The primary emulsion is triturated for at least 5 minutes. Finally, the emulsion is transferred to a graduated cylinder and brought to volume with water. The emulsion should be Labeled "Shake well before use.

2-Wet gum method:

Emulsifier is added to water to form a mucilage then oil is slowly added to emulsion.

Thequantitiesofoil,waterandgumforprimaryemulsionarecalculated.Acaciaandwateraretriturat edtoformmucilageinaporcelainmortar.TheoilisaddedinSmallamountswithconstant,rapidandlighttrituration.Whenalltheoilhasbeenadded,themixtureistriturated vigorouslyforafewminutes.Finally,theemulsionistransferredtograduatedcylinderandbroughttovolumewithwater.

•Emulsions containing more than one oily liquid:

When two or more oily liquids are present, the quantity of acacia required for each is calculated, and the sum of these quantities is used for the emulsion. Alternatively each oil may be emulsified separately before mixing.

•Emulsions containing water-soluble substances:

Most of the substances included in emulsions are water-soluble, e.g. salts, syrups, glycerin. Water-soluble substances are dissolved in the aqueous vehicle required for the approximate completion of the desired volume in this way are used in a dilute state as possible because some substances have "de -emulsifying" properties, i.e. they might unstabilize the emulsion if added in concentrated solution.

•Emulsions containing oil-soluble substances:

E.g.,Salol and naphthol
Emulsion containing oil-soluble substances, should be prepared with 50 % more Gum than required for other emulsions. The oil-soluble substances are dissolved in the Oil

before preparing the primary emulsion.

•Emulsions containing substances insoluble in either oil or water

These substances must be finely powdered in a mortar, and mixed with the acacia required for the primary emulsion. The oil is then added, and the primary emulsion prepared in the usual way.

Example: Bismuth carbonate in a castor-oil emulsion, and phenolphthalein in a liquid paraffin emulsion.

•Emulsions containing a small proportion of oily substances:

If the proportion of oil is too small, modifications must be made. Acacia emulsions containing less than 10% oil tend to cream readily. An inert oil, such as arachis oil, should be added to increase the amount of oil to 10 -20%, and so prevent this from happening.

Example

DISPERSED PHASE	DISPERSION MEDIUM	TYPE OF COLLOID	EXAMPLE
Solid	Solid	Solid Sol	Some Coloured Glasses And Gemstones
Solid	Liquid	Sol	Paints, Cell Fluids
Solid	Gas	Aerosol	Smoke, Dust

Properties Of Emulsions

- Emulsions contain both a continuous and the dispersed with the boundary coming between the phases that are called “interface”.
- Emulsions have a cloudy appearance due to many phase interfaces scattering light passing through the emulsions.
- Emulsions appear in white colour when the light is dispersed in equal proportions.
- If the emulsion is dilute, then higher-frequency and the low-wavelength type of light will be scattered in more fractions, and this kind of emulsion will appear in blue in colour. This is also referred to as the Tyndall effect.

Applications and Uses of Emulsion

Emulsions are very much famous in various fields of science. It is utilized in the tanning and dyeing industries, used in the manufacturing process of plastics and synthetic rubber.

- Usually used in cosmetics, pharmaceuticals, personal hygiene.
- Microemulsions are used to deliver vaccines to kill various microbes.
- It is used in chemical synthesis mainly in the manufacture of polymer dispersions.

- It is used in firefighting.
- Nanoemulsions such as soybean oil are used to kill microbes.
- Mayonnaise is an oil in water emulsion with egg yolk or sodium stearoyllactylate.

Electrophoresis

Electrophoresis is a class of separation techniques in which we separate analytes by their ability to move through a conductive medium—usually an aqueous buffer—in response to an applied electric field. In the absence of other effects, cations migrate toward the electric field's negatively charged cathode. Cations with larger charge-to-size ratios—which favors ions of larger charge and of smaller size—migrate at a faster rate than larger cations with smaller charges. Anions migrate toward the positively charged anode and neutral species do not experience the electrical field and remain stationary.

There are several forms of electrophoresis. In slab gel electrophoresis the conducting buffer is retained within a porous gel of agarose or polyacrylamide. Slabs are formed by pouring the gel between two glass plates separated by spacers. Typical thicknesses are 0.25–1 mm. Gel electrophoresis is an important technique in biochemistry where it is frequently used for separating DNA fragments and proteins. Although it is a powerful tool for the qualitative analysis of complex mixtures, it is less useful for quantitative work.

In **capillary electrophoresis**, the conducting buffer is retained within a capillary tube whose inner diameter is typically 25–75 μm. Samples are injected into one end of the capillary tube. As the sample migrates through the capillary its components separate and elute from the column at different times. The resulting **electropherogram** looks similar to a GC or an HPLC chromatogram, providing both qualitative and quantitative information. Only capillary electrophoretic methods receive further consideration in this section.

Note

As we will see shortly, under normal conditions even neutral species and anions migrate toward the cathode.

Theory of Capillary Electrophoresis

In capillary electrophoresis we inject the sample into a buffered solution retained within a capillary tube. When an electric field is applied across the capillary tube, the sample's components migrate as the result of two types of action: electrophoretic mobility and electroosmotic mobility. **Electrophoretic mobility** is the solute's response to the applied electrical field. As described earlier, cations move toward the negatively charged cathode, anions move toward the positively charged anode, and neutral species remain stationary. The other contribution to a solute's migration is **electroosmotic flow**, which occurs when the buffer moves through the capillary in response to the applied electrical field. Under normal conditions the buffer moves toward the cathode, sweeping most solutes, including the anions and neutral species, toward the negatively charged cathode.

Electrophoretic Mobility

The velocity with which a solute moves in response to the applied electric field is called its **electrophoretic velocity**, v_{ep}; it is defined as

$$v\text{ep}=\mu\text{ep}E \qquad (12.43)$$

where μ_{ep} is the solute's electrophoretic mobility, and E is the magnitude of the applied electrical field. A solute's electrophoretic mobility is defined as

$$\mu\text{ep}=q6\pi\eta r \qquad (12.35)$$

where

- q is the solute's charge,
- η is the buffer viscosity, and
- r is the solute's radius.

Using equation 12.34 and equation 12.35 we can make several important conclusions about a solute's electrophoretic velocity. Electrophoretic mobility and, therefore, electrophoretic velocity, increases for more highly charged solutes and for solutes of smaller size. Because q is positive for a cation and negative for an anion, these species migrate in opposite directions. Neutral species, for which q is zero, have an electrophoretic velocity of zero.

What Is Column Chromatography?

In chemistry, Column chromatography is a technique which is used to separate a single chemical compound from a mixture dissolved in a fluid. It separates substances based on differential adsorption of compounds to the adsorbent as the compounds move through the column at different rates which allow them to get separated in fractions. This technique can be used on small scale as well as large scale to purify materials that can be used in future experiments. This method is a type of adsorption chromatography technique.

Column Chromatography Principle

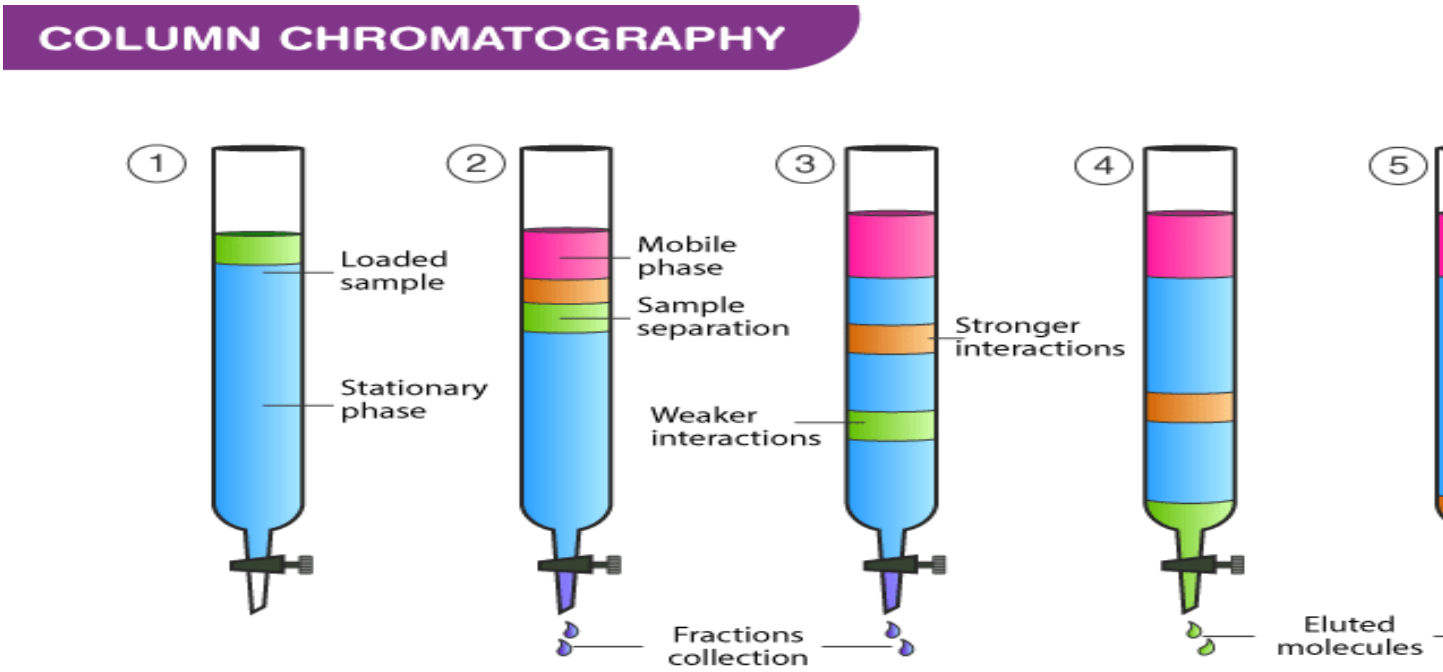
When the mobile phase along with the mixture that needs to be separated is introduced from the top of the column, the movement of the individual components of the mixture is at different rates. The components with lower adsorption and affinity to stationary phase travel faster when compared to the greater adsorption and affinity with the stationary phase. The components that move fast are removed first whereas the components that move slow are eluted out last.

The adsorption of solute molecules to the column occurs in a reversible manner. The rate of the movement of the components is expressed as:

R_f = the distance travelled by solute/ the distance travelled by solvent

R_f is the retardation factor.

Column Chromatography Diagram



Column Chromatography Diagram

Column Chromatography Procedure

Before starting with the Column Chromatography Experiment let us understand the different phases involved.

Mobile phase – This phase is made up of solvents and it performs the following functions:

1. It acts as a solvent – sample mixture can be introduced in the column.
2. It acts as a developing agent – helps in the separation of components in the sample to form bands.
3. It acts as an eluting agent – the components that are separated during the experiment are removed from the column
4. Some examples of solvents used as mobile phase based on their polarity are – ethanol, acetone, water, acetic acid, pyridine, etc.

Stationary phase – It is a solid material which should have good adsorption property and meet the conditions given below:

1. Shape and size of particle: Particles should have uniform shape and size in the range of 60 – 200μ in diameter.

2. Stability and inertness of particles: high mechanical stability and chemically inert. Also, no reaction with acids or bases or any other solvents used during the experiment.
3. It should be colourless, inexpensive and readily available.
4. Should allow free flow of mobile phase
5. It should be suitable for the separation of mixtures of various compounds.

Column Chromatography Experiment

- The stationary phase is made wet with the help of solvent as the upper level of the mobile phase and the stationary phase should match. The mobile phase or eluent is either solvent or mixture of solvents. In the first step the compound mixture that needs to be separated, is added from the top of the column without disturbing the top level. The tap is turned on and the adsorption process on the surface of silica begins.
- Without disturbing the stationary phase solvent mixture is added slowly by touching the sides of the glass column. The solvent is added throughout the experiment as per the requirement.
- The tap is turned on to initiate the movement of compounds in the mixture. The movement is based on the polarity of molecules in the sample. The non-polar components move at a greater speed when compared to the polar components.
- For example, a compound mixture consists of three different compounds viz red, blue, green then their order based on polarity will be as follows blue>red>green
- As the polarity of the green compound is less, it will move first. When it arrives at the end of the column it is collected in a clean test tube. After this, the red compound is collected and at last blue compound is collected. All these are collected in separate test tubes.

Column Chromatography Applications

- Column Chromatography is used to isolate active ingredients.
- It is very helpful in Separating compound mixtures.
- It is used to determine drug estimation from drug formulations
- It is used to remove impurities.
- Used to isolation metabolites from biological fluids.

What Is Paper Chromatography?

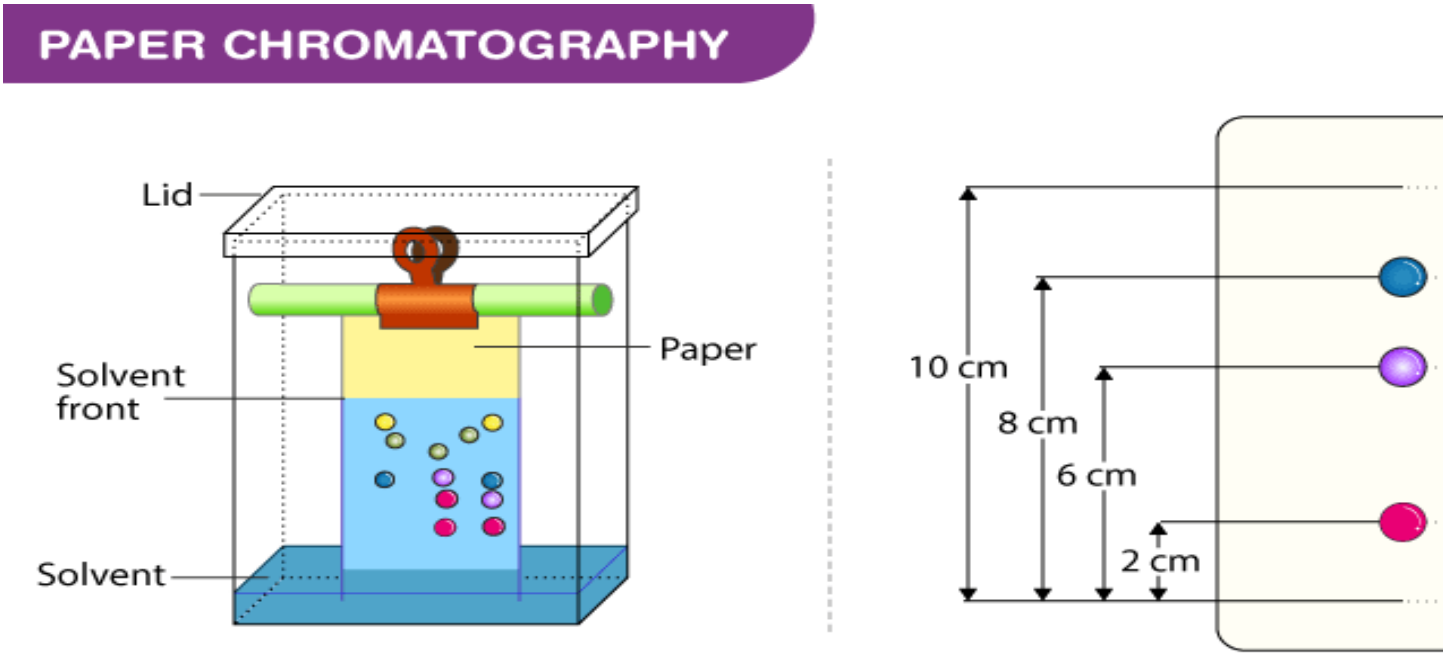
Chromatography technique that uses paper sheets or strips as the adsorbent being the stationary phase through which a solution is made to pass is called paper chromatography. It is an inexpensive method of separating dissolved chemical substances by their different migration rates across the sheets of paper. It is a powerful analytical tool that uses very small quantities of material. Paper chromatography was discovered by Synge and Martin in the year 1943.

Paper Chromatography Principle

The principle involved can be partition chromatography or adsorption chromatography. Partition chromatography because the substances are partitioned or distributed between liquid phases. The

two phases are water held in pores of the filter paper and the other phase is a mobile phase which passes through the paper. When the mobile phase moves, the separation of mixture takes place. The compounds in the mixture separate themselves based on the differences in their affinity towards stationary and mobile phase solvents under the capillary action of pores in the paper. Adsorption chromatography between solid and liquid phases, wherein the solid surface of the paper is the stationary phase and the liquid phase is the mobile phase.

Paper Chromatography Diagram



Paper Chromatography Procedure

Below we have explained the procedure to conduct Paper Chromatography Experiment for easy understanding of students.

1. **Selecting a suitable type of development:** It is decided based on the complexity of the solvent, paper, mixture, etc. Usually ascending type or radial paper chromatography is used as they are easy to perform. Also, it is easy to handle, the chromatogram obtained is faster and the process is less time-consuming.
2. **Selecting a suitable filter paper**: Selection of filter paper is done based on the size of the pores, and the sample quality.
3. **Prepare the sample:** Sample preparation includes the dissolution of the sample in a suitable solvent (inert with the sample under analysis) used in making the mobile phase.
4. **Spot the sample on the paper:** Samples should be spotted at a proper position on the paper by using a capillary tube.

5. **Chromatogram development:** Chromatogram development is spotted by immersing the paper in the mobile phase. Due to the capillary action of paper, the mobile phase moves over the sample on the paper.
6. **Paper drying and compound detection**: Once the chromatogram is developed, the paper is dried using an air drier. Also, detecting solution can be sprayed on the chromatogram developed paper and dried to identify the sample chromatogram spots.

Paper Chromatography Applications

There are various applications of paper chromatography. Some of the uses of Paper Chromatography in different fields are discussed below:

- To study the process of fermentation and ripening.
- To check the purity of pharmaceuticals.
- To inspect cosmetics.
- To detect the adulterants.
- To detect the contaminants in drinks and foods.
- To examine the reaction mixtures in biochemical laboratories.
- To determine dopes and drugs in humans and animals.

What Is 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 = dist. travelled by sample / dist. travelled by solvent

The factors affecting retardation factor are the solvent system, amount of material spotted, absorbent 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

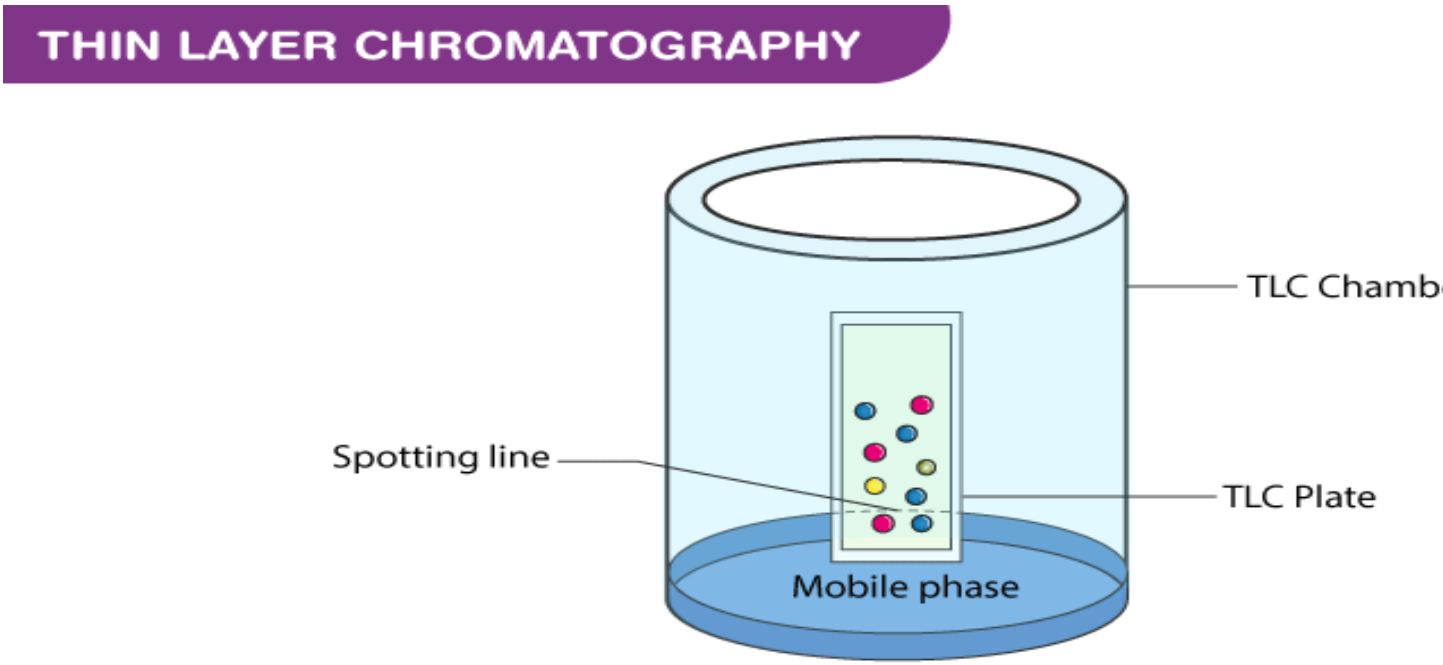


Diagram of Thin Layer Chromatography

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.

Photochemistry

Derivation of Beer Lambert Law

Beer-Lambert Law derivation helps us to define the relationship of the intensity of visible UV radiation with the exact quantity of substance present. The Derivation of Beer-Lambert Law has many applications in modern day science. Used in modern-day labs for testing of medicines, organic chemistry and to test with quantification. These are some of the fields that this law finds its uses in.

Beer-Lambert Law Statement

The Beer-Lambert law states that:

for a given material sample path length and concentration of the sample are directly proportional to the absorbance of the light.

The Beer-Lambert law is expressed as:

$A = \varepsilon Lc$

where,

- A is the amount of light absorbed for a particular wavelength by the sample
- ε is the molar extinction coefficient
- L is the distance covered by the light through the solution
- c is the concentration of the absorbing species

Following is an equation to solve for molar extinction coefficient:

$\epsilon = ALc$

But Beer-Lambert law is a combination of two different laws: Beer's law and Lambert law.

Beer-Lambert Law Formula

$I = I0e - \mu(x)$

Where,

- I is the intensity
- I_0 is the initial intensity
- x is the depth in meters
- μ is the coefficient of absorption

UNIT V

ELECTROCHEMISTRY

SPECIFIC CONDUCTIVITY

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. It is generally defined as the reciprocal of resistance of that material. SI unit of conductance is S (Siemens). **Specific conductivity** (better known as conductivity) is the measure of the ability of that material to conduct electricity. It is represented by the symbol "K". Hence, by definition,

$$G = 1R$$

$$R= \rho 1A$$

$$K= 1\rho$$

$$G =K\, Al$$

Where,

K = conductivity,

ρ = resistivity of the material

G= conductance

R= resistance

l = length

A= area of cross section

The conductance of a material depends on the nature of the material, no. of valence electrons for a material and temperature. Metals are good conductors of electricity due to their valence electrons. We observe that the conductance of materials decreases with increase in temperature.

Water in its pure state is known to have very low conductivity due to the presence of hydroxyl ions. The presence of electrolytes further enhances the conductivity as they furnish their ions in the solution. The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. Specific conductivity or conductivity of an electrolytic solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length. The conductivity of electrolytic solutions depends on:

1. The nature and the concentration of the electrolyte added
2. The size of the ions produced and their salvation.
3. Solvent nature and viscosity.
4. Temperature.

‘EQUIVALENT CONDUCTANCE’

The term ‘equivalent conductance’ can be defined as the net conductance of every ion that is produced from one gram equivalent of a given substance. It can be calculated using the following formula: $\lambda = kV$; where the term ‘V’ denotes the volume (in millilitres) that contains one gram equivalent of the given electrolyte. Another related term is ‘molar conductance’, which can be defined as the net conductance of all the ions produced when one mole of an electrolyte undergoes complete dissociation into its constituent ions. The formula for molar conductance is quite similar to that of equivalent conductance, but it is denoted by the symbol ‘μ’. The formula that can be used to calculate molar conductance is: $\mu = kV$.

It is important to note that equivalent conductance can be calculated as: equivalent conductance = (molar conductance) /n; where n = (molecular mass)/(equivalent mass)

ELECTROLYTES

These are substances that dissociate into their constituent ions in their aqueous solution and thus conduct electricity in their aqueous solutions or molten state. Example, salt solution, acid solution, base solution etc.

Electrolytes in ionic equilibrium can be further classified into strong and weak electrolytes.

Strong electrolytes are substances that upon dissociation in their ionic solution ionize completely while in the case of **weak electrolytes**, the dissociation is partial in nature.

For example, NaCl undergoes complete ionization in its aqueous solution to render sodium ions (Na^+) and chloride (Cl^-) ions, whereas, acetic acid undergoes partial ionization to render some amount of acetate ions($CH3COO^-$) and hydrogen(H^+) ions.

- In case of a strong electrolyte, the dissociation reaction is said to be complete, thus moving in the forward direction only, whereas, in case of a weak electrolyte, the reaction is said to be reversible in nature.
- In the case of the weak electrolyte, the equilibrium is established between the ions and the unionized molecules, which can be termed as ionic equilibrium. The same can be understood with the following example.

Ostwald’s Dilution Law: Degree of Dissociation

Ostwald’s dilution law is the application of the law of mass action to weak electrolytes in solution.

A binary electrolyte AB which dissociates into A^+ and B^- ions.

$AB \rightleftharpoons A^+ + B^-$

(i) For very weak electrolytes, since $\alpha <<< 1$, $(1 - \alpha) = 1$

$\therefore K=C\alpha 2K=C\alpha^{2}K=C\alpha 2\alpha=KV\alpha = \sqrt{KV}\alpha=KV$

(ii) Concentration of any ion = $C\alpha = \sqrt{CK} = \sqrt{K/V}$

Degree of ionization increases on dilution. Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

Limitations of Ostwald's Dilution law

The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes.

Ionic Equilibrium Formulas

It becomes necessary to know what fraction of the initial amount of the reactants are converted into products at equilibrium.

The fraction of the initial molecules that are converted at equilibrium is called the degree of Dissociation/ionization.

Degree of dissociation or ionization = α = (Number of reactant molecules dissociated\ionized at the start)/(Number of reactant molecules at the start)

Degree of dissociation in Ionic equilibrium can be expressed in percentage.

% Degree of dissociation or ionization = α = (Number of reactant molecules dissociated or ionized at the start)/(Number of reactant molecules at the start) × 100

Kohlrausch Law?

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, $Ë_m°$.

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, $Ë_m°$ 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, $Ë_m°$ 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, $Ë_m°$ 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.

$$\alpha = \Lambda Ë m\circ$$

Where, α = dissociation constant

Λ = molar conductivity

$Ë_m°$ = 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 week electrolytes
- Calculation of Molar Conductivity for week electrolytes at infinite dilution

Unit of Conductivity

Conductivity, in general, maybe of many types. It could be electrical, ionic, hydraulic, or thermal conductivity. However, conductivity is basically defined as a material's ability to conduct

electricity or heat. Apart from that, measurements are done in several ways and there are specific units of conductivity that are used depending on the circumstances. We will learn about some of the units below.

SI Unit of Conductivity

When we talk about electrical conductivity, the SI unit of conductivity is siemens per meter (S/m) or mho and is usually represented by Greek letter sigma, σ and its formula is given as;

$$\sigma = \frac{1}{\rho}$$

As for the si unit of thermal conductivity, it is measured in watts per meter-kelvin (W/(m K)) or watts per centimetre-kelvin (W/(cm K)). It is represented by the formula;

$$K = QLA\Delta T$$

where,

K is the thermal conductivity in W/m K,

Q is the amount of heat transfer through the material in J/s or W,

A is the area of the body in m^2

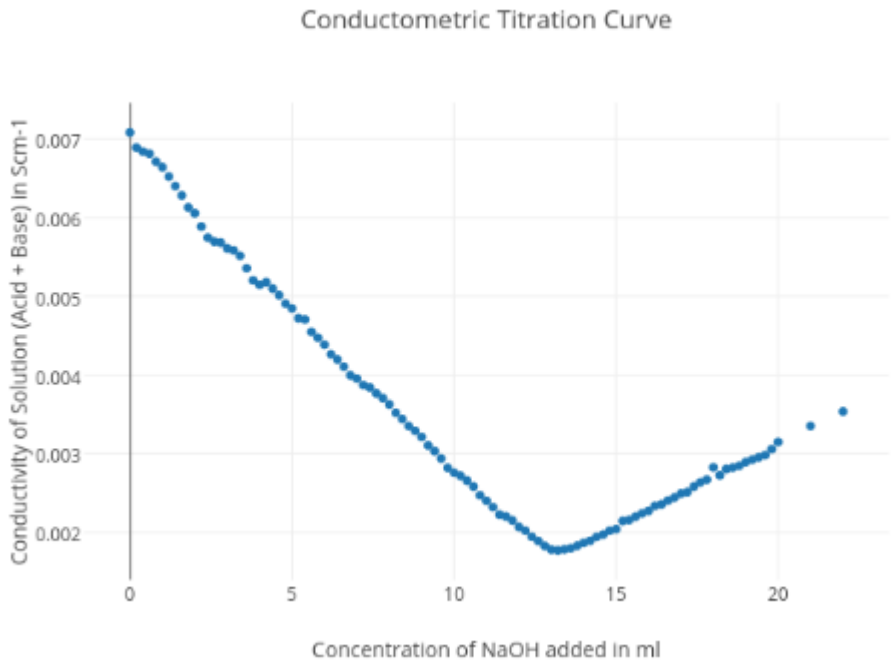
ΔT is the difference in the temperature in K.

What is 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.

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:

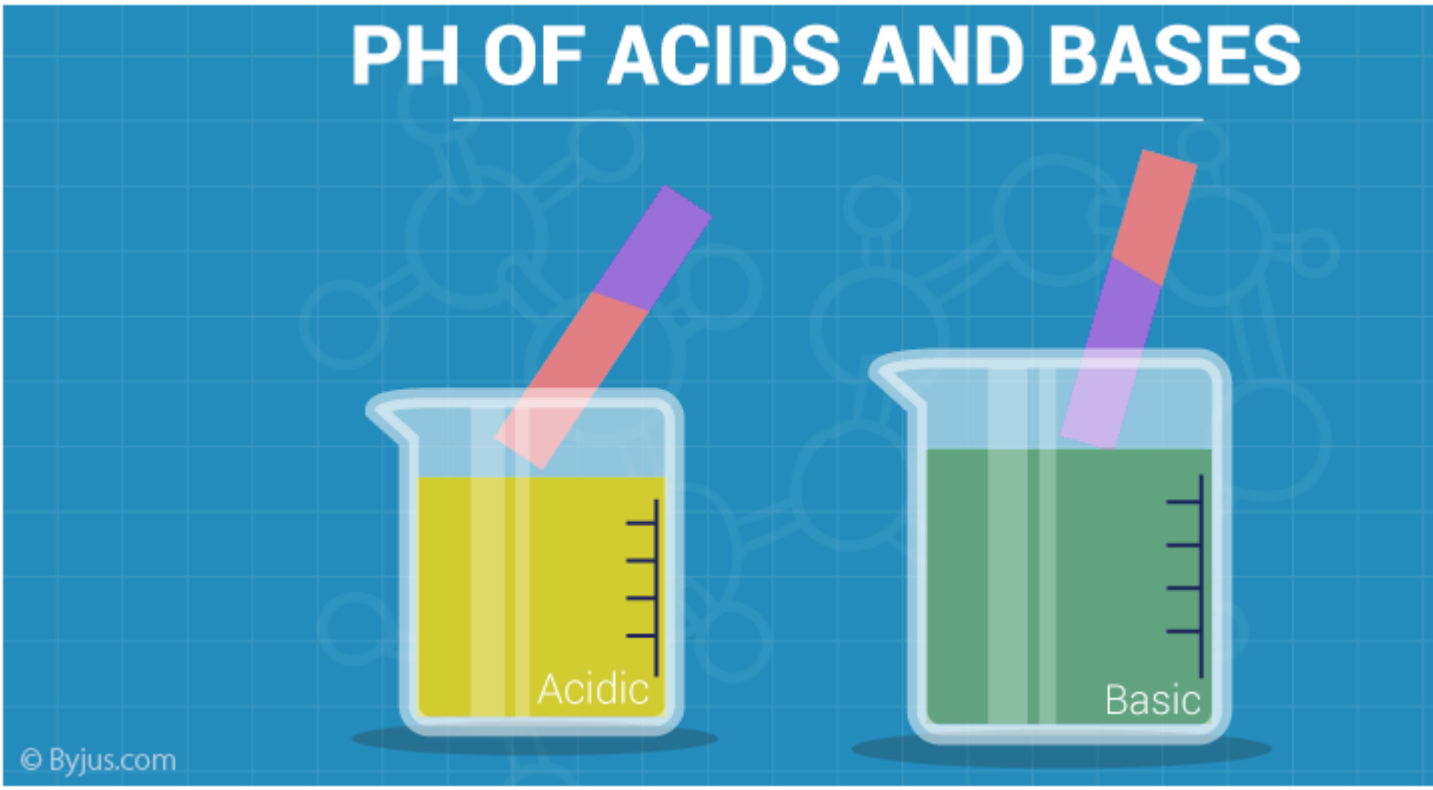
1. Only a few specific redox titrations can be done with the help of this process. This is because the conductivity of the solution is masked by relatively high hydronium ion concentration.
2. The accuracy of conductometric titration is low when the concentrations of the electrolyte are high, making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

pH and buffer

What is pH?

pH is defined as the negative logarithm of H^+ ion concentration. Hence the meaning of the name pH is justified as the power of hydrogen.

We know that all the acids and bases do not react with the same chemical compound at the same rate. Some react very vigorously, some moderately while others show no reaction. To determine the strength of acids and bases quantitatively, we use a universal indicator which shows different colours at different concentration of hydrogen ion in solution. Generally, the value of pH of acids and bases are used to quantitatively determine their strength.



pH of Acids and Bases – Red Litmus Test

pH of Acids and Bases

The pH of a solution varies from 0 to 14.

- Solutions having a value of pH ranging 0 to 7 on pH scale are termed as ***acidic*** and for the value of pH ranging 7 to 14 on pH scale are known as ***basic*** solutions.
- Solutions having the value of pH equal to 7 on pH scale are known as neutral solutions.

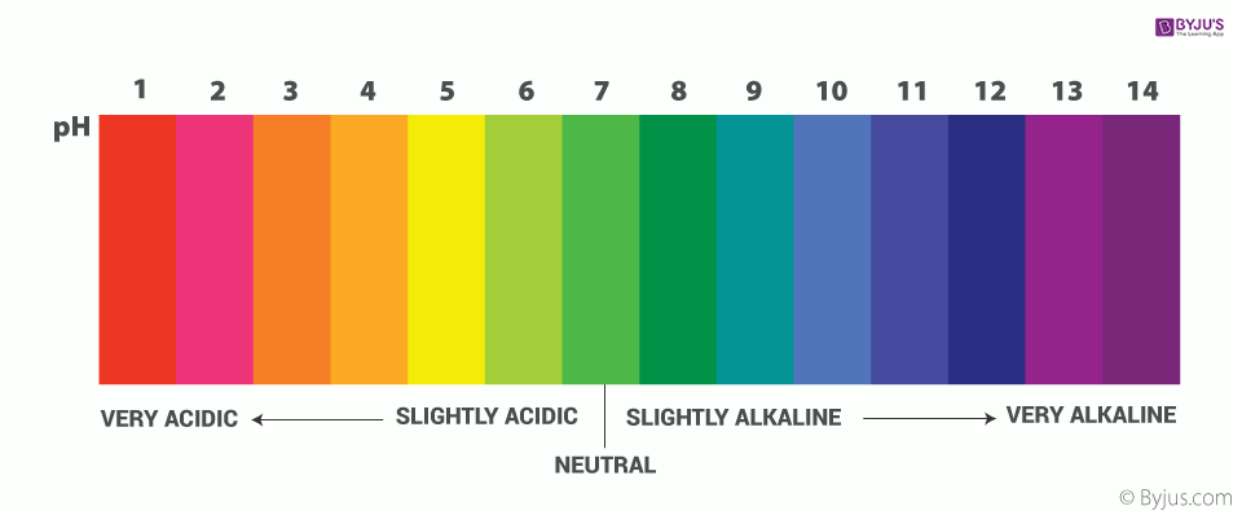
Solutions having the value of pH equal to 0 are known to be ***strongly acidic solutions***. Further, the acidity decreases as the value of pH increases from 0 to 7 whereas, solutions with the value of pH equal to 14 are termed as ***strongly basic solutions***.

The basicity decreases as the value of pH decreases from 14 to 7. The strength of acids and bases depends on the number of H^+ and OH^- ions produced. Acids furnishing more number of H^+ ions are known to be strong acids and vice versa.

The degree of ionisation of acids and bases differ for different acids and bases. It helps in the determination of the strength of acids and bases. The strength of an acid depends on the concentration of hydronium ion (H_3O^+) too. With the help of the comparison between the concentration of hydronium ion and the hydroxyl ion, we can distinguish between acids and bases.

- ***For acidic solution: $[H_3O^+] > [OH^-]$***
- ***For neutral solution: $[H_3O^+] = [OH^-]$***
- ***For basic solution: $[H_3O^+] < [OH^-]$***

pH Scale



pH Scale

The concentration of hydronium ion is conveniently expressed on a logarithmic scale. This scale is known as **pH scale**. pH of acids and bases is defined as the negative logarithm (with base 10) of activity of hydrogen ion (H^+).

What is Buffer Solution?

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

activity of enzymes, blood oxygen carrying capacity need specific hydrogen ion concentration (pH).

Solutions of a weak acid and its conjugate base or weak base and its conjugate acid are able to maintain pH and are buffer solutions.

Types of Buffer Solution

Acidic Buffers

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

- pH of these solutions is below seven
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

Alkaline Buffers

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

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

Uses of Buffer Solutions

- There exists a few alternate names that are used to refer buffer solutions, such as pH buffers or hydrogen ion buffers.
- An example of the use of buffers in pH regulation is the use of bicarbonate and carbonic acid buffer system in order to regulate the pH of animal blood.
- Buffer solutions are also used to maintain an optimum pH for enzyme activity in many organisms.
- The absence of these buffers may lead to the slowing of the enzyme action, loss in enzyme properties, or even denature of the enzymes. This denaturation process can even permanently deactivate the catalytic action of the enzymes

Working of Colorimeter

Step 1: Before starting the experiment it is important to calibrate the colorimeter. It is done by using the standard solutions of the known solute concentration that has to be determined. Fill the standard solutions in the cuvettes and place it in the cuvette holder of colorimeter.

Step 2: A light ray of a certain wavelength, which is specific for the assay is in the direction of the solution. The light passes through a series of different lenses and filters. The colored light navigates with the help of lenses, and the filter helps to split a beam of light into different wavelengths allowing only the required wavelength to pass through it and reach the cuvette of the standard test solution.

Step 3: When the beam of light reaches cuvette, it is transmitted, reflected, and absorbed by the solution. The transmitted ray falls on the photodetector system where it measures the intensity of transmitted light. It converts it into the electrical signals and sends it to the galvanometer.

Step 4: The electrical signals measured by the galvanometer are displayed in the digital form.

Step 5: Formula to determine substance concentration in test solution.

$A = \in cl$

For standard and test solutions

$\in$and l are constant

$A_T = C_T$ ….. (i)

$A_S = C_S$ ….. (ii)

From the above two equations,

$A_T \times C_S = A_S \times C_T$

$C_T = (A_T/A_S) \times C_S$

Where,

C_T is the test solution concentration

A_T is the absorbance/optical density of test solution

C_S is the standard concentration

A_S is the absorbance / optical density of standard solution

Uses of Colorimeter

- It is used in laboratories and hospitals to estimate biochemical samples such as urine, cerebrospinal fluid, plasma, serum, etc.
- It is used in the manufacturing of paints.
- It is used in textile and food industry.
- It is used in the quantitative analysis of proteins, glucose, and other biochemical compounds.
- It is used to test water quality.
- It is used to determine the concentration of hemoglobin in the blood.

What is Potentiometric Titration?

It is the procedure through which the quantity of the given test substance is determined by the measured addition of titrant until the entire test substance undergoes reaction. After the titration process, the potential difference between the two electrodes (namely the reference and indicator electrode) is measured in conditions where a thermodynamic equilibrium is maintained and the current passing through the electrodes does not disturb this equilibrium.

Potentiometric Titration Principle

Potentiometric titration is a laboratory method to determine the concentration of a given analyte. It is used in the characterization of acids. In this method, there is no use of a chemical indicator. Instead, the electric potential across the substance is measured.

Potentiometric Titration Method

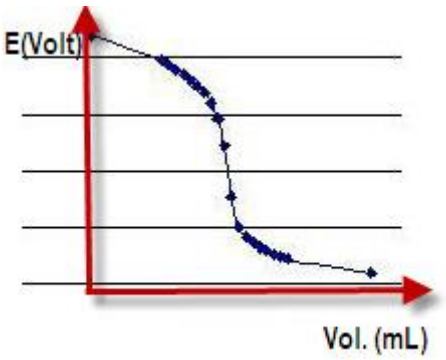
Potentiometric Titration is done via the usage of two electrodes – an indicator electrode and a reference electrode (generally a hydrogen electrode or a silver chloride electrode). One half-cell is formed with the indicator electrode and the ions of the analyte, which is generally an electrolyte solution. The other half-cell is formed by the reference electrode.

The overall cell potential can be calculated using the formula given below.

$$Ecell=Eind–Eref+Esol$$

Where the potential drop between the indicator and reference electrodes over the electrolyte solution is given by E_{sol}.

The overall cell potential, E_{cell} is calculated in every interval where the titrant is measured and added. Now, a graph is plotted with the Potential difference on the Y-axis and the volume on the X-axis as shown below.



It can be observed from the graph that the electric potential of the cell is dependant on the concentration of ions which are in contact with the indicator electrode. Therefore, the $E_{cell}$is measured with each addition of the titrant.