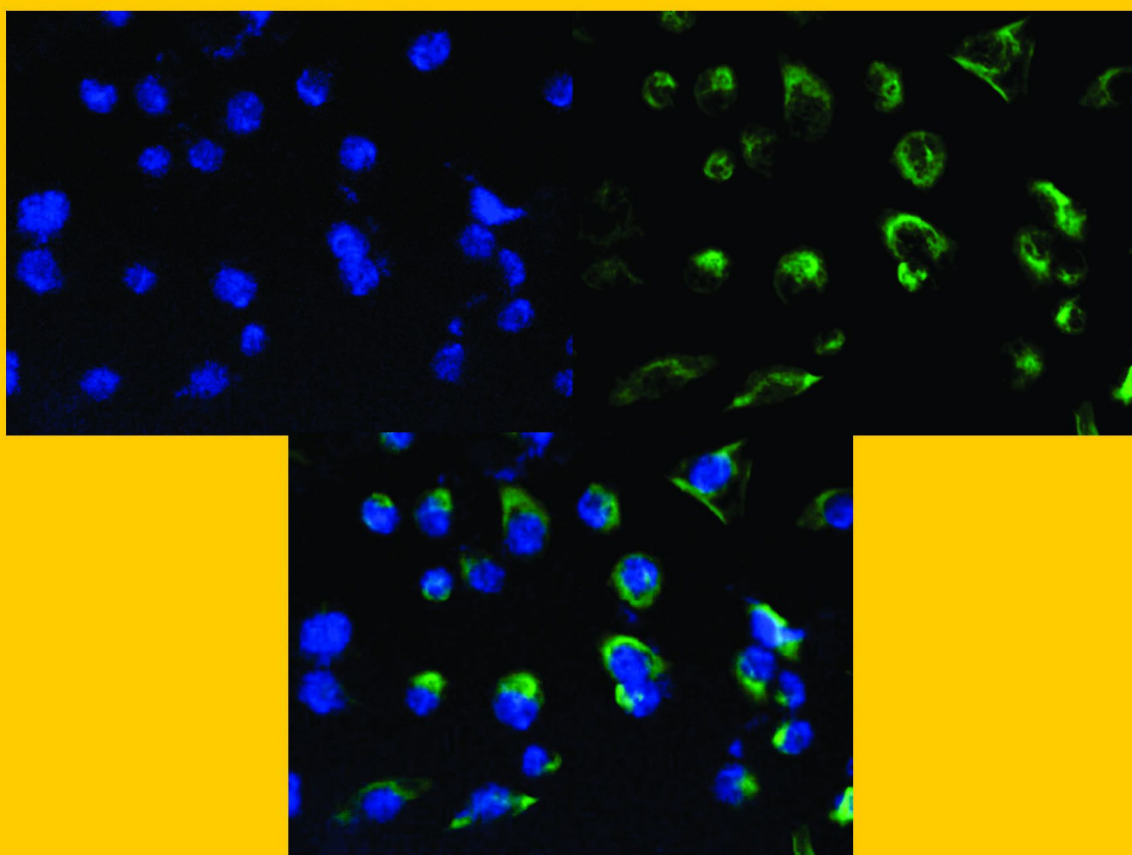


Fundamentals of Biological Chemistry : Short Notes (Volume II)



JV'n Dr. Neeraj Dholia

JAYOTI VIDYAPEETH WOMEN'S UNIVERSITY, JAIPUR

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Fundamentals of Biological Chemistry: Short Notes (Volume II)

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1. Nucleic acids

Nucleic acid may be a natural compound which will be diminished to form oxygen acid, sugars, and a mix of organic bases (purines and pyrimidines). Nucleic acids are the cell's key data-carrying molecules, and that they decide the inheritable characteristics of any animate thing by leading the method of protein synthesis. DNA (DNA) and RNA are the 2 major Forms of nucleic acids (RNA). altogether free-living species and most viruses, desoxyribonucleic acid is that the master blueprint for keeps and constitutes the genetic material. The genetic material of some viruses is RNA, however it's conjointly present altogether living organisms, wherever it plays an important role in several processes, like macromolecule synthesis.

Nucleotides: Building Blocks of Nucleic Acids

Basic structure

Polynucleotides are nucleic acids, that is, long chain-like structures created from a sequence of nucleotides thought of virtually identical building blocks. every ester consists of associate degree aromatic base containing N connected to a pentose (five-carbon) sugar, that is connected to a gaggle of phosphates successively. Four out of 5 potential nitrogen-containing bases are found in every nucleic acid: adenine (A), guanine (G), cytosine (C), thymine (T), and uracil (U). A and G are referred to as purines, and pyrimidines are conjointly referred to as C, T, and U.

The bases A, C, and G are present altogether nucleic acids; T, however, is found in desoxyribonucleic acid solely, whereas U is found in RNA. within the absence of a chemical group (-OH) on the 2' carbon of the sugar ring, the pentose sugar in desoxyribonucleic acid (2'-deoxyribose) differs from the sugar in RNA (ribose). The sugar connected to at least one of the bases is thought as a glycoside, while not an connected phosphate group. By bridging the 5'-hydroxyl group on one sugar to the 3'-hydroxyl cluster on succeeding sugar within the chain, the phosphate group binds sequent sugar residues. These glycoside linkages in RNA and desoxyribonucleic acid are referred to as phosphodiester bonds and are constant.

Biological functions of Nucleotides:

1. The fundamental units of nucleic acids are nucleotides (DNA and RNA). Though nucleoside monophosphates are present in nucleic acids, the raw materials for their synthesis are actually nucleoside triphosphates.
2. As regulatory chemicals, Cyclic Nucleotides Function. Cyclic AMP (cAMP) functions in certain hormone actions as second messengers, while cyclic GMP (cGMP) functions in responses mediated by Ca^{++} or calmodulin.
3. B-Complex Vitamin Nucleotides Act as Coenzymes. NAD^+ , NADP^+ , FMN, FAD, for instance, are coenzymes suitable for oxidation-reduction reactions.
4. Higher nucleotides act as carriers of electricity, e.g. ATP, GTP, UTP and TTP respectively. The universal energy carrier of the cell is the product of this ATP.
5. Higher nucleotides (e.g. UDP-glucose, ADP-glucose) and phospholipids are involved in the synthesis of polysaccharides (e.g. CDP and CTP).

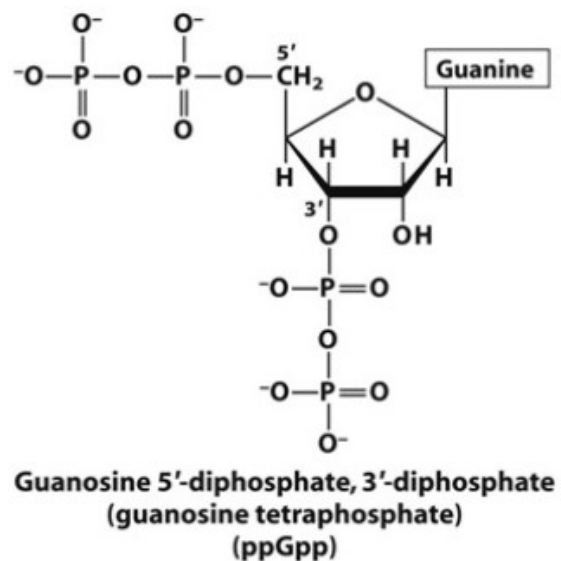
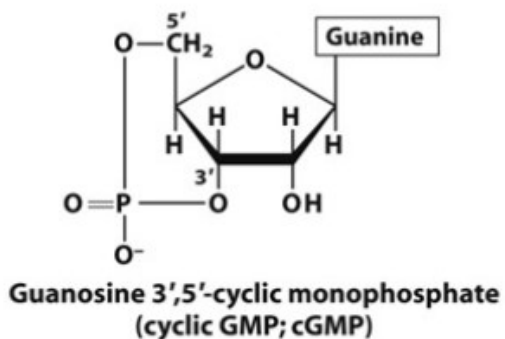
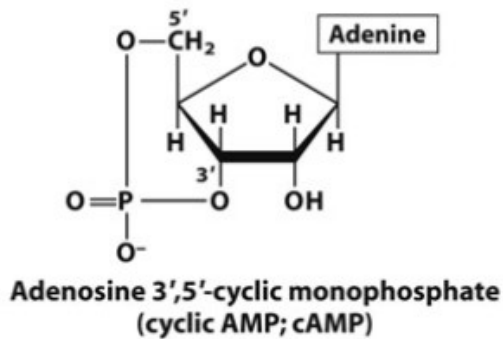


Figure: Nitrogenous base with its 3' and 5' ends in nucleotide
(Reference: Lehninger, Principles of Biochemistry)

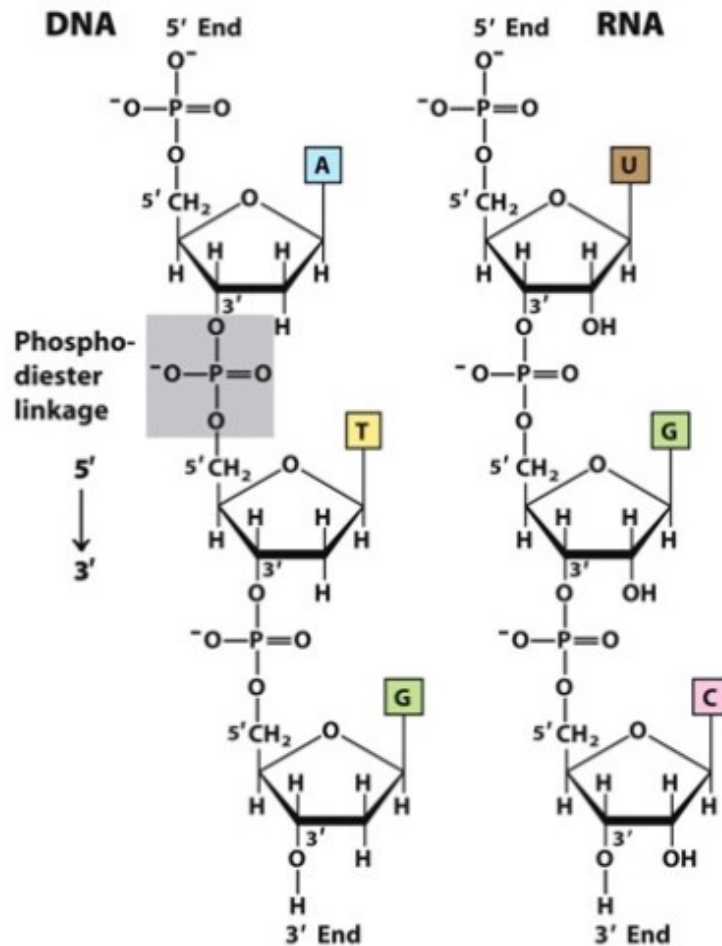
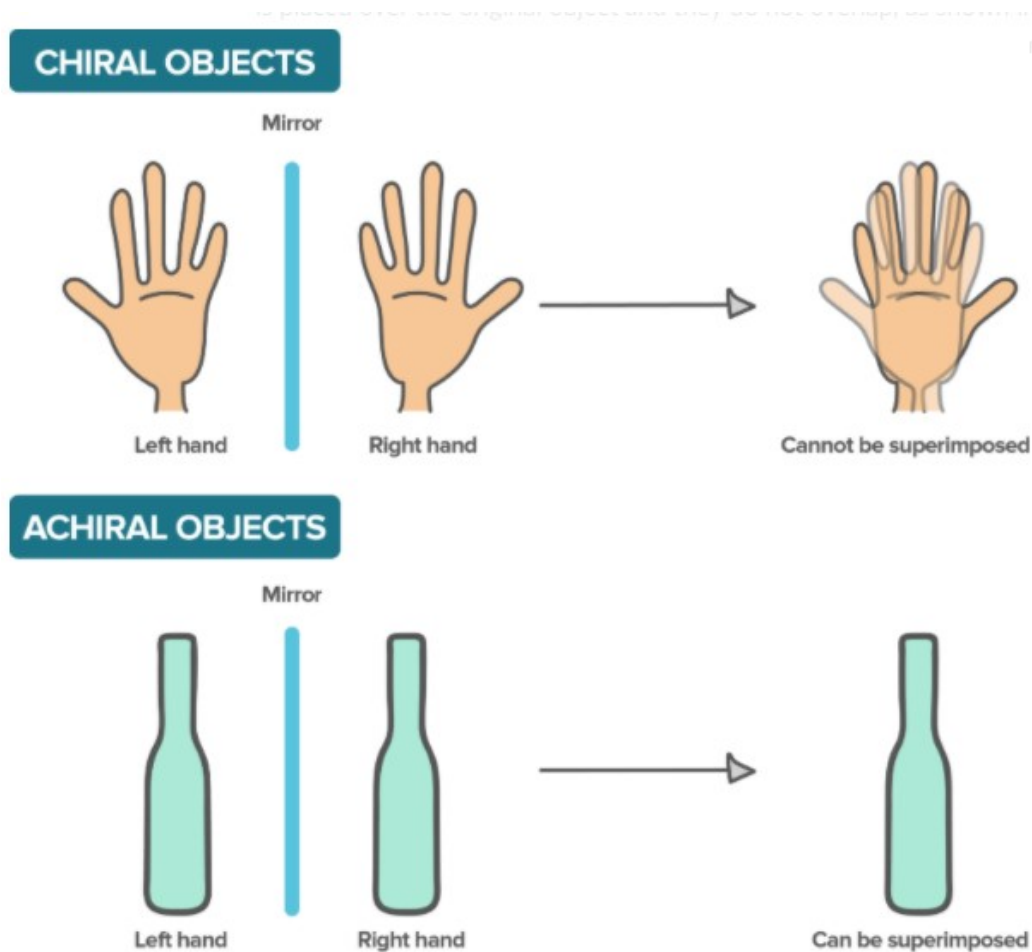


Figure: DNA and RNA. (Reference: Lehninger, Principles of Biochemistry)

2. Chiral Interactions

Chirality is derived from the Greek term for "hand" named $\chi\epsilon\iota\rho$ S (kheir). If the source and its mirror image are non-superimposable, much as our right and left side, an object is considered to be chiral. You have to ask what we mean by 'non-superimposable' now. As seen in the figure below, where the mirror image of the object is positioned over the original object and they do not overlap, then the object and its image are assumed to be non-superimposable.

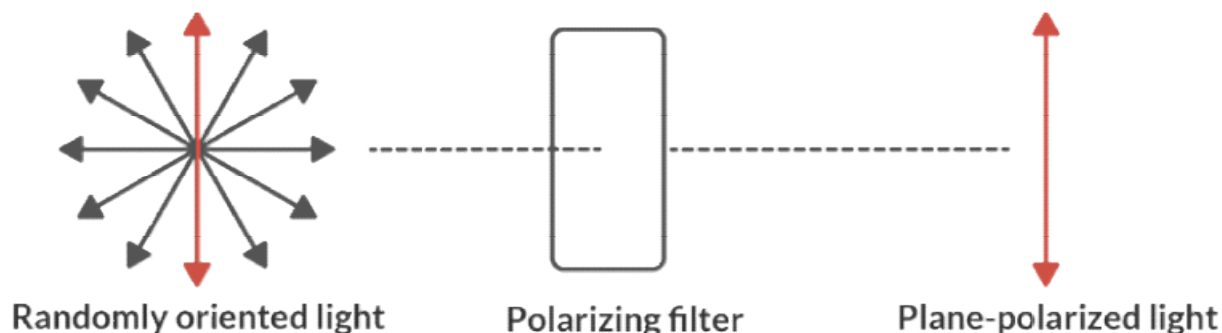


Reference: <https://www.khanacademy.org/test-prep/mcat/chemical-processes/stereochemistry/a/chiral-drugs>

Back in 1848, when he successfully isolated the two isomers of sodium ammonium tartarate, Louis Pasteur noticed molecular chirality. He noticed that the two isomeric crystals were non-superimposable mirror images of each other, possessing the same physical features, but differing

in their ability to rotate polarized light from the plane. This property has been designated as an optical operation.

In non-polarized light, in both planes, electric and magnetic fields are oriented arbitrarily. As a polarizing filter is made to flow through the non-polarized light, oscillations are directed in just one unique direction, and are considered polarized plane light.



Reference: <https://www.khanacademy.org/test-prep/mcat/chemical-processes/stereochemistry/a/chiral-drugs>

Chiral molecules are optically active, as mentioned, which means that when a plane-polarized light beam passes through a chiral molecule, it interacts with the molecule in such a way that the oscillation plane angle rotates.

In the L type, the chiral protein-making amino acids, which are translated from genetic code into the ribosome, exist. D-amino acids are, however, also present in nature. In the D configuration, monosaccharides (carbohydrate-units) are commonly found. The DNA double helix is chiral (as chiral is any kind of helix), and a right-handed turn is seen by the B-form of DNA.

Sometimes, when two enantiomers of a compound are present in animals, their flavor, odor and other biological behavior vary greatly. For instance, (+)-limonene discovered in orange (causing its odor) and (-)-limonene discovered in lemons (causing its odor) show different odors in the human nose due to various biochemical interactions. (+)-Carvone is responsible for the odor of caraway seed oil, while spearmint oil is responsible for the odor of (-)-carvone.

Even, for artificial compounds, like narcotics, in case of chiral medications, the two enantiomers often display remarkable difference in result of their biological behavior. Darvon (dextropropoxyphene) is a painkiller, while its enantiomer is an anti-cough agent called Novrad (levopropoxyphene).

3. pH, pK and Buffers

pH, pKa, and Henderson-Hasselbalch Equation

- The pKa is the pH value at which a proton would be recognized or donated by a chemical species.
- The smaller the pKa, the higher the acid and the greater the aqueous solution potential to donate a proton.
- The pKa and pH are related to the Henderson-Hasselbalch equation. It is just an approximation, however, and cannot be used for condensed solutions or for very low pH acids or high pH bases.

pH and pKa

- You know some things about a solution and how it compares with other solutions once you have pH or pKa values:
- The lower the pH, the greater the hydrogen ion concentration $[H^+]$.
- The lower the pKa, the stronger the acid and the greater its proton donation potential.
- pH depends on the solvent concentration. This is significant because it means that a weak acid can potentially have a lower pH than a strong acid that is diluted. For example, distilled vinegar (weak acid acetate) can have a lower pH than a dilute hydrochloric acid solution (a strong acid).
- On the other hand, for each molecule form, the pKa value is constant. Concentration is untouched by it.
- Even a chemical usually known as a base may have a pKa meaning since the words "acids" and "bases" literally apply to whether a species gives up or eliminates protons (acid) (base). If you have a base Y with a pKa of 13, for instance, it will accept protons and become YH, but YH will be deprotonated and become Y when the pH reaches 13. It is called a base since Y extracts protons at a pH greater than the pH of neutral water.

Buffer:

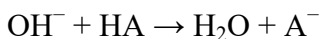
An aqueous solution composed of a combination of a weak acid and its conjugate base, or vice versa, is a buffer solution (more generally, a pH buffer or hydrogen ion buffer). Its pH changes very little when it is added to it with a small amount of strong acid or base. In a wide range of chemical uses, buffer solutions are used as a way to preserve pH at an almost constant value. There are several systems in nature which use buffering for pH control. The bicarbonate buffering system, for instance, is used to control blood pH.

Buffer solutions gain their pH transition tolerance due to the presence of a balance between the weak acid HA and its conjugate base A⁻:



Hydrogen ions (H⁺) are introduced as a strong acid is added to an equilibrium mixture of the weak acid and its conjugate base, and the equilibrium is moved to the left, in line with the theory of Le Châtelier. As a result, the concentration of hydrogen ions increases by less than the amount required with the amount of strong acid applied. Similarly, the concentration of hydrogen ion reduces by less than the amount required with the amount of alkali added as solid alkali is added to the mixture.

The simulated titration of a weak acid with pK_a = 4.7 shows the effect. In blue, the relative concentration of undissociated acid is seen, and in red, the concentration of its conjugate base. In the buffer area, pH = pK_a ± 1, centered at pH = 4.7, where [HA] = [A⁻], the pH shifts very slowly. The concentration of hydrogen ion reduces by less than the predicted amount because the bulk of the additional hydroxide ion is absorbed in the reaction.



And in the neutralization reaction, only a little is absorbed (which is the reaction that results in an increase in pH)



The pH increases quickly until the acid is more than 95 percent deprotonated, so much of the additional alkali is absorbed in the neutralization reaction.

4. Reaction mechanism

- The mechanism of reaction explains the chain of elementary reactions that must take place in order to go from reactants to products.
- In one step, reaction intermediates are formed and then consumed in a later step of the mechanism of reaction.
- The rate determining or rate-limiting step is considered the slowest step in the mechanism.
- The overall response rate is calculated by the phase rates up to (and including) the rate-determining point.

Reaction mechanisms and the rate law

As well as chemical intuition, chemists will come up with a hypothetical reaction process dependent on the experimentally defined rate law. The basic reactions that form the proposed reaction mechanism would, at the very least, add up to the total reaction. We can learn how to analyze a reaction system using kinetics in this article (and maybe just a bit of chemical intuition).

The rate determining step

We also consider the rates of each elementary step, in addition to ensuring that the elementary reactions in our reaction system add up to the total reaction equation. The overall rate of reaction is calculated by the step speeds up to (and including) the slowest specific step. In a reaction process, the slowest step is called the step of rate determination or rate limiting.

The rate limiting step is the first elementary step for our example process in the preceding section. We would therefore consider the overall rate to be comparable to the rate of NO₂ reaction rate in Elementary Stage 1

Electrophiles and Lewis Acids

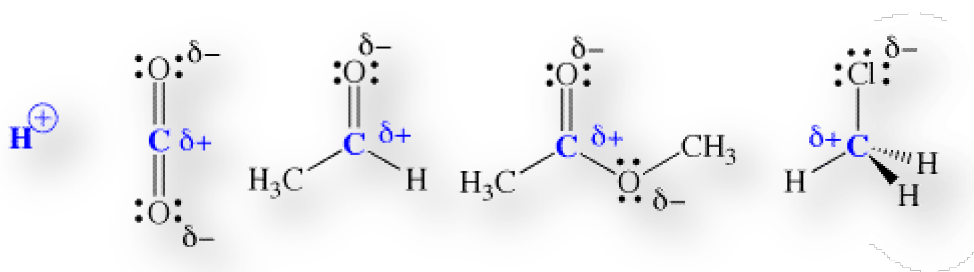
Electrophiles that are lacking in electrons and can accept a couple of electrons are considered positively loaded or neutral species. This are also considered electron-loving organisms (philic).

- The word electrophile can be separated into electron-derived "electro" and "phile," meaning loving.

- They are lacking in electrons and therefore enjoy electrons.
- They are charged positively or are charged neutrally.
- They draw electrons. Electron movement relies on mass.
- They move from a region of high density to an area of low density.
- They undergo electrophilic addition and replacement reactions with electrophilics.

Lewis acid is also considered an electrophile.

Examples:



Reference: <http://butane.chem.uiuc.edu/pshapley/genchem2/b5/1.html>

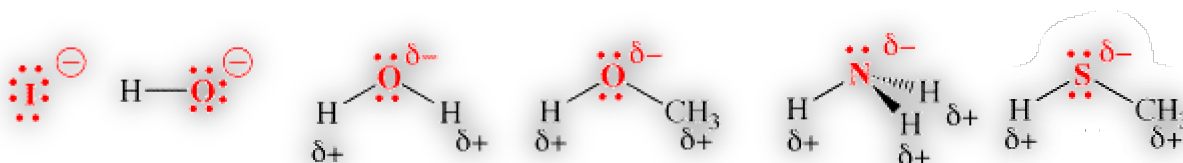
Nucleophiles and Lewis Bases

A nucleophile is a reagent composed of an atom with an incomparable or lone electron pair. As a nucleophile in electron is wealthy, it hunts for defective positions of electrons, i.e. nucleus means loving nucleus. According to the principle of Lewis acids and bases, nucleophiles act as Lewis bases.

- The word nucleophile can be divided into "nucleo" originating from the nucleus, meaning loving, and "phile."
- They are heavy in electrons and thus nucleus-loving. They are charged negatively or they are charged neutrally.
- They donate electrons.
- Electron movement is dependent on density.
- They move from a region of low density to an area of high density.
- They undergo nucleophilic addition and reactions of nucleophilic replacement.
- A Lewis base is sometimes considered a nucleophile.

For example, ammonia is a better nucleophile than water, since nitrogen is less electronegative than oxygen. What this suggests is that the nitrogen-bound single ammonia pair is more loosely contained than the solitary water pairs that are oxygen-bound.

Examples:



Reference: <http://butane.chem.uiuc.edu/pshapley/genchem2/b5/1.html>

In both biochemistry and industrial chemistry, acid-base reactions are fundamental. In comparison, acids or bases are two of the molecules we find in our houses, the grocery, and the pharmacy. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. An acid-base reaction has actually been carried out by any inexperienced chef who has cooked mayonnaise or squeezed a wedge of lemon to marinate a slice of cod. Let's first describe some of the properties of acids and bases before we explore the functionality of those reactions.

Definitions of Acids and Bases

We may describe acids as substances that dissolve to generate H^+ ions in water, whereas bases are classified as substances that dissolve to generate OH^- ions in water. This is only one possible set of meanings, in truth. While the basic properties of acids and bases have been recognized for over a thousand years, as scientists have understood more about them, the meanings of acid and base have changed significantly.

Acid was any material in ancient times that had a bitter taste (e.g., vinegar or lemon juice), produced clear color variations in plant-derived dyes (e.g., making blue litmus paper red), reacted with some metals to create hydrogen gas and a solution of salt containing a metal cation, and with the evolution of carbon dioxide, dissolved carbonate salts such as calcareous ($CaCO_3$).

A foundation, on the other hand, was any material that had a bitter flavor, felt slippery to the touch, and produced changes in color in plant tints that varied diametrically from the acid-

induced changes (e.g. turning red litmus paper blue). Although these descriptions were helpful, they were totally descriptive.

The Arrhenius Definition of Acids and Bases

The characteristic properties of acids and bases are solely due to the presence of H^+ and OH^- ions, respectively, in solution, according to Arrhenius. While the theories of Arrhenius were generally accepted, his description of acids and bases had two important shortcomings:

1. First, since acids and bases are described in terms of ions derived from water, the definition of Arrhenius extended only to aqueous solution substances.
2. Second, and more critically, the Arrhenius concept predicted that the properties of acids and bases can only be demonstrated by substances dissolving in water to produce H^+ and OH^- ions, respectively. For example, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride is not an acid-base reaction according to the Arrhenius description, since it does not include H^+ and OH^- :

The Brønsted–Lowry Definition of Acids and Bases

A more general description of acids and bases was required, due to the shortcomings of the Arrhenius definition. One was independently suggested by the Danish chemist J. in 1923. N. Brønsted (1879-1947) and the chemist from Britain, T. M. Lowry (1874–1936), who described acid-base reactions from one substance to another in terms of the conversion of a proton (H^+ ion).

According to Brønsted and Lowry, acid (a substance with at least one hydrogen atom that can dissociate into an aqueous solution to create an anion and an H^+ ion (a proton) and therefore to form an acidic solution) is any substance that can donate a proton and a base (a substance that creates one or more hydroxide ions (OH^-) and a cation when dissolved in an aqueous solution to form a simple solution).

Except that it is not limited to aqueous solutions, the Brønsted-Lowry definition of an acid is exactly the same as the Arrhenius definition. The Brønsted-Lowry description of a base, however, is even more general since only one of many compounds that can accommodate a proton is the hydroxide ion. For instance, ammonia reacts to form NH_4^+ with a proton, so NH_3

is a Brønsted-Lowry base here, and HCl is a Brønsted-Lowry acid. The Brønsted-Lowry concept is used in this text due to its more general existence, unless otherwise stated.

Strengths of Acids and Bases

Before next semester, we won't quantitatively analyze the strengths of acids and bases. Qualitatively, however, we can say that to give H^+ and the corresponding anion, strong acids react essentially fully with water. Similarly, to give OH^- and the accompanying cation, strong bases dissociate essentially entirely in water. All strong electrolytes are strong acids and strong bases. In the other hand, only a portion of the molecules of weak acids and weak bases react with water to create ions, so weak electrolytes are also weak acids and weak bases. In general, less than 5% of a weak electrolyte dissociates into solution ions, whereas more than 95% remain present in an undissociated state.

Just a few heavy acids are typically found in practice: HCl, HBr, HI, HNO_3 , HClO_4 , and H_2SO_4 (H_3PO_4 is only moderately strong). Ionic compounds having the hydroxide ion as the anion are the most typical strong bases; NaOH, KOH, and $\text{Ca}(\text{OH})_2$ are three examples. Popular weak acids include HCN, H_2S , HF, carboxylic acids such as acetic acid, and oxoacids such as HNO_2 and HClO.

Nucleophiles

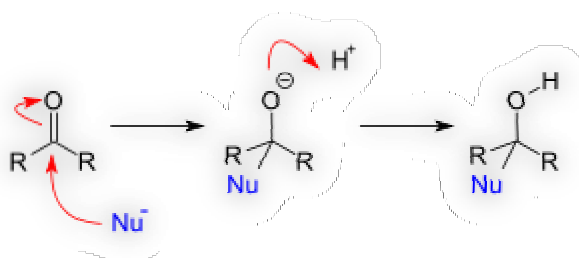
A nucleophile is a species (an ion or a molecule) that in everything else is highly drawn to an area of positive charge. Nucleophiles are either entirely negative ions, or have a heavy charge on a molecule elsewhere. We are going to look at both depend on either an oxygen atom or a nitrogen atom for lone pairs.

A nucleophilic addition reaction is an addition reaction where an electron-deficient or electrophilic double or triple bond chemical compound, a π bond, interacts with an electron-rich reactant, called a nucleophile, with the double bond vanishing and two new single bonds, or σ , being formed. The reactions are involved in the biological synthesis of compounds in the metabolism of a living organism and are used in the preparation of most modern complex organic chemicals by chemists in universities and industries such as pharmaceuticals, and so are fundamental to organic chemistry.

Additional reactions involve the presence in the electrophile of groups with multiple bonds (because double bonds and even triple bonds may both lack electron-rich sources): double bonds of carbon-heteroatom as in carbonyls, imines, and nitriles, or double or triple bonds of carbon-carbon.

Example: Addition to carbon–heteroatom double bonds

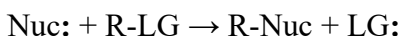
A new carbon center with two additional single, or σ , bonds is formed by nucleophilic addition reactions from nucleophiles with electrophilic double or triple bonds (π bonds). The addition of a nucleophile to double or triple carbon-heteroatom bonds such as $>\text{C}=\text{O}$ or $-\text{C}\equiv\text{N}$ reveals great diversity. These bond forms are polar (they have a significant electronegativity differential between the two atoms); their carbon atoms also bear a partial positive charge. This makes an electrophile of the molecule and the electrophilic nucleus of the carbon atom; this atom is the nucleophile's main focus.



Reference: <https://commons.wikimedia.org/wiki/File:NucleophilicAdditionsToCarbonyls.svg>

Nucleophilic substitution is a simple class of reactions in which an electron-rich compound substitutes a left group (nucleophile) (electrophile). The substrate is generally called the whole molecular body of which the electrophile and the leaving group are members. As a part of another molecule, the nucleophile essentially attempts to replace the leaving group as the primary substituent in the reaction itself.

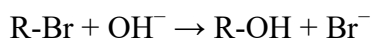
The most general form of the reaction may be given as the following:



The electron pair ($:$) from the nucleophile (Nuc) attacks a new bond forming substrate (R-LG), while the leaving group (LG) exits with an electron pair. In the present case, the principal

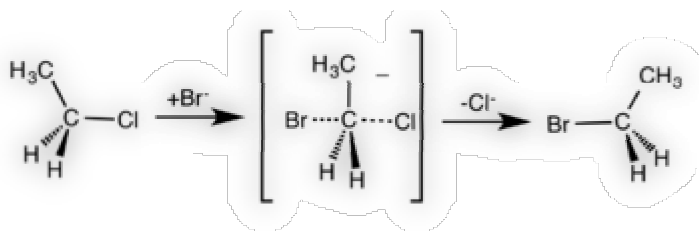
product is R-Nuc. Although the substrate is usually neutral or positively charged, the nucleophile can be electrically neutral or negatively charged.

The hydrolysis of an alkyl bromide, R-Br, under simple conditions is an example of nucleophilic substitution, where the attacking nucleophile is the OH⁻ and the leaving group is Br⁻.



At function, there are two main processes, each competing with one another. The SN1 reaction and the SN2 response are the two key pathways. S stands for chemical replacement, N stands for nucleophilic, and the number represents the reaction's kinetic order.

The addition of the nucleophile and the elimination of the leaving group occur concurrently in the SN2 reaction (i.e. concerted reaction). SN2 exists where the nucleophile is readily accessible to the central carbon atom.



Reference: https://en.wikipedia.org/wiki/Nucleophilic_substitution

SN₂ mechanism

There are a few factors in SN2 reactions that control the rate of the reaction. The 2 in SN2 means, first of all, that there are two quantities of substances that influence the reaction rate: substrate and nucleophile. For this reaction, the rate equation will be:

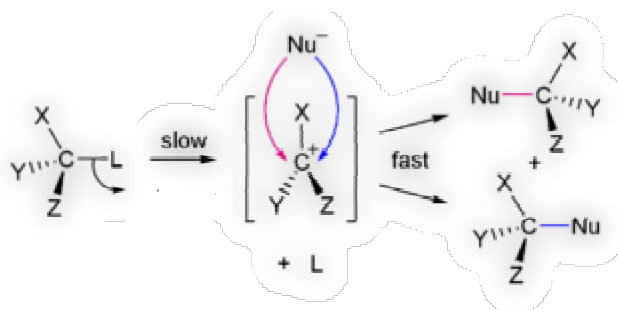
$$\text{Rate} = k [\text{Sub}] [\text{Nuc}]$$

An aprotic solvent, such as acetone, DMF, or DMSO, is optimal for an SN2 reaction. Protons (H⁺) ions are not added to the solution by protic solvents; if protons were present in SN2 reactions, they will interfere with the nucleophile and severely reduce the rate of reaction. Steric effects push the reaction speed as this reaction happens in one step. The nucleophile is 180

degrees from the leaving group in the intermediate step and the stereochemistry is reversed when the nucleophile binds to create the product.

There is still no time for the substrate to rearrange itself when the intermediate is partly bound to the nucleophile and leaving group: the nucleophile would bond to the same carbon that was connected to the leaving group. A final element that influences reaction rate is nucleophilicity; the nucleophile must attack an atom other than hydrogen.

The S_N1 reaction, by comparison, requires two phases. Where the central carbon atom of the substrate is surrounded by bulky groups, S_N1 reactions appear to be significant, both because such groups sterically interfere with the S_N2 reaction (discussed above) and because a strongly substituted carbon forms a stable carbocation.



Reference: Calvero., 2006. S_N1 reaction mechanism
(https://en.wikipedia.org/wiki/File:SN1_reaction_mechanism.png)

An additional reaction is the one in which compound shifts mean double bond or triple bond to lower bonds, such as double to single or triple to double or single, from unsaturated to saturated.

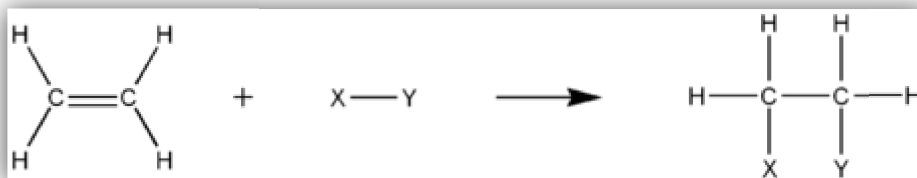
Whereas the one in which a group is replaced, such as R-X to R-OH, is a substitute.

Meanwhile, electrophiles are added in electrophilic addition and other groups are substituted by electrophiles in electrophilic replacement.

Electrophilic addition reaction

An electrophilic addition response is an addition reaction where a π bond is broken in a chemical compound and two new σ bonds are formed. A double bond or triple bond must be on the substrate of an electrophilic addition reaction.

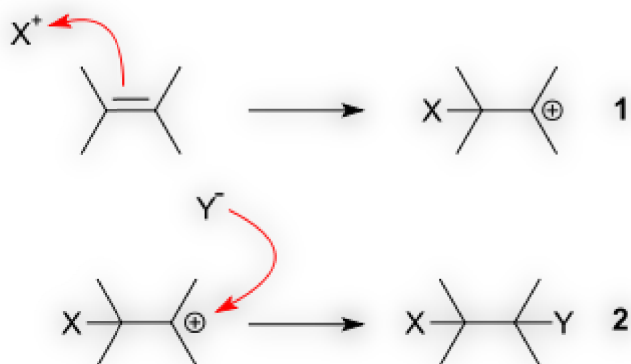
The driving force for this reaction is the formation of an electrophile X^+ with an electron-rich unsaturated $C=C$ bond that forms a covalent bond. During the $C-X$ bond formation, the positive charge on X is passed to the carbon-carbon bond, creating a carbocation.



Reference: Schizmatic, 2006. A representation of an Electrophilic addition reaction.

Above is the overall reaction.

Mechanism is shown below:



Reference: <https://commons.wikimedia.org/wiki/File:ElectrophilicAdditionmechanism.svg>

The positively charged intermediate interacts with (Y), which is electron-rich and normally an anion, in step 2 of an electrophilic addition, to form the second covalent bond.

Stage 2 is the same mechanism of nucleophilic assault observed in an S_N1 reaction.

Regioselectivity is important in all asymmetric addition reactions to carbon and is also determined by the law of Markovnikov. Organoborane compounds provide added anti-Markovnikov. Electrophilic assault on an aromatic system, rather than an additional reaction, results in electrophilic aromatic replacement.

The electrophile with the positive charge effects the creation of the overall structure in the electrophilic addition, which then also bears a positive charge, to make up for the new addition, which also occurs in the intermediate one, carrying the positive charge. The trick to understanding electrophilic addition is this intermediate, which is due to the constructive existence of the involved particles. If this is achieved, so these additions will understand the responses as positively charged reactions. As the intermediate form otherwise known as the ultimate structure of such an intermediate, the positive charge bears effects. The end product thus contains the complete structure, with the addition of Y, a nucleophile.

Few examples are:

- Dihalo addition reactions: X_2
- Hydrohalogenations: HX
- Hydration reactions: H_2O
- Hydrogenations: H_2

Electrophilic substitution reactions

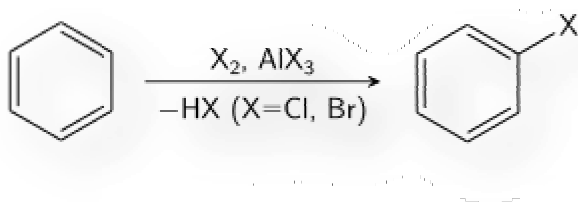
Electrophilic substitution reactions are chemical reactions where an electrophile transfers a functional group in a compound, a hydrogen-typical atom.

Two types:

Electrophilic aromatic substitution

An atom bound to the ring, normally hydrogen, is substituted by an electrophilic replacement in aromatic compounds.

The related aryl halides are obtained by aromatic halogenation with bromine, chlorine or iodine. The resulting iron or aluminum trihalide normally catalyzes this reaction.



Reference: Krishnavedala, 2014. Halogenation of benzene.

Examples:

Friedel-Crafts reactions: aromatic nitrate, aromatic halogenation and sulfonation and acylation.

Electrophilic aliphatic substitution

An electrophil displaces a functional group as electrophilically substituted with aliphatic compounds. This reaction is identical to the nuclear aliphatic substitution in which the reactant is not an electrophile, but rather a nucleophile. SE1, SE2 (front), SE2 (back) and SEi (electro-philic substitution) are all potential pathways of electrophilic aliphatic replacement, which often mimic nucleophilic SN1 and SN2 equivalents. The substratum is first ionized in a carbanion with a positive organic residue during the SE1 action process. The carbanion then rejoins the electrophile easily. The SE₂ reaction mechanism has a single transition state in which the old bond and the newly formed bond both are present.

Electrophilic aliphatic substitution reactions are:

Nitrosation

Ketone halogenation

Keto-enol tautomerism

5. Carbohydrates

- Carbohydrates are a group of carbonyl compounds (aldehydes or ketones) which occur naturally and also contain several hydroxyl groups.
- Their derivatives can also contain hydrolysis-generating compounds.
- They are also known as "saccharides" as the most available organic modules of the nature.
- Calories that are water-soluble and sweet in color are referred to as sugars.

Structure of Carbohydrates

- Carbohydrates are composed of carbon, oxygen, and hydrogen.
- For carbohydrates, the general analytical form is $(CH_2O)_n$.
- These are organic compounds with several hydroxyl groups coming off the carbon chain arranged in the shape of aldehydes or ketones.
- Easy sugars or monosaccharides are the building blocks of all carbohydrates.
- A polyhydroxy aldehyde (aldose) or a polyhydroxy ketone may be a monosaccharide (ketose).

The carbohydrates can be structurally represented in any of the three forms:

- Open chain structure.
- Hemi-acetal structure.
- Haworth structure.

Open chain structure – It is the carbohydrate form of the long straight-chain.

Hemi-acetal structure – Here the 1st carbon of the glucose condenses with the -OH group of the 5th carbon to form a ring structure.

Haworth structure – It is the presence of the pyranose ring structure.

Physical Properties of Carbohydrates

- Stereoisomerism – The same structural formula is having compounds, but they vary in spatial structure. Example: With regard to the penultimate carbon atom, glucose has two isomers. They are glucose-D and glucose-L.

- Optical Activity – It is the rotation of (+) glucose and (-) glucose-forming plane-polarized light.
- Diastereo isomers – This changes the structure with respect to C2, C3, or C4 of glucose. Examples: galactose, mannose.
- Anomerism – That is the spatial structure of the first aldonic carbon atom and the second ketonic carbon atom.

Chemical Properties of Carbohydrates

- Osazone formation: As sugars react with excess phenylhydrazine, osazone is a carbohydrate derivative. Eg. Glucosazone
- Benedict's test: Reducing sugars are converted to strong reduction species known as enediols when heated in the presence of an alkali. The solution changes its colour to orange-red/brick red as Benedict's reagent solution and reducing sugars are heated together.
- Oxidation: When their carbonyl groups oxidize to give carboxylic acids, monosaccharides are sugar reducers. D-glucose is oxidized into D-gluconic acid in the Benedict test, so glucose is known to be a sugar reducer.
- Reduction to alcohols: The C=O groups may be reduced by sodium borohydride, NaBH₄, or catalytic hydrogenation (H₂, Ni, EtOH/H₂O) into alcohols in open-chain types of carbohydrates. The products are referred to as 'alditols.'

Properties of Monosaccharides

- The majority of monosaccharides taste sweet (fructose is sweetest; 73 percent sweeter than sucrose).
- They are room temperature solids.
- They are highly soluble in water: the presence of vast amounts of OH groups makes the monosaccharides even more water-soluble than other comparable MW molecules, considering their high molecular weights.
- To produce a syrup (1 g / 1 ml H₂O), glucose can dissolve in minute quantities of water.

Classification of carbohydrates:

Single sugars (monosaccharides) and polymers, oligosaccharides, and polysaccharides are among the basic carbohydrates.

Monosaccharides

- The simplest category of carbohydrates, also referred to as basic sugars, as they cannot be hydrolyzed anymore.
- Colorless, crystalline solids that are water soluble and non-polar solvent soluble.
- There are molecules that have a free aldehyde group or ketone group.
- $C_n(H_2O)_n$ or $C_nH_{2n}O_n$ are the general formula.
- They are categorized by the number of carbon atoms they possess and also by the basis of the present functional group.
- The monosaccharides are also referred to as trioses, tetroses, pentoses, hexoses, heptoses, etc. with 3, 4, 5, 6, 7... Carbons, and also as aldoses or ketoses, based on whether they contain a group of aldehydes or ketones.
- Examples: glucose, fructose, ribulose, erythrulose.

Oligosaccharides

- Oligosaccharides are compound sugars which, on hydrolysis, yield 2 to 10 molecules of the same or different monosaccharides.
- Glycosidic linkage connects the monosaccharide units.
- It is also defined as disaccharide, trisaccharide, tetrasaccharide, etc, depending on the number of monosaccharide units.
- Oligosaccharides are known as a disaccharide, yielding 2 molecules of monosaccharides on hydrolysis, and those yielding 3 or 4 monosaccharides are known as trisaccharides and tetrasaccharides, etc.
- $C_n(H_2O)_{n-1}$ is the basic disaccharide formula, and $C_n(H_2O)_{n-2}$ and so on is that of trisaccharides.

Examples: Disaccharides include sucrose, lactose, maltose, etc.

Trisaccharides are Raffinose, Rabinose.

Polysaccharides

- They are often referred to as "glycans."
- Polysaccharides contain more than 10 units of monosaccharides and can be hundreds of units of sugar in volume.
- They yield more than 10 monosaccharide molecules for hydrolysis.
- In the identity of their repeated monosaccharide groups, in the length of their chains, in the forms of bond binding units and in the degree of branching, polysaccharides vary from each other.
- They are mainly associated with two essential functions i.e. Structural functions and energy conservation.
- Based on the form of molecules formed as a result of hydrolysis, they are further reclassified.
- They can be homopolysaccharides, containing the same type of monosaccharides, or heteropolysaccharides, i.e. different forms of monosaccharides.

Examples of Homopolysaccharides are starch, glycogen, cellulose, pectin.

Heteropolysaccharides are Hyaluronic acid, Chondroitin.

Functions of carbohydrates

Carbohydrates are molecules of plant and animal tissues that are commonly dispersed. Carbohydrates from the skeletal systems of plants and arthropods also act as food reserves for plants and animals. They are an essential source of energy needed for different metabolic activities and oxidation derives the energy.

Some of their major functions include:

- To fuel cellular reactions, living organisms use carbohydrates as available resources. For all living things, they are the most abundant dietary source of nutrition (4 kcal/gram).
- In addition to being the main source of energy, carbohydrates are immediate sources of energy in many species. Glucose is broken down to yield ATP by glycolysis/ Krebs's loop.
- Acting as energy stores, oils, and intermediates for metabolism. It is processed in livestock as glycogen and in plants as starch.

- Stored carbohydrates, instead of proteins, act as an energy source.
 - They shape structural and defensive elements, such as those of plants and microorganisms in the cell wall. Structural components in bacterial (peptidoglycan or murein) cell walls, plants (cellulose) and animals (chitin).
 - Carbohydrates are intermediates in the mechanism of fat and protein biosynthesis.
 - Carbohydrates tend to control nerve tissue and are the source of energy for the brain.
 - In order to establish surface antigens, receptor molecules, vitamins and antibiotics, carbohydrates are paired with lipids and proteins.
 - O Formation of the RNA and DNA structural structure (ribonucleic acid and deoxyribonucleic acid).
 - Many proteins and lipids are connected to them. In cell-cell contact and in interactions between cells and other elements in the cellular system, these related carbohydrates are essential.
 - They are a major component of connective tissues in animals.
 - Carbohydrates high in fiber lead to the reduction of constipation.
 - In addition, they aid in the regulation of the immune system.
- Triose monosaccharide with the molecular formula $C_3H_6O_3$ is glyceraldehyde (glyceral). It is the simplest of all the aldoses that are common. It is a crystalline, colorless, sweet solid and is an intermediate compound in the metabolism of carbohydrates. The term comes from the mixture of aldehyde and glycerol, as glyceraldehyde is glycerol with an aldehyde oxidized by one alcohol group.

d-glyceraldehyde

(*R*)-glyceraldehyde

(+)-glyceraldehyde

l-glyceraldehyde

(*S*)-glyceraldehyde

(-)-glyceraldehyde

Fischer projection	$ \begin{array}{c} \text{H}-\text{C}=\text{O} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $	$ \begin{array}{c} \text{H}-\text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{OH} \end{array} $
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Reference: Master Uegly, 2015. Fischer projection of D- and L-Glyceraldehyde.

Carbohydrates are aldehyde or ketone derivatives of polyhydroxy alcohols containing at least three general formula carbon atoms $(\text{CH}_2\text{O})_n$. These are moderately reduced compounds (some of which are connected with oxygen) that can be readily converted into energy (ATP).

Uses

- 1) Energy storage, fuel, intermediates of metabolism
- 2) Structural - DNA and RNA, cell walls in plants (cellulose), arthropods skeleton (chitin)
- 3) Recognition - attached to lipids and proteins (blood types on red blood cells = antigens)

Monosaccharides - suffix "ose" is used to designate sugars

- Building blocks --> polysaccharides (macromolecules)
- D-Configuration is the most common in sugars synthesized by living organisms. D assignment is based on the configuration of the chiral carbon furthest from the "anomeric" carbon C-1 in aldoses & C-2 in ketoses
- Two major monosaccharide classes are Aldoses and Ketoses
- Aldoses

The simplest aldose is based on D-glyceraldehyde structures. The asymmetric carbon farthest away from the aldehyde defines D and is drawn to the right. Aldoses contain an aldehyde group and per molecule have 1-4 chiral centers.

- Ketoses

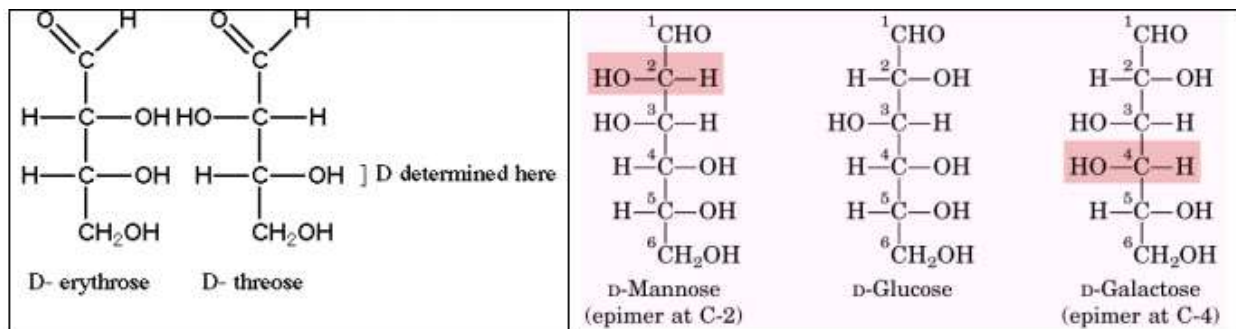
Dihydroxyacetone-based structures (simplest ketose). The asymmetric carbon farthest away from the ketone defines D and is drawn to the right. It comprises the group carbonyl. Have a chiral carbon of 1, 2 or 3 per atom.

Nomenclature

The sugar prefix indicates the number of carbons in such a manner that hexoses (e.g., glucose and fructose) contain 6 carbons and pentoses contain 5 carbons, triose 3, tetrose 4, pentose 5, hexose 6, heptose 7, and heptose 7.

- Enantiomers = isomers that are perfect mirror copies (i.e., D- and L- glyceraldehyde) o
- Diastereoisomers = not mirror images Carbohydrates are rich in stereoisomerism o (i.e., D- erythrose and D-threose)

Epimers = isomers that vary from one asymmetric carbon — Examples of hexose; Glucose vs. mannose at carbon 2 and Glucose v/s. galactose at carbon 4



Reference: Lehninger Principles of Biochemistry.

Configurations of carbohydrates:

- Asymmetric carbons are those with four distinct classes of chemicals attached.
- There are four distinct asymmetrical carbons of glucose (#2, 3, 4, 5). Get a look at glucose epimers; allose, altrose, and mannose.
- Carbons of sugar are counted starting at the end of the aldehyde or ketone group closest to the sugar group.

- The "D" or "L" label for a sugar designates the configuration of the atoms about the asymmetric carbon farthest from the aldehyde or ketone.

- Most sugars in humans are D-sugars.

- Examples:

D-Erythrose, D-Threose (four carbon)

D-Ribose, D-Arabinose, D-Xylose, D-Lyxose (five carbon)

D- Allose, D-Altrose, D-Glucose, D-Mannose (six carbon)

• Monosaccharides (aldoses & ketoses) with 5 or more carbons are most soluble in their 'ring' shape in solution.

In the ring type, inside the chain, the carbonyl carbon becomes covalently bound to another OH group.

Carbonyl carbon after cyclization becomes "anomeric" carbon

Pyran and Furan are the most common ring systems.

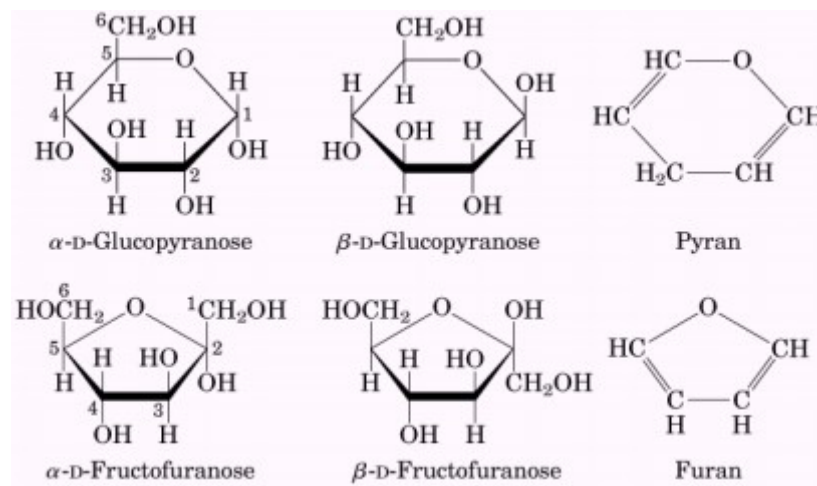


Figure: Pyranose and Furanose (Reference: Lehninger Principles of Biochemistry)

Pyranose ring - 6-membered ring (5- or 6-carbon monosaccharides)

Glucose = six-carbon aldose, C-1 reacts with C-5 OH to form pyranose ring

Conformation of hydroxyl on carbon 1, α (below plane of ring) and β (above plane of ring)

Furanose ring - Five-membered loop (most 5-carbon monosaccharides)

Fructose = 6-carbon ketose, C-2 responds to form a furanose ring with C-5 OH and C-1 responds to form a pyranose ring with C-5 OH.

Conformations

The anomeric OH group of be above or below the plane of the ring alpha-D sugars of the OH-group on the anomeric carbon below the plane of the ring β -D sugars of the OH-group on the anomeric carbon above the plane of the ring in glucopyranose after cyclization. The β form (β -D glucopyranose) is the favored form (62%), with the remaining 38% being β -D-glucopyranose . Alpha and beta forms interconvert into straight-chain forms of water (mutarotation).

Disaccharides belong to the oligosaccharides that have 2-8 monosaccharides connected by glycosidic bonds and sometimes oligosaccharides found in nature.

- Maltose, lactose, trehalose and sucrose are physiologically essential disaccharides.
- Disaccharides consist of two monosaccharides which are joined by an O-glycosidic bond covalently.
- Compared to other hydroxyl groups, the hydroxyl group formed as a result of hemiacetal formation is particularly reactive.
- This hydroxyl group present in one monosaccharide reacts with any one of the hydroxyl groups attached to C-1, C-2, C-3, C-4, or C-6 of another monosaccharide to produce 1 $\rightarrow$ 1, 1 $\rightarrow$ 2, 1 $\rightarrow$ 3, 1 $\rightarrow$ 4, and 1 $\rightarrow$ 6 linked disaccharides.
- When only one anomeric carbon is involved in the forming of glycosidic bonds, disaccharides are formed by reduction.
- If all monosaccharide anomeric carbon atoms are involved in the creation of glycosidic bonds, resulting in the formation of non-reducing disaccharides such as trehalose (aldosyl-aldosyl disaccharide) or sucrose (aldosyl-ketosyl disaccharide).

- In the case of disaccharide reduction, one end of the free anomeric carbon molecule is called the reduction end, while the other end is called the non-reducing end, where the anomeric carbon is involved in the glycosidic bond.

Glycosidic bond - Catalyzed to form an R-O-R linkage by hydrolase (dehydration reaction). In a polysaccharide, glycosidic bonds tie together the monosaccharides. The bond is formed when the anomeric hydroxyl group condenses on a second monosaccharide with an alcohol group.

One sugar's anomeric OH-group responds to another sugar with an OH-group. Reaction usually leaves one carbon "anomeric". Some of the disaccharides prevalent in nature are: Sucrose – Fructose-containing disaccharide + glucose bound to glucose alpha (1->2) (no free anomeric carbon) glucose alpha (1->2)-β-fructose, alpha-D-glucopyranosyl - (1->2)-beta-D-fructofuranoside.

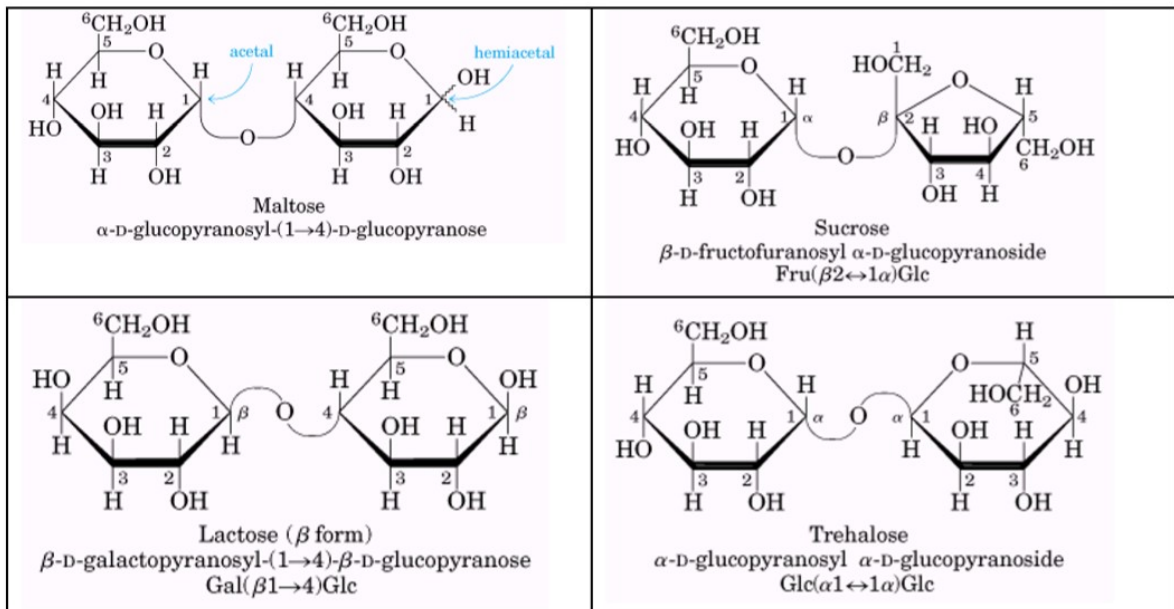
Lactose (milk sugar) – Galactose + glucose disaccharide bound to β (1->4) (free anomeric carbon) -galactose β (1->4) glucose, β-D-galactopyranosyl - (1->4) - alpha-D-glucopyranose.

Lactose intolerance: By cleaving a β-1, 4-galactosidic bond, lactase hydrolyzes lactose, a disaccharide, into galactose and glucose in the intestine. This enzyme is deficient in about one in 4 people, contributing to lactose sensitivity. As adults, up to 90% of Asians and Africans can be lactase- deficient. Owing to slow digestion, lactose accumulates in the gut. Bacteria develop lactose metabolites that contribute to the influx of fluid into the intestine. Medical signs include bloating, fatigue, cramping, diarrhea with sweat. It is necessary to eliminate lactose from the diet.

Maltose- Maltose is a disaccharide made up of two residues of glucose that are connected by a glycosidic bond between one residue of glucose C-1 and the other residue of C-4.

The structure of the glucose anomeric carbon involved in the linkage is (1-4). The second glucose anomeric carbon atom is free, so maltose is a sugar reducer.

Maltose has been reported in plants periodically. Typically, it is obtained during the germination or malting process as a result of the enzyme starch hydrolysis.



Reference: Lehninger Principles of Biochemistry.

Oligosaccharides - 2-8 monosaccharides linked by glycosidic bonds

Polysaccharides: The main classes of biomolecules include polysaccharides. They are long chains of molecules of carbohydrates comprising of several smaller monosaccharides. These complex bio-macromolecules act in animal cells as an essential energy source and form a structural part of a plant cell. Based on the monosaccharide form, it may be a homopolysaccharide or a heteropolysaccharide.

Polysaccharides may be either a simple monosaccharide chain known as a linear polysaccharide, or a branched polysaccharide.

Characteristics of Polysaccharides

Polysaccharides have the following properties:

1. In terms of flavor, they are not sweet.
2. Some are water-insoluble.
3. In nature, they are hydrophobic.

4. When desiccated, they do not form crystals.
5. It can be mined to form a white powder.
6. They are carbohydrates that have a high molecular weight.
7. They are compact and osmotically inert within the cells.
8. They are made of oxygen, carbon, and hydrogen. 2:1 is the hydrogen to oxygen ratio.

Types of Polysaccharides

Polysaccharides are categorized into two types:

- Homopolysaccharides.
- Heteropolysaccharides.

Homopolysaccharides

A polysaccharide which contains monosaccharides of the same kind is known as a homopolysaccharide. Any of the essential homopolysaccharides are:

1. Glycogen: It is consisting of a large molecular chain. It is found in fungi and animals.
2. Cellulose: The plant's cell wall is made up of cellulose. Large chains of glycosides compose it.
3. Starch: It is formed by amylose and amylopectin condensation. It is primarily present in fruits, trees, seeds, etc.
4. Insulin: It consists of a variety of molecules of fructofuranose bound together in chains. It is found in Dahlia, Artichoke, etc. tubers.

Heteropolysaccharides

A polysaccharide is classified as a heteropolysaccharide that includes various forms of monosaccharides. Any of the heteropolysaccharides that are important are:

1. Hyaluronic acid: D-glucuronic acid and N-acetyl-glucosamine are composed of this acid. It is located in tissues and skin that are connective.
2. Heparin: It consists of D-glucuronic acid, L-iduronic acid, N-sulfo-D-glucosamine, which is circulated primarily in the blood and mast cells.
3. Chondroitin-4-sulfate: D-glucuronic acid and N-acetyl-D-galactosamine-4-O-sulfate are the constituent sugars. It is found in the cartilage.
4. Gamma globulin: The base sugars of this polysaccharide are N-acetyl-hexosamine, D-mannose, D-galactose. It is present in the blood.

Functions of Polysaccharides

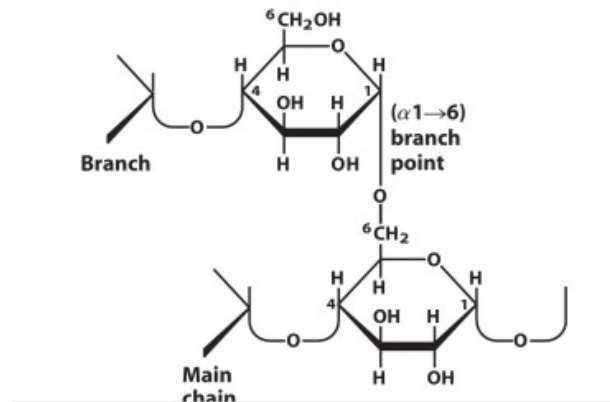
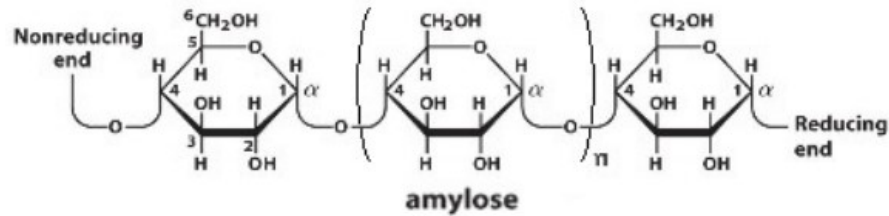
The polysaccharides in animals and plants function as a systemic organization. Some polysaccharide roles include:

1. In species, they store electricity.
2. Owing to the presence of many hydrogen bonds, the molecules that make them hydrophobic will not be invaded by water.
3. They allow for changes in the gradient of concentration, which affects the cells' intake of nutrients and water.
4. To form glycolipids and glycoproteins, often polysaccharides become covalently bound with lipids and proteins. This glycolipids and glycoproteins are used within and within the cells to transmit messages or signals.
5. They provide the cells with encouragement. The plant cell wall is composed of cellulose polysaccharide, which provides insulation for the plant cell wall. Chitin plays a significant function in supplying protection for the extracellular matrix around the cells in insects and fungi.

Cellulose: It is glucose connected to unbranched beta 1-4. In plants, it plays a structural function. Mammals are indigestible.

Amylose: D-Glucose-linked unbranched α 1-4 is

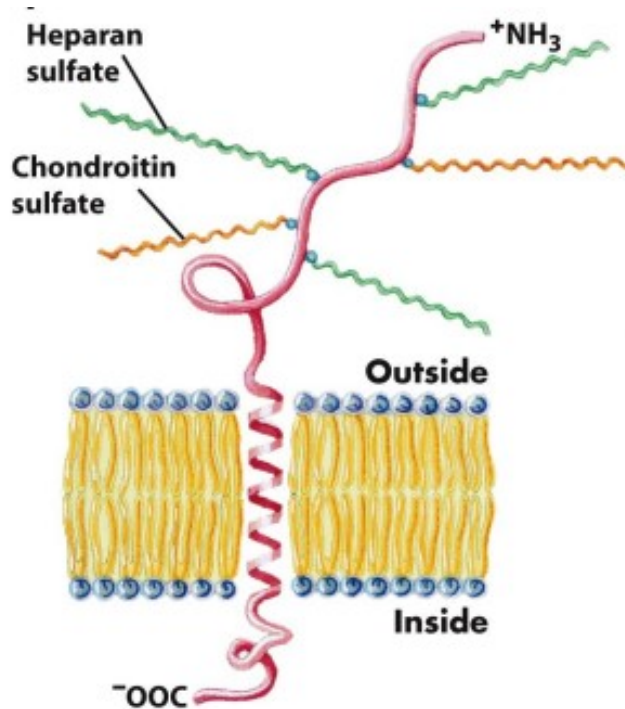
Glycogen: It is amylose for every 8-12 residues of the α 1-6 branch



Glycogen

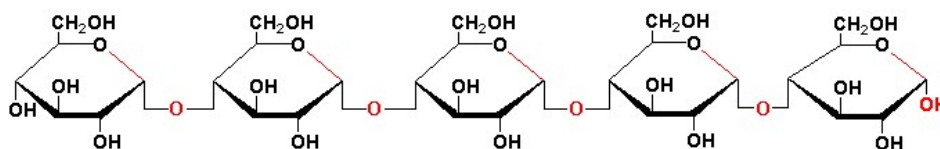
Reference: Lehninger Principles of Biochemistry.

Proteoglycans: Proteoglycans are highly glycosylated proteins. The simple proteoglycan unit consists of one or more covalently bound glycosaminoglycan (GAG) chain "core protein" (s). They are cell-surface or extracellular matrix macromolecules. It comprises of a membrane or secreted protein and one or more covalently bound glycosaminoglycan chains to the Ser-Gly-X-Gly series.



Reference: Lehninger Principles of Biochemistry

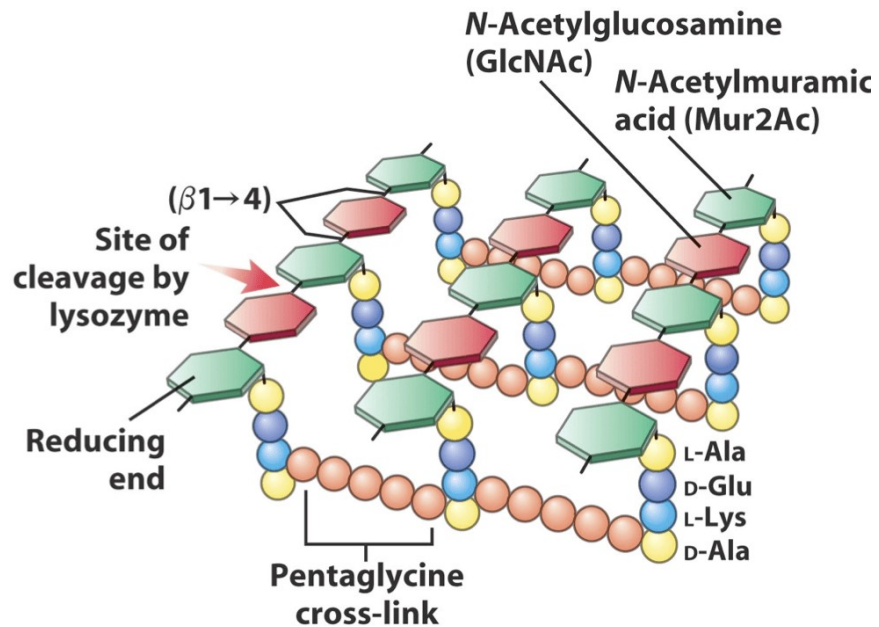
Starch: A polymeric carbohydrate composed of a large number of glucose units connected by glycosidic bonds is starch, or amylum. This polysaccharide is generated as an energy store by most green plants. It is the most popular human dietary carbohydrate and is present in staple foods such as potatoes, wheat, maize (corn), rice, and cassava in significant quantities.



Reference: Lehninger Principles of Biochemistry

An necessary and unique part of the bacterial cell wall is peptidoglycan or murein. Peptidoglycan is a heteropolymer made up of strands of glycan crosslinked by peptides. The glycan backbone is composed of N-acetylglucosamine and N-acetylmuramic acid alternating units connected by β -1,4-glycoside bonds. The subunits of peptides typically comprise four alternating L- and D-amino acids and are bound by the lactyl groups of the N-acetylmuramic

acid residues to the glycan stands. In general, cross-linking of the glycan strands occurs between the D-Ala carboxyl group at position 4 and the diamino acid amino group at position 3, either directly or by a short peptide bridge.

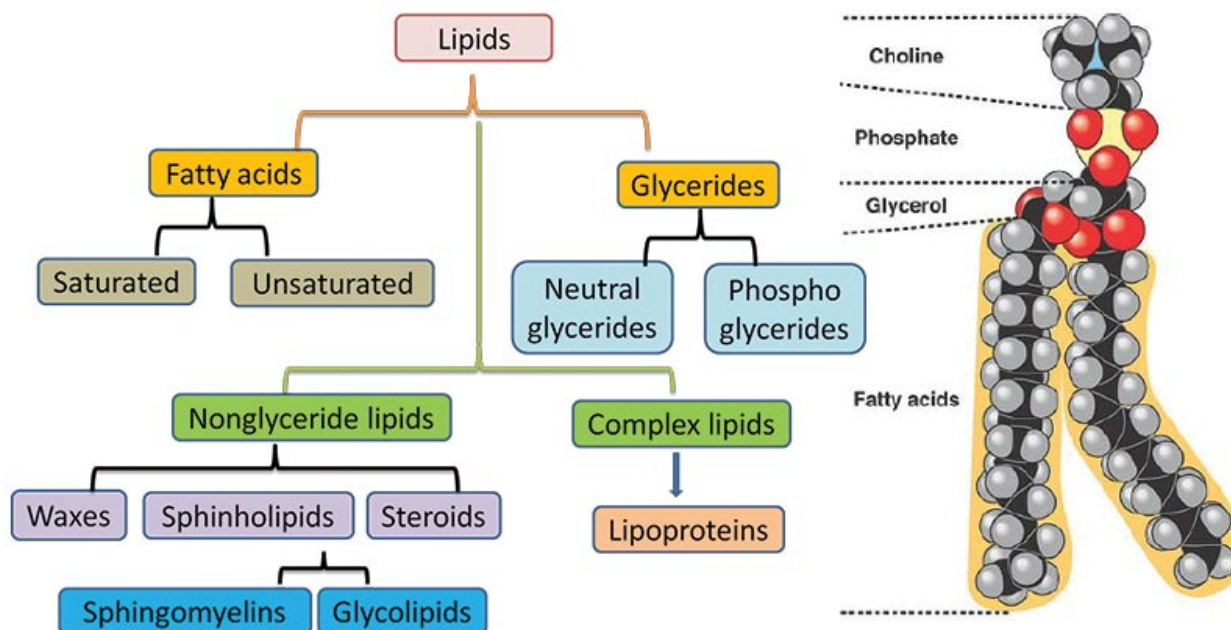


Reference: Lehninger Principles of Biochemistry

6. Lipids

Lipids are a heterogeneous group of organic compounds insoluble in water and soluble in organic solvents which are non-polar.

They exist naturally in most plants, animals, and microorganisms, and are used as components of the cell membrane, molecules of energy storage, insulation, and hormones.



Reference: Sagar Aryal, 2018. Microbe notes.

- Either liquids or non-crystalline solids at room temperature can be lipids.
- Colourless, odorless, and tasteless are pure fats and oils.
- Energy-rich organic molecules are
- Insoluble in water
- Soluble in alcohol, chloroform, acetone, benzene, etc. organic solvents
- No ionic charges
- There are high concentrations of saturated fatty acids in stable triglycerols (fats).
- There are high concentrations of unsaturated fatty acids in liquid triglycerols (oils).

Structure:

- Lipids are composed of carbon, hydrogen and oxygen components, but have a much smaller water proportion than other molecules, such as carbohydrates.
- Lipids are not polymers, unlike polysaccharides and proteins, which lack a repeated monomeric unit.
- They are made from two molecules: Glycerol and Fatty Acids.
- A glycerol molecule consists of three atoms of carbon with a hydroxyl group bound to it and atoms of hydrogen occupying the remaining positions.
- Fatty acids consist of an acid group and a hydrocarbon chain at one end of the molecule, usually denoted by the 'R' letter.
- Saturated or unsaturated, they can be.
- If a potential bond is made with a hydrogen atom, a fatty acid is saturated, so that no C = C bonds remain.
- On the other hand, unsaturated fatty acids do contain C = C bonds. One C=C bond has monounsaturated fatty acids, and more than one C=C bond has polyunsaturated fatty acids.

Structure of Triglycerides

- Triglycerides are lipids which consist of one molecule of glycerol bonded with three molecules of fatty acids.
- The bonds are covalent between the molecules and are termed Ester bonds.
- During a condensation reaction, they are formed.
- The charges are scattered uniformly around the molecule such that hydrogen bonds do not form with water molecules that make them insoluble in water.

Lipids can be classified according to their hydrolysis products and according to similarities in their molecular structures. Three major subclasses are recognized:

1. Simple lipids

- (a) Fats and oils which yield fatty acids and glycerol upon hydrolysis.
- (b) Waxes, which yield fatty acids and long-chain alcohols upon hydrolysis.

Fats and Oils

- Triacylglycerols are called all forms of compounds because they are esters consisting of three fatty acids, trihydroxy alcohol, joined to glycerol.

- The differentiation is on the basis of their physical environments at room temperature. If it is solid at 25°C, it is common to name a lipid a fat, and oil if it is a liquid at the same temperature.
- These variations in melting points indicate differences in the constituent fatty acids' degree of unsaturation.

Waxes

- Wax is a long-chain alcohol (generally mono-hydroxy) ester and a fatty acid.
- The acids and alcohols usually present in waxes have length chains on the order of 12-34 carbon atoms.

2. Compound lipids

- (a) Phospholipids which, upon hydrolysis, produce fatty acids, glycerol, amino alcohol, sphingosine, phosphoric acid and alcohol containing nitrogen.

Based on the alcohol group present, they may be glycerophospholipids or sphingophospholipids (glycerol or sphingosine).

- (b) Glycolipids that include hydrolysis of fatty acids, sphingosine or glycerol, and a starch. Depending on the alcohol group present, they can also be glyceroglycolipids or sphingoglycolipids (glycerol or sphingosine).

3. Derived lipids:

Related lipids are referred to as hydrolysis results of basic and compound lipids. Fatty acids, glycerol, sphingosine, and steroid derivatives are included.

Phenanthrene compounds that are very distinct from lipids made up of fatty acids are steroid derivatives.

Fatty acids

- Lipids are derived from two molecules: fatty acids and glycerol.
- Fatty acids consist of an acid group and a hydrocarbon chain at one end of the molecule, usually denoted by the 'R' letter.
- Saturated or unsaturated, they can be.
- If a potential bond is made with a hydrogen atom, a fatty acid is saturated, so that no C = C bonds remain.

- On the other hand, unsaturated fatty acids do contain C = C bonds. One C=C bond has monounsaturated fatty acids, and more than one C=C bond has polyunsaturated fatty acids.

Lipids are a distinct category of biological molecules, but they are composed of a hydrocarbon chain that ends with bound oxygen and hydrogen groups, and have the general property of not being at least partially soluble in water. They are important to all life forms and are the primary component of any cell membrane on Earth. For animals and other species, some of the main properties of lipids include energy conservation, while others are listed below:

1. Solubility: Lipids are soluble but insoluble in water in non-polar solvents (ether, chloroform, benzene, etc.).
2. Consistency: They are colourless, tasteless and odorless. They have a specific gravity of 0.86 and they are lighter than water. The stability of lipids depends on saturated and/or unsaturated fatty acids being present.
3. Hydrolysis: It is caused by the action of the enzyme lipase in the presence of acids or alkalis. Acid hydrolysis contributes to the formation of glycerol and the long fatty acid chain, while alkaline fat hydrolysis leads to the formation of fatty acid sodium or potassium salts such as soaps and the process is known as saponification.
4. Hydrogenation: converting liquid vegetable oil to solid vegetable ghee by reacting with hydrogen gas at a temperature of 200°C in the presence of a catalyst (Ni).
5. Emulsification: As water is rubbed with fats or oils, the large lipid molecules split into smaller emulsion-forming molecules, and the process is called emulsification.
6. Rancidity: An unpleasant and unwanted odor is created when lipids are exposed to the environment (heat, light, air, moisture) for more than 30 days. These lipid forms are referred to as rancid lipids, and the phenomenon is known as rancidity.

Rancidity is of two types:

(a) Hydrolytic and (b) Oxidative

a. Hydrolytic Rancidity: This type of phenomenon happens during fat hydrolysis due to the release of volatile acids.

b. Oxidative rancidity: The condition is called oxidative rancidity as a component of unsaturated fatty acid is oxidized to create aldehyde ketone.

Physical properties of lipids

FAs type crystals composed of layered molecular layers. The thickness of each sheet of two extended molecules is structured in such a way that the two faces are formed by the water-loving (hydrophilic) carboxylic acid groups and the inner center is outlined by the water-fearing (hydrophobic) chains. The particulars of molecular packing which vary in the formulation of various crystal structures called polymorphs in the case of particular FAs. Biologically important SFAs have melting temperatures over 27°C (81°F) and increase with the length of the hydrocarbon chain escalating.

At much lower temperatures than their saturated molecules, polyunsaturated and monounsaturated molecules liquefy. Melting temperatures are lowest of most biological molecules when the C=C is located in near proximity to the middle of the hydrocarbon chain. These molecules form viscous liquids at room temperature and the hydrophobic structure of most FAs exceeds the hydrophilic character of carboxylic acid, providing very squat aqueous solubility of these molecules. For example, with any CH₂ group, additional energy is needed to arrange the water molecules of FA in the hydrocarbon chain region, resulting in a hydrophobic effect.

The group of carboxylates separates a positively charged hydrogen ion to a very small degree in pure water, thus reflecting the equation described below:



Where R signify the hydrocarbon chain.

Chemical properties

Chemically, the most reactive element is the acidic carboxyl group (COOH) of the fatty acid. It reacts with alcohols (R'OH) to yield water molecule releasing esters (RCOOR'). In complex lipids, FA moieties are connected to other groups by the ester (main covalent) bond. The ether bond (R'-O-R, second chemical) also binds FAs and is chemically more stable than the ester bond.

In fatty acids, with the exception of C=C, the hydrocarbon component is relatively defiant to chemical attack, and various molecules react with identical double bonds. For example, hydrogen attaches to the double bond to give an SFA when platinum is present as a catalyst.

Halogens (iodine, chlorine, bromine) and their derivatives (hydroiodic acid) often retort to structure the SFAs with the double bond, but herein the halogen (one or two atoms) share the atoms of hydrogen (one or two) normally endowed in the saturated acyl chain. In enzymatically catalyzed oxidation reactions or in non-enzymatic systems, C=C may also react with oxygen. A number of products are produced by the process, many of which add to the stale smell of vegetable products and spoiled meat. It is widely understood that heavily unsaturated fatty acids are oxidized more quickly.

Sap value:

The Saponification Value or Saponification Number (SV or SN) is the number of milligrams of potassium hydroxide (KOH) needed under the stated conditions to saponify one gram of fat. It is a measure of the average molecular weight of all the fatty acids found as triglycerides in the sample (or chain length). The higher the saponification value, the smaller the average length of the fatty acids, the lighter the average triglyceride molecular weight, and vice versa. Fats or oils with a high saponification value (such as coconut and palm oil) are technically more acceptable for soap production.

Acid value:

The mass of potassium hydroxide (KOH) in milligrams that is needed to neutralize one gram of chemical material is the acid value (or neutralization number or acid number or acidity). The number of acids is a measure of the number of groups of carboxylic acids in a chemical compound, such as a fatty acid, or in a compound mixture. A known quantity of sample dissolved in an organic solvent (often isopropanol) and titrated with a known concentration solution of potassium hydroxide (KOH) using phenolphthalein as a color indicator in a standard technique.

Iodine number:

In chemistry, the value of iodine (or the value of iodine adsorption or the number of iodine or iodine index, usually abbreviated as IV) is the mass of iodine in grams absorbed by 100 grams of a chemical material. For calculating the amount of unsaturation in fats, oils and waxes, iodine numbers are also used. Insaturation happens mostly in fatty acids as double bonds and are very

reactive to halogens, in this case iodine. Therefore, the greater the value of iodine, the more fat is unsaturated. From the table, it can be seen that coconut oil is very saturated, which means it is ideal for soap production. In the other side, it is heavily unsaturated linseed oil, which makes it a drying oil.

Rancidity:

Rancidification is the mechanism by which fats and oils are fully or incompletely oxidized or hydrolysed when exposed to sunlight, light, or moisture or by bacterial activity, resulting in an unpleasant taste and odor. In fact, it is the hydrolysis or autoxidation into short-chain aldehydes and ketones of fats that are intolerable in taste and smell. Unwanted odors and tastes can result when these processes occur in food.

However, in some situations, the flavors may be attractive (as in aged cheeses). These flavours are collectively known as warmed-over flavours of processed meats.

Rancidification, since certain vitamins are susceptible to oxidation, may also distract from the nutritious value of food. Oxidative oxidation also happens in other hydrocarbons, such as lubricating oils, fuels, and industrial cutting fluids, close to rancidification.

Glycerolipid, Sphingolipid and Lipid derived from isoprene

- Glycolipids are lipids bound by a glycosidic (covalent) bond with a carbohydrate. Their function is to preserve the cohesion of the cell membrane and to promote the identification of cells, which is important for the immune response and for the tissue-forming connections that enable cells to communicate with each other. On the surface of all eukaryotic cell membranes, glycolipids are located where they reach into the extracellular environment from the phospholipid bilayer.
- Glyceroglycolipids: a sub-group of glycolipids characterized as a lipid complex by an acetylated or non-acetylated glycerol containing at least one fatty acid. Photosynthetic membranes and their functions are also correlated with glyceroglycolipids. The glyceroglycolipid subcategories depend on the attached carbohydrate.
- Glycosphingolipids: a subgroup of sphingolipid related glycolipids. In nervous tissue, glycosphingolipids are mainly found and are responsible for cell signaling.

- Sphingolipids, a set of aliphatic amino alcohols that include sphingosine, are a family of lipids containing a backbone of sphingoid bases. They were found in brain samples in the 1870s and, because of their mysterious existence, were named after the mythological sphinx. In signal transduction and cell recognition, these compounds perform important roles. Sphingolipidoses, or sphingolipid synthesis diseases, have a clear affect on neural tissue. A ceramide is a sphingolipid with a R group consisting only of a hydrogen atom. Phosphocholine, yielding sphingomyelin, and various sugar monomers or dimers, yielding cerebrosides and globosides, respectively, are other common R groups. Cerebrosides and globosides are collectively known as glycosphingolipids.
- Isoprene-derived lipids: Terpenoids or prenol lipids are often referred to. Isoprenoids refer to a class of organic compounds composed of two or more units of hydrocarbons, with five carbon atoms grouped in a particular pattern in each band. These compounds are derived from five-carbon isoprene units and are biosynthesized from a natural intermediate that is itself synthesized from acetyl-CoA, known as mevalonic acid.
- These lipids are known to be the largest group of natural products that play a wide range of roles in plant and animal physiological processes and have a variety of commercial applications.
- These compounds differ in action in living species, from pigmentation and fragrances to vitamins and sex hormone precursors. Applications in manufacturing environments vary from chemical flavorings, solvents and raw materials. More generally, these compounds are related to being the primary ingredients in perfumes and incense. But these are just a handful of the numerous industrial applications of isoprenoids, which are still growing to this day.

Behavior of lipid in water

- Self-orientation of amphipathic lipids in oil:water interfaces. Membranes, Micelles, Liposomes, & Emulsions shape them. As they contain a predominance of nonpolar (hydrocarbon) groups, lipids are typically insoluble in water. However, there are polar groups of fatty acids, phospholipids, sphingolipids, bile salts, and, to a lesser degree, cholesterol. Therefore, part of the molecule is hydrophobic or insoluble in water, and part of it is hydrophilic or soluble in water. They classify those molecules as amphipathic.

They are based on oil:water interfaces in the water phase with the polar group and in the oil phase with the non-polar group.

- In biological membranes, a bilayer of such amphipathic lipids has been considered as a basic structure. They form micelles when a critical concentration of these lipids is found in an aqueous medium. In order to promote the absorption of lipids from the intestine, aggregations of bile salts into micelles and liposomes and the development of mixed micelles with products of fat digestion are necessary. By sonicating an amphipathic lipid in an aqueous medium, liposomes can be produced. They consist of lipid bilayer spheres which enclose part of the aqueous medium.
- They are of potential therapeutic benefit as carriers of drugs in the bloodstream, targeted to particular organs, eg, particularly when paired with tissue specific antibodies. In Treatment for Cancer. Furthermore, they are used for gene transfer into vein cells and as topical and transdermal carriers.

Bile acids, bile salts, plasma lipoproteins

Bile acids are steroid acids that are primarily present in mammalian bile and other vertebrates. Diverse bile acids in the liver are synthesized. To give anions called bile salts, bile acids are conjugated with taurine or glycine residues.

Those synthesized by the liver are primary bile acids. Bacterial actions in the colon originate from secondary bile acids. In humans, the main bile salts are taurocholic acid and glycocholic acid (cholic acid derivatives) and taurochenodeoxycholic acid and glycochenodeoxycholic acid (chenodeoxycholic acid derivatives). In concentration, they are approximately equivalent. The salts of their 7- α -dehydroxylated derivatives, deoxycholic acid and lithocholic acid, are also present, with more than 90% of human bile acids being derivatives of cholic, chenodeoxycholic and deoxycholic acids.

Around 80% of the organic compounds in bile acids contain bile acids (others are phospholipids and cholesterol). An increased bile acid production causes an increase in bile flow. Bile acids make food fats and oils easier to absorb. They function as surfactants that form micelles, which encapsulate nutrients, making their absorption simpler. Prior to further processing, certain micelles are suspended in the chyme. There are also hormonal activities of bile acids within the body, particularly through the farnesoid X receptor and GPBAR1 (also known as TGR5).

Plasma Lipoproteins

Lipoproteins are complex lipid and protein aggregates ('particles') that make hydrophobic lipids compliant with the aqueous environment of body fluids and allow both vertebrates and insects to be transported across the body to tissues where they are needed. Because of their therapeutic relevance, a very high percentage of lipoprotein study deals with their health-related roles in humans, and this is illustrated by the topic that follows. It is primarily in the intestines and liver where lipoproteins are synthesized.

These aggregates are in a state of continuous change within the bloodstream, varying in form and physical shape as the different components are picked up by the peripheral tissues before the remains return to the liver. Triacylglycerols, free cholesterol, cholesterol esters and phospholipids (especially phosphatidylcholine and sphingomyelin) are the most abundant lipid constituents, while fat-soluble vitamins and antioxidants are also transported in this manner. Free (unesterified) fatty acids and lysophosphatidylcholine are bound by hydrophobic forces in plasma to the protein albumin and are detoxified in effect.

The lipoproteins that circulate are structurally and metabolically distinct from the proteolipids that contain fatty acids or other lipid moieties that are covalently connected.

Vesicles and membrane transport

A vesicle composed of liquid or cytoplasm surrounded by a lipid bilayer, is a structure inside or outside a cell. During the processes of secretion (exocytosis), uptake (endocytosis) and transfer of materials inside the plasma membrane, vesicles form naturally. They may alternatively be artificially prepared, in which case they are called liposomes (not to be confused with lysosomes). They are called unilamellar liposome vesicles if there is only one phospholipid bilayer; otherwise, they are called multilamellar. A lamellar step, similar to that of the plasma membrane, is also the membrane enclosing the vesicle, and intracellular vesicles which fuse with the plasma membrane to release their contents outside the cell. Vesicles can fuse inside the cell with other organelles as well. As an extracellular vesicle, a vesicle expelled from the cell is identified.

A number of roles are performed by Vesicles. As it is isolated from the cytosol, it is possible to make the inside of the vesicle distinct from the cytosolic environment. Vesicles are a fundamental instrument used by the cell to organize cellular substances for this purpose. In

metabolism, transport, buoyancy regulation and temporary food and enzyme storage, vesicles are involved. They will serve as chambers for chemical reactions as well.

Transport across cell membrane

In addition, all cells are isolated by a plasma membrane from their surrounding world. In addition, intracellular membranes that form the borders and internal configurations of separate organelles compartmentalize the eukaryotic cells. These biological membranes are semi-permeable in nature, so their permeability properties mean that the specific molecules and ions quickly reach the cell and the waste products exit the cell. The activity of particular transport proteins present on the cell membrane mediates these motions of solutes through the cell.

For ion movements, such as Na^+ , K^+ , Ca^{2+} , and Cl^- , as well as metabolites such as pyruvate, amino acids, sugars, and nucleotides, and even water, such proteins are therefore needed. Transport proteins are also responsible for phenomena such as neurotransmission that are biologically electrochemical.

Types of transport process:

Two types of transport process occur across the membrane.

1. Non-mediated transport
2. Mediated transport

Via the basic diffusion mechanism, non-mediated transport occurs and the driving force for the transport of a material through a medium depends on the gradient of its chemical potential. Unique carrier proteins are necessary for mediated transport. The material thus diffuses in the direction in which its concentration gradient is eliminated; at a rate proportional to the magnitude of this gradient, and also based on its solubility in the non-polar center of the membrane. Based on the thermodynamics of the system, mediated transport is divided into two groups.:

1. Passive-mediated transport, or facilitated diffusion: A particular molecule flows from high to low concentrations in this type of process.
2. Active transport: A particular molecule is transferred in this type of process from a low concentration to a high concentration, that is, against the gradient of its concentration. To make it favorable, such an endergonic mechanism must be coupled to a sufficiently exergonic system ($\Delta G < 0$).

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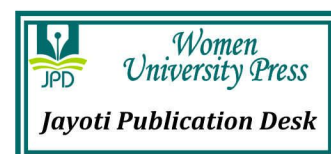
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