Chemistry and the Life

INTRODUCTION

Humans are only one of a wide variety of forms of life inhabiting the earth. Over the years, humans have considered themselves to be a unique form of life. But, what is the difference between humans and other forms of life? The difference is usually one of size, shape, or function. While there are obvious physical differences, is there really a difference in the chemistry of the various forms of life on earth. Today we believe that humans, rather than being unique, are one of many forms of life that obey certain basic principles of chemistry. This idea has slowly evolved during the past century from the work of many scientists in many fields. Let us briefly examine how this idea developed.

On the basis of countless experiments in the fields of medicine, physiology, biology, and chemistry, scientists believe today that life is a series of complex chemical reactions. All these chemical reactions, no matter how complex, obey the laws of science. No new laws of science are yet needed to account for the chemical reactions involved in the process of life. Therefore, there is no special chemistry of the living system, and cells, the basic unit of living systems, must obey the laws of chemistry.

On inescapable conclusion is reached from this view of living systems. But how can such an abstract knowledge of chemistry enable us to understand the chemistry of the complicated reactions found in living systems? The answer is the following. Before we can study the chemistry of complex molecules, we must learn the basic rules of how atoms combine to form simple molecules. Furthermore, we must learn certain principles of chemistry that have important applications to living systems. Once we understand these basic principles of chemistry, we can then examine the structure and chemical reactions of small molecules, which serve as models for the giant molecules found in living systems. We can then apply this knowledge to study the chemistry of the molecules of living systems.

The matter

Scientists define matter as **anything that has mass and occupies space.** This definition is so broad that it includes almost everything in the word.

1- Classifying matter: matter classified as either a mixture or a pure substance. A mixture contains a number of different substances more or less mixed together. A mixture has no unique set of properties. Rather, it has the properties of all the substances that are a part of it. For example, air is a gaseous mixture made up of nitrogen, oxygen, argon, water vapor, and carbon dioxide. Each of these substances retains its own physical properties in the mixture.

A mixture is either **heterogeneous** or **homogeneous**. The parts of a heterogeneous mixture are visibly different. For example, a mixture of sand and gravel is a **heterogenous mixture** because the individual pieces of sand and gravel are clearly visible. The parts of a **homogenous mixture** cannot be detected even with a microscope. For example, a salt and water solution is a homogenous mixture because the presence of the salt cannot be seen.

A mixture can be separated into its parts by using the differences in the physical properties of the parts.

2- Composition of matter : *atoms* are the fundamental units of elements. An element is a substance that contains only one kind of atom. There are only 106 elements, so there are only 106 different kinds of atoms. Many elements are quite familiar to us. The precious metals gold, silver, and platinium and the less precious but still useful metals copper, aluminum, and iron are elements. Mercury, a liquid, and helium, a gas, are other examples of elements.

Atoms combine to form *molecules*. They combine according to certain well-defined principles. A substance that contains only one kind of molecule is called a pure compound. A molecule is the smallest particle that has the properties of a pure compound.

The relationship between atoms and molecules is similar to that between the letters of the alphabet and words. There are 26 letters in the English alphabet and these can be combined according to definite rules to form millions of words. Similarly, the 106 atoms combine according to definite rules to form millions of molecules. These relatively few atoms are the fundamental units of all matter.

Matter, made up of atoms or molecules, exists in three different states: **gaseous**, **liquid**, and **solid**.

3- Physical and chemical changes: Everything in the world undergoes change.

•Chemical changes : result in the disappearance of one or more substances and the formation of new ones. For example: propane and some oxygen from the air disappear to form carbon dioxide and water vapor. Both these substances have different physical properties that distinguish them from propane and oxygen. Chemical changes are usually called *chemical reactions.*

•physical changes: No new substances are formed, for example: the freezing of water.

During chemical reactions and physical changes, energy is either released or absorbed.

4- Energy and its transfer: The word energy is used to refer activity. We also speak of the energy that can be obtained from petroleum. But we cannot see, taste, or smell energy. Unlike matter, energy does not occupy space; we can feel its effects. Energy is not a thing but is more like a characteristic of a substance.

All matter has energy. This energy has many forms. Potential, kinetic, chemical, atomic, and radiation energy are common types. The energy of any object changes whenever it undergoes a chemical reaction or physical change. This energy change occurs by transferring energy. For example; part of the energy of wood is transferred to the surrounding air when it is burned. The energy is transferred by several methods. Four of the most common are work, heat, sound, and light.

Chemical reactions involved in our body also demonstrate the transfer of energy. The food we eat provides the energy that allows our bodies to carry out the normal work of contraction and motion. Food also provides us with heat to maintain a constant body temperature. Food undergoes a series of chemical reactions in our bodies that result in the transfer of part of the chemical energy to muscles to do work and to do surroundings s heat.

5-Energy and life:

The source of all our energy is the sun. the energy transfers by sunlight to the earth, where it is stored for future use as chemical energy in the molecules of plants. This transfer occurs by a process called *photosynthesis*. By this process produce the chemical energy from precursor. This chemical energy can be used in a number of ways. The plant can be transfer a part of this energy into work and heat to allow the plant to live and grow. The plant can be used as food for humans and animals. The molecules of the plant, when digested, undergo more chemical reactions. Which transfer energy wherever needed by animals and humans.

Energy transfer, not only among the sun, plants, and animals, but also among the various parts of living organisms, is absolutely essential to life.

The transfer of energy does not stop with humans. After death, plants, animals, and humans decay. Any remaining energy is transferred into other forms outside the animal world. Although this energy is lost in a biological sense, it is never really lost. For example, the energy available to us in coal is the remains of the energy of plants that died long ago and were transformed into coal by a geological process

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The international system of units (SI)

The international system of measurement was the metric system. This is a decimal system, which means that larger and smaller parts of the basic unit are obtained by multiplying or dividing by ten. The metric system was extensively revised in 1960 and was given a new name, International System of Units. its official abbreviation is **SI**. SI is still a decimal system, and many of the units are the same in SI and metric system.

There are fractions and multiples of each basic unit of SI. Each has a characteristic name obtained by adding a prefix to the basic name of the unit. The prefix tells us how many times the basic unit has been divided or multiplied by ten.

Table (1) SI Prefixes

Prefix	Symbol	Meaning	
tera-	T	10^{12}	basic unit
giga-	G	10^{9}	= =
mega-	M	10^{6}	= =
kilo-	K	10^{3}	= =
deci-	d	10^{-1}	= =
centi-	c	10^{-2}	= =
milli-	m	10^{-3}	= =
micro-	μ	10^{-6}	= =
nano-	n	10^{-9}	= =
pico-	p	10^{-12}	= =

Let us learn the SI units of distance, mass, and volume and learn how to use these prefixes.

1- Length:

The basic unit of length or distance in SI is the *meter*. The most commonly used fractions of the meter are the centimeter and the millimeter. The kilometer is the most common multiple of the meter. This name of each units tell us the relationship between it and the basic unit.

For example: the word centimeter is the made up of two parts, the prefix centi- indicating 1/100, and the basic unit is meter. Therefore, a centimeter is one one-handredth of a meter. Similarly, a kilometer is one thousand meters, and .....et.

- Small units used to measure the short distances.
- Large units used to measure the distances between cities .

Table (2)

Prefix	Symbol	Relationship to meter
tera-meter	Tm	10^{12} m
giga-	Gm	10^{9} m
mega-	Mm	10^{6} =
kilo-	Km	10^{3} =
Meter	M	m
deci-	dm	10^{-1} =
centi-	cm	10^{-2} =
milli-	mm	10^{-3} =
micro-	μm	10^{-6} =
nano-	nm	10^{-9} =
pico-	pm	10^{-12} =

2- Mass: The terms mass and weight are used interchangeably in everyday usage. There are difference between the two terms.

***Mass**: defined as the amount of material in a certain object compared to a reference standard mass.

***Weight**: is the measurement of the attraction of the earths gravity for the mass of the object.

The SI unit of mass is the (g) gram, the most commonly used fractions are the gram (g) . the milligram (mg) and the microgram (μg).

Construct a table similar to table (2) indicating the relationship among; Tg, Gg, Mg, kg, g, dg, cg, mg, μg, ng and pg.

3- Volume: The SI unit of volume is the cubic meter. Its symbol is m^3. a cubic meter is very large unit, its not used very often by chemistry.

The liter (L) is the most commonly used unit of volume.

$$1000L = 1M^3$$

- fraction of litter are the millileter (ml) and centiliter (CL).
- One milliliter identical to one cubic centimeter, whose symbol is cm^3.

- Old symbol for cm^3 (CC).

1 cubic meter (m^3) = 1000 liters (L)
1 liter = 1000 milliliter (ml)
1 milliliter (ml) =1000 microliters (µl)

SI : TL, GL, ML, KL, L, dL, Cl, ml, and Pl.

The relationship between some standard units in the following table:

Table (3)

	U.S Unit	Abbreviations for U.S. Unit	SI Unit
Length	1 inch	in.	2.54 cm
	1 yard	yd	0.914m
	1 mile	mi	1.60 km
Mass	1 pound	Ib	454 g
	1 ounce	oz	28.4g
	1 dram	dr	3.88 g
	1 grain	gr	0.0648 g
Volume	1 pint	pt	0.473 L
	1 quart	qt	0.946 L
	1 gallon	gal	3.78 L

4- Temperature: We determine how hot or cold an object is by measuring its temperature. We measure temperature by means of thermometers. The principle of a thermometer is based on the fact that most substances expand when heated and contract when cooled. The IS unit of temperature is the Kelvin (K) .

$$K = {}^\circ C + 273.15$$

$$F = \frac{9}{5}\,{}^\circ C + 32 \qquad (F = \text{Fahrenheit})$$

Ex: convert 40°C to F ?

5-Density and Specific gravity: Often we say that lead is heavier than aluminium. Such a statement is not always correct, because it does not take into account the relative sizes of the samples of the two materials. If the two samples are the same size, it is true that the one made of lead weight more than the one made of aluminium. We express this difference in weight by saying that lead has a higher

density than aluminium. So we may be using the Density.
Density: The ratio of the mass of a material to its volume. We seen the density using the volume of the sample and mass.

$$* \text{ Density} = \frac{\text{mass of sample}}{\text{volume of sample}}$$

$$* \text{ Specific gravity} = \frac{\text{density of material}}{\text{density of water}}$$

*Density of water at 25°C is 1 g/ml

Review of terms:

-Specific gravity: The ratio of the density of any object to the density of water at same temperature.
-Atoms : The smallest partical that has all the properties of an element.
-Hydrometer: an instrument used to measure specific gravity.
-Chemical change: result in the disappearance of one or more substance and the formation of new ones. There are usually called chemical reaction.

* No new substances are formed in a physical change.

Convert form the system of units: To convert form the system of units used in united states to SI units we must know the equivalents of two systems.

Ex: convert 5IN to cm?

As: 1 IN = 2.54 cm
Therefore: 1 IN = 2.54 X 5 = 12.7 cm

Inorganic chemistry

SOLUTIONS AND COLLOIDS

Atoms : defined as the smallest representative sample of an element. Only 106 different kinds of atoms are known to exist. Each element has a symbol and a name. the symbol is made up of one or two letters taken from the name of the element. The 106 elements can be listed in a number of ways. One way is to list them alphabetically. Another and more useful way is to arrange the elements in the ***periodic table***.

Periodic Table: Arrange the elements depending of chemical and physical properties. The periodic table consist of a number of columns called ***groups***. The horizontal rows are called ***periods***. The elements in each group have similar chemical and physical properties. For example, the elements in the far right of periodic table, called the noble gases.

The element in group **IA** are called the alkali metals. Those in group **IIA** are called the alkaline earth metals the transition metals are the elements located in groups **IIIB** to **IIB**. The halogens are the elements in group **VIIA**. All the nembers of a groups have similar physical and chemical properties.

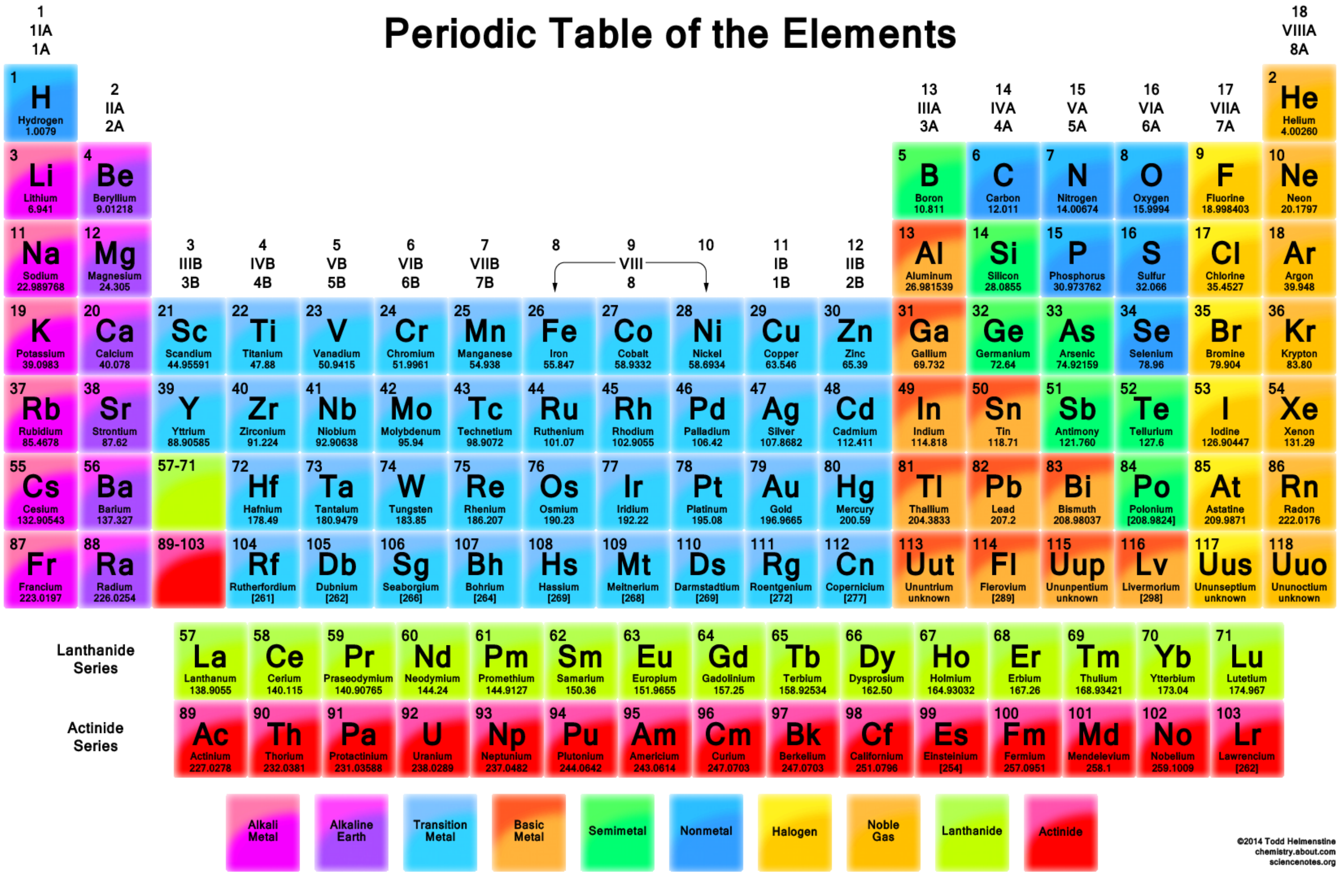
The elements are divided into three classes depended on their physical properties. Element that show a metallic luster when polished, capable of being drawn out into wire, can be hammered into sheets, and are good condectors of heat and electricity are classed as ***metals***. elements that do not have these properties are classed as ***nonmetals***. A class between these two is called the ***metalloids elements***.

Only 90 of the 106 elements are found in nature. The others are prepared in the laboratory by instruments and techniques.

There are three particles that arranged in an atom, are ***electrons***, ***protons***, and ***neutrons***. Each of these particles are characteristic properties. The discovery of these particles was a major step toward determining the structure of atoms. But how are these particles arranged in an atom?

Three important subatomic particles

Name	Charge	Mass(amu)	Symbol
Electron	-1	1/1837	$\bar{e}$
Proton	+1	1.007	H^+, P^+, P
Neutron	0	1.004	n



Periodic Table of the Elements

1 1IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.0079																	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
Lanthanide Series		57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	
Actinide Series		89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]	

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Atomic numbers: all the atoms of an element have the same atomic number. The atomic number of an element is equal to the number of protons and in same time equal number of electrons in its nucleus. The importance of this statement became clear with the discovery of isotopes.

Mass number: the mas number of an atom is the sum of the number of protons and neutrons in its nucleus. For example; the mas number of hydrogen is 1, while in deuterium is 2.

Isotopes: Atoms whose nuclei have the same number of protons but different numbers of neutrons. For example; hydrogen atoms called **deuterium** atoms have nuclei that contain one proton and one neutron. The nuclei of hydrogen atoms called **tritium** atoms, when have one proton and two neutrons. Hydrogen is not the only element that has isotopes. Many other elements have two or more isotopes.

Atomic weight: The mass of an element is a weighted average of masses of all its isotopes. For example;

Average atomic mass of C = (0.9889)(12.00)+(0.0111)(13.00)
=12.01

Ions: there are two types of ions:

Positive ions; called cations, are formed when atoms lose electron. Such Na^+.

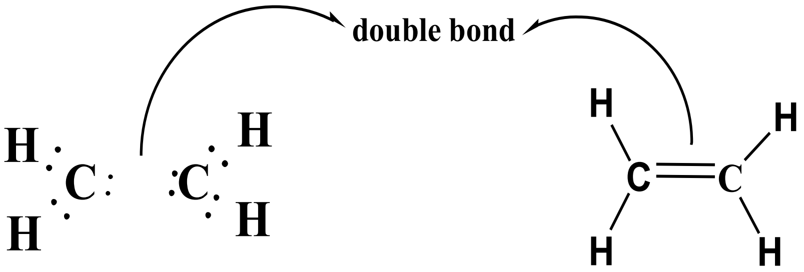
Negative ions; called anions, are formed when atoms gain electrons. Such Cl^-.

The charge on an ion is determined by the number of electrons it must gain or lose to achieve the electron arrangement of the nearest noble gas.

Chemical bonds: Molecules are made up of atoms joined together. This join is called chemical bonds.

a. ionic bonds; formed by a strong attraction between negative and positive ions. Anion and cations are formed in many chemical reactions by the transfer of one or more electrons from one element to another. For example; NaCl.

b. Covalent bonds; formed by sharing electrons to achieve a noble gas electron arrangement for each atom. Meaning a pair of electrons shared between two atoms. For example: H_2, Cl_2, O_2 and CH_2=CH_2.



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c. polar covalent bonds: The ability to attract electrons differs from atom to atom. Formed between two atoms of differents elements depends on the difference in their electronegativity. For example; in HCl (hydrogen chloride), the hydrogen and chlorine atoms share a pair of electrons. Because chlorine is more electronegative than hydrogen, the electron pair is drawn toward chlorine, giving it a partial negative charge and leaving a partial positive charge on the hydrogen.

$\delta+$ $\delta-$
H-----Cl

In a polar covalent bond, the more electronegative atom acquires a partial negative charge, and its less electronegative partner acquires a partial positive charge.

EX:	$\delta+$ $\delta-$ C-----N	$\delta+$ $\delta-$ C-----F	$\delta+$ $\delta-$ H-----O	$\delta+$ $\delta-$ H-----N

Atoms of the elements H, C, N, O, S and halogens form polar covalent bonds with atoms of other elements.

Chemical reaction: the chemical reaction occur around us, the burning of fuel, the rusting of iron, and the growth of plants and animals are all examples of chemical reactions. We represent these and other chemical reactions on paper by *chemical equations*. A chemical equation is a concise way of giving information about a chemical reaction. The compounds that react in a chemical reaction are represented by their chemical formulas in the chemical equation.

SOLUTIONS AND COLLOIDS

Solutions and colloids are essential to life. The solutions in living systems are aqueous, they are made with water. Therefore we must learn types of solutions and concentration of it, and used to explain their biologically important properties.

Solution: Homogenous mixture of molecules, atoms or ions of two or more different substance.

In the solution there are two substance which called components. One found in excess called the **Solvent**, and other is called **solute**. For example; solution of sugar in water, water is the solvent and sugar is the solute. The three states of matter can combine in nine different ways to form solution containing two components:

Taple ( ) Type of solutions

solvent	solute	Examples
liquid	liquid	Alcoholic beverages
Solid	liquid	An amalgam (mercury in silver)
Gas	liquid	-
Gas	solid	-
liquid	solid	Salt water
Solid	solid	metal alloys (brass or tin)
Gas	Gas	Air
liquid	Gas	carbonated beverages
Solid	Gas	hydrogen gas in palladium metal

-there is usually a limit to the amount of solute that can be dissolved in a solvent at particular temperature when this limit is reached, no more solute will dissolve in the solvent. When this happens we say that the solvent is saturated with solute, and called saturated solution.

Solubility: The amount of solute that dissolved in a given quantity of solvent to form the saturated solution. The solubility of a solute in a particular solvent depends on a number of factors:

1-kind of solvent
2-kind of solute
3-The temperature of the solvent
4-The pressure above the solvent.

The results of our experiences in the world have led to the very general rule that (like dissolves like). By this we mean that a polar solvent such as water is a good solvent for ionic compounds such as sodium chloride. Gasoline, a mixture of nonpolar organic compounds, is a good solvent for other nonpolar organic compounds such as oils.

The polar and nonpolar substances will not solutions such gasoline and water.

solubilities of several compounds in water

Compound	Solubility at 20°C (g/100ml)	Solubility at 100°C (g/100ml)
NaCl	36.2	39.1
NH_4Br	97.1	146.0
KBr	59.4	102.0
NH_3	47.5	6.9
KNO_3	37.8	247.0
O_2	0.00434	0.00080
Li_2CO_3	1.33	0.725
$Ca\ SO_4$	0.21	0.16

*Sometimes there is no limit to the amount of one substance that dissolve in another. This is particularly true for solution of a liquid in liquid.

1. Completely miscible: pair of liquids that are infinitely soluble in each other.

2. Partially miscible: other liquids are only slightly soluble in each other.

3. Immiscible: liquids that are insoluble in each other, ex. Gasoline immiscible water.

*Temperature of the solvent affect the solubility of the solute, in general solutes are more soluble in hot than cold solvents. Solubilities of several solids increasing greatly with increasing temperature, others increase only slightly. Other actually decrease. Above Table.

Gases are other compounds whose solubility in water decrease with increasing temperature. A familiar example is boiling water. The bubbles that form when water is heated are air escaping from solution because dissolved air is less soluble in water at higher temperatures.

Concentration of solutions

We describe the relative amounts of solute and solvent in a solution by means of units of concentration. There are several such units, and we will examine the most commonly used ones.

A- Weight/ Weight percent:

One way to specify the concentration of a solute in a solution is as a *percent by weight*. The concentration of the solute is given by the following equation (8-1):

$$\boxed{\textbf{percent by weight solute} = \frac{\textbf{weight of solute in g}}{\textbf{weight of solute in g + weight of solvent in g}} \times 100}$$

The following example shows how to express the concentration of a solute in the unit.

Example : What is the percent by weight of sugar in a solution made by dissolving 10 gm of sugar in 90 gm of water?

Step 1. Relate the quantities in equation 8-1 to those given in the problem:

Ans:

Weight of solute = 10 gm
Weight of of solute and solvent = 10+90=100gm

Then:

10gm / 100gm × 100 = 10%

Q/ Determine the percent by weoght of the solute in each of the following solutions?

(a) 1.5 gm of sodume chloride in 100gm water
(b) 3.5 gm of glucose in 250 gm of water

B- Volume/ Volume percent

A convenient way of expressing the concentration of a liquid solute dissolved in a liquid is as a percent by volume. This unit of concentration is similar to percent by weight except that volumes in milliliters are used instead of weight in gram. The equation is as following:

$$\boxed{\text{percent by volume solute} = \frac{\text{volume of solute in ml}}{\text{total volume of solution in ml}} \times 100}$$

We can express the concentration of solute in this unit, as shown in the fpllowing example.

Example: what is the percent by volume of ethyl alcohol in a solution made by diluting 10 ml of ethyl alcohol to 100 ml with water?

Ans:

Volume of solute = 10 ml
Total volume of solution = 100 ml

Then:

Percent by volume ethyl alcohol = $10/100 \times 100 = 10\%$

Q1/ Determine the percent by volume of the solute in each of the following solutions:

(a) 5 ml of rubbing alcohol diluted to 150 ml with water
(b) 15 ml of ethyl alcohol diluted to 500ml with water

C- Weight/Volume percent:

This widely used method of expressing concentration is a combination of weight and volume. This weight is usually that of the solid solute and the volume is that of the total solution. This unit is defined as follows.

$$\boxed{\text{percent by wieght/volume solute} = \frac{\text{wieght of solute in gm}}{\text{total volume of solution in ml}} \times 100}$$

To use of this unit is shown in the following example:

Example: what is the percent by weight /volume of sodium chloride in a solution made by diluted 1.5 gm of sodium chloride to 100 ml with water?

Ans:

Weight of solute = 1.5 gm
Total volume of solution = 100 ml
Place thr quantities into above equation:

$$\text{percent by wieght /volume NaCl} = \frac{1.5\text{ gm}}{100\text{ ml}} \times 100$$

$$= 1.5\%$$

Low concentrations of solute are often expressed in milligrams (*mg*) per 100 ml. this weight / volume percent unit is defined as following:

$$\boxed{\text{milligrams per 100 ml} = \text{mg / 100 ml} = \frac{\text{wieght of solute in mg}}{\text{100 ml of solution}}}$$

This unit is often used to express the concentrations of solute in blood and urea, as shown in the following:

Example: 1 ml sample of blood plasma is found to contain 3.3 mg of sodium ions. Express this concentration in mg/100ml .

Ans: solute = 3.3 mg , solution = 1 ml of blood plasma
To find out the number of mg in 100 ml of blood plasma, we set up the following proportion :

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$$\frac{3.3\ \text{mg}}{1\ \text{ml}} \ \text{x}\ \frac{\text{x}}{100\ \text{ml}}$$

By rearrange and solve for x

$$\text{x} = \frac{3.3\ \text{mg x } 100\ \cancel{\text{ml}}}{1\ \cancel{\text{ml}}} = 330\ \ \text{mg}$$

There are 330 mg of sodium ions in 100 ml of blood plasma .
Therefore we say 330 mg per 100 ml
This value is within the normal concentration range of sodium ions in blood plasma (320 – 350/ 100 ml)
This percent mg / 100 ml sometimes called mg percent.

Q/ determine the concentration of solute in each of the following solutions in mg / 100 ml.

(a) 32 mg of sugar diluted to 10 ml with water
(b) 5 ml of solution that contains 1 gm of sodium ion

D- Molar Concentration (Molarity)

We can used the moles to measure of quantities of matters. We can extend this concept to solutions by expressing the amount of solute present in 1 L of solution in terms of moles.
Molar concentration, or molarity, which defined as the number of moles of solute per liter of solution, is designated by the capital letter M.
This definition is given in the form of an equation, as following:

$$\boxed{M = \frac{\textbf{number of moles of solute}}{\textbf{number of liters of solution}}}$$

Example : Determine the molar concentration of a solution that contains 25 gm of glucose, $C_6H_{12}O_6$ in 500 ml of solution.

Ans:

Convert 25 gm of glucose into moles

Molecular weight og glucose = 180 sm/ mol

$$\textbf{Number of moles} = \frac{\textbf{25 gm}}{\textbf{180 gm}} = \textbf{0.139 mol}$$

$$\textbf{Volume in L} = \frac{\textbf{500 ml}}{\textbf{1000 ml}} = \textbf{0.5 L}$$

Then: by used equation of molarity we can measure the concentration in molarity:

$$\textbf{M} = \frac{\textbf{number of moles}}{\textbf{volume in L}} = \frac{\textbf{0.139 mol}}{\textbf{0,5 L}} = \textbf{0.278 M}$$

Q1/ How many grams of glucose are needed to make 2 L of 2 M solution?

Q2/ How many grams are needed to make 500 ml of 0.15 M sucrose ($C_{12}H_{22}O_{11}$) solution.

E= Part Per Million and Part Per Billion:

These units of concentration are widely used to report very small amounts of solute in a solution. The concentration of pollutants in water and air are usually reported in these units.

* one part per million: abbreviated ppm, contains 1 part of solute per 1 million (10^6) parts of solution. By parts we mean any unit of measure such as grams, litters, or anything else we choose.

For example, the concentration of solid pollutants in solid food is given in ppm expressed as mg of pollutant (the solute) in 1 million mg of solid food (the solution). Because 1 million mg is equivalent to 1 kg. ppm is usually defined as follows:

$$\text{ppm} = \frac{\text{wieght of solute, in mg}}{\text{wieght of solution, in kg}} \quad \text{or} \quad \frac{\text{mg of solute}}{\text{L of solution}} \quad \text{or} \quad \frac{\mu\text{L}}{\text{L}}$$

The express the concentration of small quantities of solid solute in water, the unit ppm is usually define as mg of solute per liter of solution. This change from weight to volume of solvent can be made because 1 million mg (1 kg) of water occupies approximately 1 L. this definition of ppm is also frequently used even through the solution may weight somewhat more or less than 1 kg.

Air pollution is measured in ppm on the basis of measurements of volume rather than weight. Thus, 1 ppm means that there is I μL of pollutant (the solute) per 1 million (10^6) μL (1L) of air (the solution).

One part per billion: The sensitivity of analytical methods has improved so much that parts per billion, abbreviated ppb, has become a common unit of concentration. Its use and definition are similar to those of ppm. Thus, 1 ppb contains 1 part of solute per 1 billion (10^9) part of solution. Again, the part refer to weight or volume, depending on whether the solution is a gas, liquid, or solid.

$$\text{ppb} = \frac{\text{weight of solut in } \mu\text{g}}{\text{weight of solution in kg}} \quad \text{or} \quad \frac{\mu\text{g of solute}}{\text{L of solution}} \quad \text{or} \quad \frac{\mu\text{L}}{10^3\text{L}}$$

The units ppm and ppb are extremely small. For example, 1 ppm is equivalent to 1 cent in 10,000 dollars, and 1 ppb is equivalent to 1 cent in 10 million dollars. These unit are convenient means to express very small concentrations without using exponential notation. The use of these units is shown in the following :

Example: The maximum Food and Drug Administration (FDA) tolerance of mercury in fish is 0.5 ppm. A 10 gm sample of fish is found to contain 72 µg of mercury. Does the amount of mercury in the fish exceed the FDA maximum tolerance?

Ans:
ppm = 1 part of measure unit per 1 million parts
then:

$$\text{ppm} = \frac{\text{weight of mercury in } \mu\text{g}}{\text{weit of fish sample in gm}}$$

$$= \frac{72\ \mu\text{g}}{10\ \text{gm}} = 7.2\ \text{ppm}$$

Acids - Bases and Salts

A more general definition of acids and bases was proposed by Scientists. They are defined the acids and bases compounds as the following:

***Bronsted (1923):** defined an acid as any compound or ion that donate proton (H^+), and a base any compound or ion that accepts a proton.
***Lewis (1930):** defined an acid as any compound or ion accept one pair of electron, and a base any compound or ion donate one pair of electron.
***Arrhenius (1887):** define an acid as any compound that ionize in water to form [H_3O^+], and a base any compound that ionize in water to form [OH^-].

The pronsted definition is important because it allows us to classify as acids and bases many compounds and ions that do not fit the Arrhenius definition. Consider a monoprotic acid. It is a Bronsted acid. When it donates its proton, the remainder of the molecule is no longer acid; it is now a base. Hydrogen chloride in an example of such a monoprotic acid. in water, it donates a proton to water to form a hydronium ion and a chloride ion. Hydrogen chlorideide is an acid according to both the Arrhenius and the bronsted definitions. But the chloride ion that remains after the proton is donated is a base. Chloride ion is a base because it fits the Bronsted definition. It can accept a proton to form htdrogen chloride . while chloride ion is not a base according to the Arrhenius definition.

When an acid donates a proton. The remainder of the molecule or ion is a base. These two parts of the same molecule are called a *conjugate acid-base* pair. To use hydrogen chloride again as an example, hydrogen chloride is the acid and chloride ion is its conjugate base. The two, HCl and Cl^-, are a conjugate acid-base pair. We say that hydrogen chloride is the conjugate acid of chloride ion.

There is another conjugate acid-base pair in an aqueous solution of hydrogen chloride. Hydrogen chloride donates a proton to water to form a hydronium ion. Because water accepts a proton, it is a Bronsted base. So a hydronium ion can donate a proton, so it is a Bronsted acid. Therefore water and hydronium ion are the second conjugate acid-base pair in the solution. The two conjugate acid-base pair in an aqueous hydrogen chloride solution are shown in the following equation:

$$HCl + H_2O \rightleftharpoons H_3O^+ + CL^-$$

Exercise : Identify the two conjugate acid-base pair in each of the following equation:

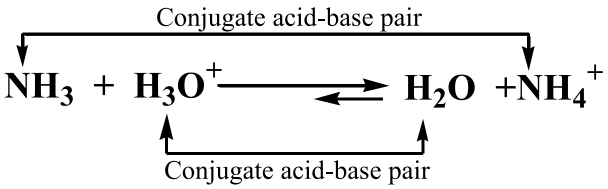
(a) $HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$

(b) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$

(c) $H_3O^+ + OH^- \rightleftharpoons H_2O + H_2O$

(d) $OH^- + C_2H_3O_2H \rightleftharpoons H_2O + C_2H_3O_2^-$

Ammonia reacts with a proton (hydrogen ion) to form an ammonium ion according to the following equation:

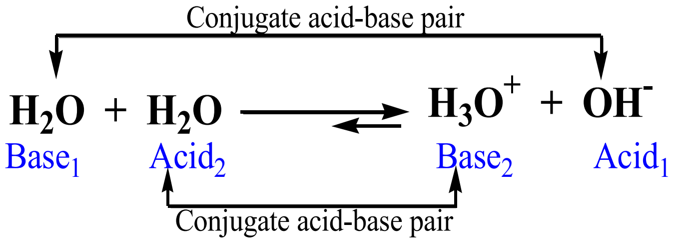


$$NH_3 + H_3O^+ \rightleftharpoons H_2O + NH_4^+$$

NH_3 is a Bronsted base, but it dosent fit the Arrhenius definition of base.

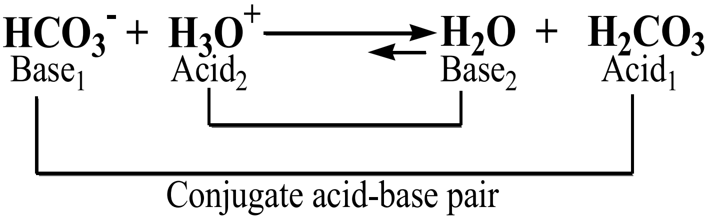
Many compounds in living systems have groups that are ammonia like others act like ammonium ions. These groups accept and donate hydrogen ions to control the acidity of body fluids.

One water molecule donates a proton to another molecule of water to form a hydronium ion and a hydroxide ion. One water molecule acts as an acid and the other acts as a base, as shown in the following equation:



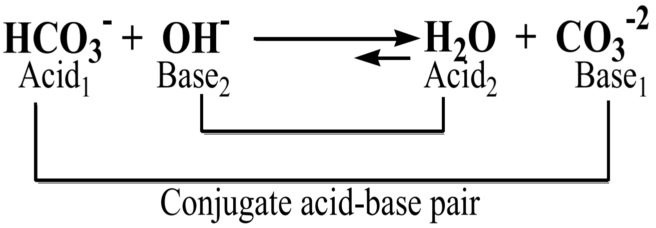
$$\underset{Base_1}{H_2O} + \underset{Acid_2}{H_2O} \rightleftharpoons \underset{Base_2}{H_3O^+} + \underset{Acid_1}{OH^-}$$

Water acts as both a Bronsted acid and a Bronsted base in this reaction. Many compounds and ions show such amphoteric behavior. The bicarbonate ion is an example of such an ion. It reacts as a base according to the following equation:



$$\underset{\text{Base}_1}{HCO_3^-} + \underset{\text{Acid}_2}{H_3O^+} \rightleftharpoons \underset{\text{Base}_2}{H_2O} + \underset{\text{Acid}_1}{H_2CO_3}$$

It also reacts as an acid, according to the following:



$$\underset{\text{Acid}_1}{HCO_3^-} + \underset{\text{Base}_2}{OH^-} \rightleftharpoons \underset{\text{Acid}_2}{H_2O} + \underset{\text{Base}_1}{CO_3^{-2}}$$

Other ions formed by the loss of one proton from a diprotic acid also show this behavior.

The compounds or ions involved in acid-base reactions can be divided into two conjugate acid-base pairs. This means that there are two acids and two bases in solution. *The stronger the acid, the weaker is its conjugate. The weaker an acid, the stronger is its conjugate base.*

- Certain acids ionize completely when dissolved in water. Such acids are called **strong acids**. Hydrogen chloride (HCl) is an example of a strong acid. When hydrogen chloride is bubbled into water, the molecules ionize to form hydrogen and chloride ions, according the following equation:

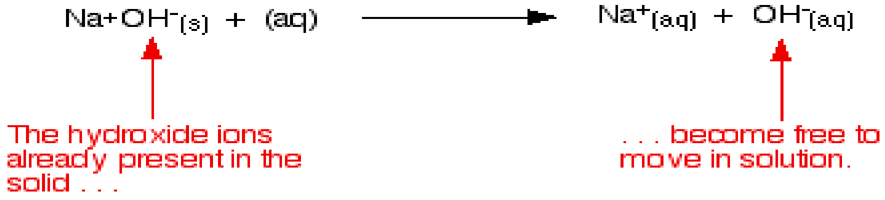
$$\underset{\text{Hydrogen chloride}}{HCl} + \underset{\text{Water}}{H_2O} \rightleftharpoons \underset{\text{Hydrogen ion}}{H_3O^+} + \underset{\text{Chloride ion}}{CL^-}$$

Other compounds that are strong acids are (HBr, $HClO_4$, HI, HNO_3, H_2SO_4, HF, HCN, H_2CO_3,$C_2H_3O_2H$).

- Bases are also called alkaline substances. Some bases exist as ions in aqueous solution and are called **strong bases**. Sodium

$$NaOH \longrightarrow Na^+ + OH^-$$

hydroxide (NaOH) is an example of a strong base. When dissolved in water, hydrated sodium ions (Na^+) and hydroxide ions (OH^-) are formed, as shown in the following equation:



Other common bases are potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$), and magnesium hydroxide ($Mg(OH)_2$), these bases all exist as ions in aqueous solution.

The strong acids are more completely ionized in solution than are weak acids. The degree of ionization of any acid is given by ionization constant, K_a. The equilibrium constant for the ionization of an acid in water is defined as its ionization constant.

Ex: Acetic acid ionization:

$$C_2H_3O_2H + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

$$K = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[H_2O]\,[C_2H_3O_2H]} \Longrightarrow K \times [H_2O] = \frac{[H^+]\,[C_2H_3O_2]}{[C_2H_3O_2H]}$$

Diprotic acids ionize in two steps:

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \Longrightarrow K_{a1} = \frac{[H^+][HCO_3]}{[H_2CO_3]}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_2^- \Longrightarrow K_{a2} = \frac{[H^+][HCO_3]}{[H_2CO_3]}$$

$PK_a = -\log K_a$

*The strength of an acid is expressed as acid ionization constant (K_a). The larger the value of PK_a meaning the weaker the acid and vice versa.

*The strength of a base is expressed as a base ionization constant (K_b). The larger the value of PK_b meaning the weaker the base and vice versa.

Ex: $$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K = \frac{[NH_4^+][OH^-]}{[H_2O][NH_3]} \Longrightarrow K \times [H_2O] = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$PK_b = -\log K_b$

Notice : The strong acids have large values of Ka than weak acids. The second ionization constant of diprotic acid is smaller than the first, and third ionization constant of H_3PO_4 is smaller than the second.

Example: Which is the stronger acid, HCN (K_a=4.93x 10^{-10}) or HF (K_a= 3.53 x 10^{-4}) ?

Ans: Decide which value of K is smaller.

4.93x 10^{-10} is smaller than 3.53 x 10^{-4} therefore, HCN is the weaker acid.

Problems:

1. Calculate the PH of a 0.025M solution of HCl (log2=0.3).

$$HCl \longrightarrow H^+ + Cl^-$$

$[H^+]$= 0.025M

PH= $-\log 2.5 \times 10^{-2}$, $\log 2.5 = 0.4$

$= -\log(10^{0.4} \times 10^{-2}) = -\log 10^{-1.6} = -(-1.6) = 1.6$

2. Find the PH of 0.1M NH_4OH (K_b=2 x 10^{-5})

$$NH_4OH \longleftrightarrow OH^- + NH_4^+$$

$[OH^-] = \sqrt{Kb \times C}$ C= Conc. of weak base

$= \sqrt{2x\ 10^{-5}}\ x\ 10^{-1}$ =1.42x 10^{-3}

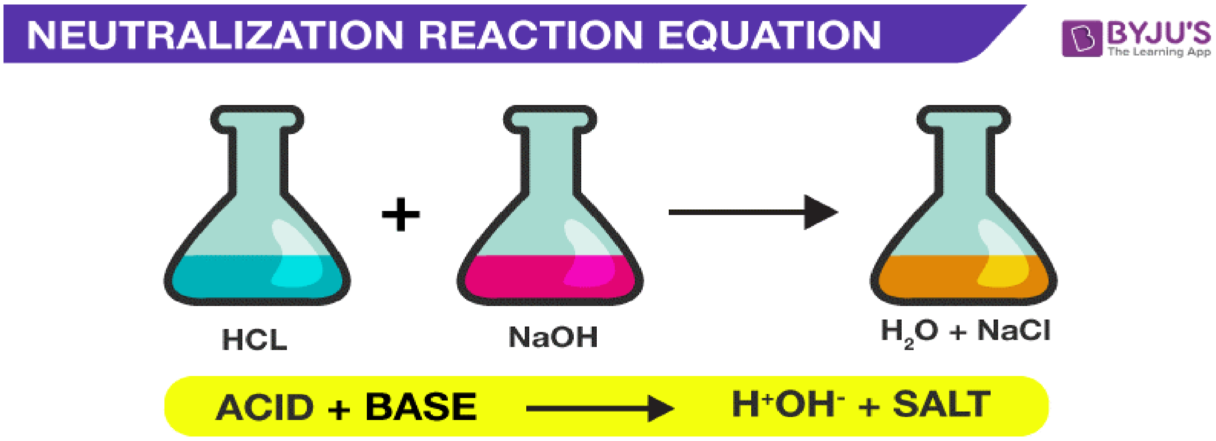
POH= 2.85

PH + POH= 14

PH=11.15

Neutralization

An acid reacts with a base to form water and a salt. For example: aqueous solutions of sodium hydroxide and hydrochloric acid react to form water and sodium chloride, as the following equation :



The resulting solution is neither acidic not basic. It is neutral, and the reaction is called a ***neutralization reaction***, because is ionic reaction that goes to completion and un-ionized molecule (H_2O) is formed.

Example of strong diprotic acids require 2 moles of base per mole of acid to be neutralized completely:

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

ACID BASE TITRATION

A titration is a method of determining the amount of acid or base in a solution. This method is based on the chemical reaction between an acid and base.

If we to know the amount of base in a certain volume of solution, we measure the amount of an acid of known concentration needed to react completely with the base. Conversely. If we have an other solution and want to know the amount of acid it contains, we measure the amount of base needed to react with all the acid.

The adding must be as drops, the color change meaning end the titration, this color change called ***endopoint*** or ***equivalence point***, referring to the balanced equation of the acid-base reaction.

*The molar ratio of base to acid is 1:1 at the equivalence point, and number of moles for acid equal to number of moles for bases

At equivalence point: **N1 V1 = N2 V2**

Acid base

Dr. Mahmoud AL-Fahdawi

Q/ It takes 35.2ml of a 0.1M HCl solution to neutralize exactly 25.0ml of NaOH solution. What is the concentration of this NaOH solution?

Acid-base balance in blood:

The PH of various body fluids is maintained by buffers. There are several different buffer systems in the body:

(1) *phosphate buffer*: Dihygrogen phosphate ($H_2PO_4^-$) and monohydrogen phosphate (HPO_4^{-2}) are one weak acid-base conjugate pair that acts as a buffer in the blood. Any acid reacts with monohydrogen phosphate according to the following equation:

$$HPO_4^{-2} + H^+ \rightleftharpoons H_2PO_4^- + H_2O$$

Dihydrogen phosphate is a weak acid that reacts with any base as follows:

$$H_2PO_4^{-2} + OH^- \rightleftharpoons HPO_4^{2-} + H_2O$$

(2) *bicarbonate buffer:* Carbonic acid-bicarbonate ion. Carbonic acid is formed by dissolving carbon dioxide in aqueous body fluids. It is a weak acid that ionizes to bicarbonate ion. The equation for these two equilibrium reactions is as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

Normally, in the body fluids such as blood, there is 24 meq/L of HCO_3^- to 1.2 meq/L of H_2CO_3.

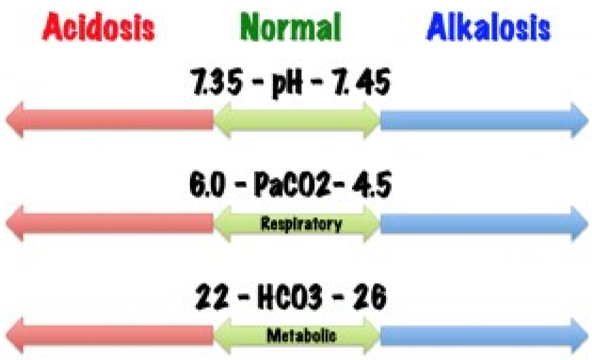
The PH of the blood is within its normal range (7.35- 7.45) when the ratio: $HCO_3^-/\ H_2CO_3 = 24/1.2 = 20/1$ is maintained. The PH of the blood becomes more acidic if the ratio HCO_3^-/ H_2CO_3 is less than 20/1. the acidic condition of the blood signified by a PH less than 7.35 is called ***acidemia***.

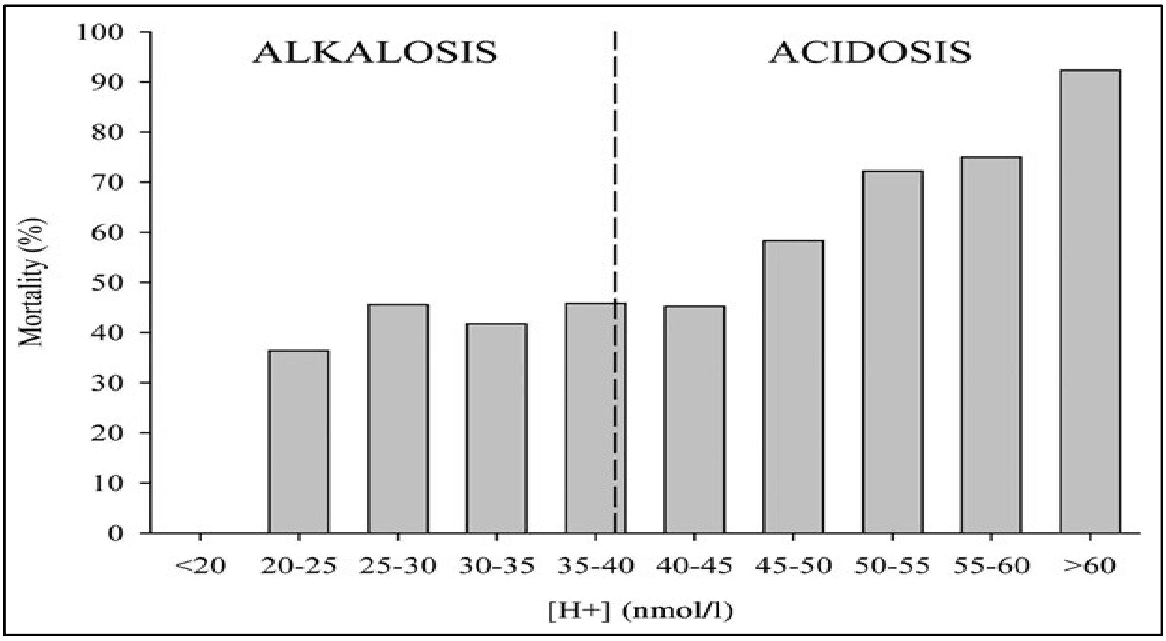
The PH of the blood becomes more basic when the ratio HCO_3^-/ H_2CO_3 becomes greater than than 20/1. the alkaline condition of the blood signified by a PH greater than 7.45 is called ***alkalemia***.
Death occurs if the PH of the blood is more acidic than 6.8 or more basic than 7.8 .

-Let us consider how the body uses the carbonic acid-bicarbonate ion buffer system to cope with an increase in either the acid or the base concentration in the blood.
First: ***acidosis***: (the physiological processes causing acidemia) occur in a patient who has illness that causes an increase in the concentration of acidic products in the blood. The acidic products react with HCO_3 to produce H_2CO_3; this causes a decrease in the ratio HCO_3^-/ H_2CO_3 .

One of the functions of both lungs and kidneys is to maintain the PH of the blood by replenishing the buffer compounds that are used up or removing any excess compounds from the body. The circulation of air into and out of the lungs, called ventilation. An increase in the amount of H_2CO_3 in the blood causes a corresponding increase in the amount of CO_2, formed from the decomposition of H_2CO_3 .

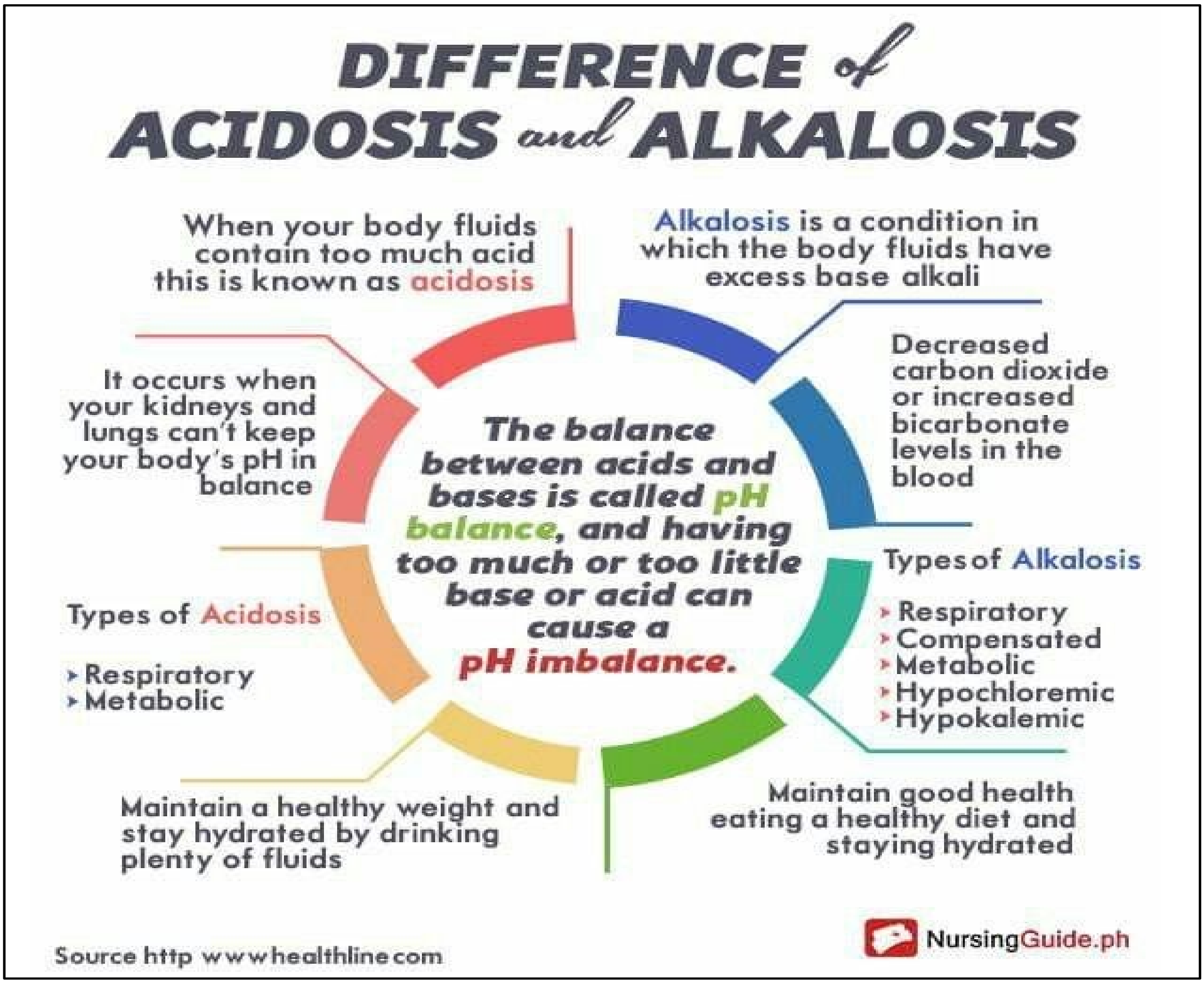
$$\boxed{H_2CO_3 \rightleftharpoons H_2O + CO_2\uparrow}$$





To lose this excess CO_2 deeper and faster breathing called ***hyperventilation***, occurs, which causes a decrease in the acidity of the blood. If this does not return the PH to normal, the kidneys can help by releasing more HCO_3^- ions into the blood and removing H^+ ions to return the HCO_3^-/H_2CO_3 ratio to its normal value and maintain the acid-base balance in the blood.

Second: Alkalosis: (the physiological processes causing alkalemia) occur in a patient who has an illness that causes an increase in the concentration of bacic products in the blood. These basic products react with H_2CO_3 to produce HCO_3^- ions; this causes an increase in the ratio HCO_3^-/H_2CO_3 . to prevent this ratio from increasing is to conserve the CO_2 in the body and use it to produce more H_2CO_3 . to do this, loss of CO_2 through lungs is minimized by slower breathing. This process called ***hypoventilation***. As before, the kidneys can help if needed by removing HCO_3^- and addition of H^+ ions to blood. Thus, the lungs and kidneys can function to maintain the PH of the blood within its normal range of 7.35 to 7.45.



DIFFERENCE of ACIDOSIS and ALKALOSIS

When your body fluids contain too much acid this is known as acidosis

It occurs when your kidneys and lungs can't keep your body's pH in balance

Types of Acidosis

- Respiratory
- Metabolic

Maintain a healthy weight and stay hydrated by drinking plenty of fluids

Alkalosis is a condition in which the body fluids have excess base alkali

Decreased carbon dioxide or increased bicarbonate levels in the blood

Types of Alkalosis

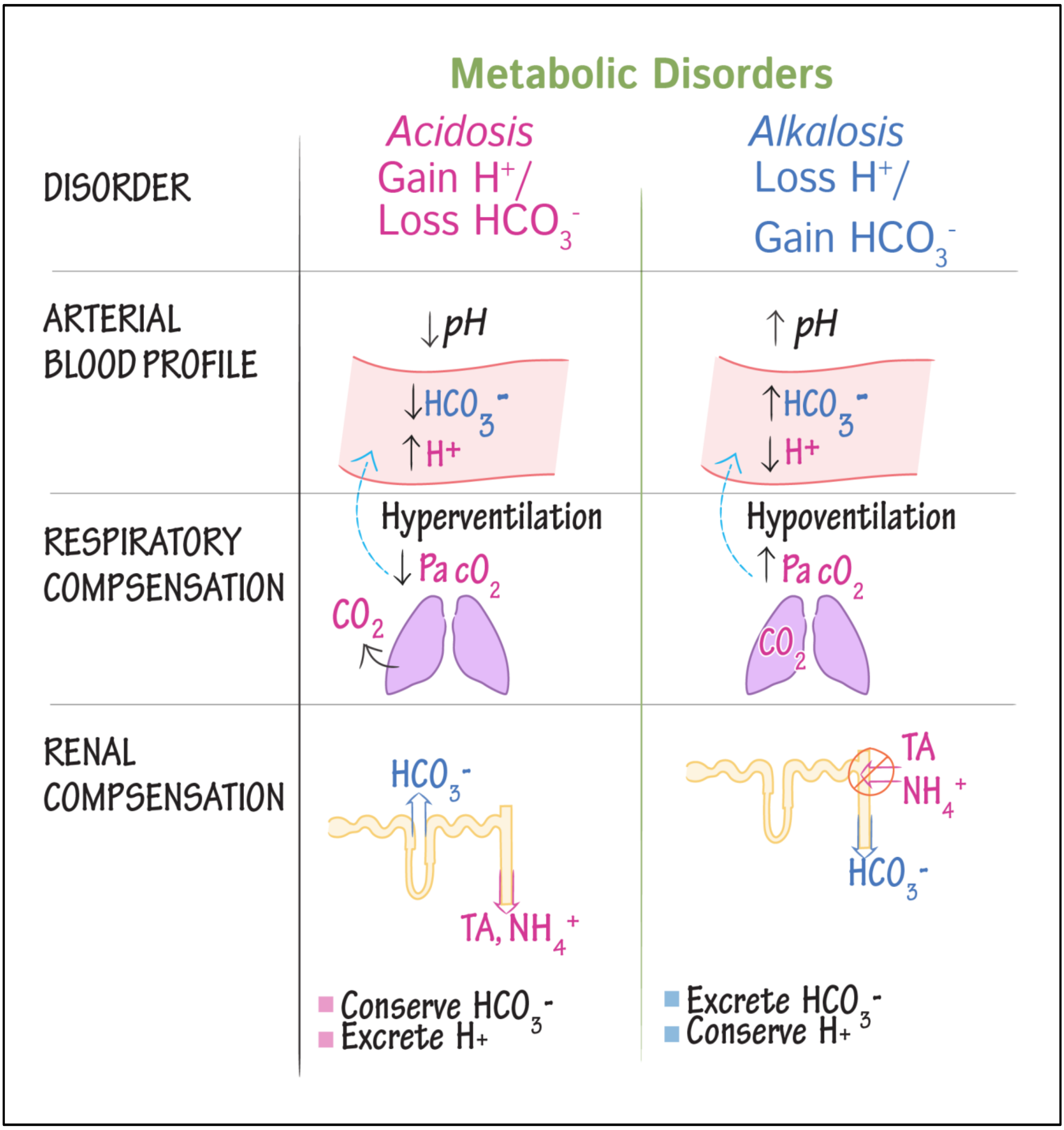
- Respiratory
- Compensated
- Metabolic
- Hypochloremic
- Hypokalemic

Maintain good health eating a healthy diet and staying hydrated

The balance between acids and bases is called pH balance, and having too much or too little base or acid can cause a pH imbalance.

Source http www.healthline.com

NursingGuide.ph



Metabolic Disorders

	Acidosis	Alkalosis
DISORDER	Gain H^+/ Loss HCO_3^-	Loss H^+/ Gain HCO_3^-
ARTERIAL BLOOD PROFILE	↓pH ↓HCO_3^- ↑H^+	↑pH ↑HCO_3^- ↓H^+
RESPIRATORY COMPSENSATION	Hyperventilation ↓$PacO_2$ CO_2	Hypoventilation ↑$PacO_2$ CO_2
RENAL COMPSENSATION	HCO_3^- TA, NH_4^+ ■ Conserve HCO_3^- ■ Excrete H^+	TA NH_4^+ HCO_3^- ■ Excrete HCO_3^- ■ Conserve H^+

Buffer systems

The Le Chatelier principle Buffer systems: *If a system at equilibrium is disturbed by an externally applied stress, the system changes in such a way that this external stress is minimized.*

BUFFER SOLUTIONS

A buffer solution is a mixture of either a weak acid and its salt, or a weak base and its salt, which resist the change in PH upon the addition of small amounts of strong bases.

Ex: ($C_2H_3O_2H$ + $C_2H_3O_2Na$) is a buffer system.

If small amount of strong acid is added; it will react with the conjugate base.

$$C_2H_3O_2^- + H_3O^- \rightleftharpoons C_2H_3O_2H + H_2O$$

Weaker base

Most of the added H^+ ions are removed from the solution and PH hardly changed.

The OH^- ions added to the buffer solution, react with molecules of acetic acid forming acetate ions and water.

$$OH^- + C_2H_3O_2H \rightleftharpoons C_2H_3O_2^- + H_2O$$

The PH of a buffer solution is determined by the PKa of the weak acid and (log) of the ratio of concentration of conjugate base to the concentration of acid. The following equation, called the Henderson-Hasselbalch equation, expresses this relationship for the buffer solution.

$$\mathbf{PH = PK_a + \log\frac{[C_2H_3O_2^-]}{[C_2H_3O_2H]}}$$

A buffer solution has a limited ability to react with acids and bases without changing its PH. It acts as buffer because it contains both members of a conjugate acid-base pair. Removal of one of these two by chemical or physical process destroys the buffer action of the solution. Buffer solutions are important in the body because they maintain the acid-base balance in the blood.

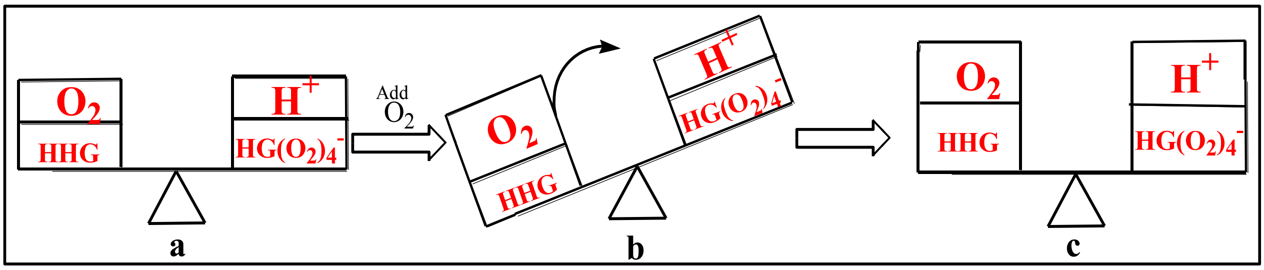
Many example of this principle are found in living systems:
*Oxygen needed by the body is carried in the blood stream to the cells as part of the molecule oxyhemoglobin. This molecule is formed in the blood by the reaction between dissolved oxygen gas obtained from air and hemoglobin in the red blood cells. This reaction is reversible. In the cells, oxyhemoglobin releases its oxygen to reform hemoglobin. We can write the equation for this reversible reaction as follows:

$$\textbf{Hemoglobin} + 4O_2 \rightleftharpoons \textbf{Oxyhemoglobin}$$

The chemical formulas and structures of hemoglobin and oxyhemoglobin are very complicated. We use the symbol HHG for hemoglobin and the symbol $HG(O_2)_4^-$ for oxyhemoglobin.

$$HHG + 4O_2 \rightleftharpoons HG(O_2)_4^- + H^+$$

The partial pressure of oxygen gas in the lungs is higher than anywhere in the body. This increases the oxygen gas concentration in the blood entering in the alveoli (the small, thin sacs of blood capillaries in the lungs). The result is a reduction in the concentration of oxygen gas and formation of more oxyhemoglobin and then to regions of the body that need oxygen. this principle is shown pictorially in the following figure.



(a) the reaction between hemoglobin and oxyhemoglobin at equilibrium. (b) Addition of oxygen disturbs the equilibrium. (c) Oxygen and hemoglobin react to form more oxyhemoglobin and H^+ to re-establish the equilibrium.

*The enzyme-catalyzed reaction of glucose-1-phosphate (G-6-P) to glucose-6-phosphate (G-6-P) as follows:

$$\text{G-1-P} \xrightleftharpoons{\text{Enzyme}} \text{G-6-P}$$

$$K=\frac{[\text{G-6-P}]}{[\text{G-1-P}]} = 20.0$$

We know from many experiments that the equilibrium constant for this reaction is 20.0 at body temperature (37 °C).

This means that concentration of G-6-P is 1.00M and the concentration of G-1-P is 0.0500M . this is an equilibrium mixture of the two compounds.

$$\frac{[\text{G-6-P}]}{[\text{G-1-P}]} = \frac{1.00\text{M}}{0.05\text{M}} = 20.0$$

IONIZATION OF WATER

The molecule of liquid water are held together by hydrogen bonds. In three-dimensional structure of water molecules, exist very small concentration of hydronium ions (H_3O^+) and hydroxide ions (OH^-). These ions are formed from water molecules by the following reaction:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad \text{------} \quad (1)$$

Formation of these ions by the breaking of a polar covelent bond in a molecule is called ***ionization***.

The number of ionize water molecule is very little, which is only one of every 550,000,000 water molecules is ionized. This is shown by the fact that the concentration of hydronium ions in water at 25 °C is only 1×10^{-7} M, because a hydroxide ions is formed with each hydronium ion, therefore the concentration of hydroxide ions is also 1×10^{-7} M.

The concentration of (H_3O^+) and (OH^-) ions change when certain substance dissolved in water. To understand how this occurs, therefore we must begin with the equilibrium constant expression for the ionization of water:

$$K = \frac{[H_3O^+][OH-]}{[H_2O]^2}$$

The concentration of water molecules is essentially constant. Thus:

$$K[H_2O]^2 = K^- = [H_3O^+][OH-]$$

The ionization of water is often written simply as:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{------ (2)}$$

From comparing equations (1) and (2) we see that:

$$[H_3O^+] \rightleftharpoons [H^+]$$ Therefore:

$$K = K_W = [H^+]\,[OH^-] = [1x10^{-7}][1x10^{-7}] = 1x10^{-14}$$

-In any aqueous solution or any neutral solution both hydronium and hydroxide ions must be present and the product of their concentration must be constant = 10^{-14}.

-As the concentration of one of $[H_3O^+]$ and $[OH^-]$ increase the concentration of the other must be decrease.

-An aqueous solution in which $[H^+]$ is grater than $[OH^-]$ is called *acidic solution*. While in *basic solution* $[OH^-]$ is grater than $[H^+]$.

Example: for each of the following solution, calculate the concentration of hydroxide ions:

(a) $[H+] = 1 \times 10^{-4}$ M **(b)** $[H+] = 1 \times 10^{-10}$ M.

$K_w = [H^+][OH^-] = 1x10^{-14}$

(a) $[OH^-] = \frac{1x\ 10^{-14}}{[H^+]} = \frac{1x\ 10^{-14}}{1x\ 10^{-5}} = 1X\ 10^{-9}M$

(b) $[OH] = 1x10^{-4}$

Exercise: Decide whether each of the following solutions is acidic, basic or neutral.

- **(a)** $[OH^-] = 1\ X\ 10^{-12}M$
- **(b)** $[H^+] = 1\ X\ 10^{-2}M$
- **(c)** $[H^+] = 1\ X\ 10^{-7}$

PH scale: Molar concentration is used to express the concentration of H^+ and OH^- ions, another way is PH.

P= function= -log[con.] to express very low concentrate.

$$PH = 0 \longrightarrow 7 \longrightarrow 14$$

acidic **neutral** **basic**

$PH = -\log[H^+]$ **$[H^+] = 1x\ 10^{-PH}$**

$[H^+]$ for pure water is **$1x\ 10^{-7}M$**

$[H^+] = 1x\ 10^{-7}M = 10^{-PH}$

PH= 7

In same way: **POH = 7**

$Kw = (1x\ 10^{-PH})\ x\ (1x\ 10^{-PH}) = 1x\ 10^{-14}$

PH+POH=14 so POH= 14-PH

Example:

(1) calculate PH and POH of solution its $[H^+]$ $1.5\ x\ 10^{-3}$

$PH = -\log[H^+] = -\log\ [1.5\ x\ 10^{-3}] = -\log 1.5 - \log 10^{-3}$

$PH = -\log 1.5 + 3 = 2.82$

$POH = 14 - PH = 14 - 2.82 = 11.18$

(2) calculate $[H^+]$ conc. Of solution that its PH= 5.25.

PH= -log $[H^+]$
LogH^+= -PH= -5.2
Auti log = 5.62 x 10^{-6}

*Body fluid differ in (1) their acidity (2) range of acidity.

-**Stomach** : PH = $1 \longrightarrow 3$

-**Urine** : PH = $4.8 \longrightarrow 7 \longrightarrow 8.4$

Has wide PH range therefore many acidic and basic substance are removed from body through urine to help maintain of blood plasma.

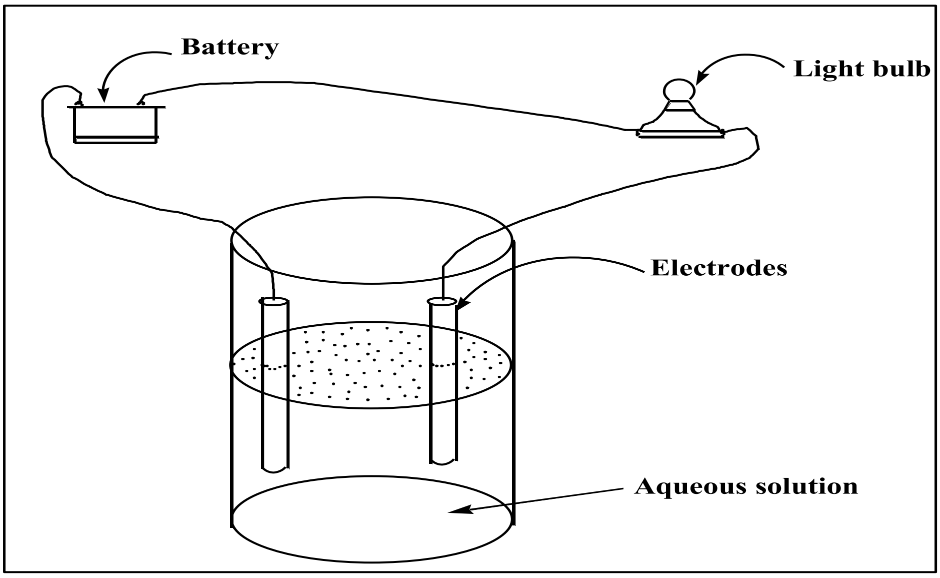
-**Blood plasma**: PH = 7.35 – 7.45 Has narrow PH range,
If PH change outside this range the ability of blood to transport oxygen is reduc

Lec:(5) -- (2023-2024) --Dr.Mahmoud S. Muter

Fluids and Electrolytes

Electrolytes and nonelectrolytes

Electricity is the flow of electrons in circuit from a battery or electrical generator along a wire back to the source. The electricity passing through the circuit can do work, such as running a motor or providing heat and light. The flow of electricity stop if the circuit is broken. An electrical circuit can also contain aqueous solution as shown in following figure.



-The circuit contain (battery, aqueous solution, light bulb of two wires called electrodes).

-The two electrode are oppositely charged.

-For electricity to flow through this circuit after the connection have been made.

-The solution must be able to conduct electricity. Glowing light bulb indicates that electricity is flow through circuit. Aqueous solutions either conduct electricity or they do not. One that conducts electricity is called an ***electrolytic solution***; one that dose not is called *a* ***nonelectrolytic solution.***

Electrolytes and Nonelectrolytes

Electrolytes		Nonelectrolytes	
NaCl	sodium chloride	$C_{12}H_{22}O_{11}$	sucrose
KI	potassium iodide	C_2H_5OH	Ethyl alcohol
LiBr	Lithium bromide	C_3H_6O	Acetone
Na_2SO_4	sodium sulfate	CH_4	Methane
KNO_3	potassium nitrate	N_2	Nitrogen
$CaCl_2$	Calcium chloride	O_2	Oxygen
LiF	Lithium floride	CO	Carbon monoxide

Electrolyte: A solute that forms an aqueous electrolytic solution.
Nonelectrolyte: A solute that forms an aqueous nonelectrolytic solution.
Hydration: is a close association of water molecule with an ion, we say that ion is hydrated. Thus according to **Arrhenius theory**, one mole of sodium chloride forms one mole of sodium ions and 1 mole of chloride ion when dissolved in water.
*Aqueous solution of electrolytes are really solutions of hydrated ions.
*The total number of ions formed per mole of electrolyte depends on the chemical formula of the electrolyte as shown in following Table.
Ex: 1 mole of calcium chloride dissolved in water forms 1 mole of hydrated calcium ions and 2 moles of hydrated chloride ions.

Number of ions formed per mole of electrolyte

chemical formula	ions formed in aqueous solution	Number of ions in 1 mol of electrolyte
NaCl	Na^+ Cl^-	$2 \times 6.02 \times 10^{23}$
LiBr	Li^+ Br^-	$2 \times 6.02 \times 10^{23}$
KNO_3	K^+ NO_3^-	$2 \times 6.02 \times 10^{23}$
$CaCl_2$	Ca^+ Cl^- Cl^-	$3 \times 6.02 \times 10^{23}$
Na_2SO_4	Na^+ Na^+ SO_4^{-2}	$3 \times 6.02 \times 10^{23}$
Na_3PO_4	Na^+ Na^+ Na^+ PO_4^{-3}	$4 \times 6.02 \times 10^{23}$

The sugar molecules surrounded by water molecules, are neutral when a pair of electrodes is placed in this solution. The sugar molecules are not attracted by their electrode. Consequently no electric current flows through the solution.

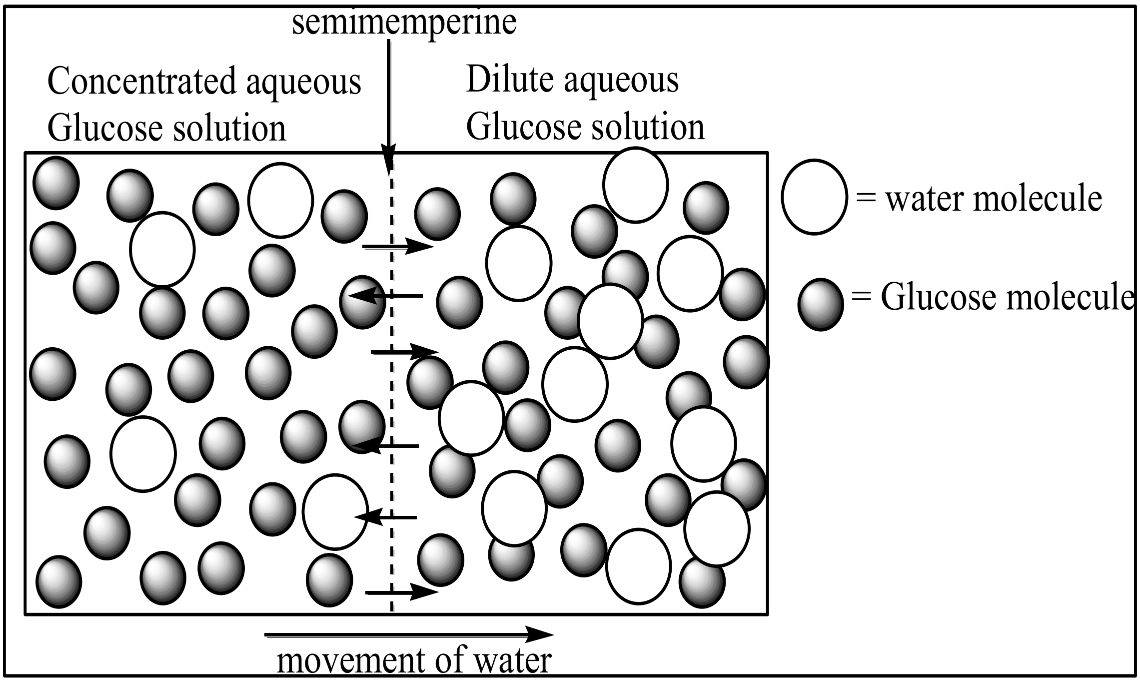
OSMOSIS AND OSMOTIC PRESSURE

Cells have limiting boundary membranes that are called plasma membranes. These membranes not only keep the cell intact but also allow the exchange of materials back and forth between the interior of the cell and its exterior surroundings. Osmosis and Dialysis are two ways that such an exchange of materials occurs.

*Osmosis: is the movement of water through an osmotic membrane from an aqueous solution that is less concentrated to one that is more concentrated.

This phenomenon that occur whenever an osmotic membrane separated two solution of different concentration. Osmotic membrane = semipermeable membrane= plasma membrane.

*Osmotic pressure: The pressure needed to prevent osmosis is called the *osmosis pressure*. Notice that a high solute concentration means high osmotic pressure. Water moves from dilute to more concentrated solutions. The purpose of this movement of water is to make the concentrations of the solution equal. In the following figure, the water moves to the solution that has the greater number of dissolved particle (Glucose).



***Colligative property:** Any property of a solution that depends on the number of dissolved particles in the solvent.

We can easily that osmotic pressure is a colligative property. For example, if we measure the osmotic pressure of a 1M aqueous sodium chloride solution, we find that it is exactly twice that of a 1M aqueous glucose solution. The reason for this difference in osmotic pressure is that sodium chloride is an electrolyte, whereas glucose is a nonelectrolyte. An aqueous solution containing 1mole of sodium chloride actually contains 1 mole of sodium ions and 1 mole of chloride ions.

*The relative osmotic pressures of two solutions are extremely important in living systems.

***Isotonic:** The two solutions that have the same osmotic pressure, for example, 1M glucose solution and a 1M urea (nonelectrolyte).

***Hypertonic:** One of the two solutions has a higher osmatic pressure, for example, 1M NaCl solution has a higher osmotic pressure than a 1M glucose solution.

***Hypotonic:** One of the two solutions that has the lower osmotic pressure than the other, for example, 1M NaCl solution has a lower osmotic pressure than a 2M LiBr solution.

* The plasma membranes of red blood cells behave as osmotic membranes. The cells contain an aqueous fluid made up of dissolved compounds. This fluid has an osmotic pressure determined by the concentration of dissolved molecules and ions in the fluid. Osmotic occurs when a red blood cell is placed in water.

*The solution inside the cell is hypertonic compared to pure water, so water enters the cell.

***Hemolysis:** The rupture of red blood cells when much water enter cell, the cells are called (*Hemolyzed*).

Osmosis also occurs when red blood cell is placed in solution of concentrated saline (sodium chloride). But the solution inside cell is hypotonic and water leave cell.

-Crenation: The process of leaving water and passes into solution and causes R. B. C to shrivel and shrink.

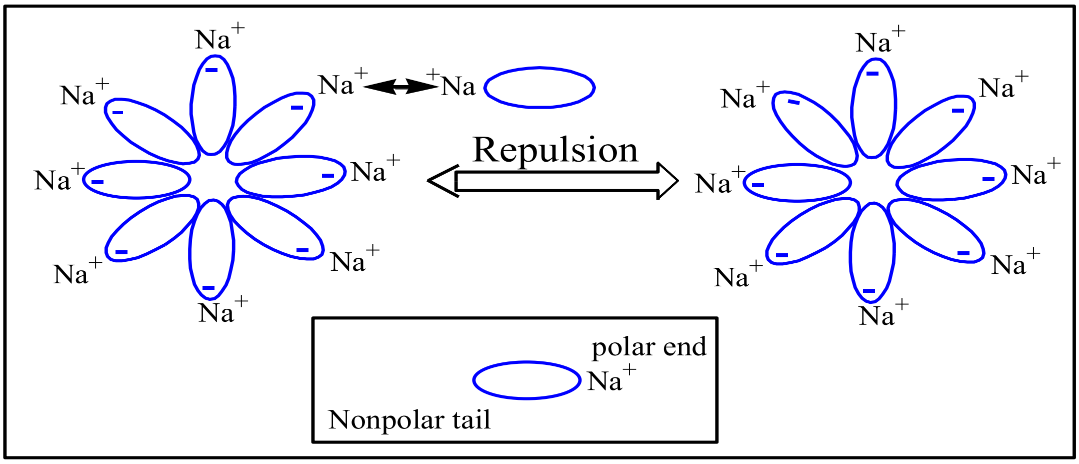
-Colloid: Mater contain particle it is size range from (1-100 nm)

-**Colloidal dispersion:** A uniform dispersion of a colloid in water.
-Dispersion substance: is the colloidal dispersion (solute)
-Dispersed substance: The continuous matter in which the colloid is dispersed (solvent).

* The dispersed and dispersion substance can be liquids, solids or gases. They can combine in nine different ways to form colloidal dispersion containing two components. but only eight of these nine possible combinations. Mixture of two gases can not be colloid dispersion because the particle of gas are individual molecules. The eight types of colloidal dispersion are given in the following Table.

Dispersed solvent	Dispersion solute	Example
Liquid	Gas	oxigen in water, clouds
Solid	Gas	Smoke
Gas	Liquid	Foams, whipped cream
Liquid	Liquid	Milk, butter, wine
Solid	Liquid	Paints, glue
Gas	Solid	Foam, rubber, pumice
Liquid	Solid	Jellies, cheese
Solid	Solid	Colored glass, gems

If the colloids are clusters of molecules, why don't the clusters increase in size unit they get large enough to settle out? The reason is that particle in the most stable colloid dispersions all have the same electrical charge can be caused by adsorption of ions to the surface of the particle, or the large particle themselves can be charged. As result the particle repel each other and can not form particle large enough to settle out as shown:



Colloids formed by attractions between complex molecules

Emulsifying agent: A Compound or substance that stabilized a colloidal dispersion for example (Soap) in mixture of oil and water. Water is immiscible with water, if we add soap to mixture the oil is emulsified by the soap.

***Dailyzing membrane**: membrane that allow small molecules and ions to pass while holding back large molecules and colloidal particle.

Dailysis: The selective passage of small molecules and ions in either direction by dialyzing membrane. Dialysis differ from osmosis in that osmotic membrane allow only solvent molecules to pass.
*The kidneys are an example of organs in the body that use dialysis to maintain the solute and electrolyte balance of the blood.
The main purpose of the kidneys are to clean the blood by removing the waste products of metabolism and control the concentration of electrolyte.
*The efficient kidneys purified 180L of blood in a 68kg (150 Ib) adult.

Chemical reactions in aqueous solutions

Many of the chemical reactions that occur in nature take place between substances dissolved in water. Reactions between ions are particularly important in water and in many body fluids salts are compounds that release ions when dissolved in water. Other compounds called acids and bases also form ions in aqueous solutions.

(1) Ionic reactions: An ionic reaction is a chemical reaction between ions or between ions and molecules. An ionic reaction occurs only if the product is one or more of the following:

a. compound insoluble in water, called a precipitate.
b. Gas.
c. compound that is soluble in water but dose not as ions, called an un-ionized compound.

*For example, let us consider what happens when we dissolve equal molar quantities of lithium chloride and sodium nitrate in water. Will the following chemical reaction occur:

$$LiCl + NaNO_3 \longrightarrow LiNO_3 + NaCl$$

The lithium and sodium ions simply exchange anions in this reaction. This type of reaction is called a double decomposition reaction.

The products lithium nitrate and sodium chloride, also exist as ions in solution. This means that an aqueous solution of the two salts is a mixture of the four ions, Li^+ , Na^+ , NO_3^- , and Cl^-. No precipitate, no gas, no un-ionized compound is formed as product product. therefore, no chemical reaction has taken place.

(2)

*Another example equimolar quantities of sodium chloride and silver nitrate are dissolved in water. Occur the following reaction:

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl\downarrow$$

The salts sodium chloride, silver nitrate are all electrolytes. In contrast, silver chloride is insoluble in water (precipitate) .
therefore, chemical reaction is ionic reaction.

Ions in body fluids

The most common cations and anions in the fluids of living systems are given in the following Table:

Cations	Anions
Na^+	Cl^-
k^+	HCO_3^-
Mg^{+2}	$H_2PO_4^-$
Ca^{+2}	HPO_4^{-2}
Fe^{+2}	—
Fe^{+3}	—

-Na$^+$, Ca^{+2} : in intercellular fluid (fluid between cells). Calcium ions are needed for healthy bones and teeth, for blood clotting, and for regulation of the heartbeat.

-K$^+$, Mn^{+2} : in cellular fluid, the Mn^{+2} ions assist enzymes in their biological roles.

-Fe^{+2} , Fe^{+3} : part of cytochrome system involved in oxidative phosphorylation and the hemoglobin contain Fe^{+2}that play very important role in the transport of oxygen and carbon dioxide.

-Cu^{+2}, Zn^{+2}, Co^{+2} and **Mn^{+2}:** assist enzymes in their biological role.

-Hg^{+2} : Extensive damage to brain and nervous system.

-Pd^{+2} : Toxic effect on kidney and nerve damage.

-O$_2$: carried in blood stream to cells as part of molecule Oxyhemoglobine.

The metallic ions present in trace amounts in living systems usually exist as complex ions. A complex ion is made up of one or more metallic cations surrounded by other ions or molecule. These other ions or molecules contain nitrogen, oxygen, or sulfur atoms that form bonds with the metallic cation. A simple example of a complex ion is the one formed between cupric ion and ammonia. Four ammonia molecules react with each cupric ion to form the complex ion shown in the following equation:

$$Cu^{+2} + 4NH_3 \longrightarrow Cu(NH_3)_4^{+2}$$

Many large molecules in living systems contain ammonia. The nitrogen atoms contained in these molecules form complex ions with metallic cations. In this way, the metallic cation is bound to the molecule and becomes part of the living system.

Sometimes the reaction of a metallic cation and a large molecule is poisonous to the living system. This is case with the ions of mercury (Hg^{+2}) and lead (Pb^{+2}). Both are particularly poisonous to humans. Lead ions have a toxic effect on the kidneys and cause nerve damage. Mercuric ions cause extesive damage to the brain and nervous system. These ions react with the sulfur atoms of large molecules involved in many important functions of the body. The result is that the molecules are disrupted and are prevented from performing their normal functions. Many of the reactions of ions and molecules in living systems are in a state of chemical equilibrium.

Chemical Equilibrium

We learned that a chemical reaction is reversible when the products react to reform the reactants. Reversible reactions are usually in a state of chemical equilibrium. to understand chemical equilibrium, let us examine the formation of ammonia from nitrogen and hydrogen according Haber process for manufacture of feltilizer.

$$\boxed{\underbrace{N_2 + 3H_2}_{V= 32\%} \longrightarrow \underbrace{2NH_3}_{v= 68\%}}$$

The reaction occurs when a mixture of 3 moles of hydrogen and I mole of nitrogen, the heated to 200 C are subjected to a pressure of 30 atm. We find that some hydrogen and nitrogen are still present. In fact, 32 percent of the volume of gases is still hydrogen and nitrogen; only 68 percent is ammonia.

The reverse reaction occurs when we start with pure ammonia. Under the same reaction conditions ammonia decompose to hydrogen and nitrogen. The ammonia is still present and we find that 68 percent of ammonia and 32 percent of nitrogen and hydrogen.

A chemical reaction is in a state of equilibrium when the amount of products formed per second by the forward reaction exactly equals the amount of products lost per second by the reverse reaction. This reaction express by the following equation :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The quantities of products and reactants present at equilibrium in any reaction are related to each other by equilibrium constant expression. For the reaction of hydrogen, nitrogen, and *equilibrium constant* expression is:

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

The symbol K is called the *equilibrium constant*. This constant is a ratio of the concentrations of the products to the concentrations of the reactants. The general form of this ratio depends on the *balanced equation* for the equilibrium reaction, temperature, and the pressure. The equilibrium constant for an equilibrium reaction

will always have the same value at the same temperature and pressure.
Examples :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad K=\frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

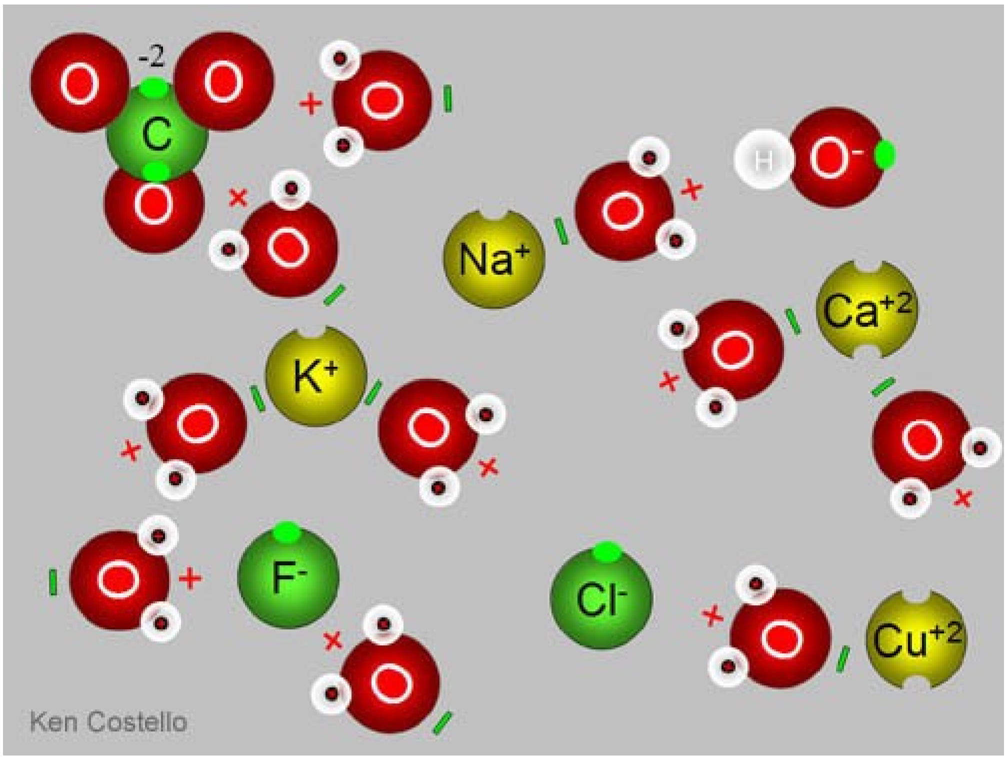
$$3O_2 \rightleftharpoons 2O_3 \qquad K=\frac{[O_3]^2}{[O_2]^3}$$

$$Cl_2 + 2HBr \rightleftharpoons Br_2 + 2HCl \qquad K=\frac{[Br]^2[HCl]^2}{[Cl][HBr]^2}$$

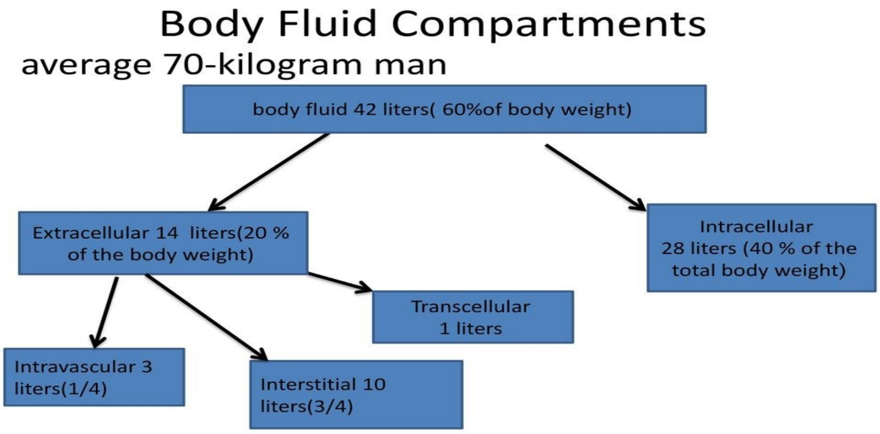
When the equilibrium constant is greater than 10^2, most of the reactants have been converted to products. Thus the *products are favored in an equilibrium reaction whose equilibrium constant is greater than* 10^2. conversely, when the equilibrium constant is less than 10^{-2}, only a very small amount of product is formed. Therefore, the *reactants are favored in an equilibrium reaction whose equilibrium constant is less than* 10^{-2}. if the equilibrium constant is between 10^{-2} and 10^2, neither product not reactant is greatly favored, and *both are present at equilibrium*.

Ions in body fluids

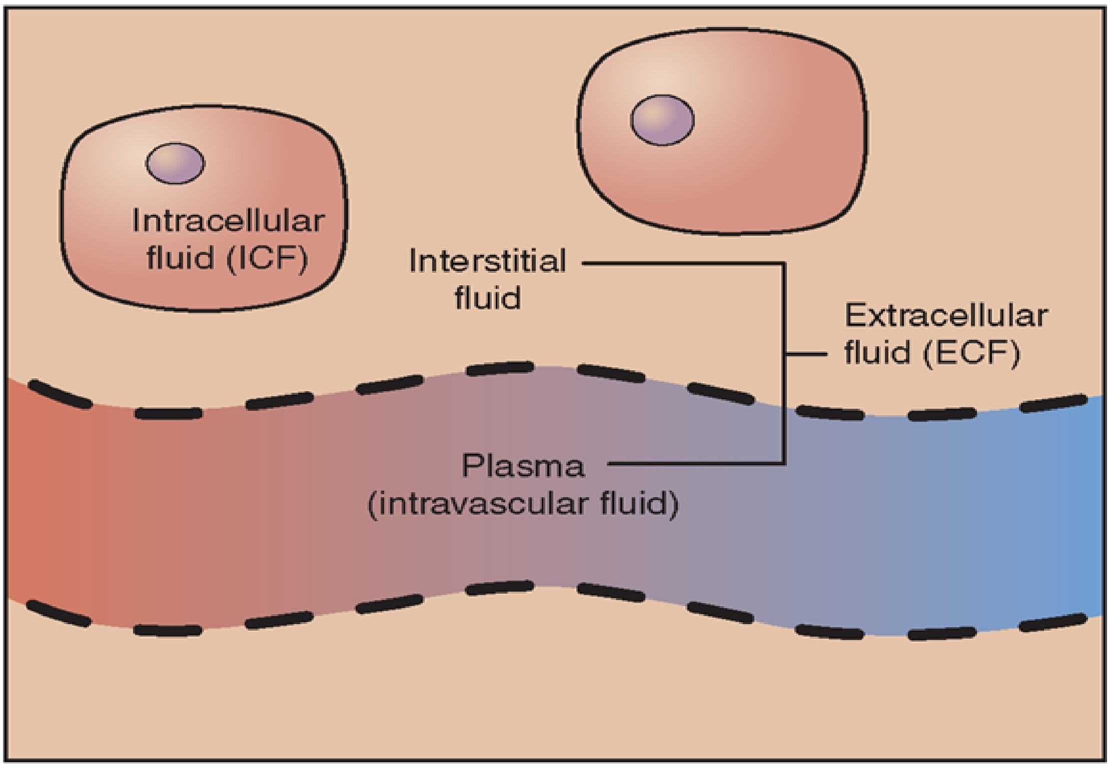
Introduction: A body fluid refers to any fluid produced by a living organism. In humans,The major component of the human body is water, which accounts for 63% of an adult male. and in female increased body fat content is associated with ageing , obesity, Consequently, the percentage of water in women falls to 52%, Dissolved within this water are carbon dioxide (CO2) nutrients, proteins and charged particles (ions).



the body fluid can be classified into two major types according to location:



(1) intracellular fluid (ICF): the fluid inside the cells. It makes up about 67% of the total body water composition in humans. The body fluid within the cell composed mainly of water dissolved ions, and other molecules.



(2) extracellular fluid (ECF):

The extracellular fluid is the body fluid located outside the cell(s). It makes up about 26% of the total body water composition in humans.

All fluids outside cells, its divide to:-

- interstitial fluid (ISF): exists in the spaces between cells and lie outside the vascular system. The interstitial fluid, the fluid filling up the spaces between cells, is the major constituent whereas the transcellular. The fluid found in the intercellular spaces composed of water, amino acids, sugars, fatty acids, coenzymes, hormones, neurotransmitters, salts, and cellular products. It bathes and surrounds the cells of the body, and provides a means of delivering materials to the cells, intercellular communication, and removal of metabolic waste.

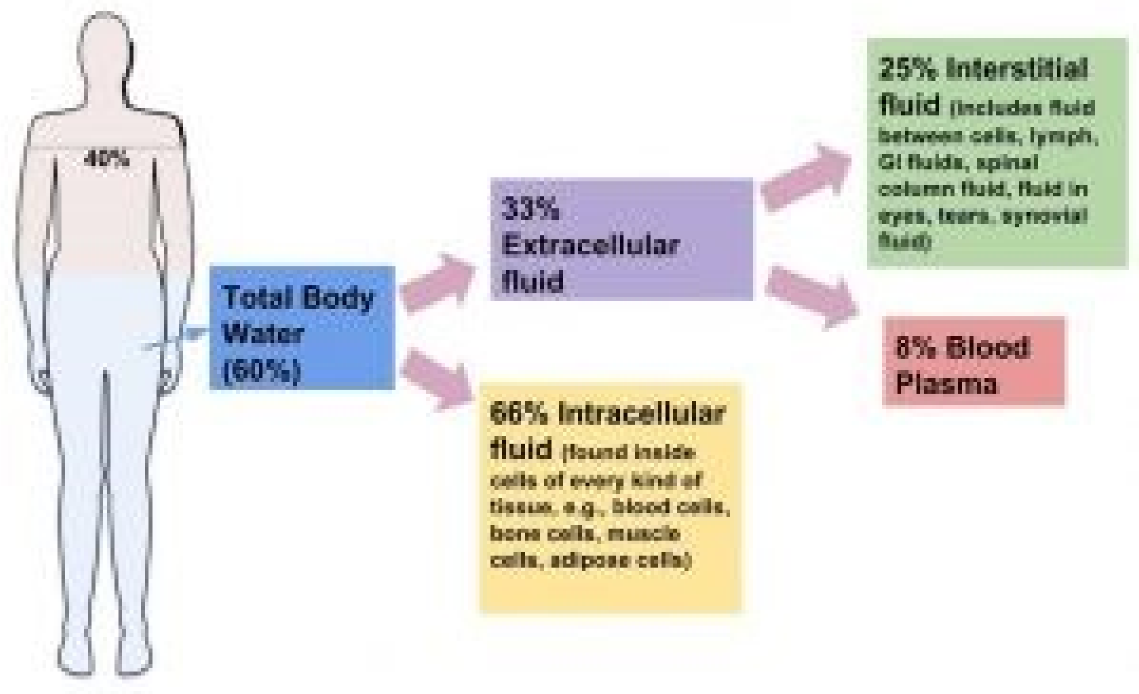
- intravascular fluid (IVF): exists as blood plasma in blood vessels.
intravascular fluid and plasma are in a state of continual exchange via pores in the highly permeable capillary membrane. The two fluids therefore have a similar composition, with the exception of large proteins, which are trapped within the capillaries in the vascular system.
Intravascular fluid (blood plasma), interstitial fluid, lymph and trans cellular fluid make up the extracellular fluid. The transcellular fluid is the smallest component of the extracellular fluid.

-Transcellular fluid (i.e): the fluid filling up the spaces of chambers formed from the linings of the epithelial cells, is the least.

Blood plays a major role in the body's defense against infection by carrying **blood** waste away from our cells and flushing them out of the body in **urine**, **feces**, and **sweat**.

Examples of body fluids are as follows:

- amniotic fluid
- bile
- blood plasma
- breast milk
- cerebrospinal fluid
- gastric juice
- lymph
- mucus
- saliva
- serous fluid
- semen
- sweat
- tears
- urine



The importance of body fluids:

1- helps to protect the cushion joints and organs.
2- Fluid helps to prevent dehydration.
3- Fluid helps your kidneys work to produce urine and remove waste from the body, and keeping the urinary tract healthy.
4- Rapid Specific Method for Determination of Aldosaccharides in the body
5- helps to control body temperature.
6- helps to carry nutrients around the body, and prevent constipation by keeping stools soft and regular.

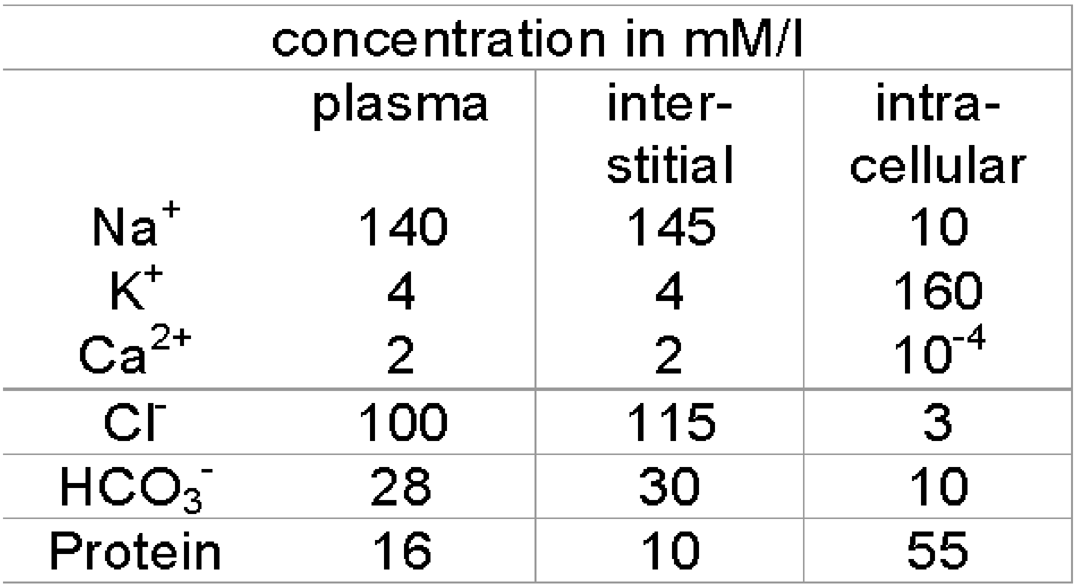
Body fluid Composition

(1) Intracellular Fluid Composition: The cytosol or intracellular fluid consists mostly of water, dissolved ions mainly cations and anions, small and large molecules, water-soluble molecules (such as proteins), metabolic blood gasses, hormones, and glucose. This mixture of small molecules is extraordinarily complex, as the variety of enzymes that are involved in cellular metabolism is immense.

These enzymes are involved in the biochemical processes that sustain cells and activate or deactivate toxins. Most of the cytosol is water, which makes up about 70% of the total volume of a typical cell. The pH of the intracellular fluid is 7.4 . The cell membrane separates cytosol from extracellular fluid, but can pass through the membrane via specialized channels and pumps during passive and active transport.
The concentrations of the other ions in cytosol or intracellular fluid are quite different from those in extracellular fluid. The cytosol also contains much higher amounts of charged macromolecules, such as proteins and nucleic acids, than the outside of the cell.

In contrast to extracellular fluid, cytosol has a high concentration of potassium ions and a low concentration of sodium ions. The reason for these specific sodium and potassium ion concentrations are Na+/K ATPase pumps that facilitate the active transport of these ions. These pumps transport ions against their concentration gradients to maintain the cytosol fluid composition of the ions.

(2) Extracellular fluid Composition The extracellular fluid is mainly cations and anions. The cations include: sodium (Na+ = 136-145 mEq/L), potassium (K+ = 3.5-5.5 mEq/L) and calcium (Ca2+ = 8.4-10.5 mEq/L). Anions include: chloride (mEq/L) and hydrogen carbonate (HCO3- 22-26 mM). These ions are important for water transport throughout the body.



concentration in mM/l			
	plasma	inter-stitial	intra-cellular
Na^+	140	145	10
K^+	4	4	160
Ca^{2+}	2	2	10^{-4}
Cl^-	100	115	3
HCO_3^-	28	30	10
Protein	16	10	55

Plasma is mostly water (93% by volume) and contains dissolved proteins (the major proteins are fibrinogens, globulins, and albumins), glucose, clotting factors, mineral ions (Na+, Ca++, Mg++, HCO3- Cl- etc.), hormones and carbon dioxide (plasma being the main medium for excretory product transportation). These dissolved substances are involved in many varied physiological processes, such as gas exchange, immune system function, and drug distribution throughout the body.

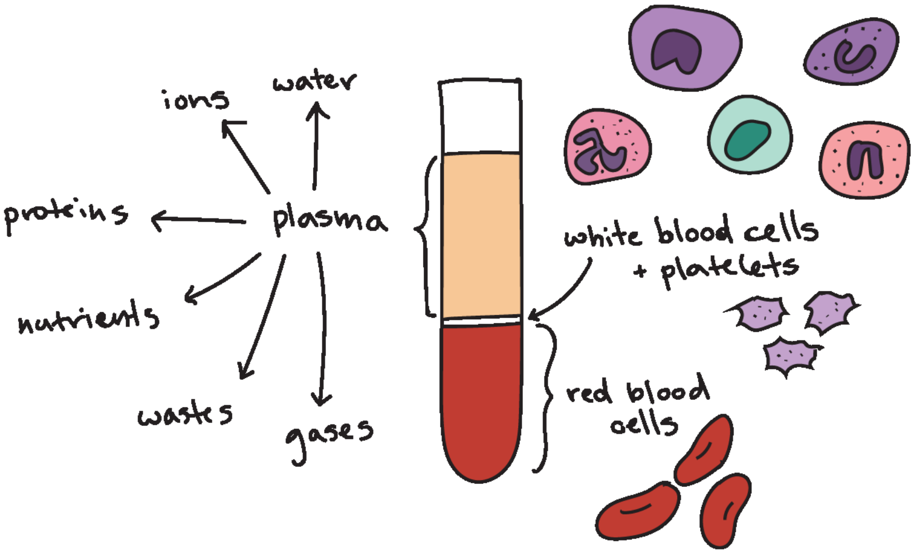
Because of its composition, therefore, serves as a delivery medium for nutrients and waste products. It is also a crucial site for various homeostatic mechanisms. For example , in humans, the normal glucose concentration of extracellular fluid that is regulated by homeostasis is approximately 5 mM. The pH of extracellular fluid is tightly regulated by buffers around 7.4. The volume of extracellular fluid is typically 15 L (i.e. 12 L is interstitial fluid and 3 L is plasma).

(3) Blood Plasma Composition

Plasma contains about 90 percent water, with 10 percent being made up of ions, proteins, dissolved gases, nutrient molecules, and wastes.

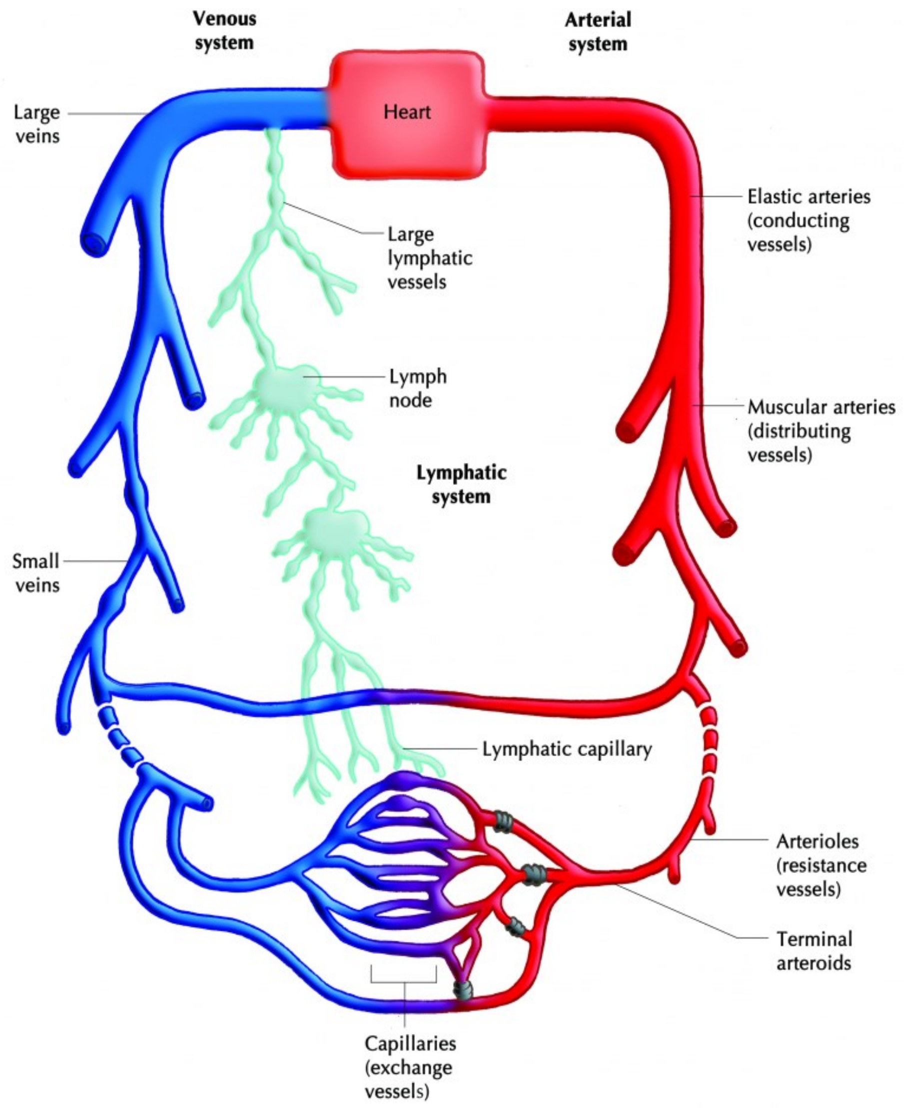
Plasma proteins are the most abundant substances in the plasma and are present in three major types, namely, albumin, globulins, and fibrinogen. They play specialized roles as follows:

Plasma that separates from blood in coagulation.The water substance in which all blood cells are suspended in, until movement by the heart pushes them along the bloodstream.



(4) Lymph composition

Lymph, derived from a Latin word, is fluid which flows through the lymphatic system that composed of lymph nodes and lymph vessels or channels, yellowish to almost colourless, slightly alkaline, It is very much similar to blood plasma, water (96%), inorganic and organic substances (4%), but has lesser number of calcium, proteins, phosphoeous, and high amount of glucose concentration. however lymph contains mainly of white blood cells, and (chlorides , bicarbonates) more than plasma.

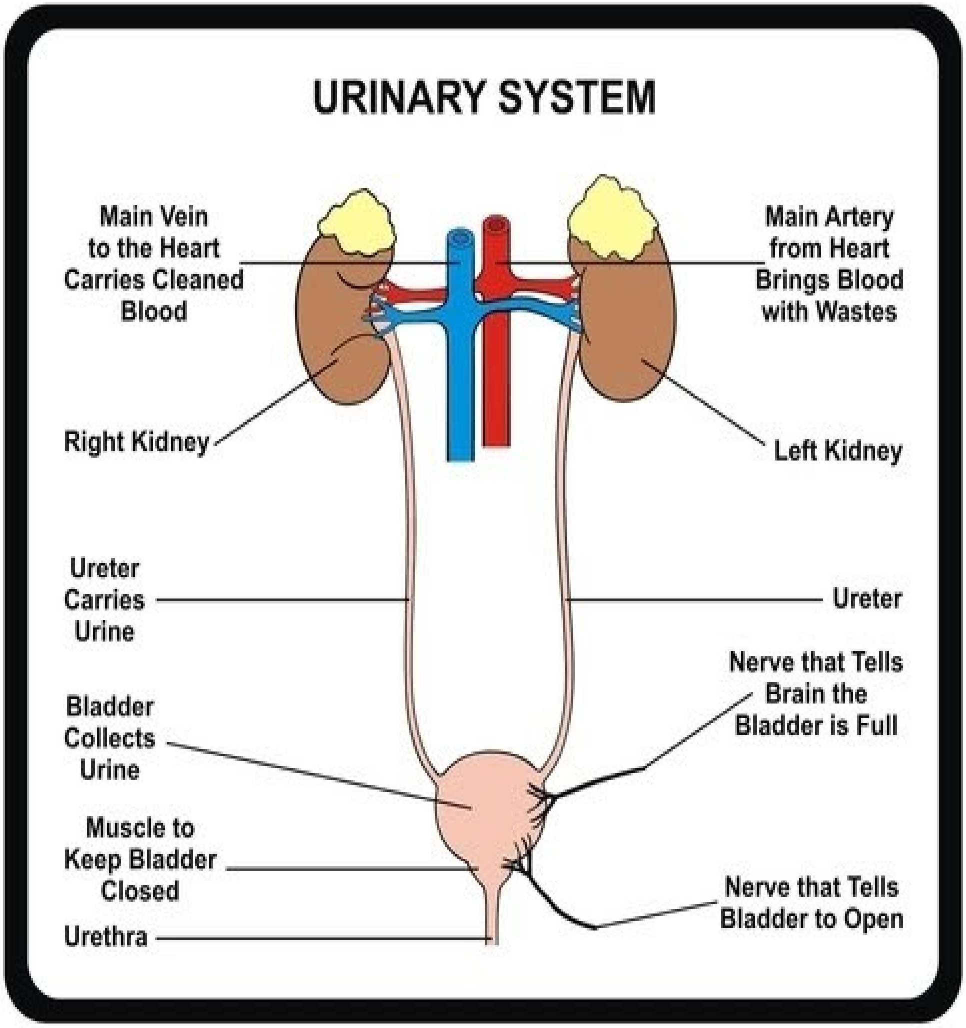


Body Fluid Regulation and Excretion

The body requires a particular volume of fluid within it in order to function normally. Most of the fluids which are taken into the body by drinking or eating are excreted by the kidneys to make sure the body does not have too much fluid (fluid over-load) or too little fluid (dehydration).

A relatively small amount of fluid is excreted from the body by sweating, opening bowels and breathing, but most of the fluid excretion occurs by urine production in the kidneys.

Healthy kidneys are extremely good at regulating the amount of fluid in the body. If a person drinks an extra 1.5 litres of fluid in a day, the kidneys will excrete an extra 1.5 litres of urine.



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Pollution

introduction

The environment has been taken care of in general, and the issue of pollution in particular, and at various levels, whether on the public formal education institutions or the non-formal education institutions. In spite of the great interest in environmental education programs, the reality of this situation is still that environmental care and importance are modest and insufficient to effect the desired effect in developing environmental awareness.

The world has known since the beginning of the twentieth century a set of developments in the relationship of man to the environment, as this century was marked by a set of transformations that caused severe impacts on the environment. The most notable of these transformations are the massive industrialization that the whole world and the developed countries in particular have known, in addition to the massive demographic explosion. These transformations have caused serious environmental problems, perhaps the most important of which is pollution that has affected all aspects of life. This is what imposed on those concerned with the environment, health, education and information in society, shedding light on the environment, providing environmental education that develops awareness of community members, alerting them to the dangers of environmental pollution, and most importantly, directing their behavior to caring for and preserving the environment. The topic of pollution and environmental studies has received the attention of specialists and international public opinion, so there are numerous seminars and conferences dealing with environmental issues and problems. Everyone has been warned that the fundamental solution to the current environmental crisis ازمة requires a major change in human attitudes towards their environment, and educational institutions must achieve this through environmental education curricula مناهج that provide an environmental culture that results in changes in behavior (Park, 1988). As the curriculum contains environmental educational experiences helps to broaden learners' perceptions, and increases their knowledge of how to deal with the environment . The issue of pollution is one of the most important study topics included or that must include environmental educational concepts, which one must acquire and adhere to.

DEFINITION

Chemical pollution is defined as the presence or increase in our environment of chemical pollutants that are not naturally present there or are found in amounts higher than their natural background values. Most of the chemicals that pollute the environment are man-made, resulted from the various activities in which toxic chemicals are used for various purposes.

The chemicals in their gaseous, liquid, and solid states that are characterized by their effict, toxicity, or explosive potential, or to corrosive events, or that have other characteristics that could result in a risk to the environment and public health, whether alone or when related to other materials. There is no doubt that the industry is one of the most important sources that produce chemical pollutants in our world today due to the multiplicity of industries and the tremendous progress in the industrial application of modern science, which is known as technology and is considered the most chemical pollutants resulting from industry have the ability to accumulate in the body of living things It reaches toxic degree.

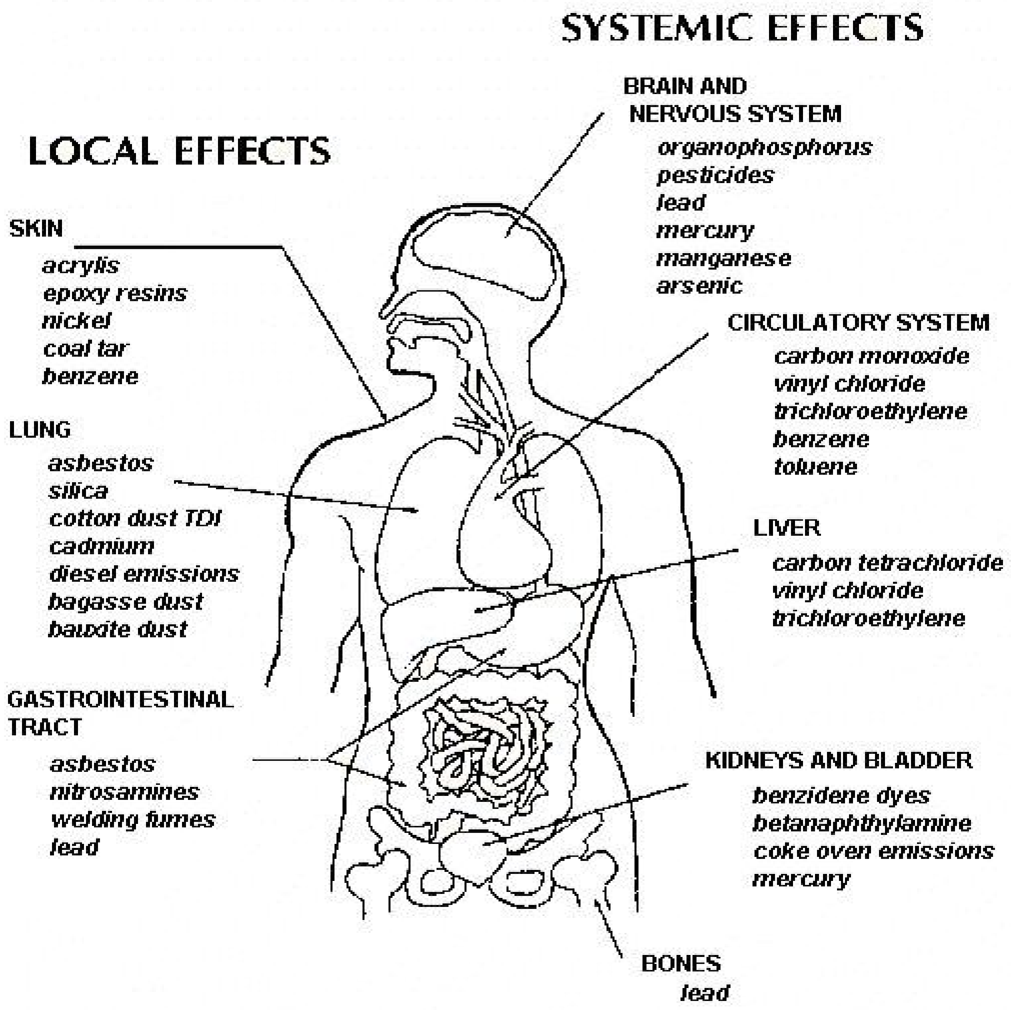
Sources of pollution

pollution is divided into two types:
natural pollution and industrial pollution.

Natural pollution : pollution is the source whose source is due to natural phenomena الظواهر that occur from time to time, such as البراكينvolcanoes, thunderboltsالصواعق, and storms العواصف that may carry huge amounts of sand and dust, and damage cropsالمحاصيل, so natural pollution is therefore sources of natural origin, and there is no income for man in it.

Industrial pollution: -Industrial pollution results from human action and activity, and finds its source in man's industrial, service, and entertainment activities, etc., and in his increasing uses of modern technology manifestationsالمظاهر and its various innovations. It responsible for the emergence of the pollution problem in our time, and reaching this degree The serious threatتهديد to life and the survival of man on the surface of the earth, and among the most important sources of industrial pollution, industrial and commercial waste and what is emitted by car exhaust, and factory chimneys that leave toxic (chlorine, fluorine and carbon) compounds, and others.

Chemical substances effects of human healthy

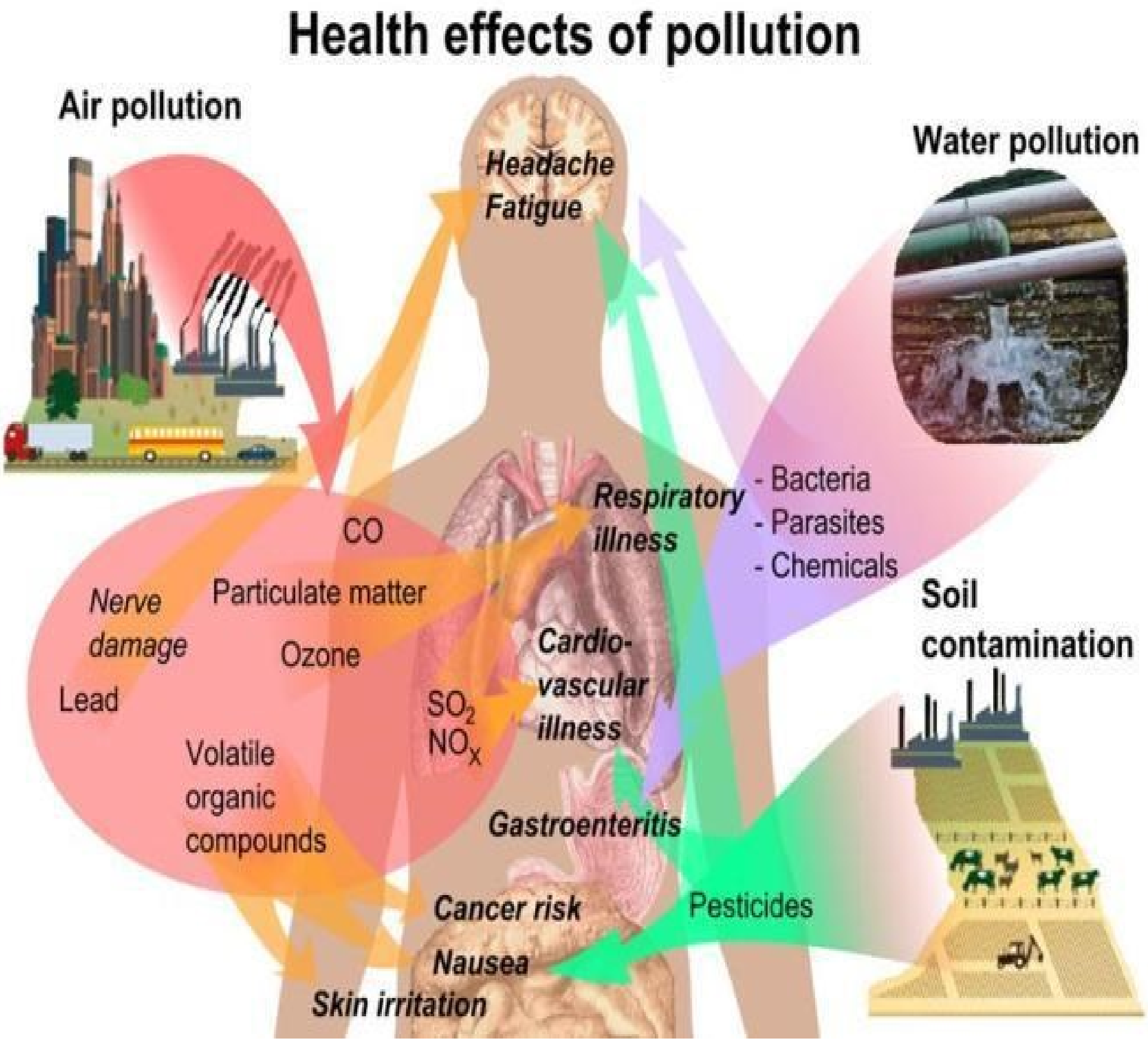


- **The severity الخطر of industrial pollution depends on several factors, including:** شدة التلوث

1. The area from which industrial pollutants are emitted
2. Time period for pollution.
3. The degree of concentration of pollutants.
4. Physical, chemical and biological properties of pollutants.
5. The ability to decompose and assimilate in the environmental environment in which it is placed.
6. Toxicity relative to humans and other organisms.

- The general pollutants classified according to the property of harmful مضار substances or products into environment to:

(Water pollution, Air pollution, Soil pollution, Nuclear pollution and Biological pollution)



MAIN TYPES OF CHEMICAL POLLUTION: These chemicals can react with tissues in the body and change the structure and function of the organ, cause abnormal growth and development of the individual, or bind with the genetic material of cells and cause cancer. One of the central tenets of the study of such effects (toxicology) is that the dose of a chemical determines its overall effects and that most chemicals can be dangerous at high exposure

1. **Inorganic pollutants**: Inorganic pollutants are released into the environment due to activities of mining, industry, transportation and urbanالحضاريه activities. Environmental risks associated with inorganic pollutants vary widely due to several complex interactions at both intracellular and extracellular levels. Toxic heavy metals and metalloids interact quite strongly with soil constituents as compared to salts of alkali metals, rate of which however, depend on the element and their speciation.
2. **Organic pollutants**: More of organic compounds used in industry and medical field there are we exposure in daily life, They're used for drugs and cleaning applications and as solvents in a wide range of products such as fuels, paints, inks, preservatives and pesticides , therefore causes more pollutions, So can have serious impacts of human health. and many can be absorbed through intact skin and absorbed into the bloodstream; and may be have more major route of entry into the body.
3. **Nuclear (Radiation) pollutants**:

Radiation warning symbol
(nuclear power plants)
محطات الطاقة النووية

Radiation pollution means the leakage of radioactive materials into one of the components of the environment, such as water, air, and soil. It is considered one of the most dangerous types of environmental pollution in our time, as it is not seen, smelled, does not feel. Without any resistance, and without any indication of its presence, and without first having an effect, and when radioactive materials reach the cells of the body, they cause visible and hidden damage that often leads to human life, and radioactive contamination may occur from natural sources such as radiation from outer space and gases Radioactive mounting from the cortex Z, or from industrial sources of nuclear power stations of atomic reactors and radioactive isotopes used in industry, agriculture, medicine or other.

Radioactivity is toxic because it forms ions when it reacts with biological molecules. These ions can form free radicals, which damage proteins, membranes, and nucleic acids. Radioactivity can damage DNA (deoxyribonucleic acid) by destroying individual bases (particularly thymine), by breaking single strands, by breaking double strands, by cross-linking different DNA strands, and by cross-linking DNA and proteins. Damage to DNA can lead to cancers, birth defects, and even death.

4. **Biological pollutants**: Biological or biological pollution is considered one of the oldest forms of pollution known to man, and this pollution arises as a result of the presence of visible or invisible living organisms such as bacteria, fungi and others in the environmental medium such as water, air or soil, so the mixing of disease-causing organisms with food that The person eats it, the water he drinks, or the air that he inhales causes biological pollution, which leads to disease.

- The effect of chemical pollutants on human health There is no شكdoubt that the human body is poisoned by chemical pollutants if exposed to it, and poisoning is the occurrence of a demolition in the biological composition of some parts of the body and acute poisoning occurs as a result of exposure to toxic gases for twenty-four hours, while chronic poisoning occurs as a result of exposure to pollutants for a long period of time intermittent. Man can control solid or liquid chemical pollutants for easy identification, collection and disposal in remote places. As for gas chemical pollutants, they are rapidly spreading and some cannot be seen, which is difficult to collect if they are spread. There are three ways by which gas pollutants enter the human body and are:

- Through the respiratory system when breathing.
- Through the digestive system when eating foods and drinks.
- Through the skin, especially in the injured areas.

Type of Industrial pollutants:

1. Solid pollutants, which are those pollutants resulting from many industries, such as dust resulting from the cement industry, for example.
2. Liquid pollutants such as the solutions of the chemical materials that the factories throw into the waterways.
3. Gas pollutants such as gases and harmful smoke from industrial chimneys and oil refineries.

Most important organs of the body affected by toxic pollutants are the kidneys and liver, where pollutants accumulate, as the skin and eye sensitivity are a sign of the presence of substances with an unhealthy effect in the atmosphere, and the fear of the effect of chemical pollutants on human health is not limited to the surrounding pollutants but rather leads to fear of using Chemicals in the various products that a person uses daily and that are included in food and drink items such as preservatives and flavors added to food. The World Health Organization issues lists of these materials to stop use in the food industry in the countries of the world.

hazards of environment Pollution

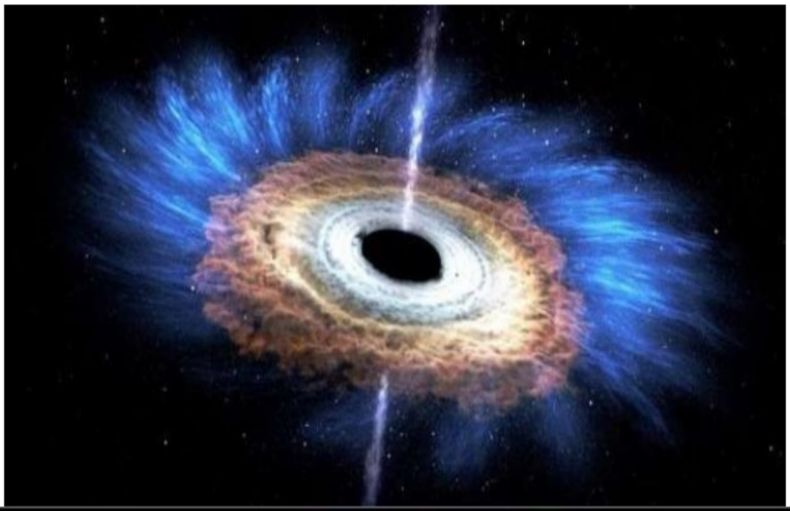
1. Poisoned marine organisms, which may cause their death, thus affecting the food chain in the ecosystem.
2. Damage to living organisms that live on Earth, whether they are microorganisms, plants or animals, as it loses soil fertility, and may lead to desertification.
3. Global warming occurs, which may cause environmental disasters, such as: global warming, as well as melting ice in the Arctic and which causes the percentage of water on the earth to rise, and thus drown.

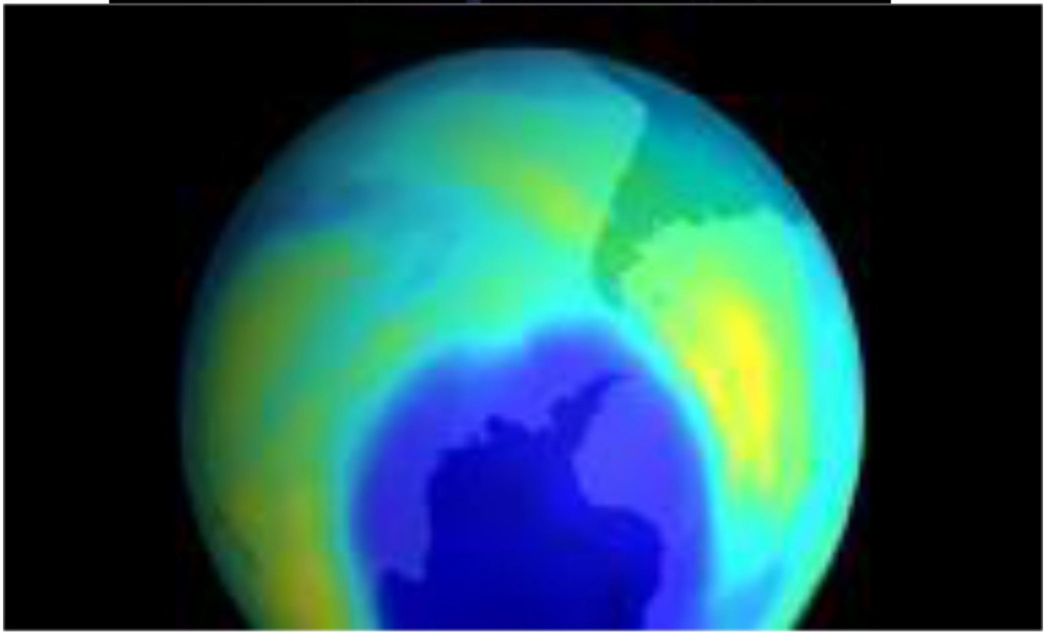
4. It leads to a hole in the ozone layer, which leads to an increase in the harmful UV rays reaching the earth, which affects human life.

Gases pollutants such oxides of salver, carbon, and nitrogen as well as the chloroflurocarbon compounds are broken by UV radiation releasing chlorine and fluorine free radical those react woth ozone of stratosphere cause decomposed it:

$SO_2 + O_3 \rightarrow SO_3 + O_2$, $NO + O_3 \rightarrow NO_2 + O_2$

$CF_2Cl_2 \rightarrow Cl^{\bullet} + C^{\bullet}F_2Cl$, $Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$





5. Acid rain causes corrosion various impacts and buildings due to the rise in the proportions of some gases.

$SO_2 + H_2O_2 \rightarrow H_2SO_4$

$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$ $CO_2 +$

$H_2O \rightarrow H_2CO_3$

The Effects of Chemical Pollution

Chemical pollution can be caused by a variety of chemicals from a variety of sources and can involve a variety of health effects from simple digestive problems to chemical intoxication and sudden death by poisoning. The effects are usually related to the exposure to high amounts and accumulate of chemicals in body. Chemical pollution leads to various serious diseases, generally by consuming poisonous food, drinking highly contaminated water, or breathing contaminated air.

Chemical intoxication can have severe health effects that may trigger immediate symptoms and diseases or delayed effects which may appear after weeks or months since the exposure occurred. This is based on the type of pollutants and on the amounts to which you are exposed. **CAUTION, never assume that all is OK if no health effects appear immediately!**

Chemical compounds intoxication are organic or inorganic chemicals that are the main causes of chemical pollution. The most common chemical pollutants are those compounds used across large areas and which are persistent, meaning they do not easily degrade in nature. Examples are most pesticides, herbicides, insecticides used in agriculture and gardening, as well as chlorinated solvents used in many industrial processes and dry-cleaning activities.

The chemical industry is another example in this sense, mainly because it is usually linked to polluted waste streams. In fact, the waste streams from chemical industry are now strictly controlled and treated before being released into the environment. But this was not always the case in the past and many rivers and surface water bodies were contaminated by the numerous waste streams coming from various chemical plants, as well as other industrial sources. Even though measures were taken to reduce this type of pollution, its effects are still visible.

Chemical intoxication is caused by exposure to chemical pollutants and can have immediate effects or delayed effects, which may appear after weeks or even months after the exposure occurred. Severe chemical intoxication may cause the death of the person that inhales an increased quantity of such substances.

HOUSEHOLD CHEMICALS involve a variety of chemical products and mixtures that can easily become chemical pollutants when released into the environment. Even the everyday detergents are chemical compounds that may pollute our environment! Read the labels of detergent products to confirm that they contain a variety of potentially hazardous chemicals. Such : (Pesticides, Fertilizers, Preservatives, Colorants and Flavor of Food and Cleaning substance and Drugs).

Containers labelled with chemical hazard warning signs

Pesticide risk of the health and environmental

pesticides have been commonly used to control pests causing release the pesticides component into the environment.

The intensive use of pesticide leads to an increased risk of contamination of the environment and harmful effects on varity biological, food security, and water sources.

The released pesticides into the environment and their impacts of the ecosystem and human health, such DDT, dieldrin, and other toxic have more affected of the healthy, because transfer to the humans by the foods of animals and plants.

Methods of prevention of environmental pollution

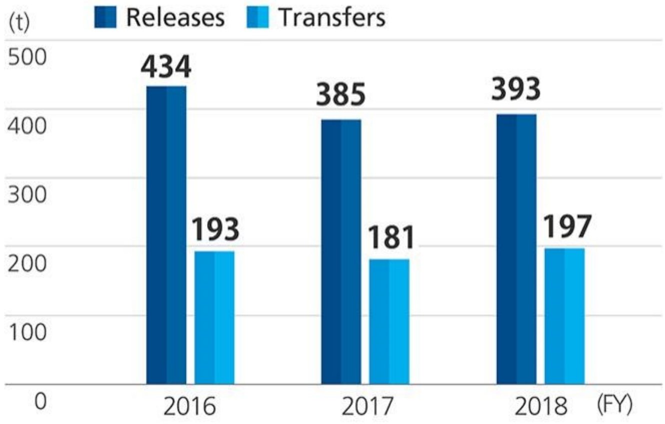
Take preventive precautions.

1. Maintaining hygiene in its various forms, including: personal hygiene, clean working environment, water, and soil.
2. Ensure the correct use of pesticides.
3. Waste disposal and disposal in the right way.
4. Getting rid of rodents and insects and eliminating them permanently.
5. Noise reduction.
6. Continuation in afforestation and erection of retaining walls in order to reduce the capacity of air pollutants.

Control of pollutant release and transfer register (PRTR) Substances

PRTR system: This system is for the control of chemical substances that are harmful to human health or the ecosystem. Under this system, businesses ascertain the amounts of harmful chemical substances they have released into the atmosphere, water, or soil, or transferred to locations outside of their business facilities, and report this data to the national government. The national government then uses this data and estimates to summarize and disclose volumes of chemical substances released or transferred.

Report of Amounts of PRTR Substances Released or Transferred
(Contain manganese, chromium, nickel, and lead as alloy substances)



Symbols of Handling, Releases, and Transfers of PRTR Substances

No.	Substance	Amount Used (kg)	Amount Released (kg)	Amount Transferred (kg)
412	Manganese and its inorganic compounds	2,535,608	0	21,200
300	Toluene	771,721	190,919	47,785
80	Xylene	203,756	18,742	1,899
87	Chromium and chromium(III) compounds	178,801	0	28,294
273	1-dodecanol	165,089	84,320	52,808
296	1,2,4-trimethyl benzene	159,894	66,436	23,955
53	Ethyl benzene	67,158	2,541	191
374	Hydrogen fluoride and its water-soluble salts	61,335	1,557	14,029
71	Ferric chlorides	49,985	0	0
297	1,3,5-trimethylbenzene	30,531	19,596	1,331

No.	Substance	Amount Used (kg)	Amount Released (kg)	Amount Transferred (kg)
88	Hexavalent chromium and its compounds	29,814	0	124
308	Nickel	29,168	0	0
302	Naphthalin	7,948	195	52
407	Polyoxyethylene = alkylether	5,882	5,746	80
392	n-hexane	4,676	1,859	661
438	Methylnaphthalene	4,604	23	0
321	Vanadium compounds	3,618	0	0
304	Lead	3,297	0	0
133	Ethylene glycol monoethyl ether acetate	3,245	26	0
207	2,6-Di-tert-butyl-4-cresol	2,598	833	1,765

No.	Substance	Amount Used (kg)	Amount Released (kg)	Amount Transferred (kg)
245	Thiourea	2,125	0	2,125
411	Formaldehyde	1,118	26	5
277	Triethylamine	1,101	62	16
	Total	4,323,070	392,882	196,320

Common Substances

- Formaldehyde
- Mercury
- Lead
- Asbestos
- Hazardous/Toxic Air Pollutants
- Per- and Polyfluoroalkyl Substances (PFAS)
- Pesticide Chemicals
- Polychlorinated Biphenyls (PCBs)

References:

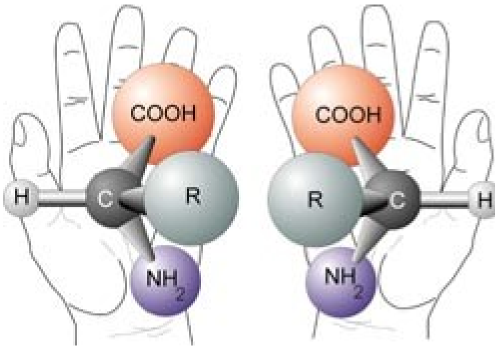
- *Environmental chemistry*
- *Emerging pollutants*
- *Chemical pollutants*
- *Environmental health*

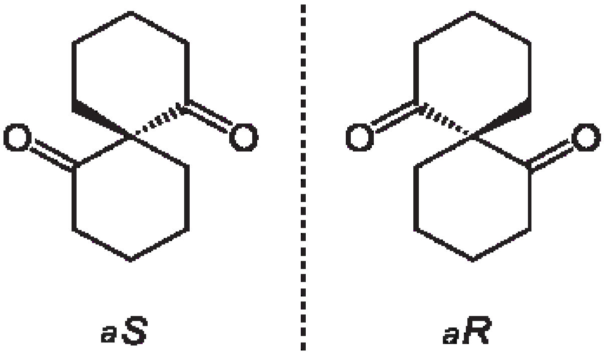
Medical chemistry (First course) First year

LEC (10)

Chirality in Biological Systems

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a non-superimposable set of two molecules that are mirror images of one another. The existence of these molecules are determined by a concept known as chirality. The word "chiral" was derived from the Greek word for hand, because our hands are a good example of chirality since they are non-superimposable mirror images of each other.





The opposite of chiral is **achiral**. Achiral objects are superimposable with their mirror images. If the molecules are superimposable, they are identical to each other. Try to line up your left hand perfectly with your right hand, so that the palms are both facing in the same directions.

The same thing applies to some molecules. A chiral molecule has a mirror image that cannot line up with it perfectly - the mirror images are non-superimposable. There are many of the biological molecules such as our **DNA, amino acids and sugars**, are chiral molecules.

This must mean that enantiomers have properties that make them different from their mirror image molecule. One of these properties is that chiral molecules do not have a **plane of** symmetry or an internal mirror plane.

So, a chiral molecule cannot be divided into two identical halves. Another property of chiral molecules is **optical activity**.

Organic compounds, molecules created around a chain of carbon atoms (more commonly known as the carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy. Since potential energy can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing the same atomic connectivity as another but differing in structural arrangements. This section is devoted to a specific type of isomer called stereoisomers and their property of chirality (Figure 5.1.1).

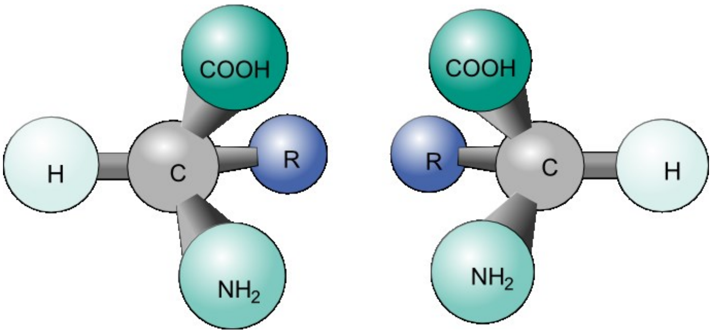


Figure 5.1.1. *Two enantiomers of a tetrahedral complex.*

The concepts of steroisomerism and chirality command great deal of importance in modern organic chemistry, as these ideas help to explain the physical and theoretical reasons behind the formation and structures of numerous organic molecules, the main reason behind the energy embedded in these essential chemicals. In contrast to more well-known constitutional isomerism, which develops isotopic compounds simply by different atomic connectivity, stereoisomerism generally maintains equal atomic connections and orders of building blocks as well as having same numbers of atoms and types of elements.

What, then, makes stereoisomers so unique? To answer this question, the learner must be able to think and imagine in not just two-dimensional images, but also three-dimensional space. This is due to the fact that stereoisomers are isomers because their atoms are different from others in terms of spatial arrangement.

Metals and DNA:

Chiral metal complexes provide unique molecular probes for DNA. Chiral reagents that "recognize" different local structures along the DNA strand have been designed by a process in which the asymmetry in shape and size of the complex is matched to that of the DNA helical groove. As a result, the chiral metal complexes provide very sensitive probes for local helical structure, both left- and right-handed. Direct coordination of chiral complexes to the DNA bases adds an element of sequence selectivity to the probe design. With a suitable reactive metal center, reagents that target chemically specific sites along the strand may be developed. One such chiral reagent, which cleaves left-handed DNA sites with photoactivation, has been useful in mapping this distinct conformation and examining its biological role. The conformation-specific molecular cleaver, much like a DNA-binding enzyme, recognizes and reacts at discrete sites along the DNA strand. These site-specific chiral metal complexes provide exciting new tools for probing the local variations in DNA structure and its role in the regulation of gene expression.

Chiral Metal Complexes

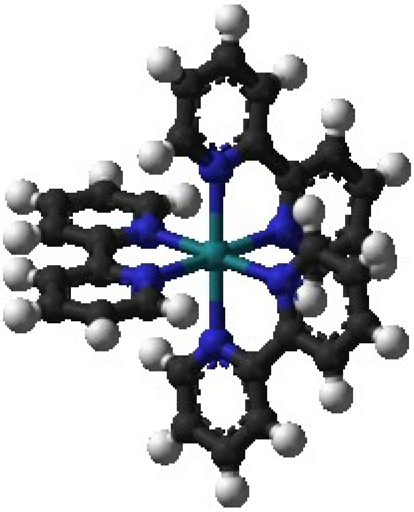
Chiral Metal Complexes As molecular recognition continues to gain importance in the biological and physical sciences as well as in the technologies of molecular electronics and optics, so has the need for efficient syntheses of chiral molecules. Chemists use of chiral organometallic molecules in discriminate between enantiotopic atoms, groups, or faces in achiral molecules and catalyze production of a broad array of natural or unnatural substances of excellent enantiomeric purity. Because of their ability to efficiently multiply chirality, even on an industrial level, these catalysts promise to exert a general impact on molecular science and engineering.

Biological importance

Many biologically active molecules are chiral, including the naturally occurring amino acids (the building blocks of proteins) and sugars.
Most scientists believe that Earth life's "choice" of chirality was purely random, and that if carbon-based life forms exist elsewhere in the universe, their chemistry could theoretically have opposite chirality.

Enzymes, which are chiral, often distinguish between the two enantiomers of a chiral substrate. One could imagine an enzyme as having a glove-like cavity that binds a substrate. If this glove is right-handed, then one enantiomer will fit inside and be bound, whereas the other enantiomer will have a poor fit and is unlikely to bind.

Ruthenium-tris(bipyridine) cation



Chirality is a symmetry property, not a property of any part of the periodic table. Thus many inorganic materials, molecules, and ions are chiral. Quartz is an example from the mineral kingdom. Such noncentric materials are of interest for applications in nonlinear optics.
In the areas of coordination chemistry and organometallic chemistry, chirality is pervasive and of practical importance. A famous example is tris(bipyridine)ruthenium(II) complex in which the three bipyridine ligands adopt a chiral propeller-like arrangement.

Chiral ligands confer chirality to a metal complex, as illustrated by metal-amino acid complexes. If the metal exhibits catalytic properties, its combination with a chiral ligand is the basis of asymmetric catalysis.

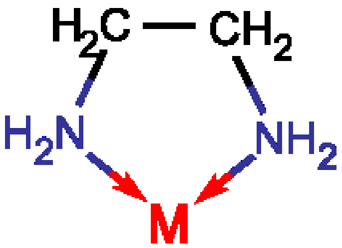
Chelating agents:

Chelation therapy

Some ligands called chelating agents, can bond with a metal ion in two or more places, forming stable complexes. Chelating agents are almost organic molecules or anions. Some chelating agents are used for the treatment of heavy metal poisoning in chelation therapy. A chelating agent that has two coordinating atoms is called bidentate; one that has three, tridentate; and so on.

Mainly atoms like S, N and O function as ligand atoms in the form of chemical groups like $–SH$, $–S\text{-}S$, $–NH_2$, $=NH$, $–OH$, $–OPO_3H$, or $>C=O$.

bidentate ligand



Chelation therapy:

Has the intent of removal toxic metal ions from the organism (that act as toxins) or of attenuating their toxicity by converting them in less toxic compounds, or of transferring them from the site where they exert their toxic action to a compartment where this cannot be executed.

A toxin is a poisonous substance produced within living cells or organisms.

Characteristics of ideal chelator

1- High stability of the formed complexes
2- Slectivity toward the target metal ion.
3- Slow biochemical metabolism of the chelating agent.
4- Good intestinal absorbtion (as drug).
5- Easy excertion of toxic metal in the complexed form by kidneys.
6- High water solubility.
7- High exchange rate of metal between natural ligands and chelator
8- Ability to penetrate cell memberance.

Uses of chelation therapy

Some examples of clinical scenarios where chelation therapy is indicated include:

1- Poisoning with heavy metals including lead, mercury, and arsenic

2- Overdose of medications containing metal ions

3- Accumulation of large amounts of iron in the body due to repeated blood transfusions (thalassemia) patients who require frequent blood transfusions.

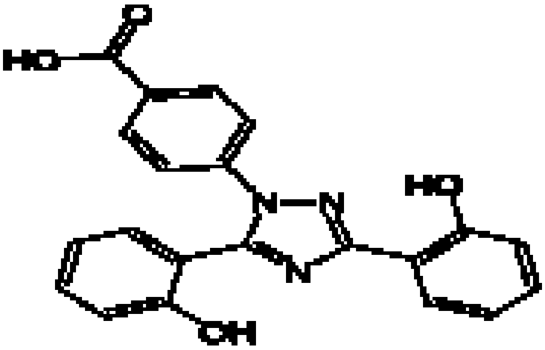
4- Accumulation of large amounts of copper in the body due to Wilson's disease, a condition where the body is unable to excrete copper normally.

Wilson's disease :**Disorder in which copper accumulates in tissues**.

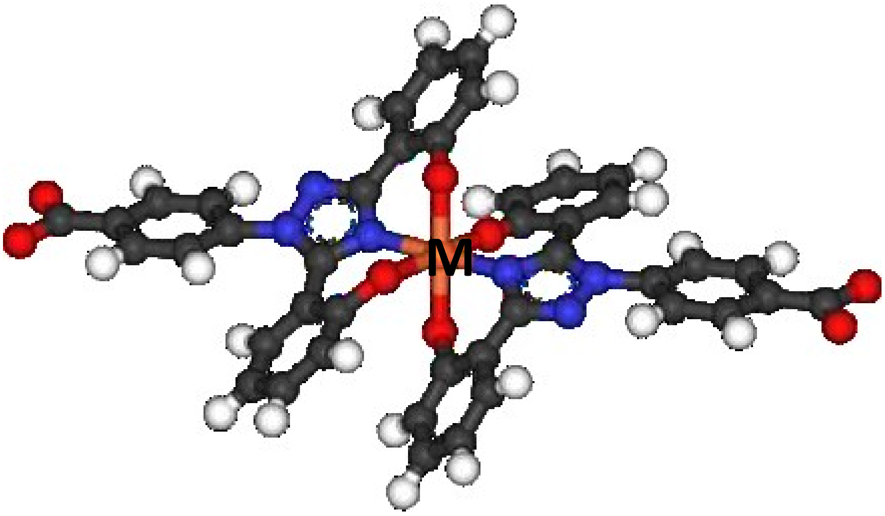
Thalassemia: **The abnormal hemoglobin formed results in improper oxygen transport and destruction of red blood cells.**

The most commonly used chelating agents today are :

1-Deferasirox



Binding mechanism of deferasirox:

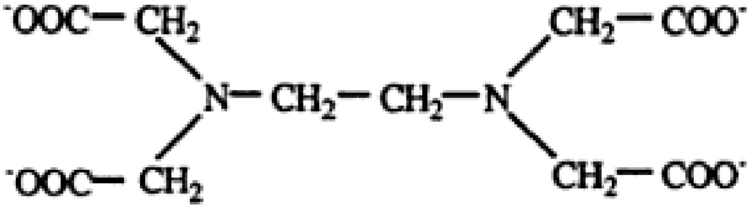


The tridentate structure results in the chelator binding iron (III) in a 2:1 ratio. This results in an iron complex coordinated by 4 oxygen and two nitrogen atoms. Despite the protein binding, good tissue penetration is seen with faster mobilization of tissue iron.

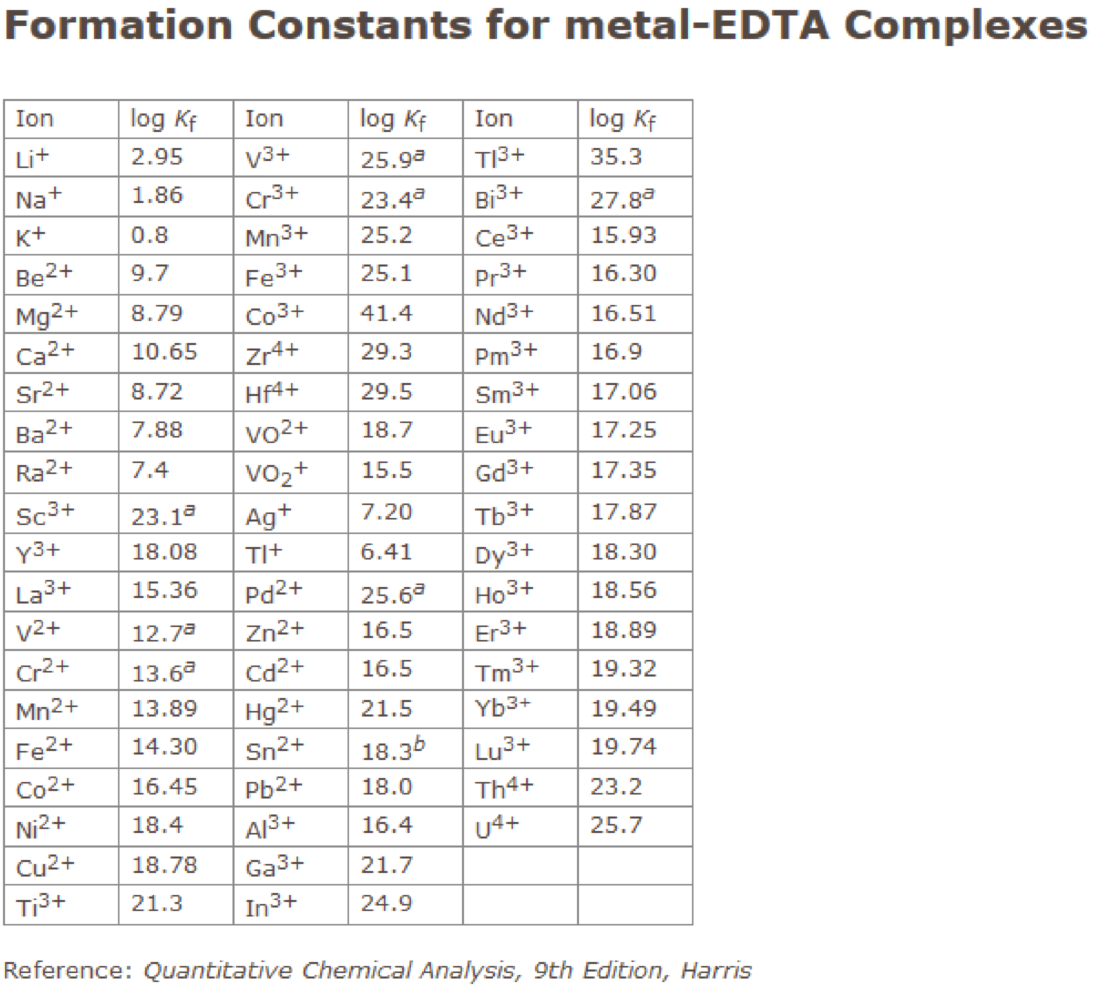
iron overload indicates accumulation of iron in the body from any cause.

Transfusional hemosiderosis is the accumulation of iron in the liver and/or heart

2-EDTA: (Ethylenediaminetetraacetic acid) (usually in its calcium disodium form).



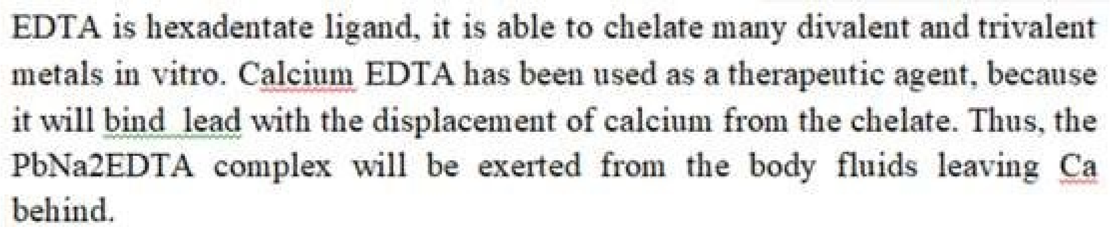
EDTA chelation of metal ions by deprotonated EDTA, a medication used in the management and treatment of heavy metal toxicity. It is in the chelating class of drogs.



Formation Constants for metal-EDTA Complexes

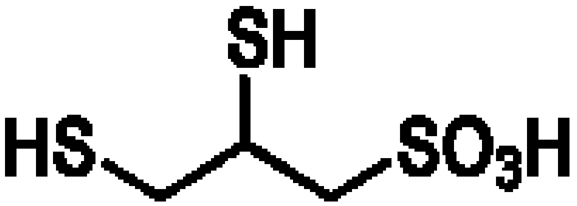
Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

Reference: *Quantitative Chemical Analysis, 9th Edition, Harris*



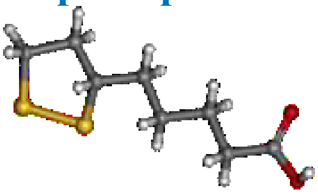
EDTA is hexadentate ligand, it is able to chelate many divalent and trivalent metals in vitro. Calcium EDTA has been used as a therapeutic agent, because it will bind lead with the displacement of calcium from the chelate. Thus, the PbNa2EDTA complex will be exerted from the body fluids leaving Ca behind.

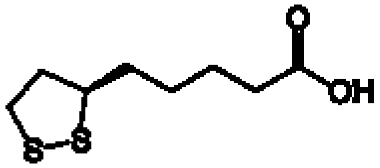
3-Dimercapto-propane sulfonate (DMPS)



Recommended for the treatment of acute arsenic and acute mercury poisoning

4-Alpha lipoic acid (ALA)



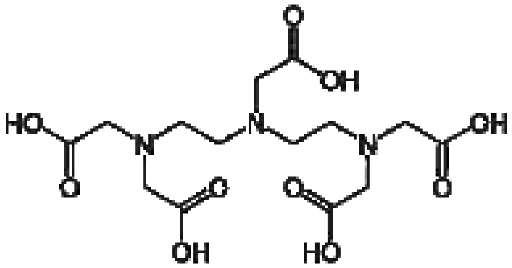


Lipoic acid administration can significantly enhance biliary excretion of inorganic mercury in rat experiments.

It has the potential to cross the blood–brain barrier in humans.

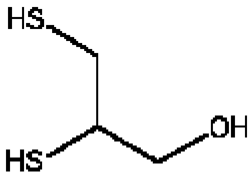
Bblood–brain barrier (BBB) is a highly selective permeability barrier that separates the circulating blood from the brain extracellular fluid (BECF) in the central nervous system (CNS)

5-Diethylene triamine pentaacetic acid (DTPA)



The trisodium calcium ($CaNa_3$-DTPA) and trisodium zinc ($ZnNa_3$-DTPA) are the only currently approved chelation drugs designed for removal the transuranic actinides plutonium (Pu), Americium (Am) and Curium (Cm)

6-Dimercaprol (BAL) **(British anti-lewisite)**

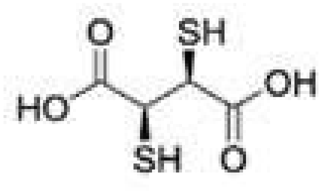


Used for the treatment of lead, arsenic and mercury poisoning.

Arsenic and some other heavy metals act by chemically reacting with adjacent thiol residues on metabolic enzymes, creating a chelate complex that inhibits the affected enzyme's activity. Dimercaprol competes with the thiol groups for binding the metal ion, which is then excreted in the urine.

7-Dimercaptosuccinic acid (DMSA)

Has been recommended for the treatment of lead and arsenic poisoning in human body. It is also effective against lead poisoning in children



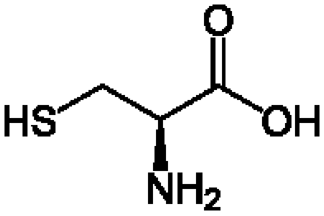
DMSA

Mechanism of binding :

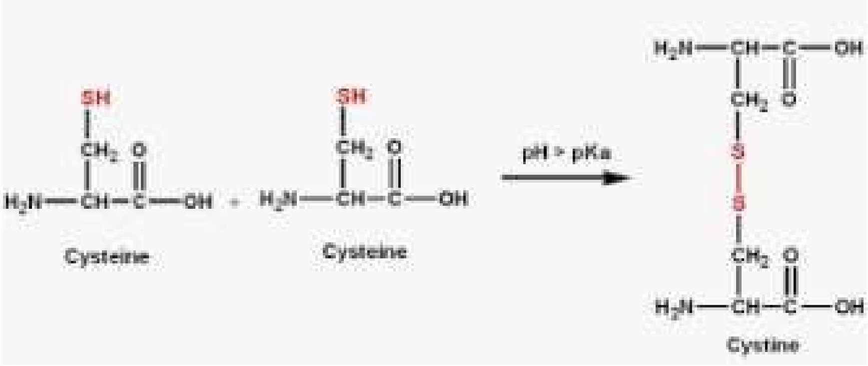
Removal the arsenic from the body

1- Arsenic (As) combines with thiol group of protein present in human body to form complex of arsenic- protein (complex-1).

2- DMSA has the ability to make free the affected protein by removing arsenic from the complex-1 in the human body according to the following mechanism

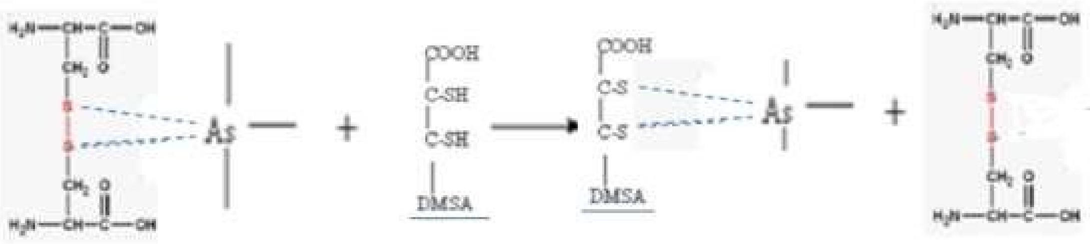


Cysteine



disulfide bond

Protein (disulfide bond) toxic As complex 1



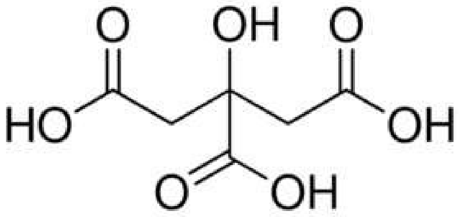
Protein (disulfide bond) DMSA complex 2 free protein

Chelating agents and dentistry

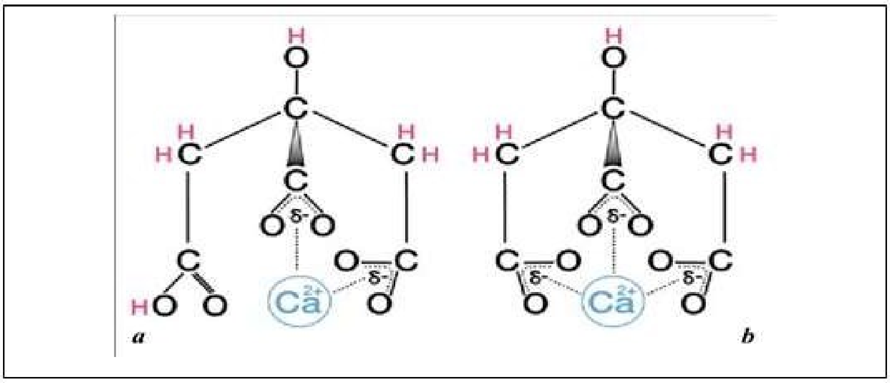
Chelating agents were introduced in dentistry for aid in preparation of narrow canals to soften the canal dentin, increase dentin penetrability and remove smear layer

Decalcifying agents are acidic substances that combine with lime (calcium-containing inorganic mineral) in bone salts, teeth, dentin, etc., forming water-soluble compounds that easily can be removed.

Citric acid as chelating agent



Citric acid structure



a: in acidic pH lost two hydrogen

b: in basic pH lost three hydrogen

The chelating properties of citric acid can enhance the erosive process by interacting with saliva as well as directly soften and dissolving tooth mineral. Up to 32% of calcium in saliva can be complexed by citrate at concentrations common in fruit juices, thus reducing the super saturation of saliva and increasing the deriving force for dissolution with respect to tooth minerals. Calcium-chelating agents may directly dissolve tooth mineral.

Tooth erosion happens when acids wear away the enamel on teeth. Enamel erosion can be caused by excessive soft drink consumption (high levels of phosphoric and citric acids) and excessive amount of citrus fruits.

EDTA as chelating agent

EDTA is used for 1 minute at the end of instrumentation to remove the smear layer so as to improve the antibacterial effect of locally used disinfecting agents in deeper layer of dentin

Removal of the smear layer is accomplished with acids or other chelating agents such as EDTA after cleaning and shaping, irrigation with 17% EDTA for 1 minute followed by a final wash with NaOCl is a recommended method. Chelators remove the inorganic compenents and leave the organic tissue elements intact. NaOCl is then necessary for removing of the remaining organic components.

Dental erosion is a combination of the mineral being dissolved by attack from the hydrogen ion and mineral dissolving by calcium being complexed by anions, especially those with strong chelating action such as citric acid and EDTA.

For research purposes, EDTA is a well known chelating agent that is used to demineralize bone and teeth samples for histological evaluation, it can demineralize at neutral pH because of the strength of the binding with calcium ions

Proteolysis-chelation theory

It was proposed by Schatz in 1966.
Concept: Simultaneous microbial degradation of the organic components and the dissolution of the minerals of the tooth by the process known as chelation.
It considers that, initially during dental caries, proteolytic breakdown of the organic portion of the entire enamel matrix takes place. Following this, a chelating agent is formed by the combination of proteolytic breakdown products, and acquired food debris, which facilities tooth decay. The whole process is helped by the bacterial enzymes which facilitate tooth decay.

The chelating agent, which is formed, is always negatively charged (mostly due to its protein content) and release the positively charged calcium ions (Ca^{++}) from the enamel or dentine. So chelation can be defined as a process that involve the complexing of a metallic ion to a complex substance by a coordination bond which results in a highly stable, poorly dissociated and weakly ionized compound called chelate. This theory explains that the destruction of organic matrix of the enamel as well as its mineral contents.

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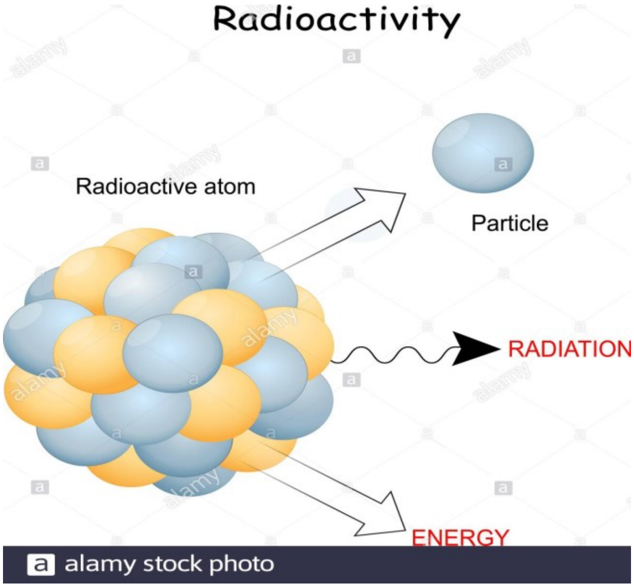
Radiochemistry

Radioactivity:

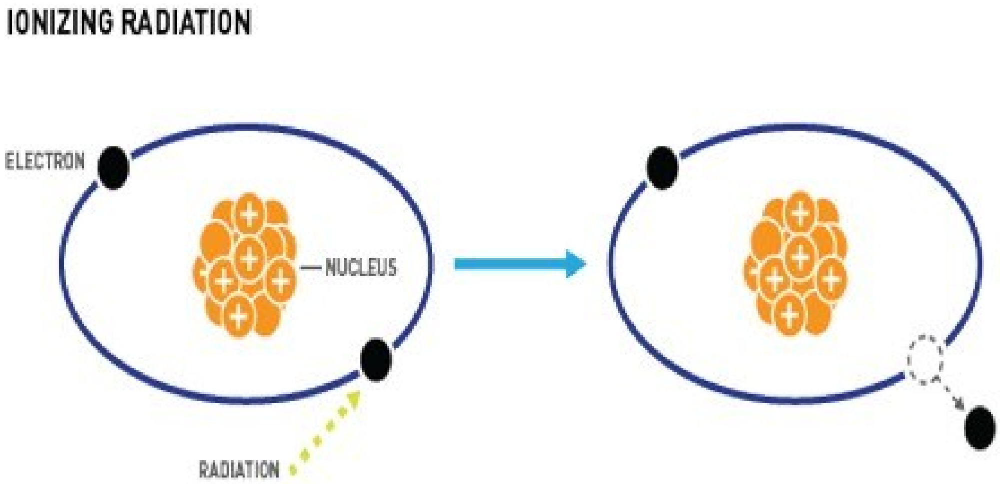
We learned in previous that there are **isotopes** of almost all the elements, ***isotopes*** can be defined as atoms whose nuclei have the same number of protons but different number of neutrons. Most of these isotopes are **stable**, but some are **unstable**. The nuclei of unstable isotopes undergo spontaneous nuclear reactions that cause particles and energy, called ***nuclear radiation***, to be given off. The emission of these particles and energy by an isotope is called ***radioactivity***. Only a few isotopes found in nature are radioactive.



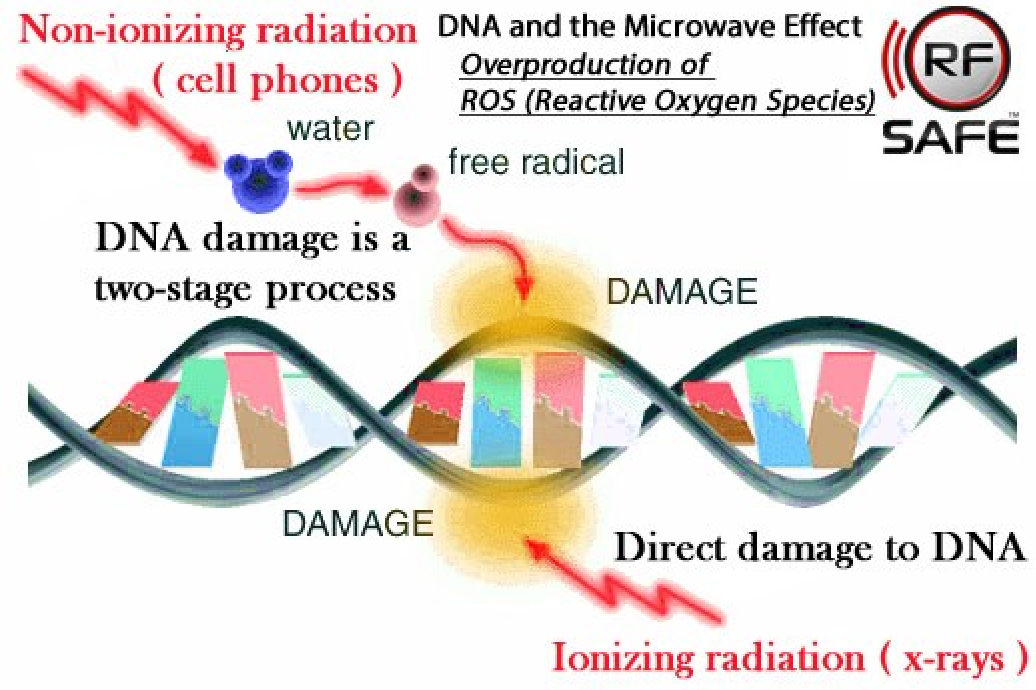
Radioactive isotope used now days in:

1. Abundant energy.
2. Nuclear weapons.
3. Radiation therapy.

Nuclear reactions: Atoms do change from one kind to another when they emit radiation. This change occurs during a nuclear reaction, when nucleus of an isotope emits **α** or **β** particles. When this happens, the nucleus gains or loses positive charge. The radiation from radioactive isotopes and x-rays can form ions in matter by knocking electrons off the atoms and molecules in its path. For this reason, it is called ***ionizing radiation***.



The chief effects of radiation on living systems are due to these ionization reaction. Repeated exposure to low levels of radiation seems to have a number of major effects on health. among them are cancer (carcinogenic effects), damage to the fetus, and genetic damage.



Dr. Mahmoud AL-Fahdawi

For example as the following nuclear equation:

$$\begin{array}{l} \text{Mass no.} \dashrightarrow \\ \text{atomic no.} \dashrightarrow \end{array} {}^{40}_{19}\text{K} \longrightarrow {}^{40}_{20}\text{Ca} + {}^{0}_{-1}\beta$$

$${}^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

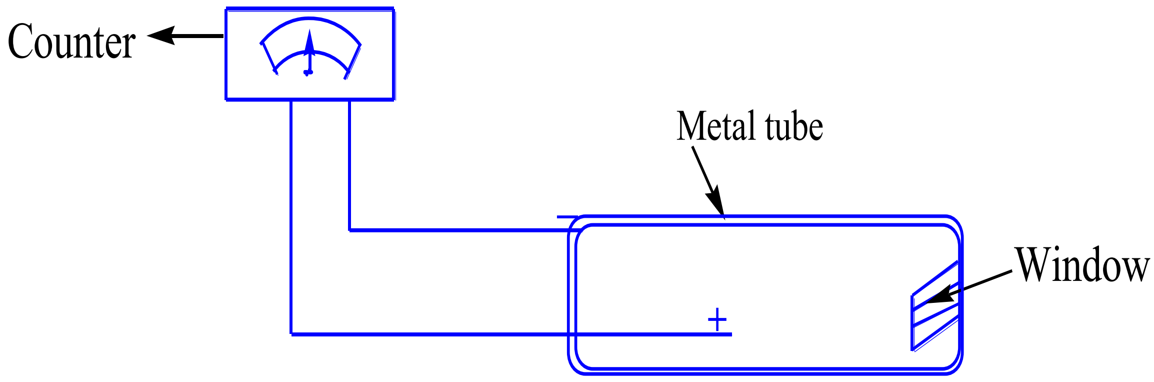
Detecting ionizing radiation:

Radiation disturbs the electronic environment of the atoms and molecules that it encounter. There are three methods of detecting ionizing radiation frequently used:

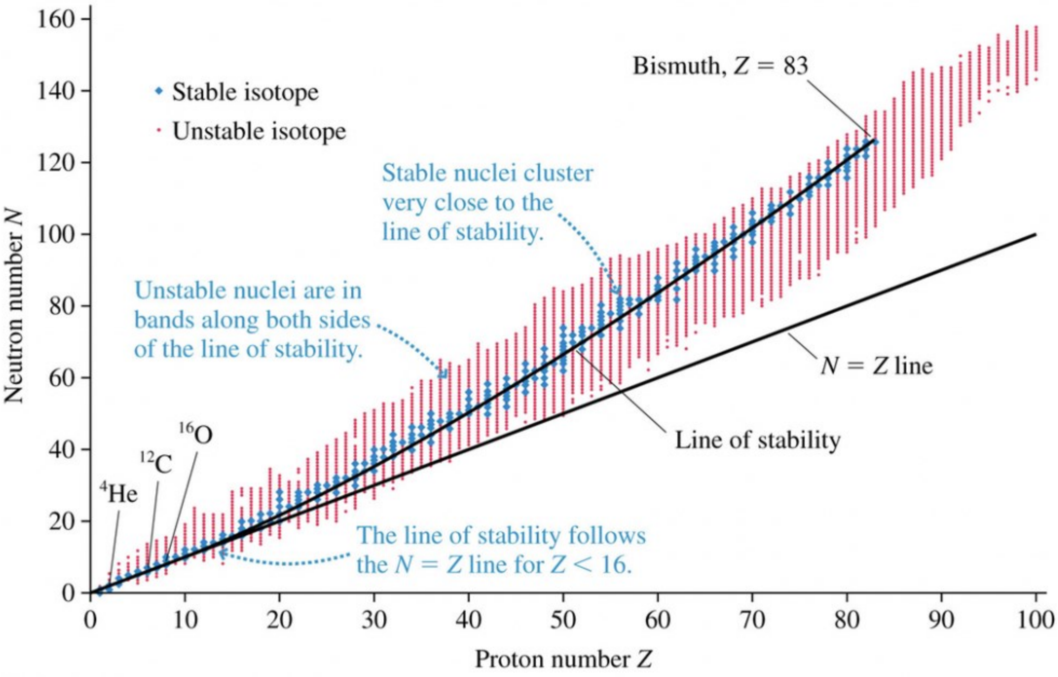
1. photographic method; photographic film and paper shielded from light are exposed by ionizing radiation. This exposure is detected by developing the film in the usual way.
2. Scintillation counter; (liquid and solid), the solid contains a surface coated with a special substance (NaI with Ti) gives off flashes of light when hit ionizing radiation (invisible transformed to visible light).
3. Geiger counter; consist of :

a. Metal tupe
b. Inert gas
c. Large potential difference maintained between metal and wire.

m



Nuclear stability: nuclear force is a strong force of attraction between nucleons (proton & neutron). Protons and neutrons have energy levels. Nuclei with certain no. of protons or neutrons appear to be stable (Magic no.)
Isotopes with even number of p or n are generally more stable.



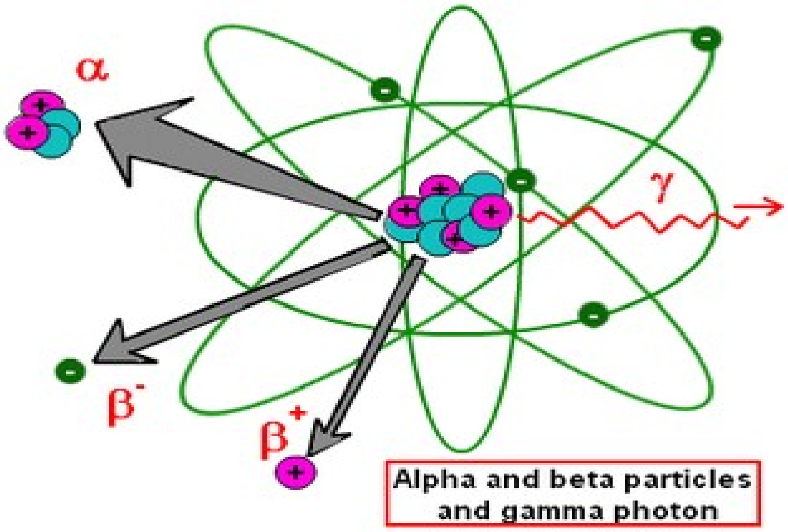
Naturally occurring radioactive substances:
All elements of atomic number more than 83 (Bi) are radioactive. There are three series (families) of naturally occurring radioactive substances:

1. Uranium series: U^{-238} **Uranium** $\longrightarrow$ $\longrightarrow$ **decay** $\longrightarrow$ Pb^{-206} **stable**

2. Actinium series: U^{-235-} **actino uranium** $^{227}\mathrm{Ac}$ $\longrightarrow$ **decay** $\longrightarrow$ Pb^{-207} **stable**

3. Thorium series: Th^{-232} $\longrightarrow$ $\longrightarrow$ **decay** $\longrightarrow$ Pb^{-208} **stable**

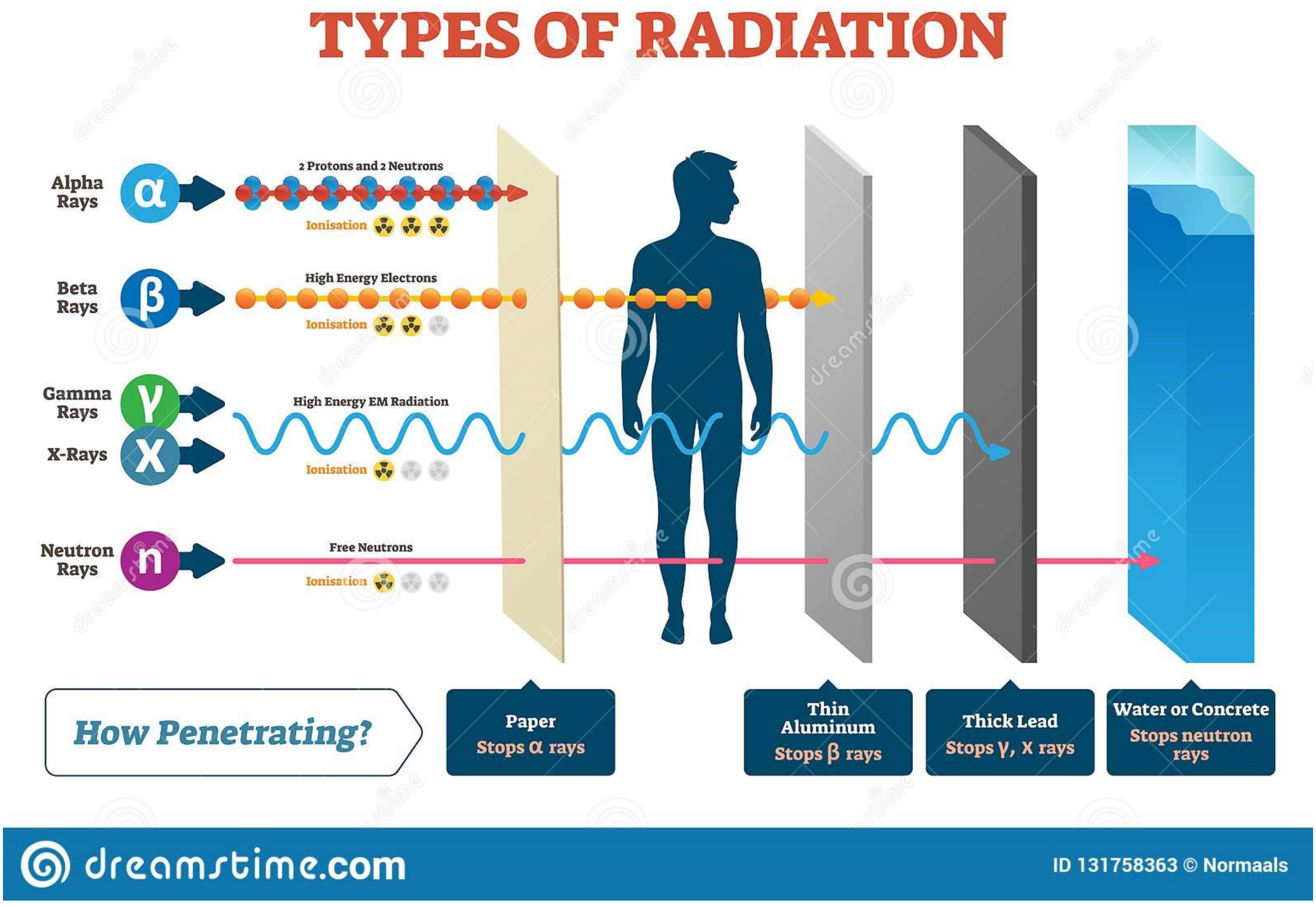
Tape of radiation:



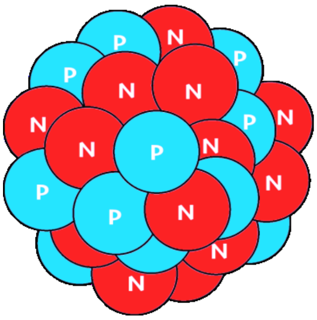
(1) **Alpha radiation (α):** is a stream of particles moving at about one-tenth of speed light. Each particle is the nucleus of a helium atom ($^4_2He^{2+}$). They are large and heavy, so they cannot travel very far, they cannot penetrate the skin. If a substance that emits α-particles gets inside the body by being inhaled or swallowed, the α can damage internal organs.

(2) **Beta particle (β):** is a stream of particles, but the particles are electrons. The electrons are produced within the nucleus by the transformation of a neutron into a proton and an electron. The proton stays in the nucleus and the electron is emitted. An electron is smaller than helium nucleus, travels much faster, and can penetrate the skin to a depth of a few centimeters.

(3) **Gamma radiation (γ):** is not a particle, but a form of energy similar to light waves, x-rays.
This radiation has high energy and can penetrate deep within the body and cause serious damage.



(4) Neutron radiation(n) consists of a free neutron, usually emitted as a result of spontaneous or induced nuclear fission. Able to travel hundreds of meters in air, they are however able to be effectively stopped if blocked by



(5) **Positron (β^+)**: also called **positive** electron, **positively charged** subatomic particle having the same mass and magnitude of **charge** as the electron and constituting the antiparticle of a negative electron.

Properties of nuclear radiation

Types of Radiation	*Composition*	*Symbol*	*Mass (a.m.u)*	*Charge*	*Penetration (cm)*
Alpha	**He nucleus**	$(\alpha)\,{}^{4}_{2}He$	**4**	**+2**	**0.01**
Beta	**electron**	$(\beta)\,{}_{-1}^{0}e$	**1/1837**	**-1**	**1**
Gamma	**energy**	(γ)	**0**	**0**	**100**
Neutron	**neutron**	$(n)\,{}^{1}_{0}n$	**1**	**0**	**>100**
Positron	**positron**	$(\beta^{+})\,{}^{0}_{1}e$	**1/1846**	**+1**	**1**

Examples:

$$* \quad {}^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He \qquad -\alpha-$$

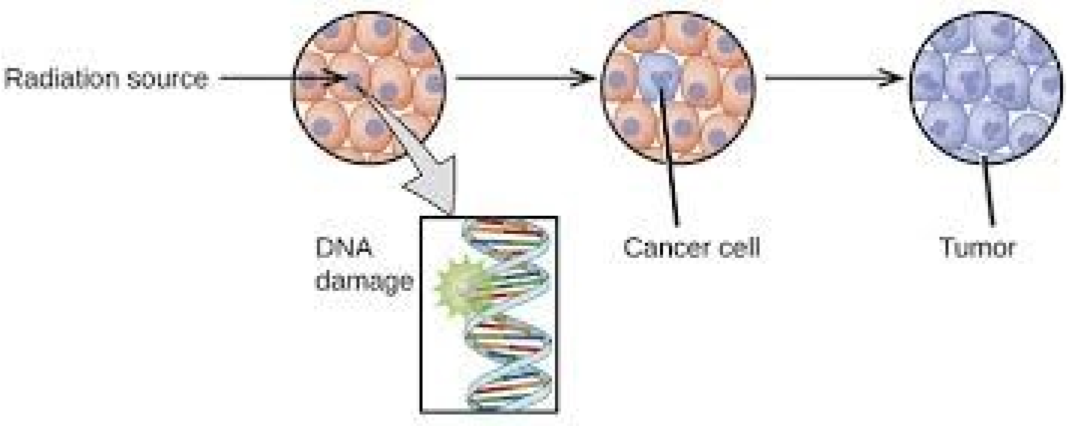
$$* \quad {}^{16}_{7}N \longrightarrow {}^{16}_{8}O + {}^{0}_{-1}e \qquad -\beta-$$

$$* \quad {}^{99m}_{43}Tc \longrightarrow {}^{99}_{43}Tc + \gamma \qquad -\gamma-$$

$$* \quad {}^{131}_{53}I \longrightarrow {}^{131}_{54}Xe + \beta + \gamma$$

Radiation causes cancer, skin cancer, bone cancer, leukemia and other cancers are products of exposure to radiation.

Genetic risk of exposure to radiation is more difficult to determine. Genetic damage is caused by damage to the genes in the nuclei of cells. The damage to the structure of the gene may cause death or variety of physical defects in the following generation.



Exposure to radiation is dangerous. But is there any level of exposure below which radiation has no effect. According to one theory:

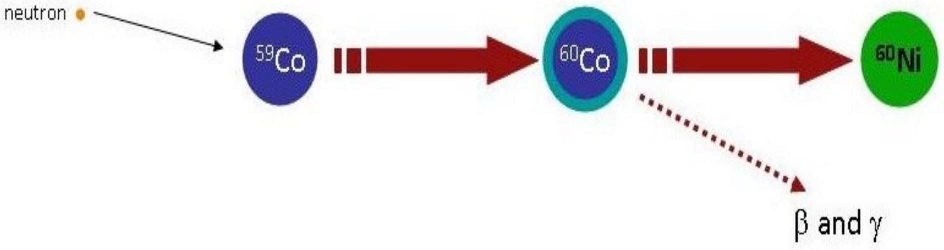
1. **Threshold theory:** no damage is occur below a certain level of radiation, called the threshold value.
2. **Linear theory:** the risk of damage is proportional to exposure, even down to very low levels of radiation.
3. **Current view:** is a compromise of these two theories; there is a risk of damage even at low levels of radiation, but risk is extremely small.

Artificial Radioactivity:

Artificial isotopes can be made when non-radioactive isotope nucleus is bombarded with proton, neutron or Alpha particle such as:

$${}^{197}_{79}\mathrm{Au} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{198}_{79}\mathrm{Au} \qquad \text{tracer in liver}$$

$${}^{98}_{42}\mathrm{Mo} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\mathrm{e} \qquad \text{tracer}$$

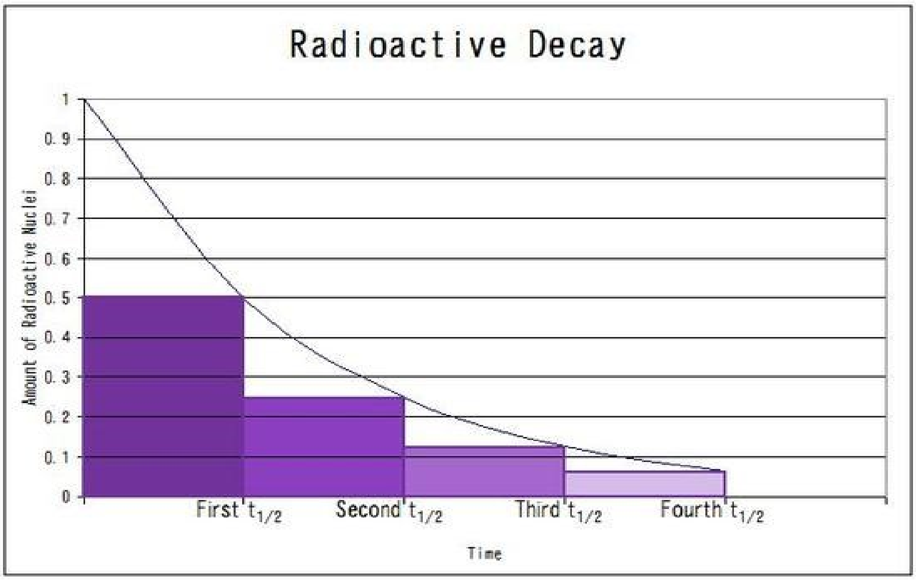


Half-life ($t_{1/2}$):

Half-life: is the time required for half of given quantity to change to another isotope.

Each radioactive isotope has a characteristic half-life values of the half-lives of naturally occurring isotope range from milliseconds to several billion years.
For example:

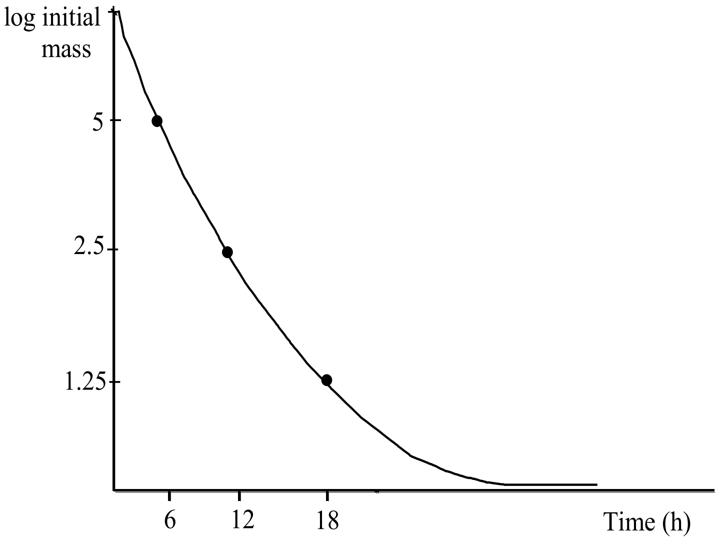
Element	Isotope	Half-Life
Hydrogen	${}^{3}_{1}H$	12.3 Yr
Carbon	${}^{14}_{6}C$	5700 Yr
Sodium	${}^{24}_{11}Na$	15 Yr
Uranium	${}^{235}_{92}U$	710 millionYear



The importance of the half-life is that it tell us how long a sample of the isotope will exist. The value of the half-life of a radioactive isotope is independent of sample size.
For example: the amount of the sample of thorium-234 is 10gm, 1kg, or 10gm, half of it will decay in 24.1 days.

$$ {}^{234}_{90}\mathbf{Th} \xrightarrow[\text{24.1 days}]{\text{half-life}} {}^{234}_{91}\mathbf{Pa} + {}^{0}_{-1}\beta $$

Ex: The decay scale of **Tc^{-99m}** ($t_{1/2}$ =6h) is :



The remaining mass can be calculated as following:

$$\boxed{n = \frac{\text{time elapsed}}{\text{half-life}}}$$

n= no. of half-life elapsed

$$\boxed{\text{mass}_{\text{remain}} = \frac{\text{mass initial}}{2^n}}$$

In addition to how long a radioactive isotope will last, we also want to know how much radiation it gives off, for this reason we need units to measure the radiation given off by radioactive isotopes.

Radiation Dosages:

The basic unit of radioactivity:

Curie (Ci): is the level of radioactivity caused by 3.7 x 10^{10} radioactive disintegrations per second. It is independent of the size of the radioactive sample.

Picocurie (10^{-12} Ci), and millicurie (10^{-3} Ci), are generally used.

Becquerel (Bq): is the SI unit of radioactivity. One Ci is equal to $3.7x10^{10}$ becquerel.

Ci= 3.7×10^{10} Bq

Rad (D): radiation absorbed dose. The energy absorbed by tissue.

Gray (Gy): the SI unit of absorbed dose.

100 rad = 1 Gy

Rem : No. of rem= RBE X no. of Rad

Where: RBE=Factor called relative biological equivalent (effectiveness) .

RBE of $\alpha = 10$ cause more damage

RBE of $\beta = 1$

RBE of $\gamma = 1$

RBE of $n = 5$

LD_{50} Value: the dose, in rem, that is fatal to 50% of the population within 30 days.

The LD50 value for human is estimated to be 500 rem.

The LD50 values of mammals are 250-1000 rem.

The LD50 values of insects are 50000 rem.

Microorganisms can tolerate even more.

END LEC

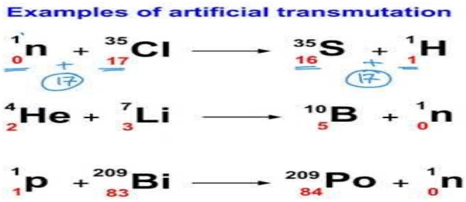
Lec:(7)---220-2021---Dr.Mahmoud S. Muter

Radiochemistry

Transmutation:

Changing one element into another, either in nature or in the laboratories. This can be done by bombardment reaction, accelerator is needed. The reaction occurs when particles of atomic or subatomic size strike atoms of an element and change them into another.

$$\underset{\text{target}}{{}^{9}_{4}\text{Be}} + \underset{\text{bombarding particle}}{{}^{4}_{2}\text{He}} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$



Examples of artificial transmutation

$${}^{1}_{0}\text{n} + {}^{35}_{17}\text{Cl} \longrightarrow {}^{35}_{16}\text{S} + {}^{1}_{1}\text{H}$$

$${}^{4}_{2}\text{He} + {}^{7}_{3}\text{Li} \longrightarrow {}^{10}_{5}\text{B} + {}^{1}_{0}\text{n}$$

$${}^{1}_{1}\text{p} + {}^{209}_{83}\text{Bi} \longrightarrow {}^{209}_{84}\text{Po} + {}^{1}_{0}\text{n}$$

Accelerator is a device that increases the speed of a charged atomic or subatomic particle. Circular accelerator (Cycletron) is used and operation is based on:

a) A charged particle is repelled by another of like charge.

b) A charged particle moves in a curved path when magnetic field is applied.

Medical uses of radioactive isotopes:

Diagnostic techniques in **nuclear medicine use radioactive** tracers which emit gamma rays from within the body. These tracers are generally short-lived **isotopes** linked to chemical compounds which permit specific physiological processes to be scrutinised. They can be given by injection, inhalation, or orally.

Therapeutic applications of radioisotopes typically are intended to destroy the targeted cells. This approach forms the basis of radiotherapy, which is commonly used to treat cancer and other conditions involving abnormal tissue growth, such as hyperthyroidism. In radiation therapy for cancer, the patient's tumor is bombarded with ionizing radiation, typically in the form of beams of subatomic particles, such as protons, neutrons, or alpha or beta particles, which directly disrupt the atomic or molecular structure of the targeted tissue. Ionizing radiation introduces breaks in the double-stranded DNA molecule, causing the cancer cells to die and thereby preventing their replication.

1. Treatment of cancer :

Isotopes must be chosen carefully because:

- **a.** The half-life must be long enough to do job; yet, short enough to disappear without subjecting body to unnecessary radiation.
- **b.** No isotope emit α–particle used.

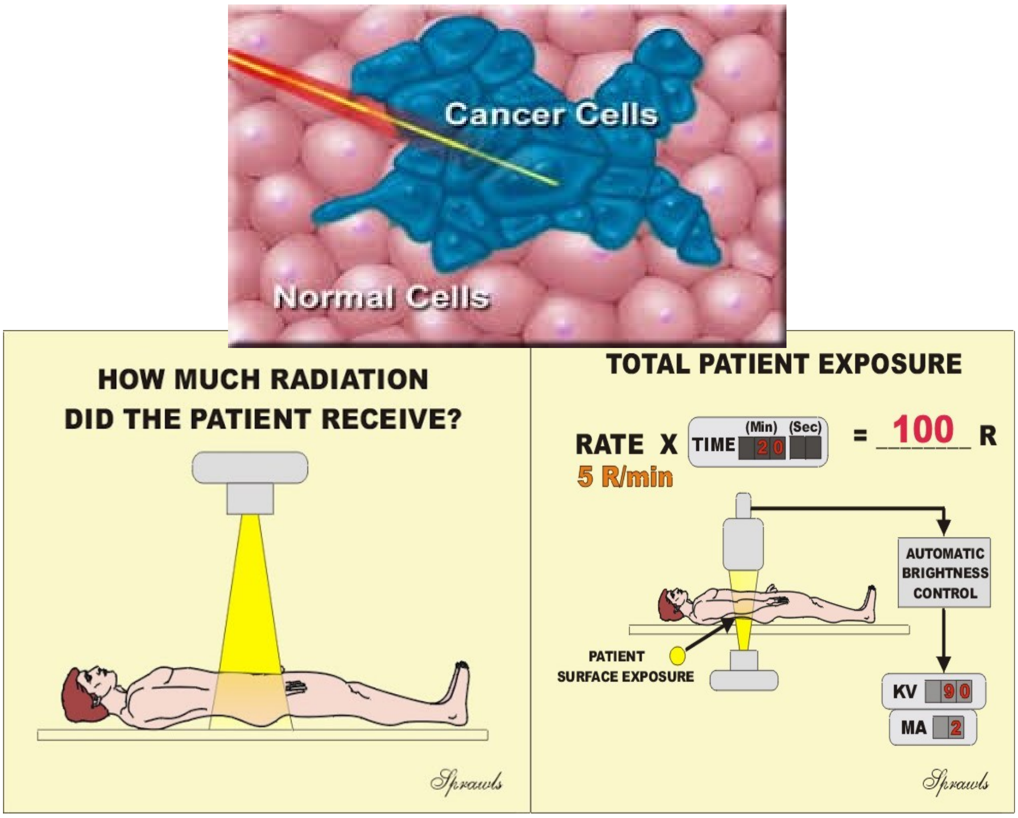
Co^{-60} used as external source,

$^{123}_{53}\mathbf{I}$, $^{131}_{53}\mathbf{I}$ used internally to treat thyroid cancer.

$^{32}_{15}\mathbf{P}$ used to treat leukemia.

$^{99}_{43}\mathbf{Tc}$ used to scans Brain, Kidney, and Lung

$^{24}_{11}\mathbf{Na}$ diagnose blockages in circulatory system.

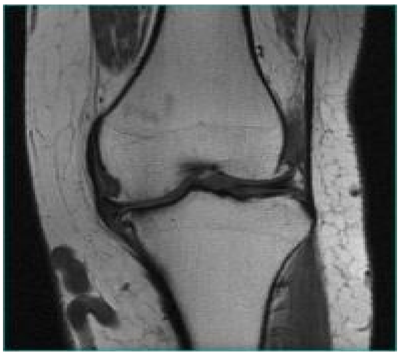


2. Magnetic Resonance Imaging (MRI):

Nuclear transition occurs in the microwave region of the electromagnetic radiation under the influence of magnetic field.

An image (based on microwave absorption) is generated, stored in computer. Differences between normal and malignant tissue may clearly be seen in the final image.

MRI of a knee

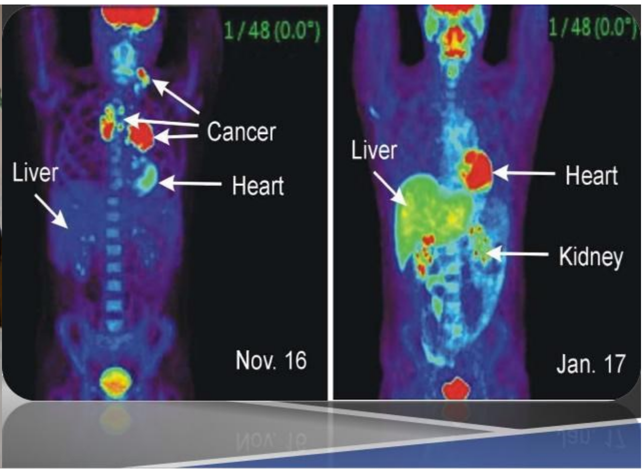


3. Positron Emission Tomography (PET):

It is a technique for following biochemical processes within the organs (brain, heart, ...) of the human body.

PET scan produces an image of a two and three-dimensional slice through a body organ of a patient.

The PET scan uses a mildly radioactive drug to show up areas of your body where, Some isotopes used in PET scans are C-11, N-13, O-15 and F-18. All have short half-lives, so the radiation dosage to the patient is minimal. This scan can sometimes detect disease before it shows up on other imaging tests. cells are more active than normal. It's used to help diagnose some conditions including cancer.



Energy and nuclear reactions:

nuclear chemistry, nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into two or more smaller, lighter nuclei. The fission process often produces gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay.

Uranium atoms are bombarded with slow neutrons (thermal) cause splitting nucleus. This called ***fission reaction.***

U-235 is the only naturally occurring isotope which undergoes this reaction.

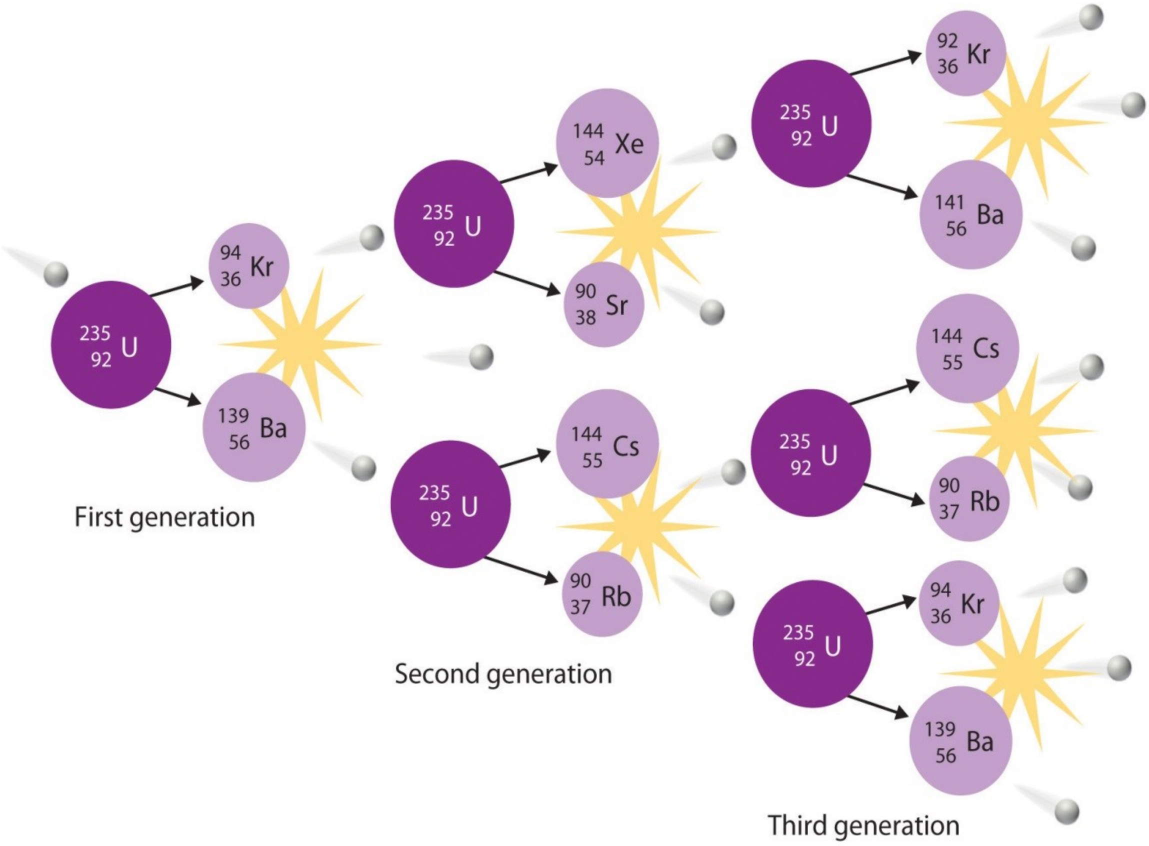
The other two isotopes which undergoes fission reaction are ^{239}Pu and 233U and both are artificial isotopes and produced in breeder reactors. Pu-239 and U-233 are fissionable fuel and can be produced as following:

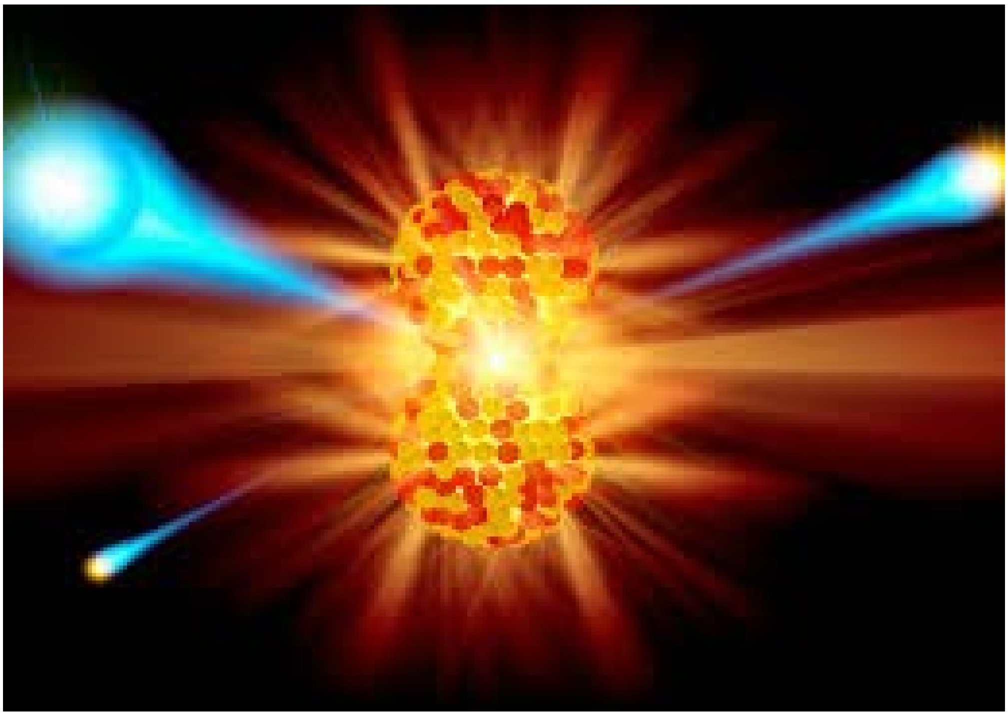
$$\underset{\text{fast}}{{}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n}} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow[\beta]{} {}^{239}_{92}\mathrm{Np} \xrightarrow[\beta]{} {}^{239}_{94}\mathrm{Pu}$$

$$\underset{\text{fast}}{{}^{232}_{90}\mathrm{Th} + {}^{1}_{0}\mathrm{n}} \longrightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow[\beta]{} {}^{233}_{91}\mathrm{Pa} \xrightarrow[\beta]{} {}^{233}_{92}\mathrm{Pu}$$

*In fission reaction, large amount of energy released, neutrons, and γ radiation as well as other elements and heat.

A chain reaction is shown, start by neutron strikes an atom of uranium-235 and causes it to split into two, three, or four neutrons. These neutrons can strike other uranium-235 atoms and cause them to undergo fission reactions. Each fission reaction produces more neutrons, which cause more fission reactions, which cause more fission reactions. It is the emission of neutrons by a fission reaction that keeps the chain reaction going. The amount of material needed for chain reaction to continue is called ((***Critical Mass***)).





fission reaction

Cancer chemistry

The cells in the body of humans can convert at any time from a healthy cell to a cancerous cell.

cancerous cells occur when exposure of Some things, such as exposure the tissue to radiation and chemicals, can cause change in cells, because those things interaction and chemically adheres to DNA and changes its structure, and causes changing the properties of cells and their natural division. increases the risk of cancer occurring at any moment, and increase with accumulating exposure of carcinogens .

The nature of cells can also change with age and less efficient functioning of the body. The danger of this change in the nature of cells is clearly evident when it comes to genes and some proteins responsible for cell growth, which speeds up the formation of cancer cells that can reproduce rapidly and uncontrollably.

Cancer is a group of diseases involving abnormal cell growth with potential to spread to other parts of the body. These contrast with benign tumors which do not spread. Possible signs and symptoms include a lump, abnormal bleeding, prolonged cough, unexplained weight loss, and a change in bowel movements. More 100 types of cancers affecting of humans.

Classification

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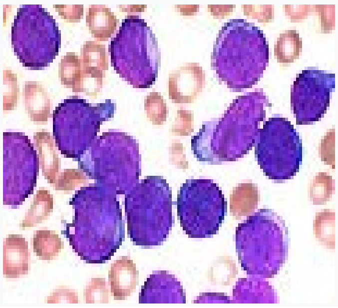
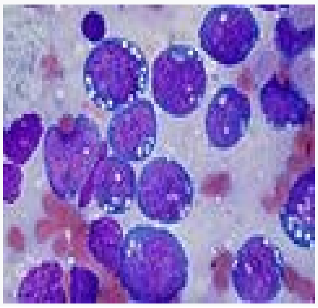
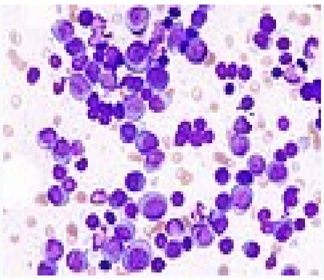
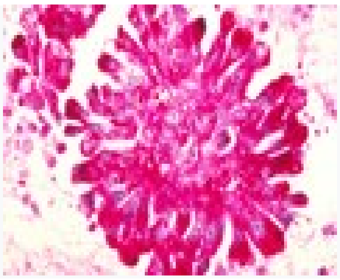
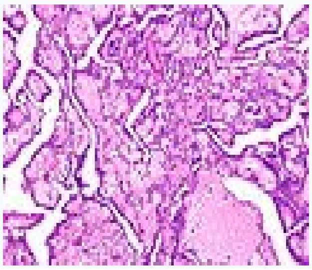
Carcinoma


Leukaemia


Lymphoma


Myeloma


Sarcoma


Mesothelioma

Carcinogens

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1. Tobacco smoking: The most common exposure to the stimulant, prepared from the leaves of the tobacco plant, is through burning it and smoking it from a cigarette or hookah pipe into the mouth and then releasing it.
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4. Arsenic in drinking water: The highly toxic chemical which is used to make certain alloys used in the manufacturing industry, can get into the drinking water supply, particularly in ground water. Arsenic is known to cause skin cancer, and linked to causing liver, lung, kidney, and bladder cancer.
5. Iron and steel founding: Studies of iron and steel founding workers in various parts of the world showed them to have a significantly increased risk for lung cancer. Exposures in the iron and steel founding industry are complex and include a wide variety of known genotoxic and carcinogenic substances including metals and formaldehyde.
6. Isopropanol manufacture: variety of industrial, household and pharmaceutical uses. Isopropyl alcohol solution is found in rubbing alcohol, hand sanitiser, and disinfecting pads.
7. Alcoholic beverages: Alcoholic beverage consumption is a cause of breast, colorectal, larynx, liver, esophagus, oral cavity and pharynx cancers, and as a probable cause of pancreatic cancer.
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12. Thioles comp.
13. Styrene

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16. Diethyl sulfate
17. Selenium sulfide
18. Thiourea
19. Toluene comp.
20. Urethane
21. Acetaldehyde
22. Formaldehyde (formalin)
23. 1,3-Butadiene
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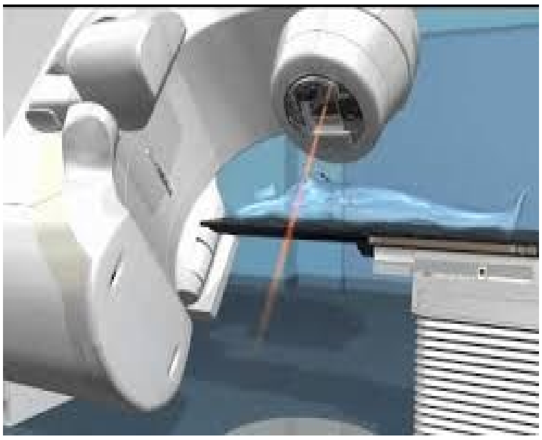

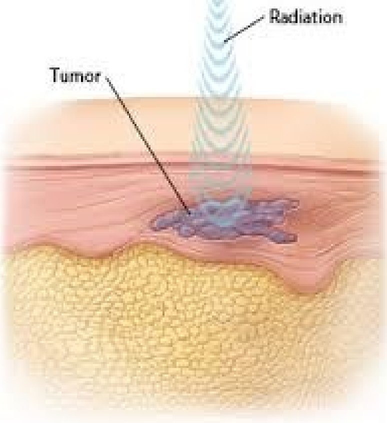

Cancer chemistry

Lec: (12) ♥♥♥ 2023-2024 ♥♥♥ Dr. Mahmoud S. Muter

The cells in the body of humans can convert at any time from a healthy cell to a cancerous cell.

cancerous cells occur when exposure of Some things, such as exposure the tissue to radiation and chemicals, can cause change in cells, because those things interaction and chemically adheres to DNA and changes its structure, and causes changing the properties of cells and their natural division. increases the risk of cancer occurring at any moment, and increase with accumulating exposure of carcinogens .

The nature of cells can also change with age and less efficient functioning of the body. The danger of this change in the nature of cells is clearly evident when it comes to genes and some proteins responsible for cell growth, which speeds up the formation of cancer cells that can reproduce rapidly and uncontrollably.

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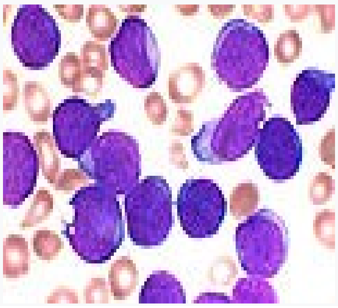
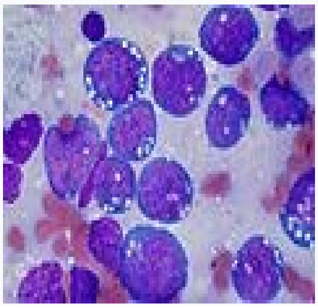
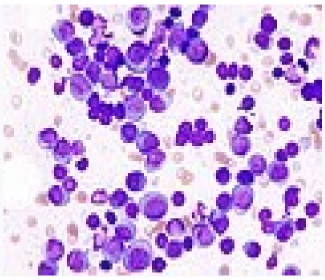
Carcinoma


Leukaemia


Lymphoma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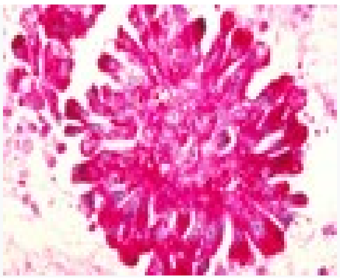
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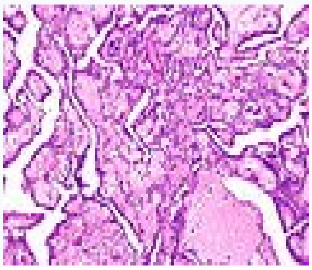
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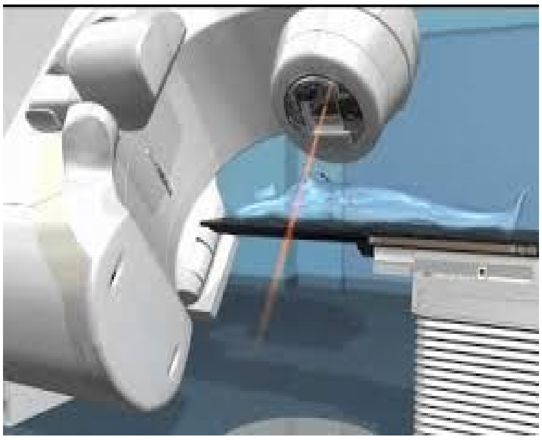
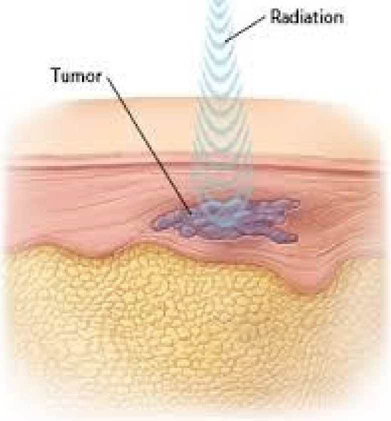
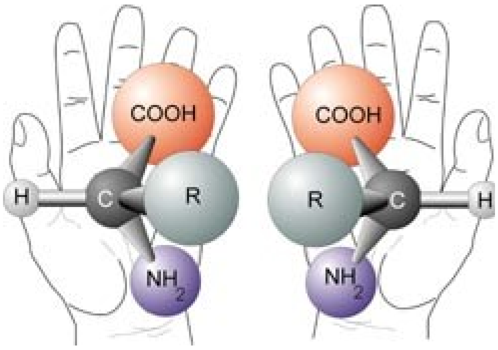
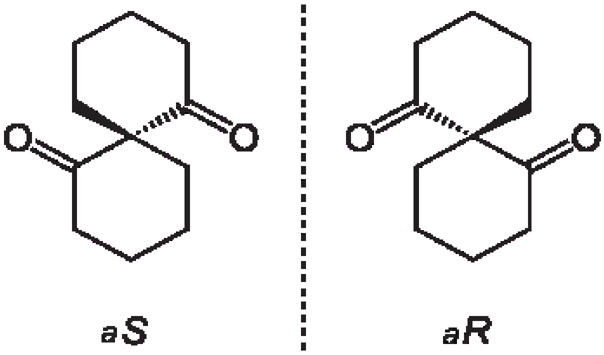




Biological chirality of molecules

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a non-superimposable set of two molecules that are mirror images of one another. The existence of these molecules are determined by a concept known as chirality. The word “chiral” was derived from the Greek word for hand, because our hands are a good example of chirality since they are non-superimposable mirror images of each other.





The opposite of chiral is **achiral**. Achiral objects are superimposable with their mirror images. If the molecules are superimposable, they are identical to each other. Try to line up your left hand perfectly with your right hand, so that the palms are both facing in the same directions.

The same thing applies to some molecules. A chiral molecule has a mirror image that cannot line up with it perfectly - the mirror images are non-superimposable. There are many of the biological molecules such as our **DNA, amino acids and sugars**, are chiral molecules.

This must mean that enantiomers have properties that make them different from their mirror image molecule. One of these properties is that chiral molecules do not have a **plane of symmetry** or an internal mirror plane. So, a chiral molecule cannot be divided into two identical halves. Another property of chiral molecules is **optical activity**.

Organic compounds, molecules created around a chain of carbon atoms (more commonly known as the carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy. Since potential energy can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing the same atomic connectivity as another but differing in structural arrangements. This section is devoted to a specific type of isomer called stereoisomers and their property of chirality (Figure 5.1.1).

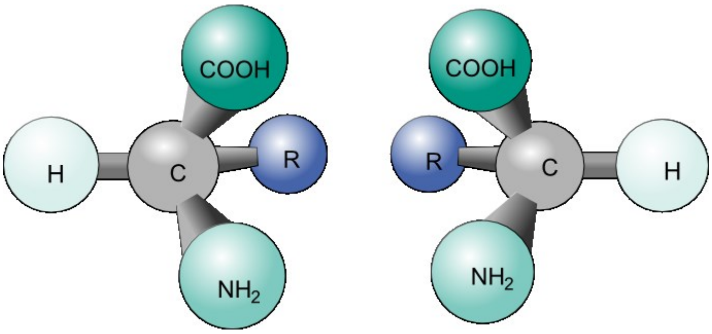


Figure 5.1.1. *Two enantiomers of a tetrahedral complex.*

The concepts of steroisomerism and chirality command great deal of importance in modern organic chemistry, as these ideas help to explain the physical and theoretical reasons behind the formation and structures of numerous organic molecules, the main reason behind the energy embedded in these essential chemicals. In contrast to more well-known constitutional isomerism, which develops isotopic compounds simply by different atomic connectivity, stereoisomerism generally maintains equal atomic connections and orders of building blocks as well as having same numbers of atoms and types of elements.

What, then, makes stereoisomers so unique? To answer this question, the learner must be able to think and imagine in not just two-dimensional images, but also three-dimensional space. This is due to the fact that stereoisomers are isomers because their atoms are different from others in terms of spatial arrangement.

Metals and DNA:

Chiral metal complexes provide unique molecular probes for DNA. Chiral reagents that "recognize" different local structures along the DNA strand have been designed by a process in which the asymmetry in shape and size of the complex is matched to that of the DNA helical groove. As a result, the chiral metal complexes provide very sensitive probes for local helical structure, both left- and right-handed. Direct coordination of chiral complexes to the DNA bases adds an element of sequence selectivity to the probe design. With a suitable reactive metal center, reagents that target chemically specific sites along the strand may be developed. One such chiral reagent, which cleaves left-handed DNA sites with photoactivation, has been useful in mapping this distinct conformation and examining its biological role. The conformation-specific molecular cleaver, much like a DNA-binding enzyme, recognizes and reacts at discrete sites along the DNA strand. These site-specific chiral metal complexes provide exciting new tools for probing the local variations in DNA structure and its role in the regulation of gene expression.

Chiral Metal Complexes

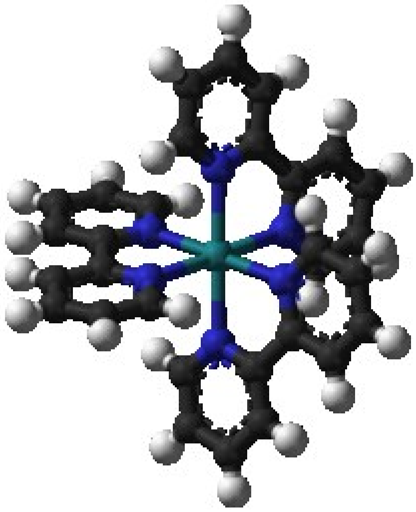
Chiral Metal Complexes As molecular recognition continues to gain importance in the biological and physical sciences as well as in the technologies of molecular electronics and optics, so has the need for efficient syntheses of chiral molecules. Chemists use of chiral organometallic molecules in discriminate between enantiotopic atoms, groups, or faces in achiral molecules and catalyze production of a broad array of natural or unnatural substances of excellent enantiomeric purity. Because of their ability to efficiently multiply chirality, even on an industrial level, these catalysts promise to exert a general impact on molecular science and engineering.

Biological importance

Many biologically active molecules are chiral, including the naturally occurring amino acids (the building blocks of proteins) and sugars.
Most scientists believe that Earth life's "choice" of chirality was purely random, and that if carbon-based life forms exist elsewhere in the universe, their chemistry could theoretically have opposite chirality.

Enzymes, which are chiral, often distinguish between the two enantiomers of a chiral substrate. One could imagine an enzyme as having a glove-like cavity that binds a substrate. If this glove is right-handed, then one enantiomer will fit inside and be bound, whereas the other enantiomer will have a poor fit and is unlikely to bind.

Ruthenium-tris(bipyridine) cation



Chirality is a symmetry property, not a property of any part of the periodic table. Thus many inorganic materials, molecules, and ions are chiral. Quartz is an example from the mineral kingdom. Such noncentric materials are of interest for applications in nonlinear optics.
In the areas of coordination chemistry and organometallic chemistry, chirality is pervasive and of practical importance. A famous example is tris(bipyridine)ruthenium(II) complex in which the three bipyridine ligands adopt a chiral propeller-like arrangement.

Chiral ligands confer chirality to a metal complex, as illustrated by metal-amino acid complexes. If the metal exhibits catalytic properties, its combination with a chiral ligand is the basis of asymmetric catalysis.

First -dentistry-SECOND SEMISTER

Lecture (1) 2022-2023 Dr. Mahmoud

ORGANIC CHEMISTRY

(Alkanes, Alkenes and Alkynes)

Organic Chemistry *: The chemistry of carbon and its chemical compounds. Carbon atoms have four polar covalent bonds with atoms of other elements or other carbon atoms.*

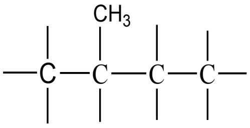
Carbon atoms can form thousands of long chains , or rings of all size, the chains and rings can having branches and crosslinks to the carbon atoms of these chains and rings there are attached with other atoms. Chiefly hydrogen, but also fluorine, chlorine, bromide, iodine, oxygen, nitrogen, sulfur, phosphors and many others.

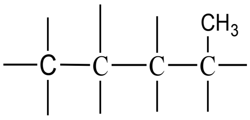
Organic chemistry is a field of immense of the food importance to technology it's the chemistry of dyes and drugs, paper, ink, paints and plastic, gasoline and rubber tires, it's the chemistry we eat and the clothing we wear.

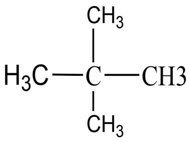
Organic chemistry is fundamental to biology and medicine. A side from water, living organisms are made up chiefly of organic compounds, the molecules of molecular biology, are organic molecules ultimately biological processes are a matter of organic chemistry.

- ***Structural formulas****: organic compounds tell us how the atoms arrangement in a different forms in the molecule. The chemical formula loses some of its usefulness because we fiend that one chemical formula dose not always represent just one compound. For example three different organic compounds all have the same chemical formula,* C_5H_{12} *. These three compounds are isomers .*

Structure formula :







Chemical formula : C_5H_{12} C_5H_{12} C_5H_{12}

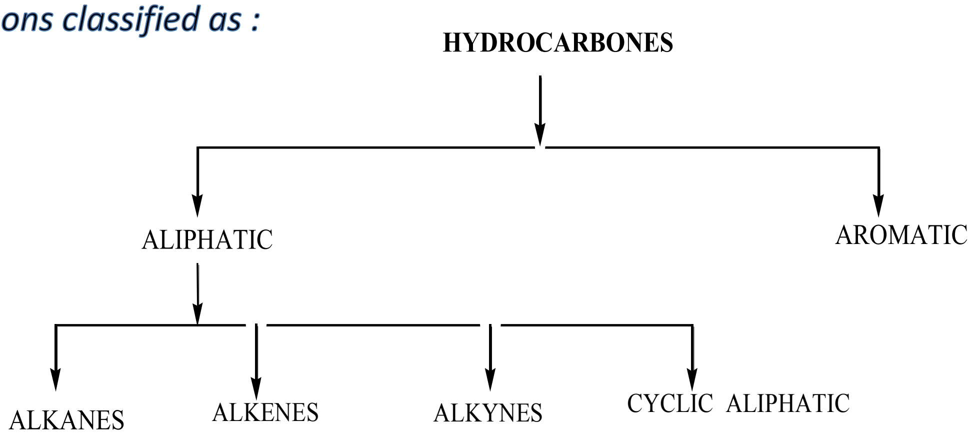
- *Chemical formulas provide us with information about the number and kinds of atoms in a molecule .*

- *Structural isomers: compounds, that have the same chemical formulas but differ in their structural formulas . the structural isomers dose not find in the methane, ethane and propane, its start from butane, pentane......et.*

Hydrocarbons : *Organic compounds contain carbon and hydrogen atoms.*

The petroleum (complex mixture of hydrocarbons) and natural gas formed as the result of a geological process that started millions of years ago for organic material, From plants and animals were buried with sediments from oceans and rivers. With the passing time, the sediments were slowly subjected to great pressures and bacterial action, which formed gas and petroleum deposits.

Hydrocarbons classified as :



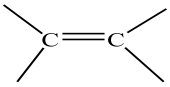
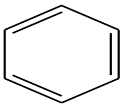
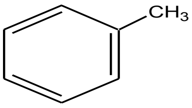
1. *Alkanes : that contain only single bonds between carbons atoms .*
2. *Alkenes : that contain one or more carbon - carbon double bonds .*
3. *Alkynes : that contain one or more carbon - carbon triple bonds .*

4. *Cyclic aliphatic : that forms deferent cyclic such tricyclic, tetracyclic, pentacyclic, hexacyclic, …. and more.*
5. *Aromatic hydrocarbons : that contain six electrons (3 π bonds) in a six member ring and may be contain single and double bonds.*

Function groups : *The specific atoms or groups that formed bond with carbon atom such as CL, OH, SH, NH_2 or ………et .These groups at which reactions occur are called function groups.*

Function groups can be organized chemical reaction in to classes . this is the way that we organize the study of organic chemistry.

Table of function groups

function groups	**class of compounds**	**Example**
	Alkene	$2HC=CH2$
$HC\equiv CH$	Alkyne	$HC\equiv CH$
	Aromatic	

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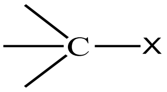
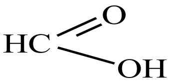
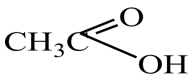
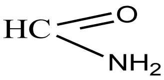
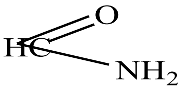
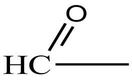
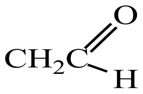
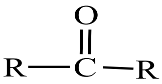
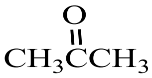
 (X=F, Cl, Br, I)	Halide	CH_3Cl
$R-OH$	Alcohol	$CH_3\,OH$
$R-O-R$	Ether	$CH_3\,O\,CH_3$
$R-NH_2$	Amine	CH_3NH_2
	Carboxylic acid	
	Amide	
	Aldehyde	
 $R-\overset{O}{\overset{\|}{C}}-R$	Ketone	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$

International Unit of Pure and Applied Chemistry (IUPAC)

1. **Alkanes**: can be naming alkanes according to the number of carbon atom in compound

C1 naming methane

C2 = ethane

C3 = propane

C4 = butane

….. et

Other naming by adding the ending …ane to the Greek name for the number of carbon atoms in the compound, like pentane = penta = 5 .

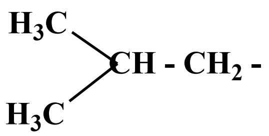
- **Branched chain alkanes are named by using the following rules:**

1- **Determine the longest continuous chain of carbon atoms in the molecule .**

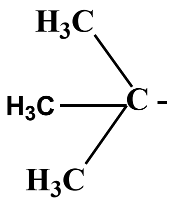
2- Carbons or function groups that have replaced … one

3- If the substituent is a hydrocarbon group, this group is named by changing the …ane to ….yl for example:

$-CH_3$	Methyl
$CH_3-CH_2-CH_2-$	Propyl
$CH_3-CH_2CH_2CH_2-$	n- butyl



Iso- butyl ,



t- butyl

Physical properties:

For all alkanes general the boiling point and melting point increase as the number of carbon atoms increase. Fewer than five Carbon atoms are gases, where as those containing five to ten Carbon atoms are liquids . alkanes containing 11 or more carbon atoms viscose liquids, and alkanes containing 20 or more carbon atoms are wax like solids.

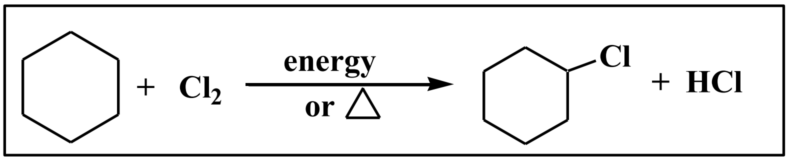
Alkanes contain only single covalent bond, C-C or C-H because the electronegativity of carbon and hydrogen are nearly the same.

Alkanes have lower boiling points than most other organic compounds of comparable molecular weight.

CHEMICAL REACTIONS OF ALKANES :

1. Chlorination : ex: $RH + Cl_2 \xrightarrow[\text{or } \Delta]{\text{light energy}} RCl + HCl$

The symbol RH represent the alkane where R is an alkyl or cyclo-alkyl group. Chlorination of an alkane is a substitution reaction :



2. Oxidation : oxidizing reagents are ($K_2Cr_2O_7$, $KMnO_4$) :

ex: $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

ex: $CH_4 + O_2 \longrightarrow C + 2H_2O$

PREPARATION OF ALKANE :

Each of the smaller alkanes, form methane through n-pentane and isopentane can be obtained in form by fractional distillation of petroleum and natural gas:

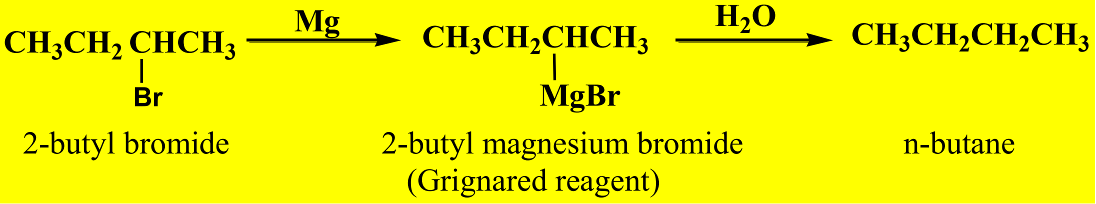
1- Hydrogenation of alkenes:

$CH_2{=}CH_2 + H_2 \longrightarrow CH_3-CH_3$

2- Reduction of alkyl halides :

a. Hydrolysis of Grignard reagent:

Ex:

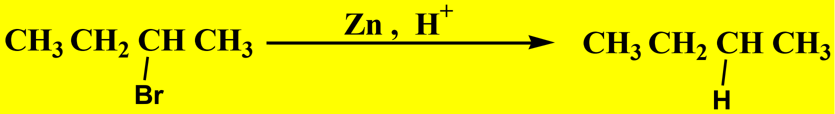


$$\underset{\text{Br}}{CH_3CH_2CHCH_3} \xrightarrow{Mg} \underset{\text{MgBr}}{CH_3CH_2CHCH_3} \xrightarrow{H_2O} CH_3CH_2CH_2CH_3$$

2-butyl bromide — 2-butyl magnesium bromide (Grignared reagent) — n-butane

b. Reduction metal and acid:

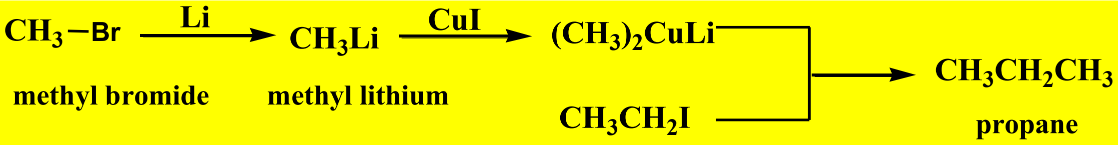
Ex:



$$\underset{\text{Br}}{CH_3\,CH_2\,CH\,CH_3} \xrightarrow{Zn\,,\ H^+} \underset{\text{H}}{CH_3\,CH_2\,CH\,CH_3}$$

3. Coupling of alkyl halides with organometallic compounds:

Ex:



$$CH_3-Br \xrightarrow{Li} CH_3Li \xrightarrow{CuI} (CH_3)_2CuLi \;+\; CH_3CH_2I \longrightarrow CH_3CH_2CH_3$$

methyl bromide — methyl lithium — propane

PREPARATION OF ALKENES :

1. Dehydrohalogenation of alkyl halides :

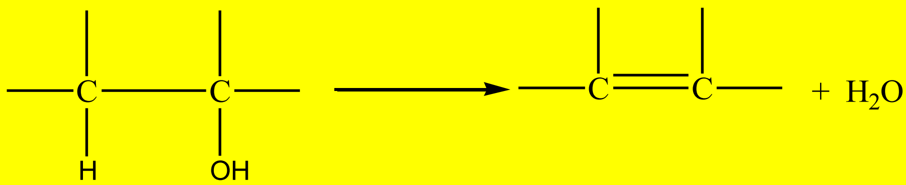
Ex:

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{KOH} CH_3CH_2CH{=}CH_2$$

n-butyl chloride — n-butene

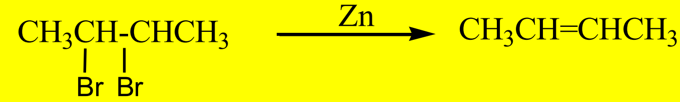
2. Dehydration of alcohols:

EX:



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + H_2O$$

3. De halogenation:



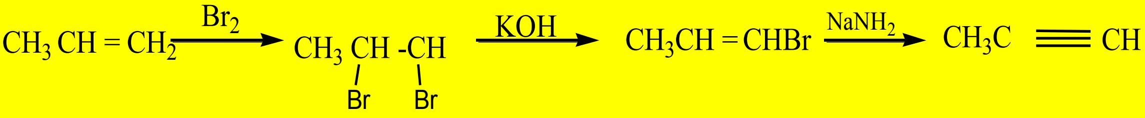
$$CH_3\underset{Br}{CH}-\underset{Br}{CH}CH_3 \xrightarrow{Zn} CH_3CH=CHCH_3$$

2-3-dibromobutane 2-butene

PREPARATION OF ALKYNES:

1. Dehydrohalogenation of alkyl dihalids:

Ex:



$$CH_3CH=CH_2 \xrightarrow{Br_2} CH_3\underset{Br}{CH}-\underset{Br}{CH} \xrightarrow{KOH} CH_3CH=CHBr \xrightarrow{NaNH_2} CH_3C\equiv CH$$

propene 1,2-dibromopropane 1-bromo-1-propene propyne

2. Reaction of sodium acytylides with primary alkyl halides:

Ex:

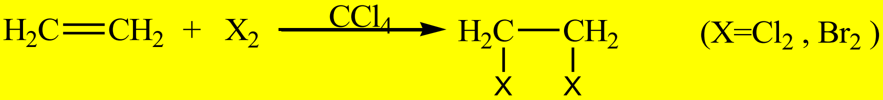
$$HC\equiv CH \xrightarrow{NaNH_2} -C\equiv C^{-}:Na^{+} + Rx \longrightarrow -C\equiv C-R + NaX$$

REACTIONS OF ALKENES:

1. Hydrogenation:

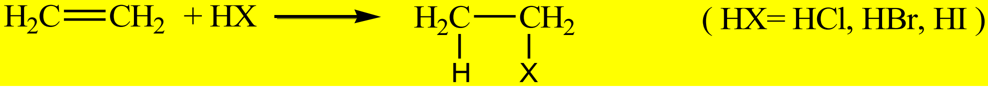
$$H_2C=CH_2 + H_2 \xrightarrow{Ni} H_3C-CH_3$$

2. Halogenation:



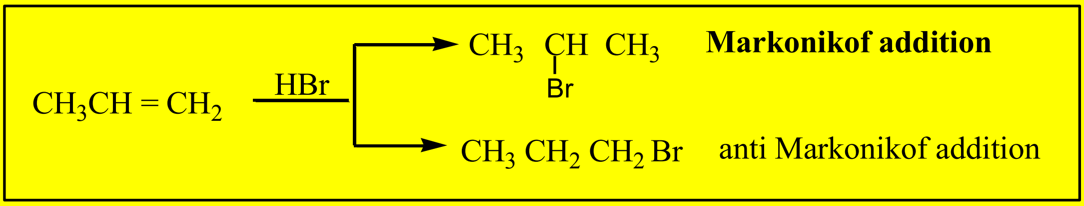
$$H_2C=CH_2 + X_2 \xrightarrow{CCl_4} H_2\underset{X}{C}-\underset{X}{CH_2} \quad (X=Cl_2 , Br_2)$$

3. Addition of hydrogen halides:



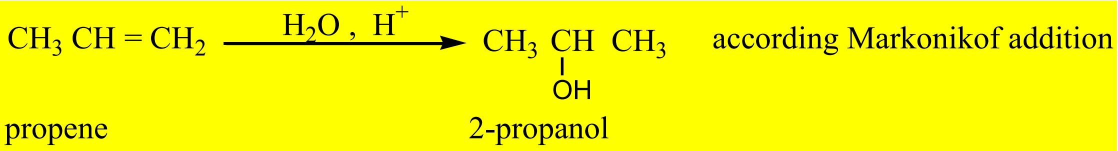
$$H_2C=CH_2 + HX \longrightarrow H_2\underset{H}{C}-\underset{X}{CH_2} \quad (HX= HCl, HBr, HI)$$

this addition depend of Markonikof addition:



$$CH_3CH=CH_2 \xrightarrow{HBr} \begin{cases} CH_3\underset{Br}{CH}CH_3 & \textbf{Markonikof addition} \\ CH_3CH_2CH_2Br & \text{anti Markonikof addition} \end{cases}$$

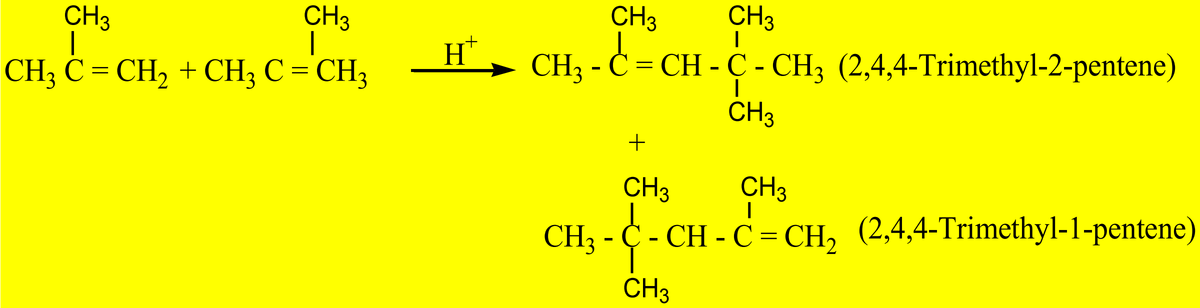
4. Addition of water (hydration):



$CH_3CH=CH_2 \xrightarrow{H_2O\ ,\ H^+} CH_3\underset{OH}{\underset{|}{CH}}CH_3$ according Markonikof addition

propene 2-propanol

5. Dimerization: since the alkenes produced contain exactly twice the number of carbon and hydrogen atoms as the original isobutylene, they are known as dimers (di=tow, mer=part) of isobutylene, and the reaction is called dimerization. Other alkenes undergo analogous dimerization.

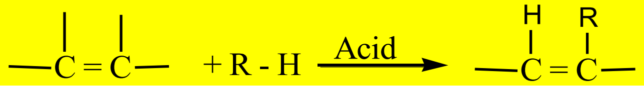


$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3\overset{CH_3}{\overset{|}{C}}=CH_3 \xrightarrow{H^+} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$ (2,4,4-Trimethyl-2-pentene)

$+$

$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH-\overset{CH_3}{\overset{|}{C}}=CH_2$ (2,4,4-Trimethyl-1-pentene)

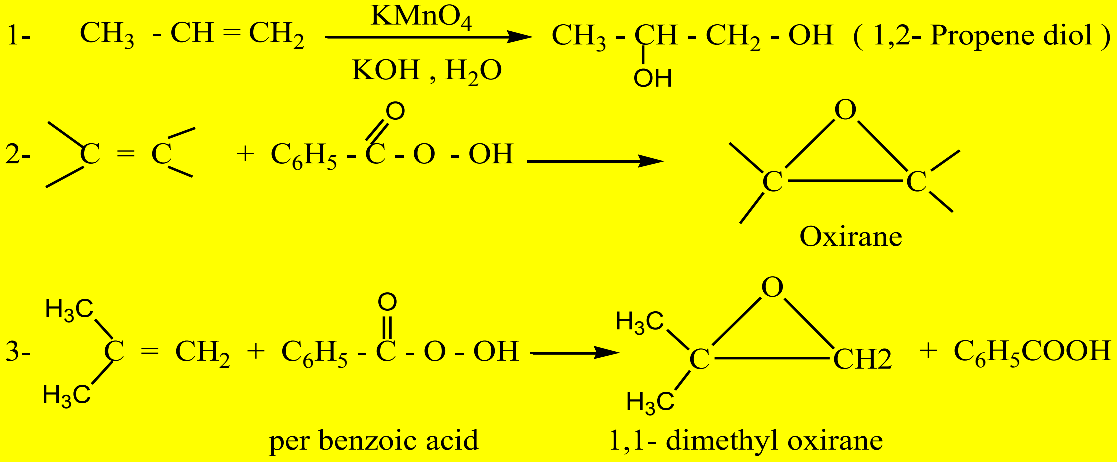
6. Alkylation:



$-\overset{|}{C}=\overset{|}{C}- \quad + R-H \xrightarrow{Acid} -\overset{H}{\overset{|}{C}}=\overset{R}{\overset{|}{C}}-$

7. Oxidation: oxidation reagents are:
   - a- $KMnO_4$
   - b. O_3 (Ozone)
   - c. Per acids (RCO_3H)

Ex:



1- $CH_3-CH=CH_2 \xrightarrow[KOH\ ,\ H_2O]{KMnO_4} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-OH$ (1,2- Propene diol)

2- $+\ C_6H_5-\overset{O}{\overset{\|}{C}}-O-OH$

Oxirane

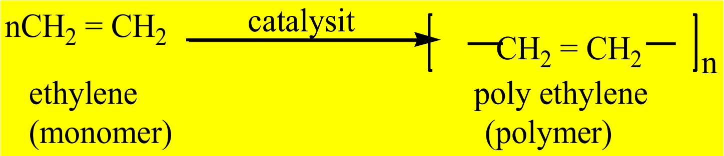
3- $=CH_2\ +\ C_6H_5-\overset{O}{\overset{\|}{C}}-O-OH$ $+\ C_6H_5COOH$

per benzoic acid 1,1- dimethyl oxirane

Markonikof role: the hydrogen of acid (HX) is add to the carbon of the double bond containing the greatest number of hydrogens.

8. Polymerization: with a catalyst, an alkene can be made to add to another alkene to form dimer. The reaction need not stop at this point. The dimer can add to another

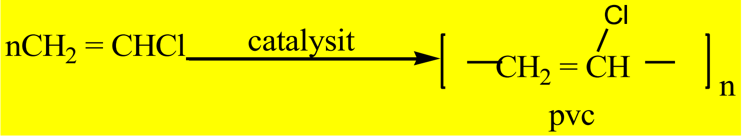
alkene to form a trimer. This reaction can continue untell a high molecule is formed the process is called polymerization to produce polymer.



$$\underset{\substack{\text{ethylene}\\ \text{(monomer)}}}{nCH_2 = CH_2} \xrightarrow{\text{catalysit}} \underset{\substack{\text{poly ethylene}\\ \text{(polymer)}}}{[-CH_2 = CH_2-]_n}$$

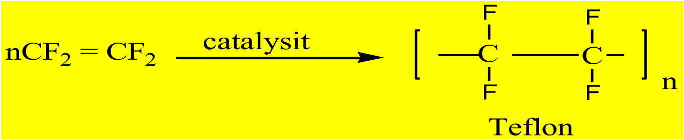
n: is a molecules number of chain that form several hundreds to several thousands.

Several halogen containing monomers, vinyl chloride form polyvinyl chloride called (PVC) by polymerization:



$$nCH_2 = CHCl \xrightarrow{\text{catalysit}} \underset{\text{pvc}}{[-CH_2 = \overset{Cl}{CH} -]_n}$$

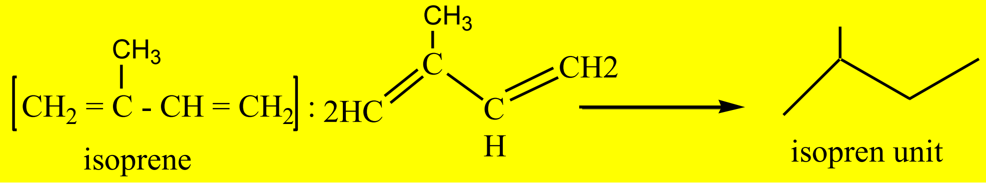
This polymer is widely used to make plastic bottles, Toflon, which is made from them monomer Tetraflouro ethylene is one of the most chemically inert of all organic substances . for this reason it is widely used as a containing for cooking .



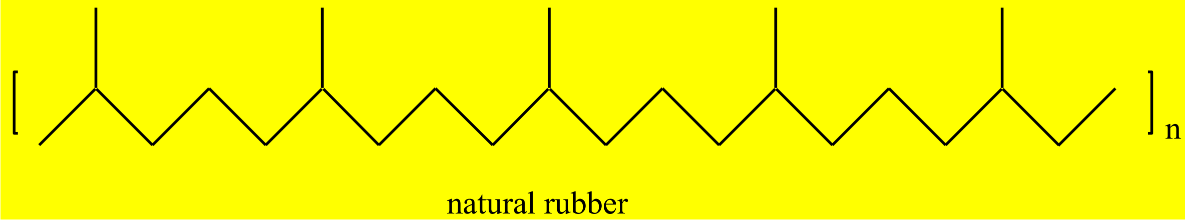
$$nCF_2 = CF_2 \xrightarrow{\text{catalysit}} \underset{\text{Teflon}}{[-\overset{F}{\underset{F}{C}} - \overset{F}{\underset{F}{C}} -]_n}$$

Polymerization in living systems:

Polymerization also occurs in living system, a large number of compounds called terpenes are found in living system. These compounds are all polymers made of repeating five-carbon unit that is structurally related to isoprene:

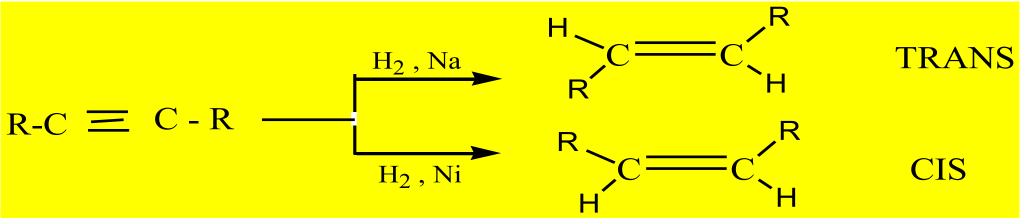


Natural rubber is an example of polymer made by combine thousands of isoprene unit:



Reaction of alkynes:

Addition hydrogen, halogen and hydrgenhalids to alkynes is very much like addition to alkenes, except that here tow molecules of reagent can be consumed for each triple bond. It is generally possible, by prepare selection of conditions, to limit reaction to the first stage of addition. Can be reduction to alkenes product cis-alkene and trans alkene as shown:



Dr. MAHMOUD ALFAHDAWI

First -dentistry-SECOND SEMISTE

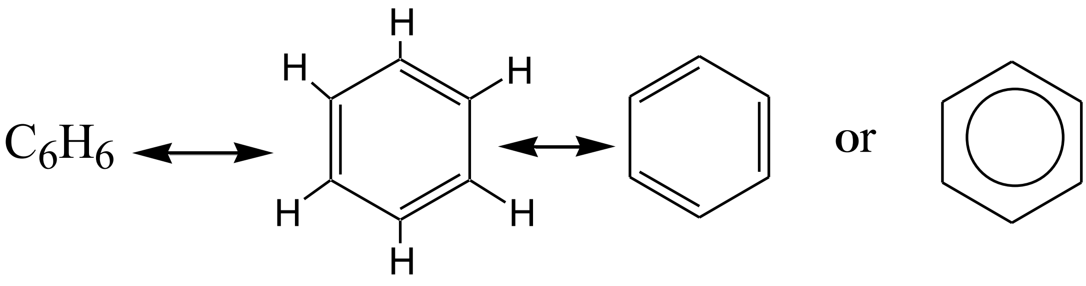
Lecture (2) **2022-2023** **Dr. Mahmoud**

AROMATIC COMPOUNDS

The benzene and compounds that resemble benzene in the structure and chemical behavior. Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons. Some compounds that posies structure of benzene.

The aromatic to be aromatic compounds must have a molecule that contain cyclic clouds of delocalized π electrons above and below the plane of the molecule. They are compounds whose molecular formulas would lead us to expect a high degree of un saturating and yet which are resistant to the addition reactions. Benzene has six carbon atoms, six hydrogen atoms and six π electrons , by x-ray methods determining the geometry of molecules.

By using these facts the structure of benzene is :



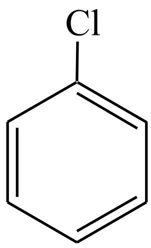
(Structure formula of benzene)

Naming aromatic compounds :

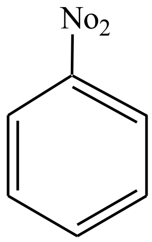
1. *When bonding only one group with benzene, the compound naming by write group name and after it benzene word, as the following examples :*

F : floro,   Cl : Chloro ,   Br : Bromo and   I : Iodo

ex:

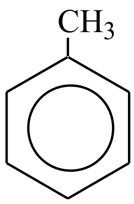


Chloro benzene

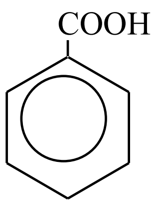


nitro benzene

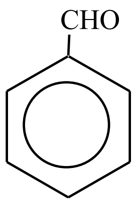
2. There are some common naming (afloat) such the following :



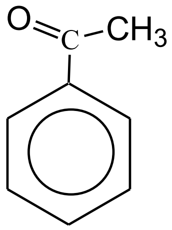
Toluene



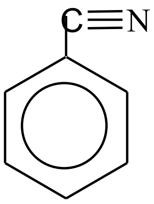
Benzoic acid



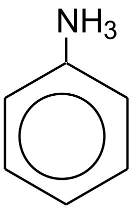
Benzaldehyde



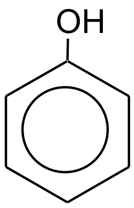
Acetophenone



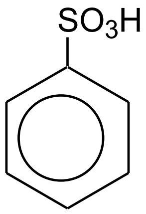
Benzonitrile



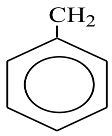
Aniline

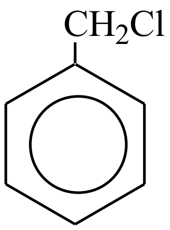


phenol

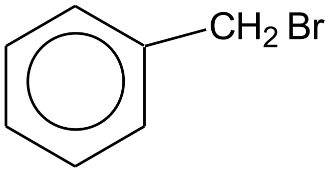


Benzenesolfonic acid

3. The compound  naming Benzyl when bonding with another group naming by benzyl followed group name as the following example :



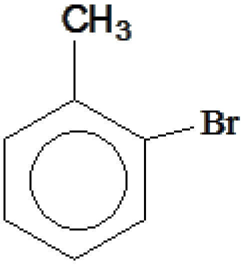
Benzyle Chloride



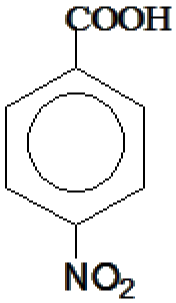
Benzyle Bromide

4. If a bonding two similar groups with benzene ring to naming compound must write site of group with main name :

   Ex :

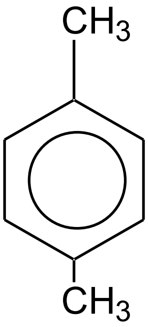


O - bromo toluene

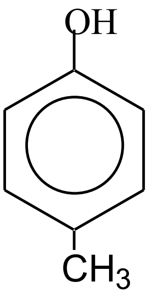


P - nitro benzoic acid

5. Two compounds very important are :



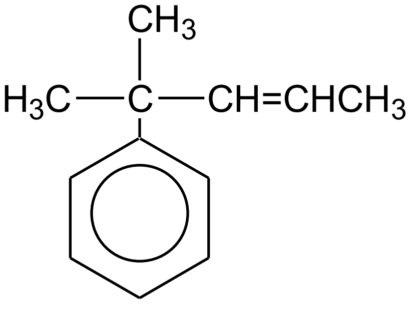
Xylene



Cresol

6. If the complex group bonding with benzene ring, when naming this type compounds the ring benzene called phenyl group :

Ex:

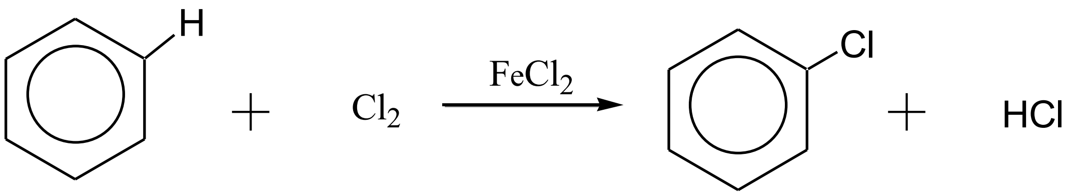


4- Methyl - 4-phenyl - 2- pentene

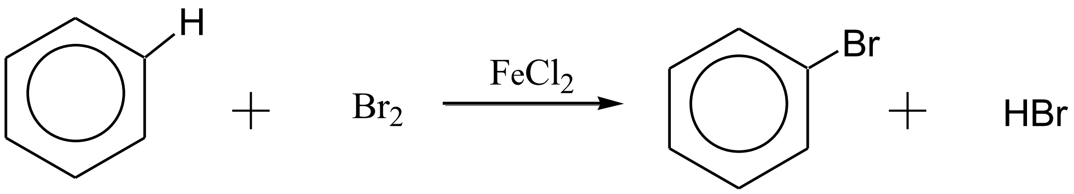
REACTION OF BENZENE

1. Substitution reaction of aromatic compounds when benzene ring don’t bonding with group :

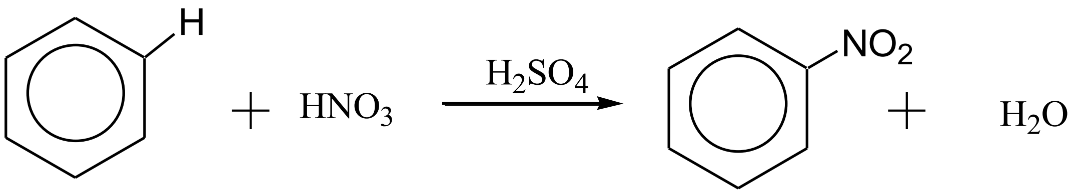
- Chlorination :



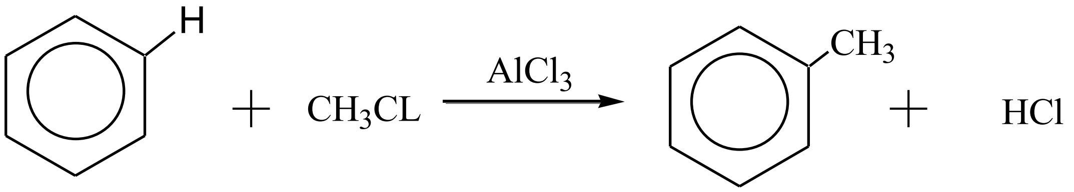
- Bromination :



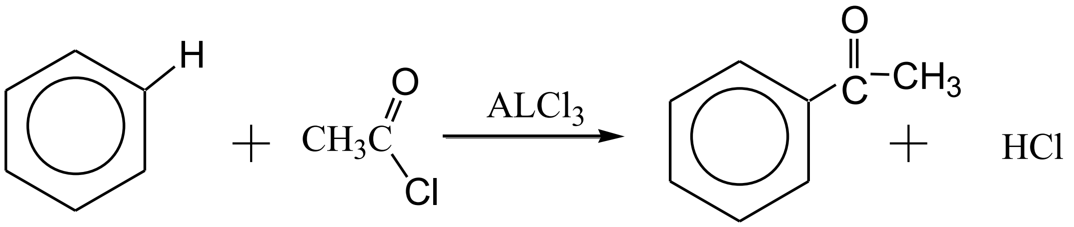
- Nitration :



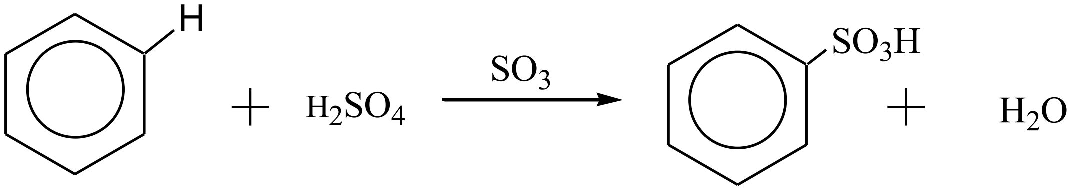
- Friedel-Crafts alkylation



- \- Friedel - Grafts acylation :



•-Sulfation :



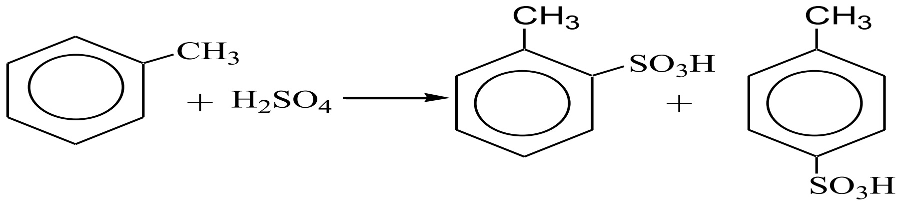
2- when benzene ring bonding with another group. This group called oriented group because is determined site of substituted (ortho , meta or para) as the following:

a- Groups oriented toward ortho and para :

1. $-NH_2$, $-NHR$, $-NR_3$
2. –NHAr , $-N(Ar)_2$
3. – OH , -OR , -Oar
4. –NHCOR, -NHCOAr
5. Alkyl groups
6. Halogens

Ex:

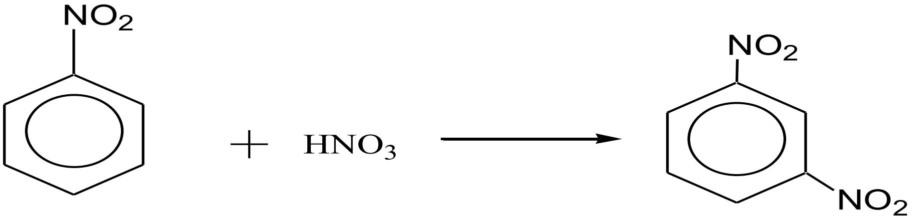
EX:



Toluen 32% Ortho 62% Para 6% meta

b. Groups orientation toward meta – *m*

$-NO_2$, -CN , $-CO_2H$, -CHO , -COR ,- SO_3H, $-NH_3$, $-NH_2R$, NHR_2 , NH_2Ar, $-NH(Ar)_2$ EX:



93% meta

93% toward m and 7% toward O (neglected)

Note: when benzene ring bonding with another group, this group make more active or little activated .

For example:

-Activating group: the methyl group of toluene makes the ring more reactive than the un substituted benzene . the methyl group is therefore an benzene group.

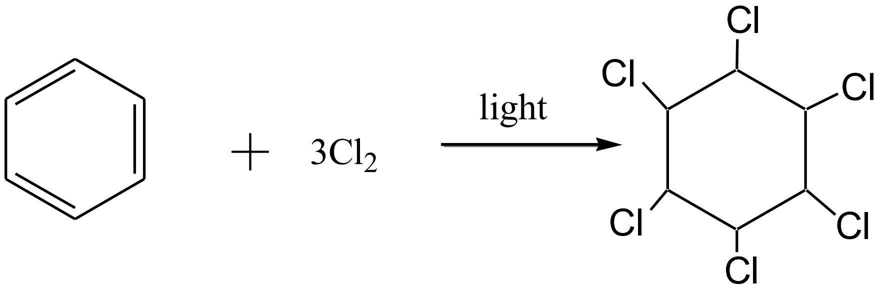
- deactivating group: The nitro group makes the ring less reactive than the un saturated benzene**.**

Generally groups that direct ortho and para are activating groups where as groups that direct meta are also deactivating.

*The halogens are the exception to this rule they direct ortho and para but are de activating.

Other reactions of aromatic compounds:

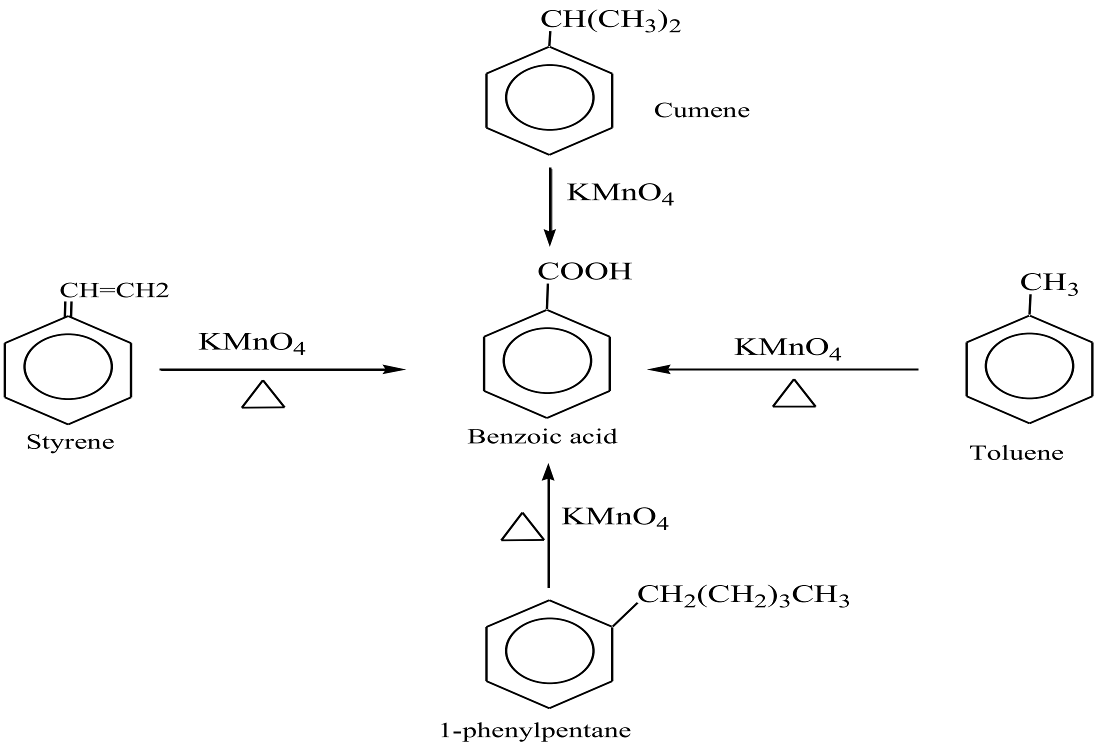
1. Addition reactions:



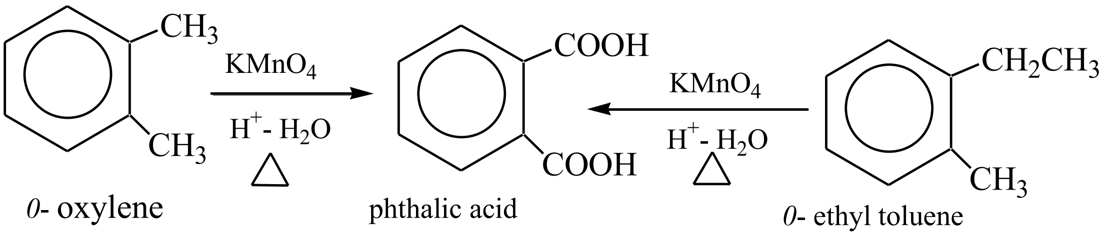
1,2,3,4,5,6 hexachlorocyclo hexane

*The catalyst factor play very important rule in the reaction, when the catalyst is $FeCl_3$ the reaction is Substitution. When the catalyst is light is addition.

2. formation of benzoic acid by the oxidation of four different mono alkyl benzene:

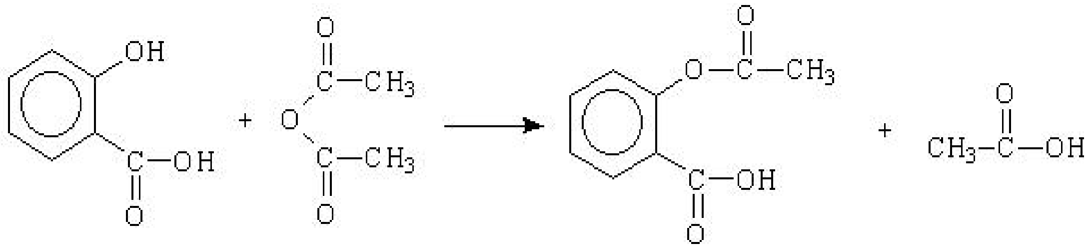


If the benzene ring contain more one bonding alkyl group, there are both groups suffering oxidation to -COOH :



3-Synthesis of Aspirin

The reaction that is used for the synthesis is shown below. In this reaction, an excess of acetic anhydride ($C_4H_6O_3$) is added to a measured mass of salicylic acid ($C_7H_6O_3$) in the presence of a catalyst, sulfuric acid (H_2SO_4). The mixture is heated to form the acetylsalicylic acid ($C_9H_8O_4$) and acetic acid ($C_2H_4O_2$). After the reaction takes place, water is added to destroy the excess acetic anhydride and cause the product to crystallize. The aspirin is then collected, purified by recrystallization, and its melting temperature measured.



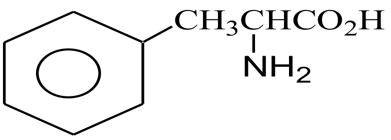
Salicylic acid ($C_7H_6O_3$) Acetic anhydride ($C_4H_6O_3$) Acetylsalicylic acid ($C_9H_8O_4$) Acetic Acid ($C_2H_4O_2$)

(Aspirin)

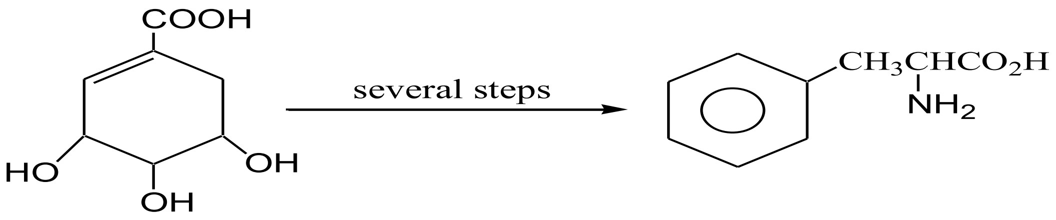
AROMATIC COMPOUNDS IN NUTURE

Derivative of benzene: The are differ in the kind and number of substituents attached to the basic structure for example:

Phenyl alanine



Phenyl alanine is prepared from nonaromatic compound (shikimic acid)



shkimic acid phenyl alanine

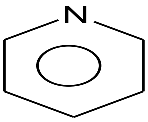
Aromatic Heterocyclic compound :

They are compound which contain another element as well as carbon and hydrogen atoms, (usually nitrogen) These elements called heteroatoms.

Examples:

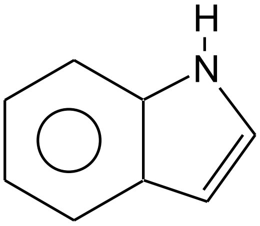
1. **Pyridine** : can be regarded as benzene in which one carbon has been replaced by a nitrogen atom:

Pyridine

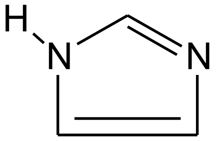


2. **Indole** : is an aromatic hetrocyclic compound containing a pyrole ring and a benzene ring.

Indole



3. **Imidazole :** is a compound that contains two nitrogen atoms in a five member ring:



First -dentistry-SECOND SEMISTE

Lecture (2) 2022-2023 Dr. Mahmoud

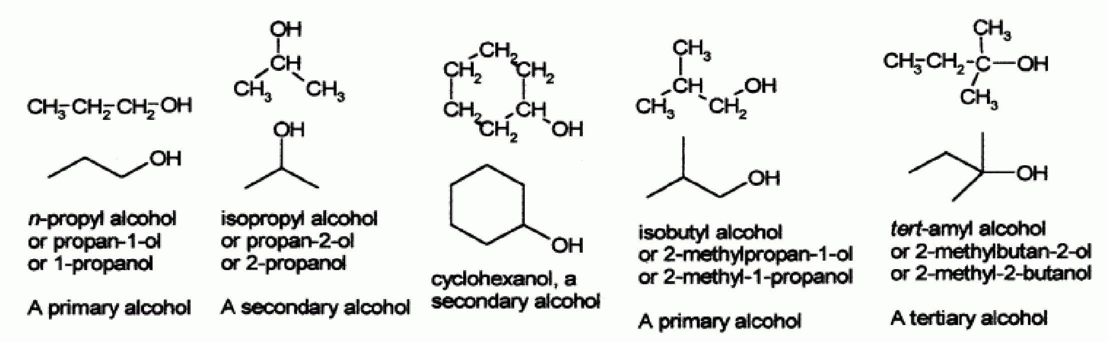
Alcohols, Penols, Ethers and Thiols

To many people alcohol means an intoxicating drink. However, to organic chemists, the word alcohol refers to a class of compounds that contain an OH group, called a hydroxyl or hydroxy group, bonded to an alkyl group. One specific example of this type of compound is ethyl alcohol, CH_3CH_2OH, the intoxicating ingredient to many drinks.

Alcohol can be viewed as organic analogues of water in which one hydrogen is replaced by an alkyl group.

Classifying and naming alcohol

Alcohols are classified according to their structure. Thus, primary alcohol is a compound in which the hydroxyl group is bonded to primary carbon. In a secondary alcohol the hydroxyl group is bonded to secondary carbon. In a tertiary alcohol the hydroxyl group is bonded to a tertiary carbon.



Naming:

The name consists of two words. The first word is the name of alkyl group to which the hydroxyl group is bonded, and the second is the word alcohol.

IUPAC name	common name	formula
methanol	methyl alcohol	CH_3OH
ethanol	ethyl alcohol	CH_3CH_2OH
2-propanol	isopropyl alcohol	$(CH_3)_2CHOH$

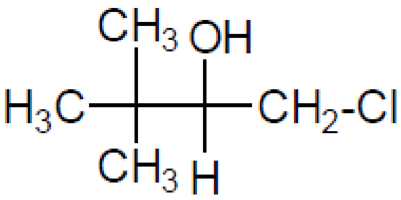
1-butanol	*n*-butyl alcohol	$CH_3(CH_2)_3OH$
2,2-dimethyl-1-propanol	neopentyl alcohol	$(CH_3)_3CCH_2OH$
cyclopentanol	cyclopentyl alcohol	cyclo-C_5H_9OH
1-nonanol	*n*-nonyl alcohol	$CH_3(CH_2)_8OH$
1-decanol	*n*-decyl alcohol	$CH_3(CH_2)_9OH$
2-propen-1-ol	allyl alcohol	$H_2C{=}CH{-}CH_2OH$
phenylmethanol	benzyl alcohol	$Ph{-}CH_2OH$*
diphenylmethanol	diphenylcarbinol	Ph_2CHOH*

Alcohols containing more than five carbons are best named by *IUPAC* rules:

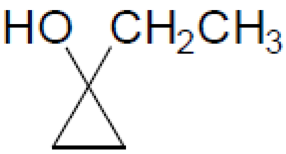
1. **The longest continuous chain of carbon atoms that contains the hydroxyl group is taken as a parent chain.**
2. **The parent name is obtained by substituting the ending –ol for the ending –e of the corresponding alkane.**
3. **The chain is numbered to give the lowest number to the carbon bonded to hydroxyl group.**
4. **The suffix –ol is used for one hydroxyl group, diol for two, triol for three, and so forth .**

$C_2H_4(OH)_2$	Ethane-1,2-diol
$C_3H_6(OH)_2$	Propane-1,2-diol
$C_3H_5(OH)_3$	Propane-1,2,3-triol
$C_4H_6(OH)_4$	Butane-1,2,3,4-tetraol

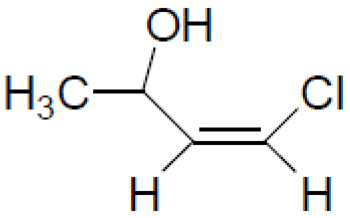
$C_5H_7(OH)_5$	Pentane-1,2,3,4,5-pentol
$C_6H_8(OH)_6$	Hexane-1,2,3,4,5,6-hexol
$C_7H_9(OH)_7$	Heptane-1,2,3,4,5,6,7-heptol



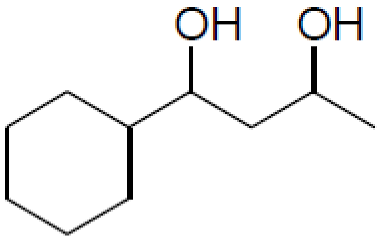
1-chloro-3,3-dimethyl-2-butanol



1-ethylcyclopropanol



)-4-chloro-3-buten-2-ol

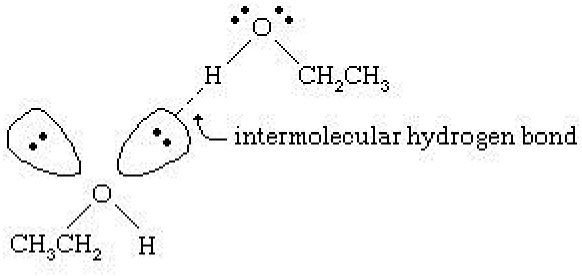


1-cyclohexyl-1,3-butanediol

Physical properties of alcohols

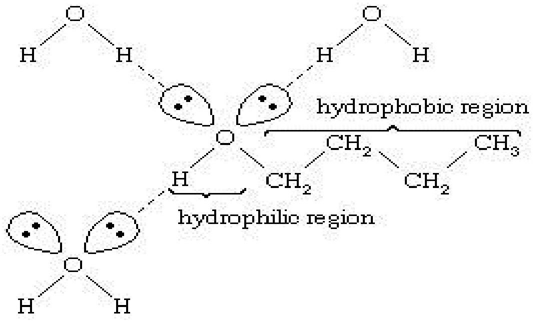
Most of the common alcohols are colorless liquids at room temperature. Methyl alcohol, ethyl alcohol, and isopropyl alcohol are free-flowing liquids with fruity odors. The higher alcohols—those containing 4 to 10 carbon atoms—are somewhat viscous, or oily, and they have heavier fruity odors. Some of the highly branched alcohols and many alcohols containing more than 12 carbon atoms are solids at room temperature.

The boiling points of alcohols are much higher than those of alkanes with similar molecular weights. For example, ethanol, with a molecular weight (MW) of 46, has a boiling point of 78 °C (173 °F), whereas propane (MW 44) has a boiling point of −42 °C (−44 °F). Such a large difference in boiling points indicates that molecules of ethanol are attracted to one another much more strongly than are propane molecules. Most of this difference results from the ability of ethanol and other alcohols to form intermolecular hydrogen bonds.



The oxygen atom of the strongly polarized O−H bond of an alcohol pulls electron density away from the hydrogen atom. This polarized hydrogen, which bears a partial positive charge, can form a hydrogen bond with a pair of nonbonding electrons on another oxygen atom.

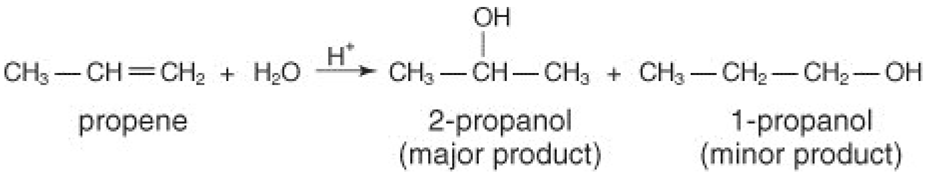
Water and alcohols have similar properties because water molecules contain hydroxyl groups that can form hydrogen bonds with other water molecules and with alcohol molecules, and likewise alcohol molecules can form hydrogen bonds with other alcohol molecules as well as with water. Because alcohols form hydrogen bonds with water, they tend to be relatively soluble in water. The hydroxyl group is referred to as a hydrophilic ("water-loving") group, because it forms hydrogen bonds with water and enhances the solubility of an alcohol in water. Methanol, ethanol, n-propyl alcohol, isopropyl alcohol, and t-butyl alcohol are all miscible with water. Alcohols with higher molecular weights tend to be less water-soluble, because the hydrocarbon part of the molecule, which is hydrophobic ("water-hating"), is larger with increased molecular weight. Because they are strongly polar, alcohols are better solvents than hydrocarbons for ionic compounds and other polar substances.



Alcohol preparation

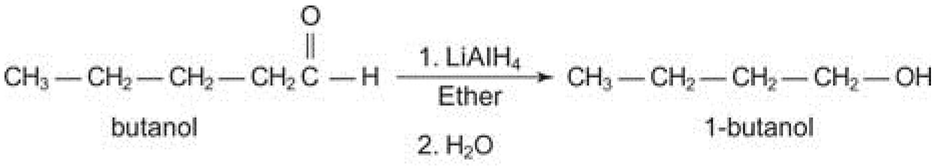
- *Hydration of alkenes:*

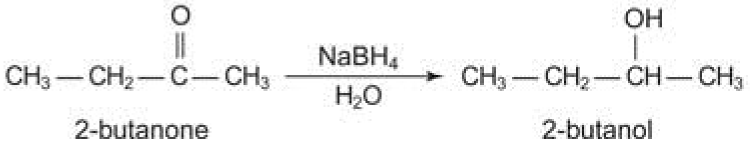
The water can be added to the double-bonded carbons of an alkene in a Markovnikov's manner. As shown in the following figure, a hydrogen ion catalyzes the Markovnikov's addition.



- *Reduction of aldehydes and ketones:*

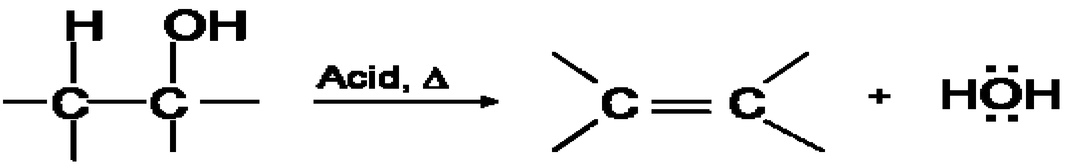
Alcohol can be prepared by adding hydrogen to the carbon oxygen double bond.





Reactions of alcohols

1- **Dehydration**: alcohol reacts with concentrated sulfuric acid to eliminate a molecule of water to form alkene.

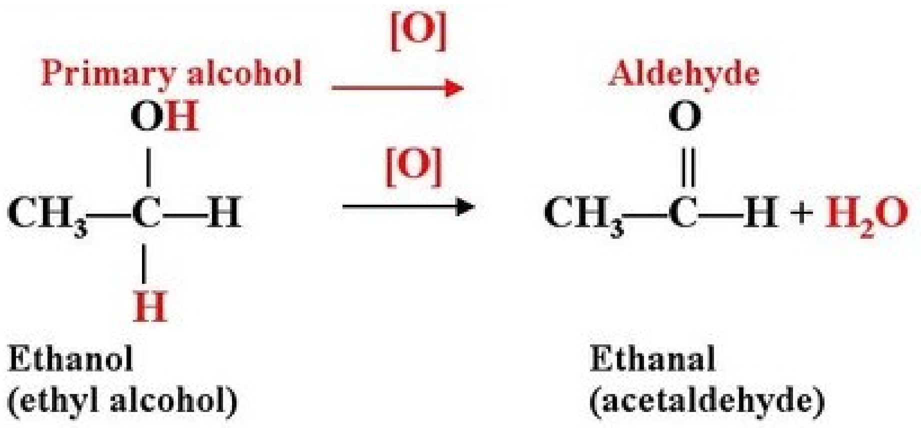


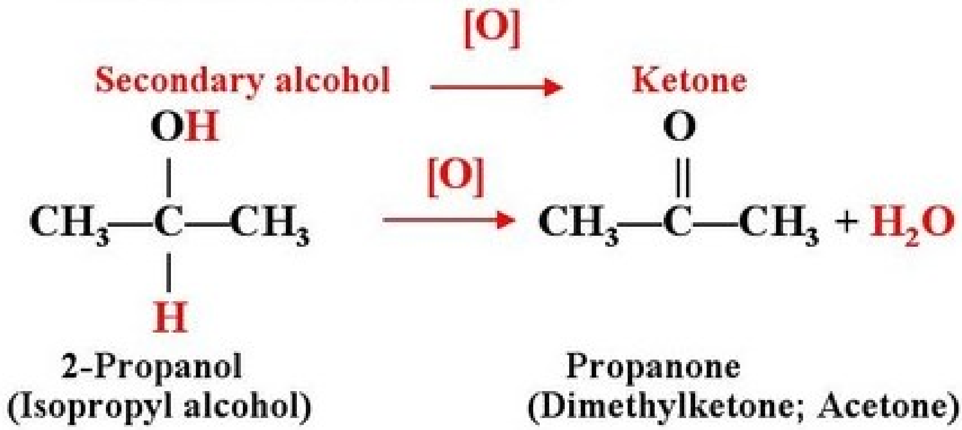
In general the ease of dehydration of alcohol is tertiary > secondary > primary.

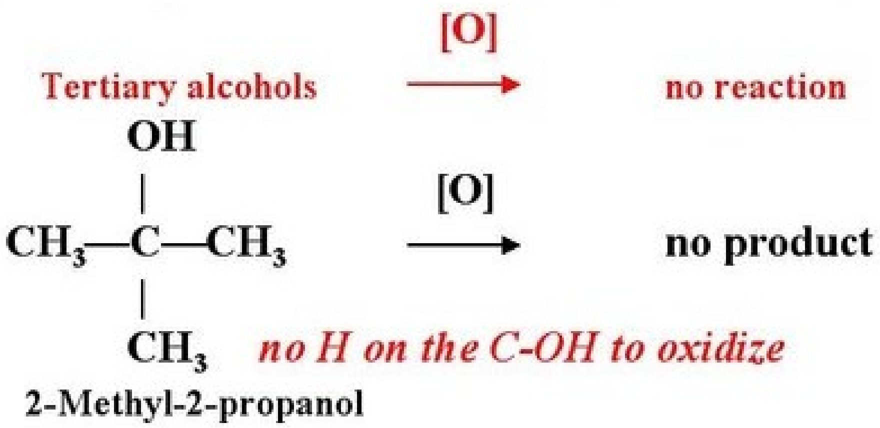
2- **Ester formation**: alcohols react with carboxylic acid in the presence of strong acid catalyst to form a class of compound called esters.

$$R\text{-}OH + R'\text{-}COOH \rightarrow R'\text{-}COOR + H_2O$$

3- **Oxidation**: the products of oxidation of alcohols depend on the structure of alcohol. Primary alcohols are first oxidized to aldehydes, which are further oxidized to carboxylic acid. Secondary alcohols form ketons on oxidation, and tertiary alcohols are not easily oxidized







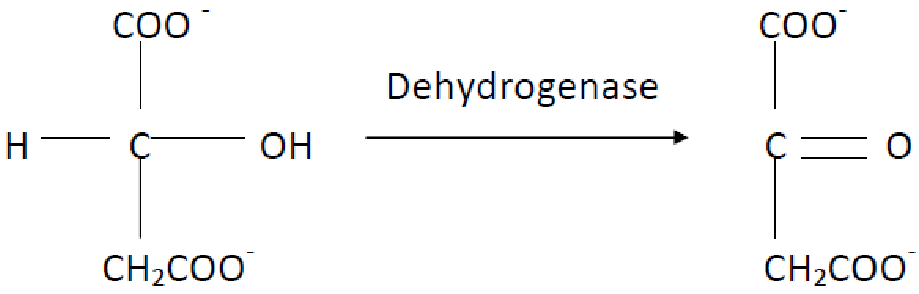
4- **Ether formation**: ether forms when dehydrations takes place at low temperature

$$CH_3{-}OH + HO{-}CH_3 \xrightarrow{H^+} CH_3{-}O{-}CH_3 + H_2O$$

Two Methanol **Dimethyl ether**

Oxidation of alcohol in living systems

The oxidation of alcohols is an important reaction in living systems. Enzymes called dehydrogenase catalyze these reactions. One example is the oxidation of malate to oxaloacetate, which occurs in citric acid cycle.



$$\begin{array}{c} COO^- \\ | \\ H{-}C{-}OH \\ | \\ CH_2COO^- \end{array} \xrightarrow{\text{Dehydrogenase}} \begin{array}{c} COO^- \\ | \\ C{=}O \\ | \\ CH_2COO^- \end{array}$$

Malate Oxaloacetate

This reaction is very stereospecific. Only L-malate ion is oxidized, the other enantiomers D- malate ion, does not react with this enzyme.

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First -dentistry-SECOND SEMISTE Lecture (4)

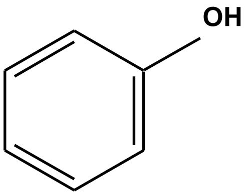
2022-2023 Dr. Mahmoud

PHENOLS

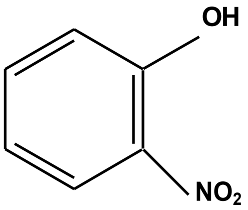
Aromatic hydroxy compounds in which the hydroxy group is attached to an aromatic .ring are called **phenols**

Properties of phenols:

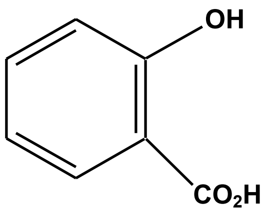
Simple phenols are liquids or low- melting solids, frequently with a very characteristic odor, moderately soluble in water and very soluble in most organic solvents. Simple phenols are generally very toxic, some like phenol itself being absorbed through the skin with the production of severe burns. Typical examples of phenols are:



Phenol

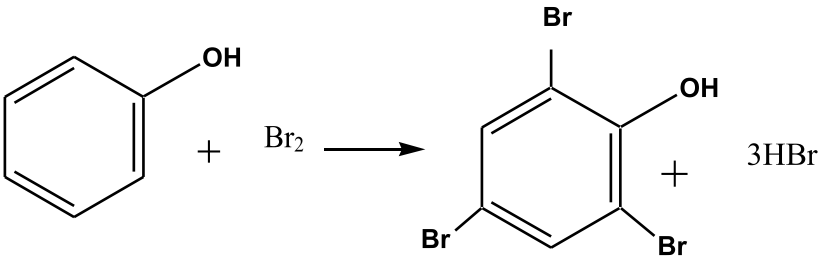


2- Nitrophenol



Salicylic acid

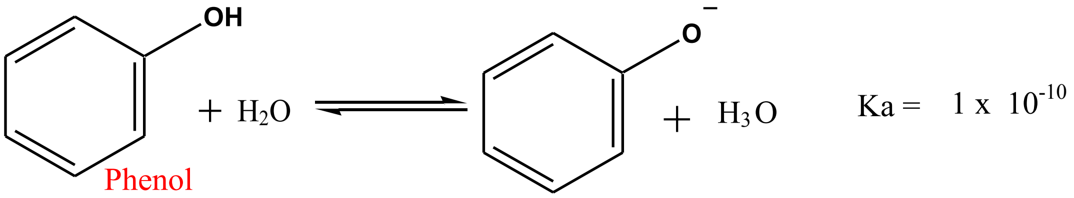
Phenols undergo electrophilic aromatic substitution reactions. The hydroxyl group is strongly activating and ortho-, para- directing. For example, phenol itself reacts with bromine without catalyst to form 2,4,6-tribromophenol:



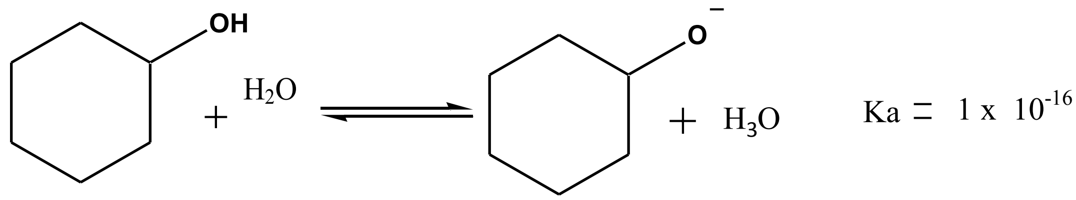
Phenol

2,4,6-Tribromophenol

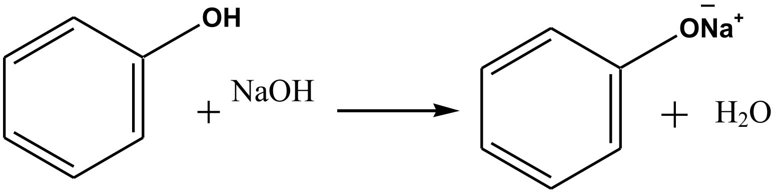
Phenols differ from alcohols in important way:‖ they are much stronger acids than are alcohols:”



Phenol

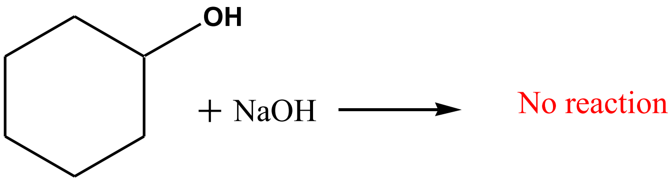


cyclohexanol



phenol

sodium phenoxide

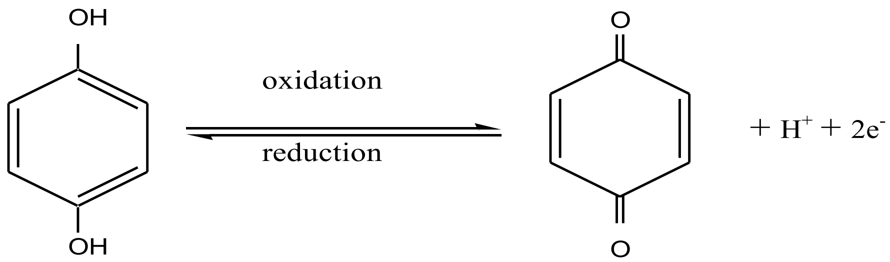


cyclohexanol

Phenol, or carbonic acid as it is sometimes, has antiseptic properties in dilute solution. In fact, all phenolic compounds appear to have germicidal properties. Several commercial germicides contain phenols. Lyso® contains o-phenylphenol, and n-hexylresorcinol is the active ingredient in Sucrets® Iozenges and several mouthwashes

hexachlorophene was used in germicidal soaps, some toothpaste and deodorants until it was discovered to have undesirable side effects.

Aromatic 1,2- and 1,4-dihydroxy compounds are phenol that undergo an important oxidation-reduction reaction. For example, hydroquinone is easily oxidized to quinine. This reaction is reversible, because quinone is easily reduced to hydroquinone:



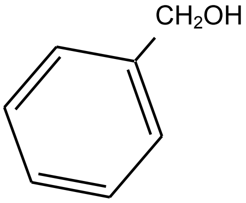
Hydroquinone

Quinone

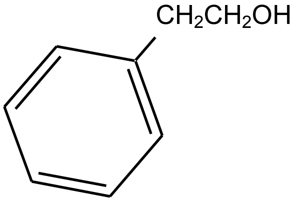
Hydroquinone and quinones are important in the respiratory systems of living systems. When hydroquinone is oxidized, it loses two electrons. In effect it transfers two electrons from itself to anther molecule. It is this property that makes hydroquinone are involved in transferring electrons to molecular oxygen in the respiratory system. One such compound is ubiquinone(also known as coenzyme .

AROMATIC ALCOHOLS

Aromatic compounds, which contain a hydroxy group on a side chain, behave like typical alcohols. Typical examples of these compounds are:



Benzyl alcohol



2- phenylethanol

Ethers

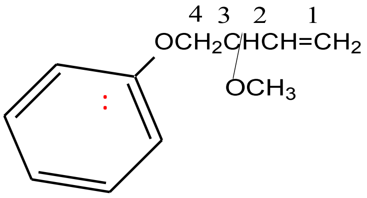
Ethers are compounds that containing oxygen atom bonded to two alkyl groups, two aryl groups or one aryl and one alkyl group. The simpler ethers are usually known by their common names .

$CH_3CH_2OCH_2CH_3$ diethyl ether.

-To name ethers by the IUPAC rules, the more complicated group attached to the oxygen is chosen as the parent. The other group and the oxygen are considered as subustituents on this chain for example:

$$\underbrace{CH_3O}_{\text{substituent}}\ \underbrace{CH = CH_2}_{\text{parent chain}}$$

-The Substituent is named as a prefix and its name is constructed by replacing the-yl of the alkyl name of phenyl by –oxy. Example



3-Methoxy-4-phenoxy-1-butene

Chemically ethers are moderately inert. They do not react with reducing agents or bases under normal conditions. However, they extremely volatile and highly flammable (easily oxidized in air) .Ethers may be prepared by the dehydration reaction between two alcohol molecules. The reaction requires heat and acid:

$$\mathrm{ROH} \quad + \quad \mathrm{R'OH} \xrightarrow[\text{heat}]{H^+} \mathrm{ROR'} \quad + \quad H_2O$$

Alcohol Alcohol Ether water

Dithyl ether was the first anesthetic used. It functions as by interfering with the central nervous system. It functions by accumulating lipid material of the nerve cells, thereby interfering with nerve impulse transmission. This result in **analgesia**: a lessened perception of pain..

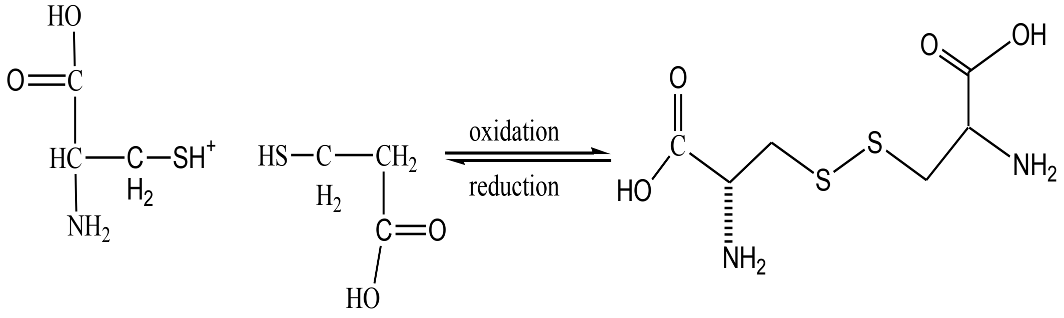
Epoxides are special kinds of ethers. These compounds are special because they have a three member ring that contains an oxygen atom. They are far more reactive than typical ethers.

One example of an epoxide in nature is squalene 2,3-epoxide. This compound is formed in a series of reactions that leads to the biosynthesis of cholesterol

Thiols

Thiols are sulfur analogs of alcohols. The IUPAC names of thiols are formed by adding the suffix- thiol, and so forth to the name of the parent hydrocarbon. Common names are obtained by first naming the alkyl group followed by the word mercaptan

- Thiols are more volatile than are the corresponding alcohols and have a very disagreeable odor. Various thiols are found in nature, e.g. 1-propanethiol is released when an onion is peeled and thiols are responsible for the odor of garlic. Thiols are highly reactive and are present in small quantities in living system where they play key roles:
- Thiols are involved in protein structure and conformation. It is the ability of two thiol groups to easy undergo oxidation to a disulfide bond (-S-S-) that is responsible for this involvement. Cysteine is an amino acid that contains a sulfhydryl group. Cysteine is found in many proteins and plays an important role in the conformation of the protein by forming disulfide bonds with other cysteine molecules within the protein:

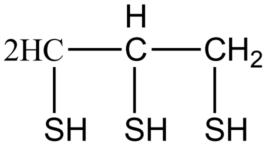


Cystien Cysteine Cysteine

- Forming Disulfide Bonds

Many extra cellular proteins contain disulfide cross-links (intracellular proteins almost never do). The cross-links can only be established after the protein has folded up into the correct shape

- **BAL (British Anti-Lewisite**) is used as an antidote for mercury poisoning. The two thiol groups of BAL complex with mercury and remove it from the system before it can do any damage.



$$\underset{\mathrm{SH}}{\mathrm{2HC}}-\underset{\mathrm{SH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{SH}}{\mathrm{CH_2}}$$

BAL

- **Coenzyme A** is a thiol that serves as a –carrier of acetyl groups (CH3CO-) in biochemical reactions. It plays a central role in metabolism by shuttling acetyl groups from one reaction to another. Coenzyme A is made up of the nucleotide ADP, the vitamin pantothenic acid, and the thiolcontaining β mercaptoethyl amine group. when the two-carbon acetate group is attached to the coenzyme A, the product is acetyl coenzyme A (acetyl CoA). The bond between coenzyme A and the acetyl group is a high- energy thioester bond. it can release a great deal of energy when the bond is broken an thus the acetyl group can participate in other biochemical reactions.

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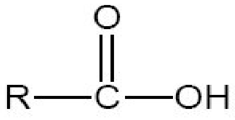
First -dentistry-SECOND SEMISTE

Lecture (5) 2022-2023 Dr. Mahmoud

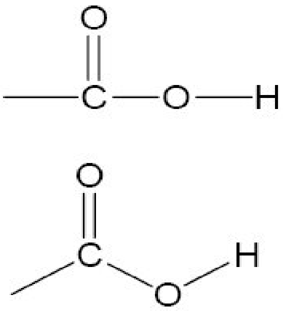
Carboxylic Acids

Carboxylic acids are weak organic acids which contain the **carboxyl group** (RCO_2H):



$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

a **carboxylic acid**



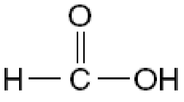
the **carboxyl** group

$RCOOH$ RCO_2H

condensed ways of writing the carboxyl group

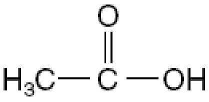
The tart flavor of sour-tasting foods is often caused by the presence of carboxylic acids.

Carboxylic acids occur both in nature and in the laboratory. Vinegar, for example, is a dilute solution of acetic acid, CH3COOH(aq); butanoic acid, CH3CH2CH2COOH(aq), is responsible for the rancid odor of spoiled butter; and hexanoic acid, CH3(CH2)4COOH(aq), is partially responsible for the characteristic odor of goats. In fact, hexanoic acid is often called caproic acid from the Latin name for goat,. The two simplest carboxylic acids are:



$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

methanoic acid
(formic acid)



$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$

ethanoic acid
(acetic acid)

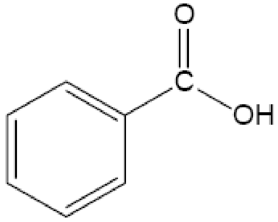
Methanoic acid and ethanoic acid are generally referred to by their common names, formic acid and acetic acid, respectively.

Acetic acid is a clear, colorless liquid with a pungent odor. Household vinegar is an approximately 5% acetic acid solution. The pure compound is commonly called glacial acetic acid because it freezes at 18° C.

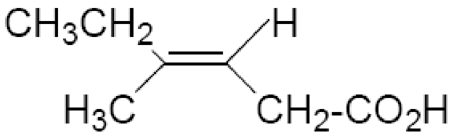
Formic acid is responsible for the irritants in certain plants, such as stinging nettles. Formic acid is a colorless, fuming liquid that is very soluble in water. It is the major irritant in ant bites and was first isolated by the distillation of ants.

Nomenclature of Carboxylic Acids

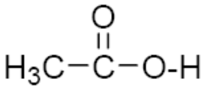
- Select the longest carbon chain containing the carboxyl group. The -e ending of the parent alkane name is replaced by the suffix -oic acid.
- The carboxyl carbon is always numbered “1
- Name the substituents attached to the chain in the usual way.
- Aromatic carboxylic acids (i.e., with a CO2H directly connected to a benzene ring) are named after the parent compound, benzoic acid.



Benzoic acid

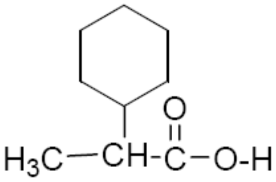


4-methyl-3-hexenoic acid



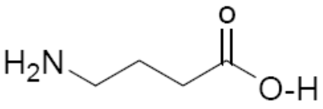
$$H_3C-\overset{O}{\overset{\|}{C}}-O-H$$

ethanoic acid



$$H_3C-\underset{}{\overset{\text{C}_6\text{H}_{11}}{CH}}-\overset{O}{\overset{\|}{C}}-O-H$$

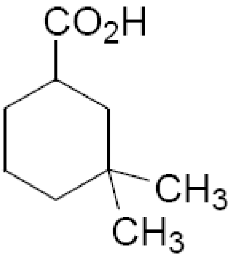
2-cyclohexylpropanoic acid



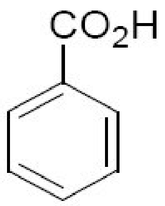
4-aminobutanoic acid

Cycloalkanes with carboxyl substituent are named as cycloalkanecarboxylic acids.

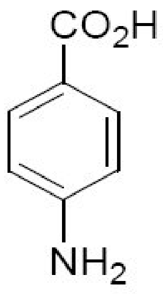
3,3-dimethylcyclohexanecarboxylicacid



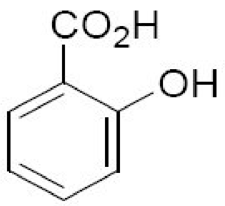
Aromatic acids of the form $Ar-CO_2H$ are named as derivatives of benzoic acids, with ortho, meta and para indicating the location relative to the carboxyl group.



benzoic acid



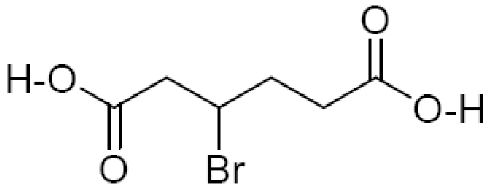
p-aminobenzoic acid



o-hydroxybenzoic acid

Dicarboxylic Acids

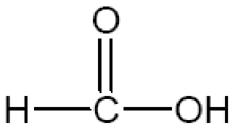
Aliphatic dicarboxylic acids are named by simply adding the suffix -dioic acid to the root name.
The root name comes from the longest carbon chain containing both carboxyl groups.
Numbering starts at the end closest to a substituent.

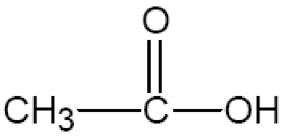


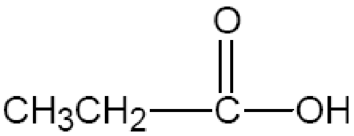
3-bromohexanedioic acid

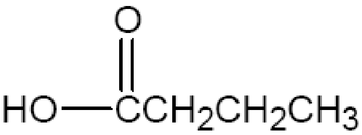
Examples: Naming Carboxylic Acids

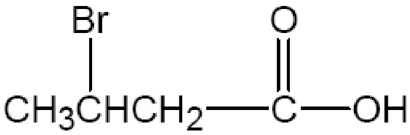
- Name the following compounds:

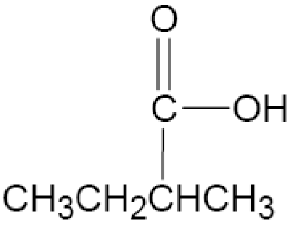

$\mathrm{H-\overset{\overset{O}{\|}}{C}-OH}$

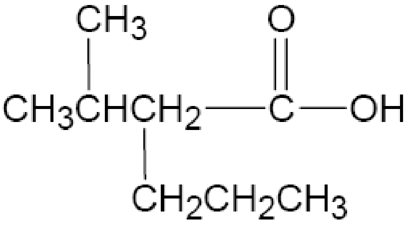

$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OH}$

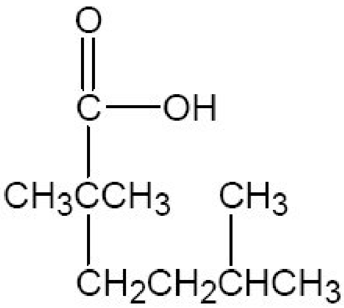

$\mathrm{CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH}$

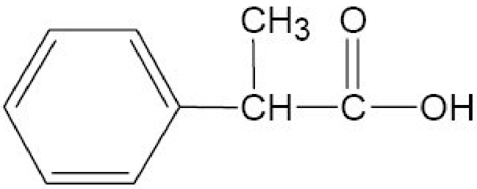

$\mathrm{HO-\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3}$

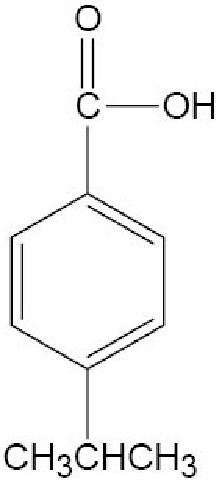

$\mathrm{CH_3\overset{\overset{Br}{|}}{C}HCH_2-\overset{\overset{O}{\|}}{C}-OH}$

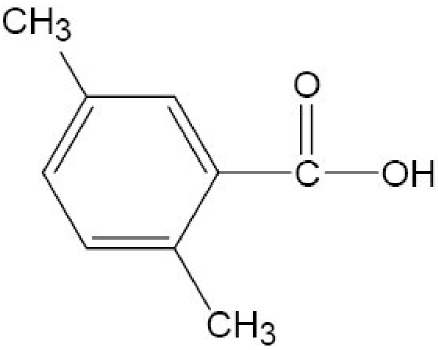

$\mathrm{CH_3CH_2\overset{\overset{\overset{O}{\|}}{C}-OH}{\overset{|}{C}}HCH_3}$

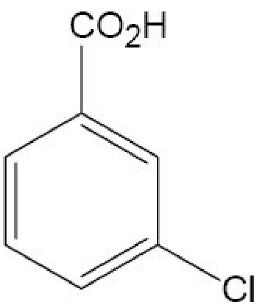

$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_2CH_2CH_3}{|}}{C}H_2-\overset{\overset{O}{\|}}{C}-OH}$


$\mathrm{CH_3\overset{\overset{\overset{O}{\|}}{C}-OH}{\overset{|}{C}}CH_3}$, $\mathrm{\underset{|}{}CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3}$





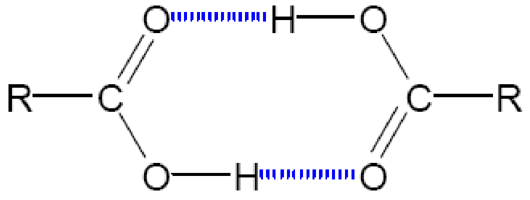




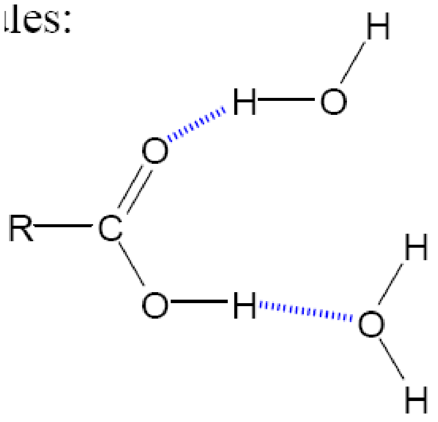
- Draw structural formulas for the following molecules:
  - 2-methylpropanoic acid
  - 2,2,5-trimethylhexanoic acid
  - 4,5-dimethyl-3-nitrooctanoic acid
  - *para*-bromobenzoic acid
  - 2,4,6-trinitrobenzoic acid
  - 4-ethylpentanedioic acid (what's wrong with this name?)

Physical Properties of Carboxylic Acids

- Carboxylic acids hydrogen bond to themselves to form a **dimer**:

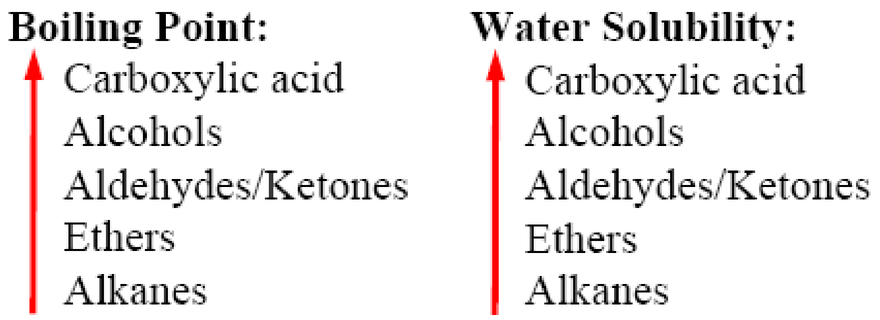


- Carboxylic acids also form hydrogen bonds to water molecules:



- Since carboxylic acids can form more than one set of hydrogen bonds, their boiling points are usually higher than those of other molecules of the same molecular weight (MW).

- Low-MW carboxylic acids are generally liquids at room temp. (often, they are somewhat oily); higher- MW carboxylic acids are generally waxy solids.
- Short-chain carboxylic acids are also generally more soluble in water than compounds of similar MW, since they can hydrogen bond to more than one water molecule.
- As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases and the solubility in water decreases.
- Many carboxylic acids that are liquids at room temperature have characteristically sharp or unpleasant odors.
- Like most acids, carboxylic acids tend to have a sour taste (e.g., vinegar, citric acid, etc.).

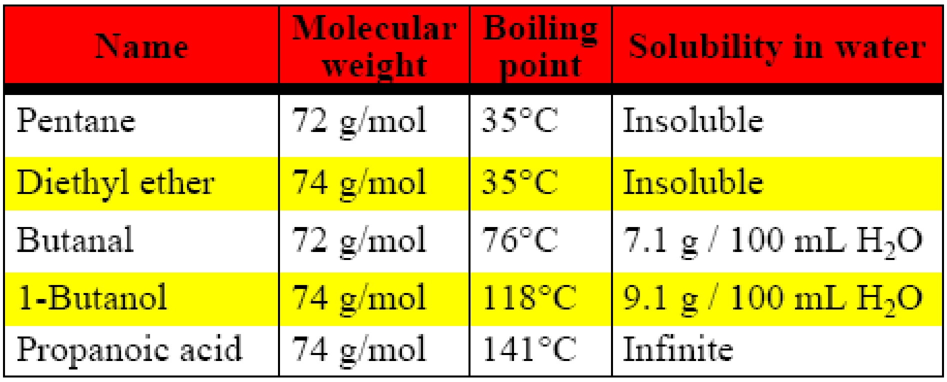


Boiling Point:

Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:

Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes



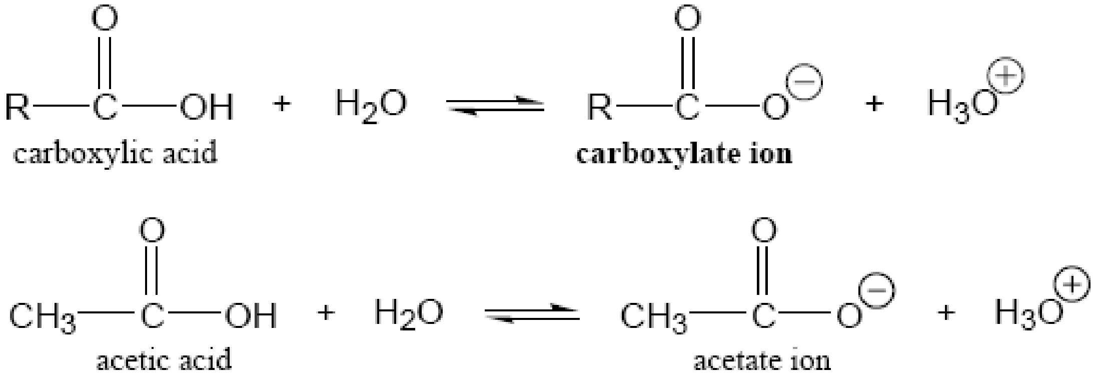
Name	**Molecular weight**	**Boiling point**	**Solubility in water**
Pentane	72 g/mol	35°C	Insoluble
Diethyl ether	74 g/mol	35°C	Insoluble
Butanal	72 g/mol	76°C	7.1 g / 100 mL H_2O
1-Butanol	74 g/mol	118°C	9.1 g / 100 mL H_2O
Propanoic acid	74 g/mol	141°C	Infinite

Examples: Predicting Physical Properties

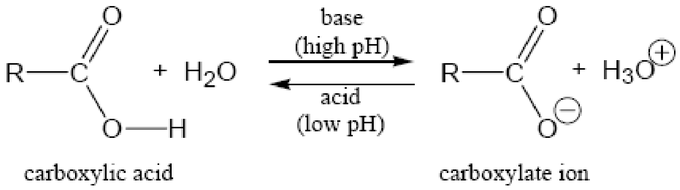
- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)
  - 1-pentanol
  - hexane
  - butanoic acid
  - pentanal
- Which member of each of the following pairs of compounds would you expect to have a higher solubility in water?
  - 2-butanone *or* propanoic acid
  - hexanoic acid *or* ethanoic acid

The Acidity of Carboxylic Acids

- Carboxylic acids are weak acids; in water, they dissociate to produce hydronium ions and **carboxylate ions**:



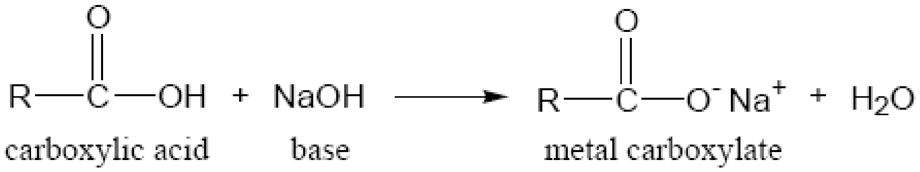
- The dissociation of a carboxylic acid is a reversible reaction, and the position of the equilibrium can be affected by the addition of acid (low pH) or by adding base (high pH):



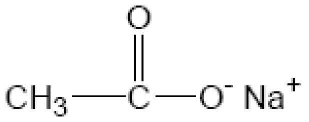
- At the *physiological pH* of 7.4 (the pH of most body fluids) the carboxylate form of most carboxylic acids is the predominate form.

Carboxylate Salts

- Carboxylic acids react with strong bases such a sodium hydroxide (NaOH) and potassium hydroxide (KOH) to produce carboxylate salts.
- Carboxylate salts are named by naming the metal first and changing the **-ic acid** ending of the carboxylic acid name to **-ate**.

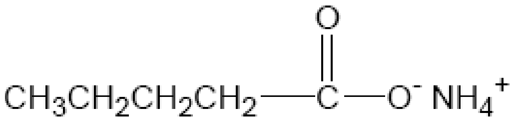


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- Na^+ + H_2O$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- Na^+$$

sodium ethanoate
(sodium acetate)

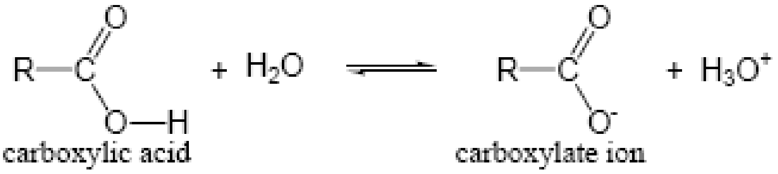


$$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O^- NH_4^+$$

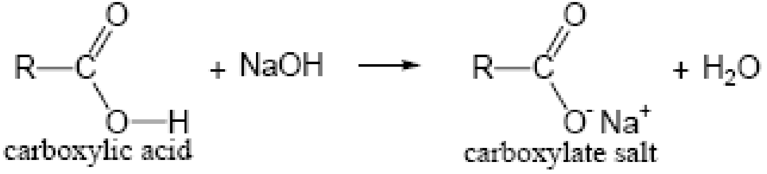
- Carboxylate salts are ionic compounds, and are typically solids at room temperature.
- Because they contain charges, carboxylate salts are typically much more soluble in water than the carboxylic acids from which they are derived.

Reactions of Carboxylic Acids

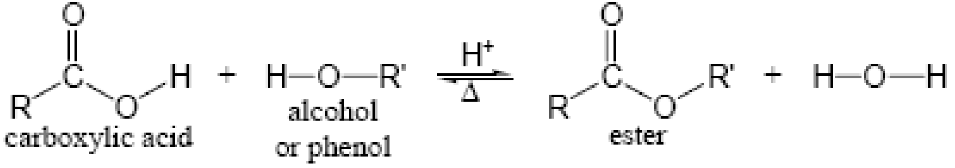
1. **Reaction of a carboxylic acid with water to form a carboxylate ion.**



2. **Reaction of a carboxylic acid with a base to form a carboxylate salt and water.**



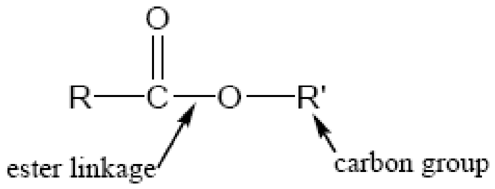
3. **Reaction of a carboxylic acid with an alcohol to produce an ester and water.**

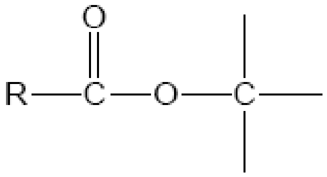


Carboxylic acids derivatives

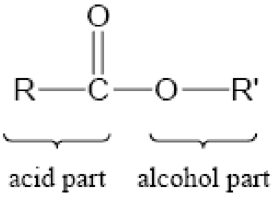
Esters

- An **ester** is a derivative of a carboxylic acid in which there is a carbon group connected to the single-bonded oxygen:



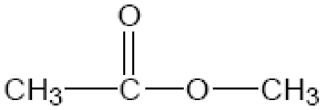


Nomenclature of Esters



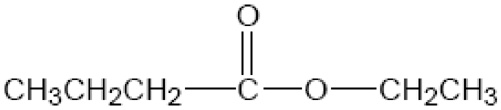
$$\underbrace{R-\overset{\overset{O}{\|}}{C}}_{\text{acid part}}-\underbrace{O-R'}_{\text{alcohol part}}$$

- Name the alkyl or aromatic portion contributed by the "alcohol part" first.
- The "acid part" is named as a carboxylic acid, with the **-ic acid** suffix changed to **-ate**.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$$

Methyl ethanoate

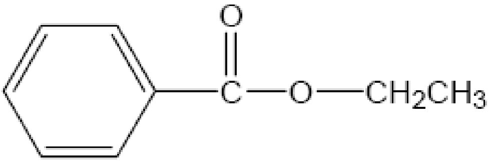


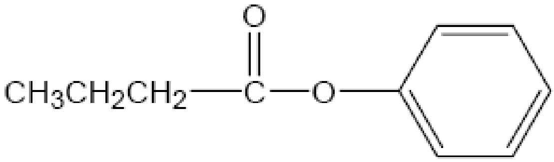
$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$$

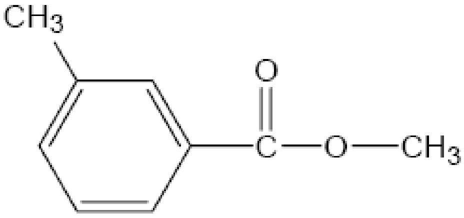
Ethyl butanoate

Examples: Ester Nomenclature

- Name the following compounds:

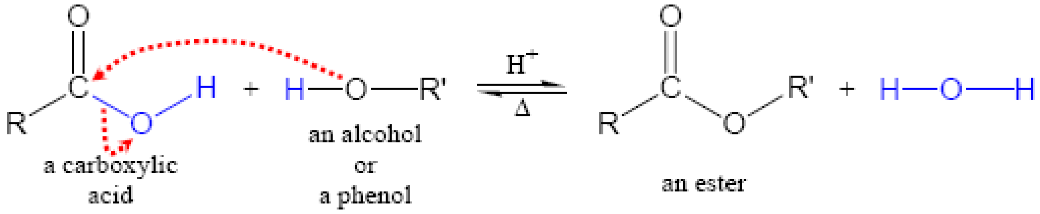






Synthesis of Esters:

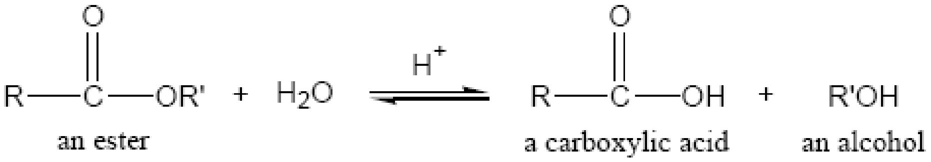
- The simplest way to synthesize an ester is to heat a carboxylic acid with an alcohol or phenol (plus an acid catalyst); the oxygen of the alcohol adds to the carboxyl group, splitting out a molecule of water in the process (an *esterification reaction*).



Reactions of Esters:

-Ester Hydrolysis

- Esters may be broken apart under *acidic conditions* by water (a **hydrolysis** reaction) to form a carboxylic acid and an alcohol.

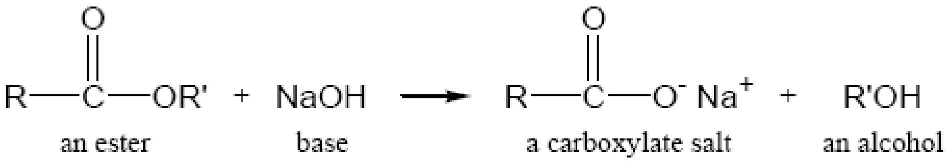


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH$$

- This is essentially the reverse reaction of the synthesis of esters from carboxylic acids and alcohols.

Saponification

- Esters may be broken apart under *basic conditions* by sodium hydroxide or potassium hydroxide to form carboxylate salts and alcohols.

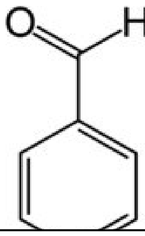


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- Na^+ + R'OH$$

- This reaction is important in the production of **soap**

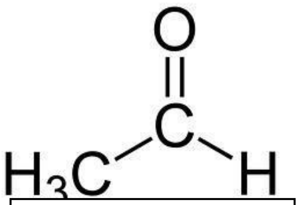
Aldehydes and Ketones

Aldehydes and ketones are two more classes of compounds that contain the carbonyl group. An aldehyde contain a carbonyl group whose carbon is bonded to one hydrogen and either an alkyl or an aryl group. For example:



Benzaldehyde

Aromatic aldehyde

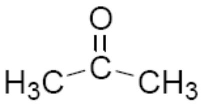


Acetaldehyde

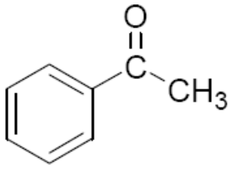
Aliphatic aldehyde

The aldehyde is often written RCHO.

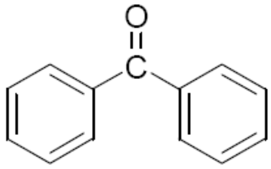
Ketones contain a carbonyl group whose carbon is bonded to two alkyl groups, two aryl groups, or one alkyl and one aryl group. For example:



acetone



acetophenone



benzophenone

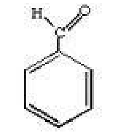
Naming aldehydes and ketones

Common names

Common names are always used for aldehydes of five carbons or less. They are obtained from the name of carboxylic acid formed by oxidation of the aldehyde. The –oic acid ending of the name of carboxylic acid is replaced by –aldehyde. Thus, the aldehyde that yields formic acid when oxidized is caused formaldehyde, the aldehyde that yields acetic acid when oxidized is called acetaldehyde, etc. examples:

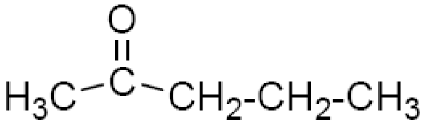
CH_3CH_2CHO propionaldehyde

$CH_3CH_2CH_2CHO$ butylaldehyde



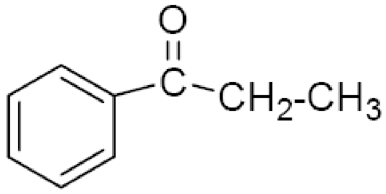
BENZALDEHYDE

IUPAC nomenclature requires ketones to be named by replacing the -e ending of the alkyl name with -one. Alkane → alkanone

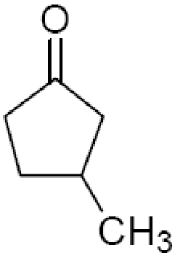


$$H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

2-pentanone

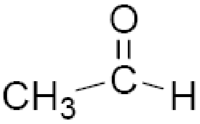


1-phenyl-1-propanone



3-methylcyclopentanone

Systematic names (IUPAC) for aldehydes are obtained by replacing -e with -al.



$$CH_3-\overset{\overset{O}{\|}}{C}-H$$

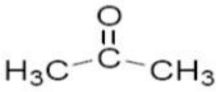
ethanal

$H_3C-CH_2-CH=CH-CHO$

pent-2-enal

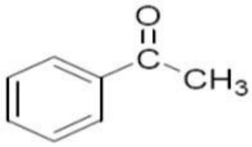
Common Names of ketones

The wide spread use of carbonyl compounds means many common names are entrenched in their everyday use.

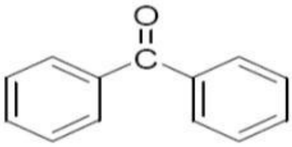


$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

acetone



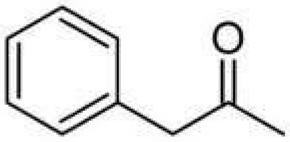
acetophenone



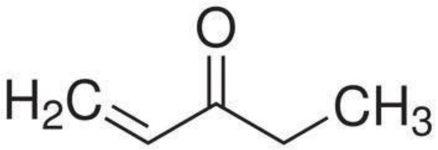
benzophenone

Also the common names of ketones are formed by placing the names of groups attached to the carbonyl group as a prefixes to the word ketone.

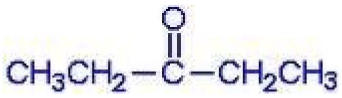
The names are written as separate words. For example:



Benzyl methyl keton

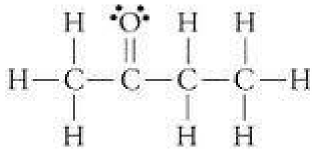


Ethyl vinyl ketone



$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

Di ethyl ketone

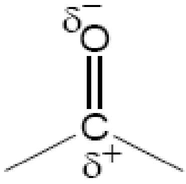


Ethyl methyl ketone

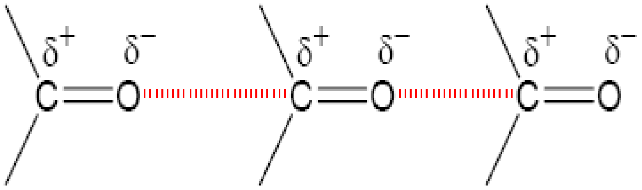
Physical Properties of Aldehydes and Ketones

The Polarity of the Carbonyl Group

- Carbonyl compounds are polar, containing a dipole along the carbon-oxygen double bond.



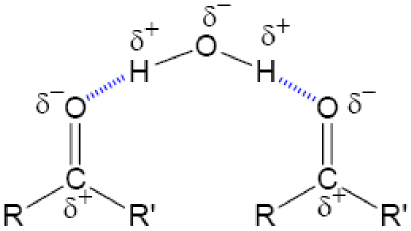
- This creates weak attractive forces between carbonyl compounds, but these attractions are not as strong as those that result from hydrogen-bonding.

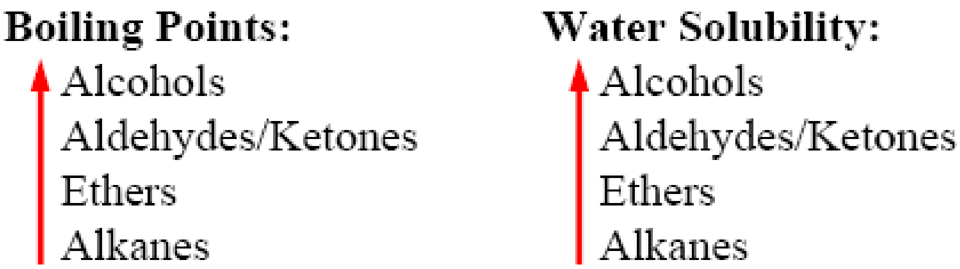


- Since there is no hydrogen on the carbonyl oxygen, aldehydes and ketones *do not form hydrogen bonds with themselves*.
- Aldehydes and ketones therefore have boiling points that are in between those of alcohols and hydrocarbons of the same molecular weight:

– Alcohols form hydrogen bonds, and have high boiling points.
– Hydrocarbons are nonpolar, and have low boiling points.
– Aldehydes and ketones are polar, so they have higher boiling points than hydrocarbons, but they are not as polar as molecules which can hydrogen bond.

- Carbonyl compounds cannot hydrogen-bond to each other, but they can hydrogen-bond to water through the carbonyl oxygen.
- Low-molecular weight aldehydes and ketones are water-soluble; water solubility decreases as the size of the molecule increases.



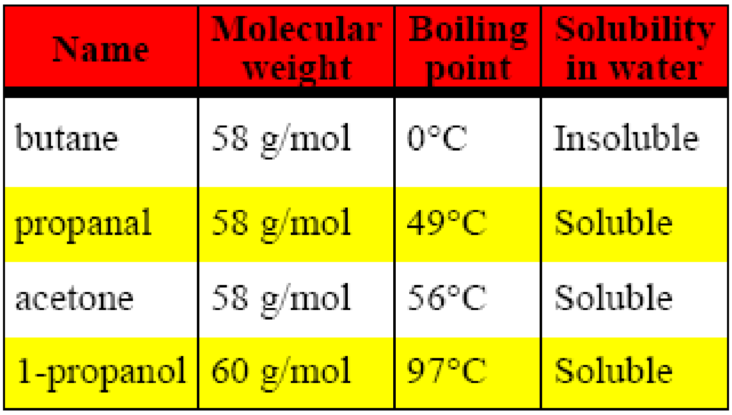


Boiling Points:

Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:

Alcohols
Aldehydes/Ketones
Ethers
Alkanes



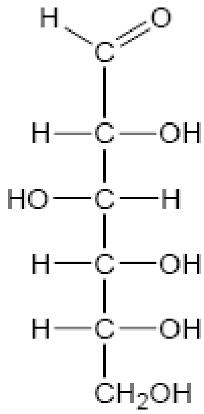
Name	Molecular weight	Boiling point	Solubility in water
butane	58 g/mol	0°C	Insoluble
propanal	58 g/mol	49°C	Soluble
acetone	58 g/mol	56°C	Soluble
1-propanol	60 g/mol	97°C	Soluble

Examples: Predicting Boiling Points

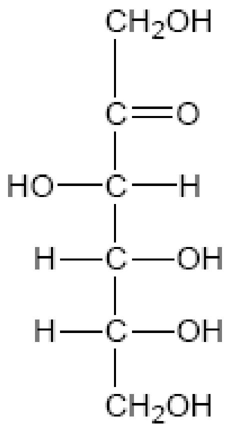
- Arrange the following compounds in order of increasing boiling point:

– 2-pentanone
– 2-methylpentane
– 2-pentanol

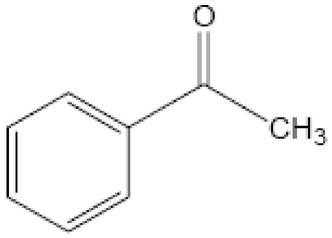
Important Aldehydes and Ketones



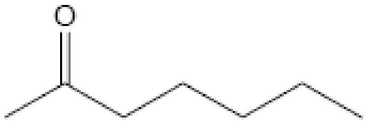
Glucose
One of the most important of the **carbohydrates**, which are *polyhydroxy aldehydes and ketones*; the metabolism of glucose is a major source of energy for living organisms



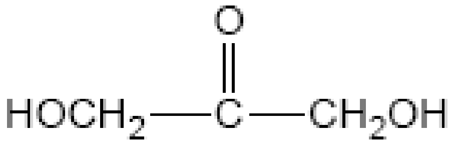
Fructose
Another important carbohydrate; a major component of corn syrup; found in honey, syrups, and preserves; in combination with glucose it forms the disaccharide **sucrose**.



Acetophenone
Used in perfumery, and as an organic solvent; also used in the synthesis of some pharmaceuticals

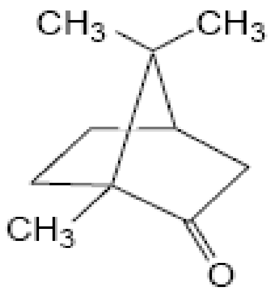


2-Heptanone
Found in oil of clove; also present in the odor of many fruits and dairy products, and is also responsible for the odor of blue cheese.



$$HOCH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2OH$$

Dihydroxyacetone
Active ingredient in "bronzers" that provide fake suntan coloration; reacts with dead, outer skin cells to produce a darker color; fades as the dead skin cells slough off.



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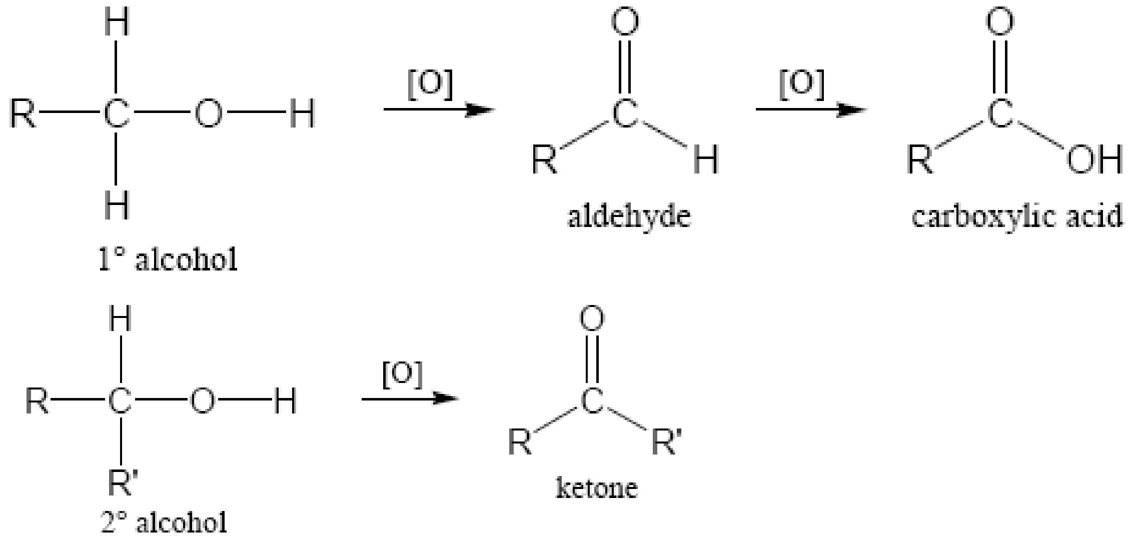
Camphor
Isolated by steam distillation from the camphor tree of China and Japan. Camphor is a counter-irritant (produces a superficial inflammation to reduce deeper inflammation) and antipruritic (anti-itching) medication; it appears to selectively stimulate cold sensors. It also stimulates the respiratory systems and inspires deep breathing, but can cause convulsions and respiratory collapse in larger doses.

Preparing aldehydes and ketones

Alcohol can be oxidized as we learned. Primary alcohols are oxidized first to aldehyde, which are then further oxidized to carboxylic acid. Secondary alcohols are oxidized to ketones.

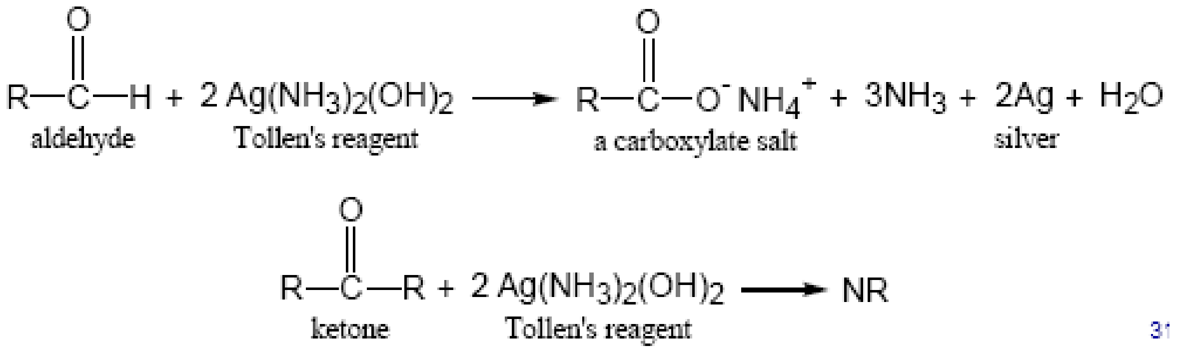


To use the oxidation of primary alcohol as a method of preparing aldehydes, it is necessary to stop the reaction at the intermediate aldehyde stage. This can be done by removing the aldehyde from the reaction mixture as soon as it formed. This can be done quite easily by distillation, because aldehydes have lower boiling points than that of alcohols. By carrying out the oxidation at a temperature slightly above the boiling point of the aldehyde.

Tests for aldehydes:

- **Tollens' reagent** is a mild oxidizing agent composed of silver ions in an aqueous basic solution of ammonia.

- Aldehydes are oxidized to carboxylate salts (since the solution is basic), and the silver ions are reduced to solid silver, which coats the bottom of the test tube with a "silver mirror."
- Ketones are not oxidized, so no silver mirror forms.



$$R-\overset{O}{\overset{\|}{C}}-H + 2\,Ag(NH_3)_2(OH)_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-NH_4^+ + 3NH_3 + 2Ag + H_2O$$

aldehyde, Tollen's reagent, a carboxylate salt, silver

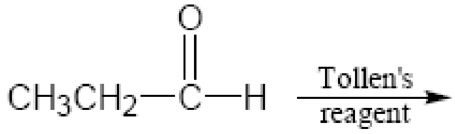
$$R-\overset{O}{\overset{\|}{C}}-R + 2\,Ag(NH_3)_2(OH)_2 \longrightarrow NR$$

ketone, Tollen's reagent

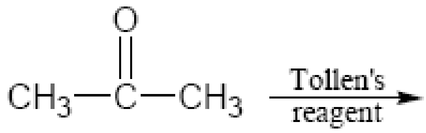
Another reagent often used to test for aldehydes is the Fehling's solution. The aldehyde is oxidized to the carboxylate ion and the cupric ion is reduced to cupric oxide, which precipitate as a red solid.

Examples: The Tollens' Test

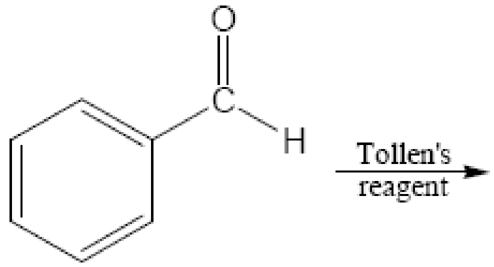
- What observations would be made in the following reactions?



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{reagent}]{\text{Tollen's}}$$



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{reagent}]{\text{Tollen's}}$$

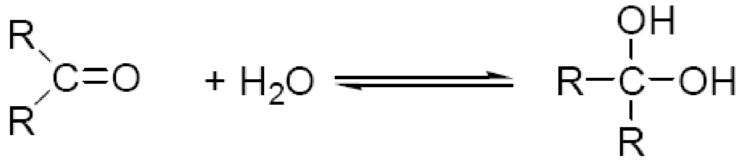


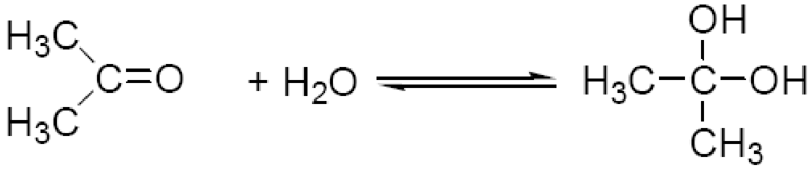
Unknown $\xrightarrow[\text{reagent}]{\text{Tollen's}}$ silver ppt

Reactions of Aldehydes and Ketones:

Addition reactions of aldehydes and ketones

1- **Addition of water (hydration)**: In aqueous solution, ketones and aldehydes are in equilibrium with their hydrates.



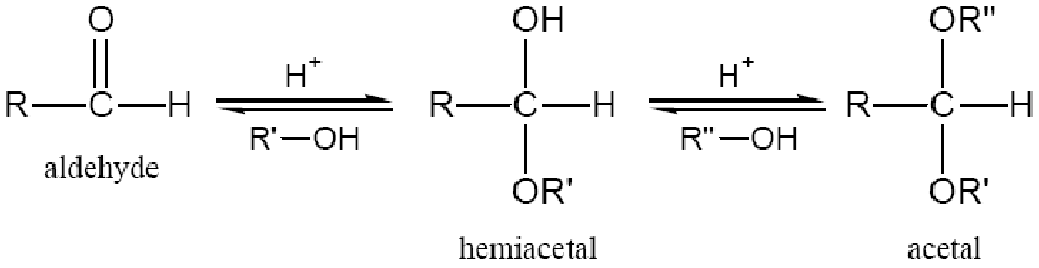


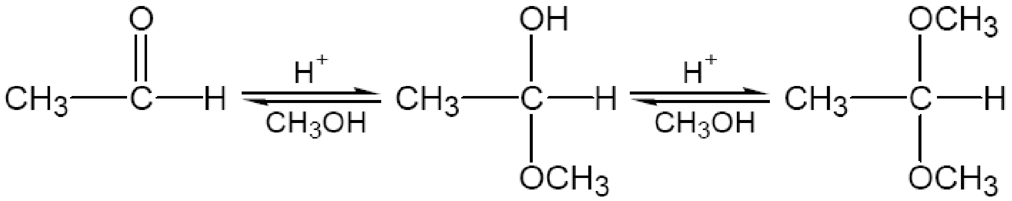
Aldehydes are more likely to form hydrates since they have the larger partial positive charge on the carbonyl carbon (larger charge = less stable = more reactive).

2- Addition of alcohols:

- Addition of Alcohols to Aldehydes

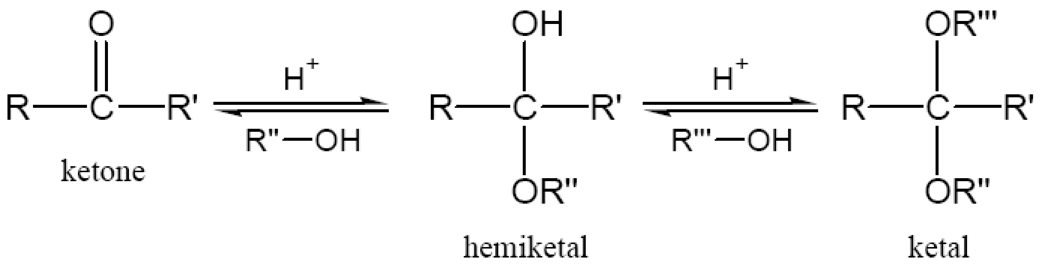
• Aldehydes react with alcohols first to form **hemiacetals**, which then react with excess alcohol to produce **acetals**.

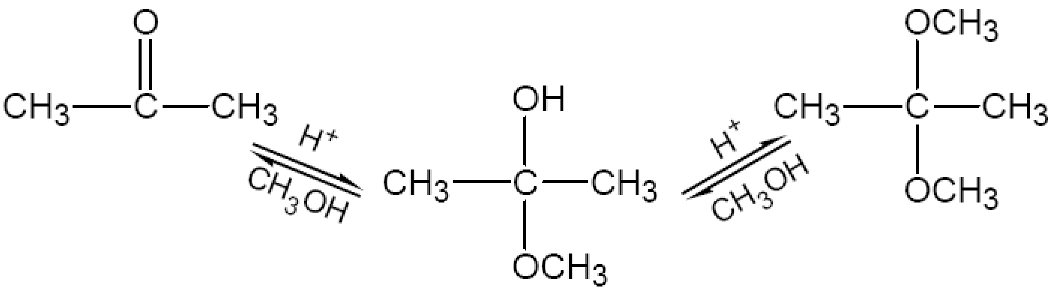




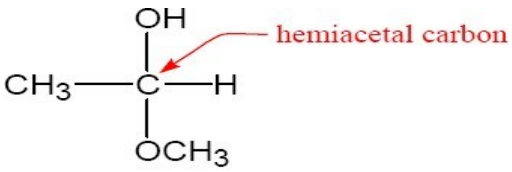
- Addition of Alcohols to Ketones

• Ketones react with alcohols first to form **hemiketals**, which then react with excess alcohol to produce **ketals**.

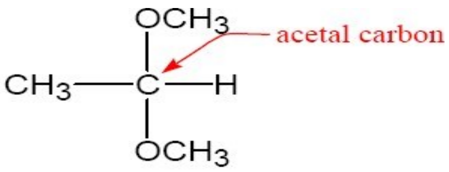




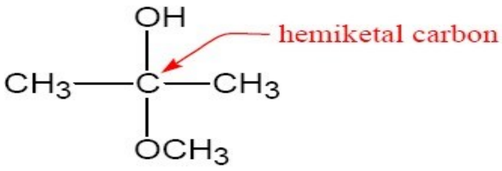
Hemiacetals, Acetals, Hemiketals, and Ketals



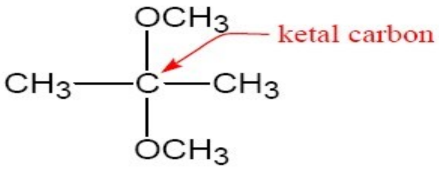
a **hemiacetal**



an **acetal**

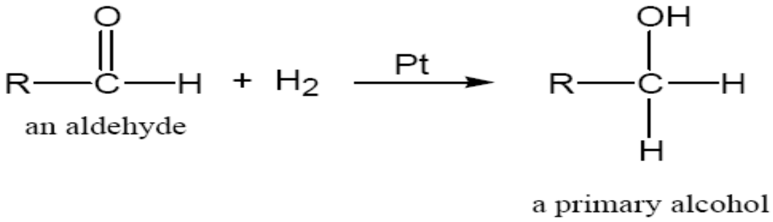


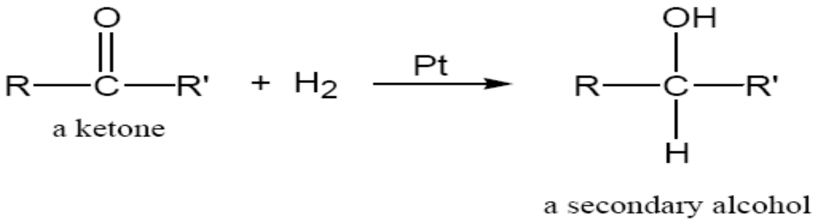
a **hemiketal**



a **ketal**

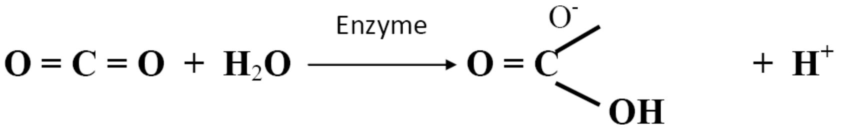
3- Hydrogenation (reduction) of aldehydes and ketones: Hydrogenation of aldehydes and ketones with hydrogen gas and a platinum catalyst produces alcohols.





4- Addition reactions of aldehydes and ketones in living system:

One of the simplest addition reactions of a carbonyl group in living systems is the enzyme catalyzed reaction of carbon dioxide to bicarbonate ion according to the following equation:

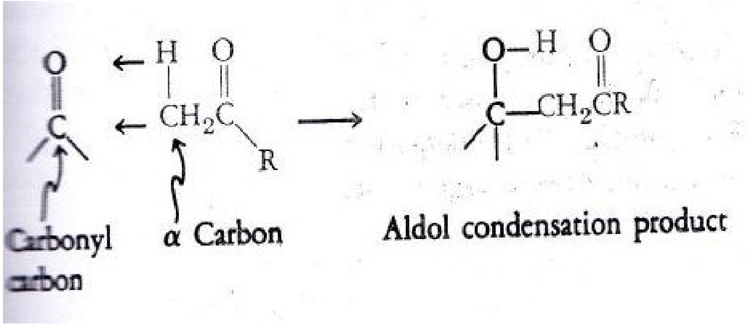


The enzyme that catalyzes this reaction is widely distributed in mammals. It is especially active in tissues that are involved in respiration, such as blood cells.

5- Condensation reactions: In condensation reactions, two compounds are joined together (or condensed) to form a large compound:

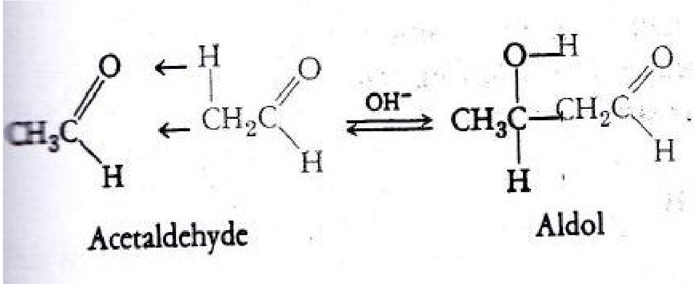
- **Aldol condensation**: this is a reaction in which the carbonyl carbon of one molecule forms a bond with the α-carbon of another carbonyl containing molecule.

For example:



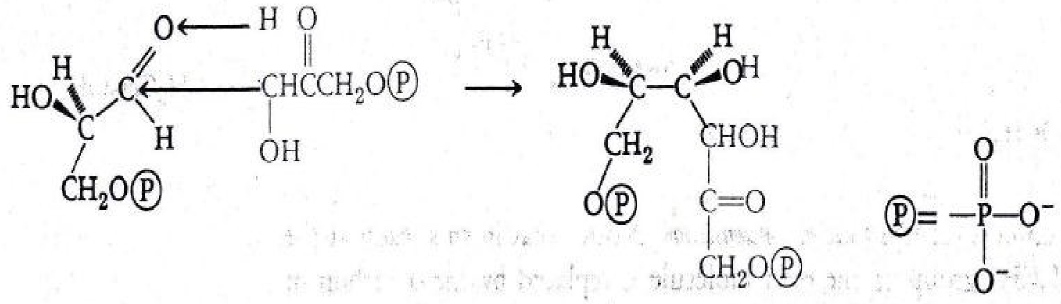
The name of aldol is derived from the structure of the product, which is both aldehyde and alcohol. Notice that this reaction is reversible. The revers reaction is called a retro-aldol condensation.

The aldol condensation is an equilibrium. The equilibrium constant for formation of products is favorable for most Aldehydes. However, for ketones, the reaction is much less favorable.



* Condensation reactions In living system

carbohydrates are prepared in the living systems by an enzyme-catalyzed aldol condensation:



19-1

D-Glyceraldehyde 3-phosphate

1,3-Dihydroxyacetone-phosphate

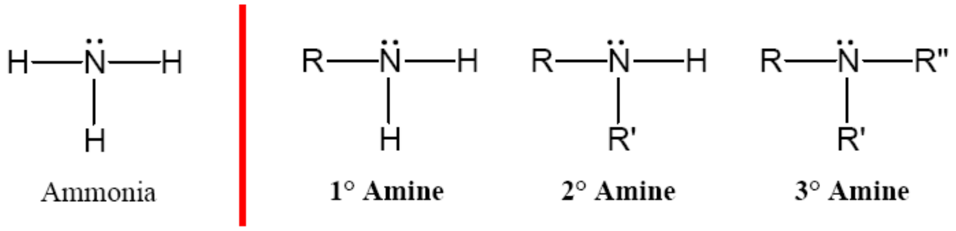
D-Fructose 1,6-diphosphate

AMINES AND AMIDES

After your study to this lecture you will be able to understand:

- The names of these compounds
- Their physical properties
- Their reactions
- Their preparations
- Eventually you have to compare between these and the former compounds to distinguish the physical properties for every compound.

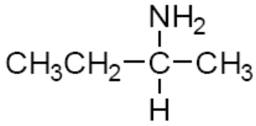
Amines are derivatives of ammonia with one or more alkyl groups bonded to the nitrogen. Amines can be classified as primary, secondary or tertiary, meaning one, two and three alkyl groups bonded to the nitrogen respectively.



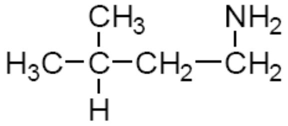
Nomenclature

The IUPAC nomenclature is analogous to that for alcohols, except the -e ending is replaced with -amine.

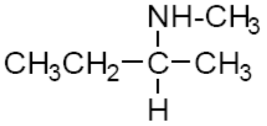
Other substituents on the carbon chain are given numbers, and the prefix N- is used for each substituent on nitrogen.


$CH_3CH_2-\underset{H}{\overset{NH_2}{C}}-CH_3$

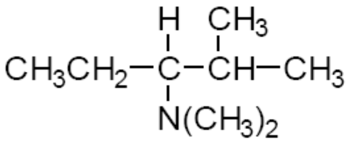
2-butanamine


$H_3C-\underset{H}{\overset{CH_3}{C}}-CH_2-\overset{NH_2}{CH_2}$

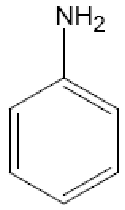
3-methyl-1-butanamine


$CH_3CH_2-\underset{H}{\overset{NH-CH_3}{C}}-CH_3$

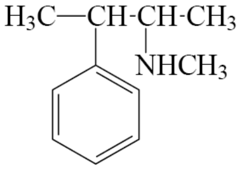
N-methyl-2-butanamine


$CH_3CH_2-\underset{N(CH_3)_2}{\overset{H}{C}}-\overset{CH_3}{CH}-CH_3$

2,N,N-trimethyl-3-pentanamine

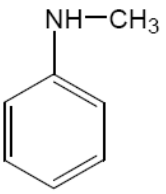


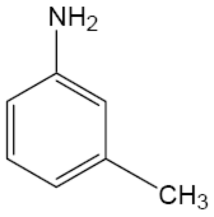
aniline

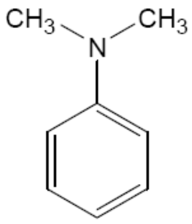


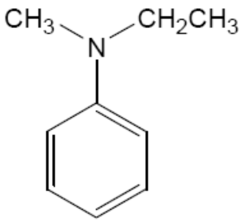
2-(N-methylamino)-3-phenylbutane

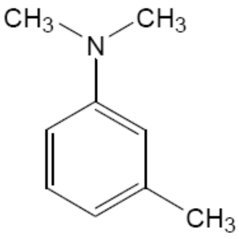
Aromatic amines are called by their historical/trivial names, with phenylamine being called aniline.

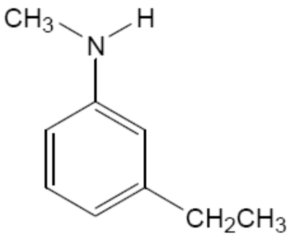


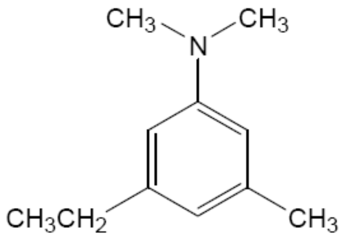






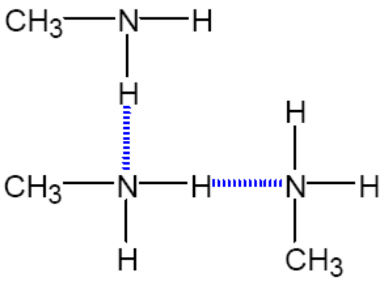


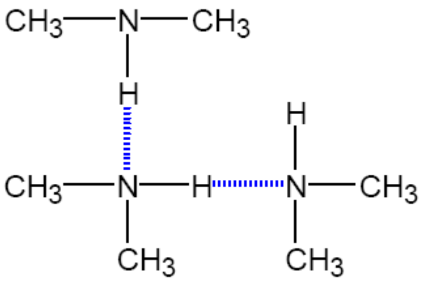




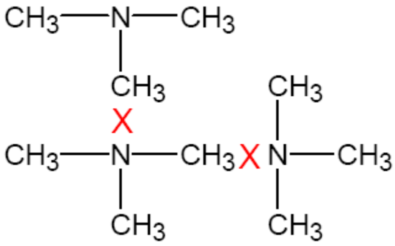
Physical Properties of Amines

- 1° and 2° amines can hydrogen bond to each other:





- 3° amines cannot hydrogen bond to each other:



- Nitrogen is less electronegative than oxygen, so the N—H bond is not quite as polar as the O—H bond.

– Hydrogen bonds from N—H’s are not as strong as those resulting from O—H’s.

– Hydrogen bonding between 1° and 2° amines is not as strong as those found in alcohols or carboxylic acids.

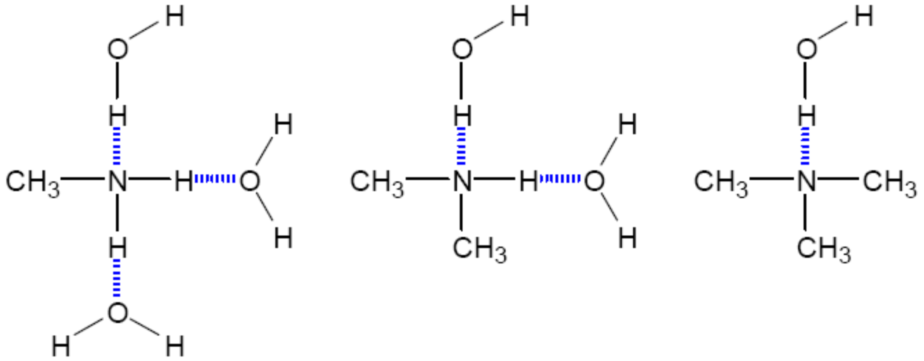
- 1° and 2° amines have lower boiling points than alcohols of similar molecular weight.
- 3° amines, since they do not hydrogen bond to each other, have boiling points similar to hydrocarbons of the same molecular weight.

Boiling Point:

Carboxylic acid
Alcohols
1°/2° Amines
3° Amines/Alkanes

Name	Molecular weight	Boiling point
Acetic acid	60.0 g/mol	118°C
1-propanol	60.1 g/mol	97°C
propyl amine	59.1 g/mol	48°C
ethylmethylamine	59.1 g/mol	36°C
trimethylamine	59.1 g/mol	2.9°C
butane	58.1 g/mol	-0.5°C

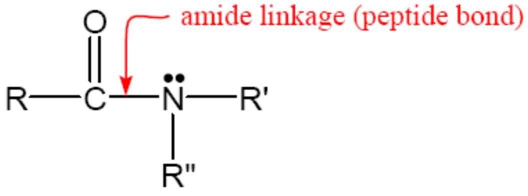
- 1°, 2°, and 3° amines can all form hydrogen bonds with water.
- Low-molecular weight amines are generally water soluble.



- Low molecular-weight amines tend to have sharp, penetrating odors similar to ammonia
- Higher molecular-weight amines often smell like rotting fish, and are often found in decaying animal tissues.

Amides

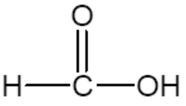
- **Amides** contain a nitrogen which is directly attached to a carbon in a carbonyl group:



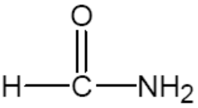
Amide

Nomenclature of Amides

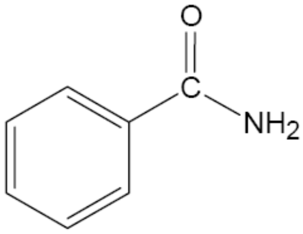
- Amides are named by changing the *-oic acid* ending of the corresponding carboxylic acid to **-amide**. If alkyl groups are attached to the nitrogen, they are named as N-alkyl substituents.


$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

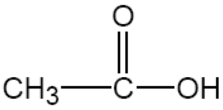
methanoic acid
(formic acid)


$H-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

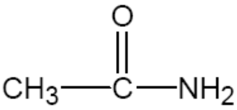
methanamide
(formamide)



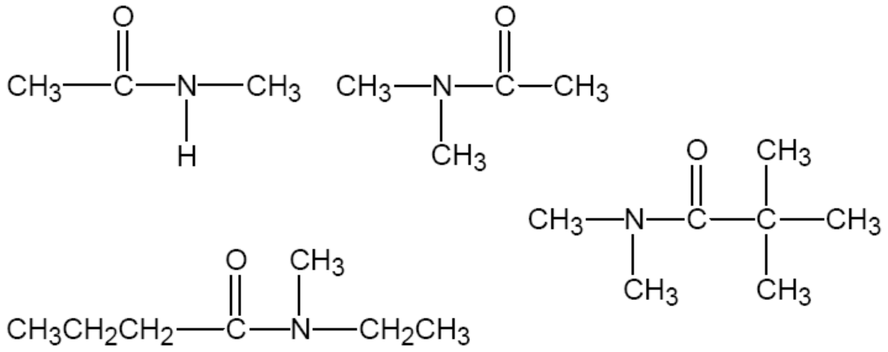
benzamide


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

ethanoic acid
(acetic acid)


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

ethanamide
(acetamide)



$CH_3C(=O)NHCH_3$

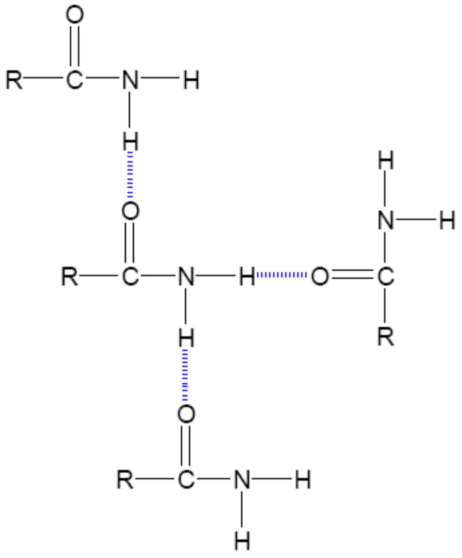
$CH_3N(CH_3)C(=O)CH_3$

$CH_3N(CH_3)C(=O)C(CH_3)_3$

$CH_3CH_2CH_2C(=O)N(CH_3)CH_2CH_3$

Physical Properties of Amides

- N,N-unsubstituted amides can form a complex network of hydrogen bonds. They tend to have high melting points and also high boiling points.



- N-substituted amides often have lower melting points and boiling points than N,N-unsubstituted amides because fewer hydrogen bonds can form.
- N,N-disubstituted amides cannot form hydrogen bonds, and have even lower melting points and boiling points.
- All amides can hydrogen bond with water, so lowmolecular weight amides are water-soluble.

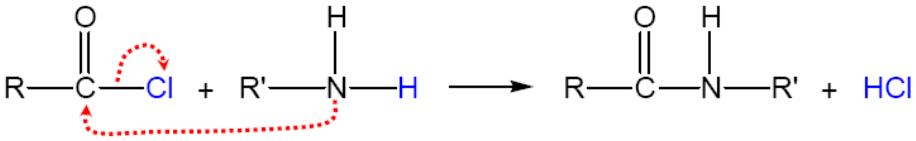
Boiling Point:

↑ N,N-unsubstituted amides
N-substituted amides
N,N-disubstituted amides

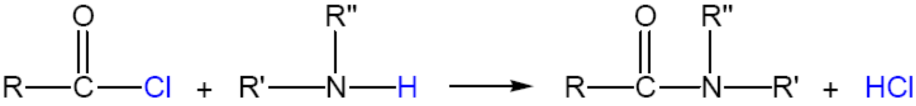
- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.) N-ethylethanamide, butanamide,N,N-dimethylethanamide.

Amide Formation

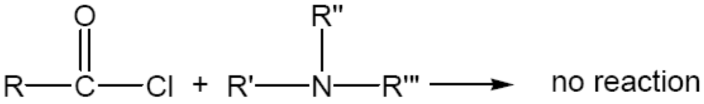
- Amides are formed when acid chlorides react with 1° or 2° amines; 3° amines cannot form amides:



$$R-\overset{\overset{O}{\|}}{C}-Cl + R'-\overset{\overset{H}{|}}{N}-H \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R' + HCl$$



$$R-\overset{\overset{O}{\|}}{C}-Cl + R'-\overset{\overset{R''}{|}}{N}-H \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\overset{R''}{|}}{N}-R' + HCl$$



$$R-\overset{\overset{O}{\|}}{C}-Cl + R'-\overset{\overset{R''}{|}}{N}-R''' \longrightarrow \text{no reaction}$$

First -dentistry-SECOND SEMISTE

Lecture (7) 2022-2023 Dr. Mahmoud

Carbohydrate

Carbohydrate are the most abundant organic molecules in nature. They have a wide range of functions. Including providing a significant fraction of the energy in the diet of most organisms. The empiric formula for many carbohydrates is $(CH_2O)_n$, hence the name ((hydrate of carbon)). Carbohydrates are distributed in plants and animals, in plants glucose is synthesized from CO_2 and H_2O by photosynthesis, and stored as starch or converted to the cellulose of the plant framework.

Animals can synthesize some CH_2O from fat and proteins but the bulk of animals CH_2O is derived from plants.

Biochemical importance: Glucose is the most important CH_2O:

1. Glucose is a major fuel of the tissues of mammals.
2. Converted to other CH_2O having highly specific functions, such as glycogen for storage and ribose and deoxy ribose in nucleic acids.
3. The most dietary CH_2O is glucose which is absorbed in to the blood stream and converted in the liver.
4. Serving as cell membrane components that mediate some forms of intercellular communication.
5. formation of exoskeleton of many insects.
6. Disease associated with carbohydrate metabolism include diabetes. Mellitus, galactosemia, glycogen storage diseases and lactose intolerance.

Classification and structure of CH_2O

1. **Monosaccharides:** simple sugars can be classified according to the number of carbon atoms they contain, in contrast may be classified in two type according to oxidized function group, are called aldoses and ketoses:

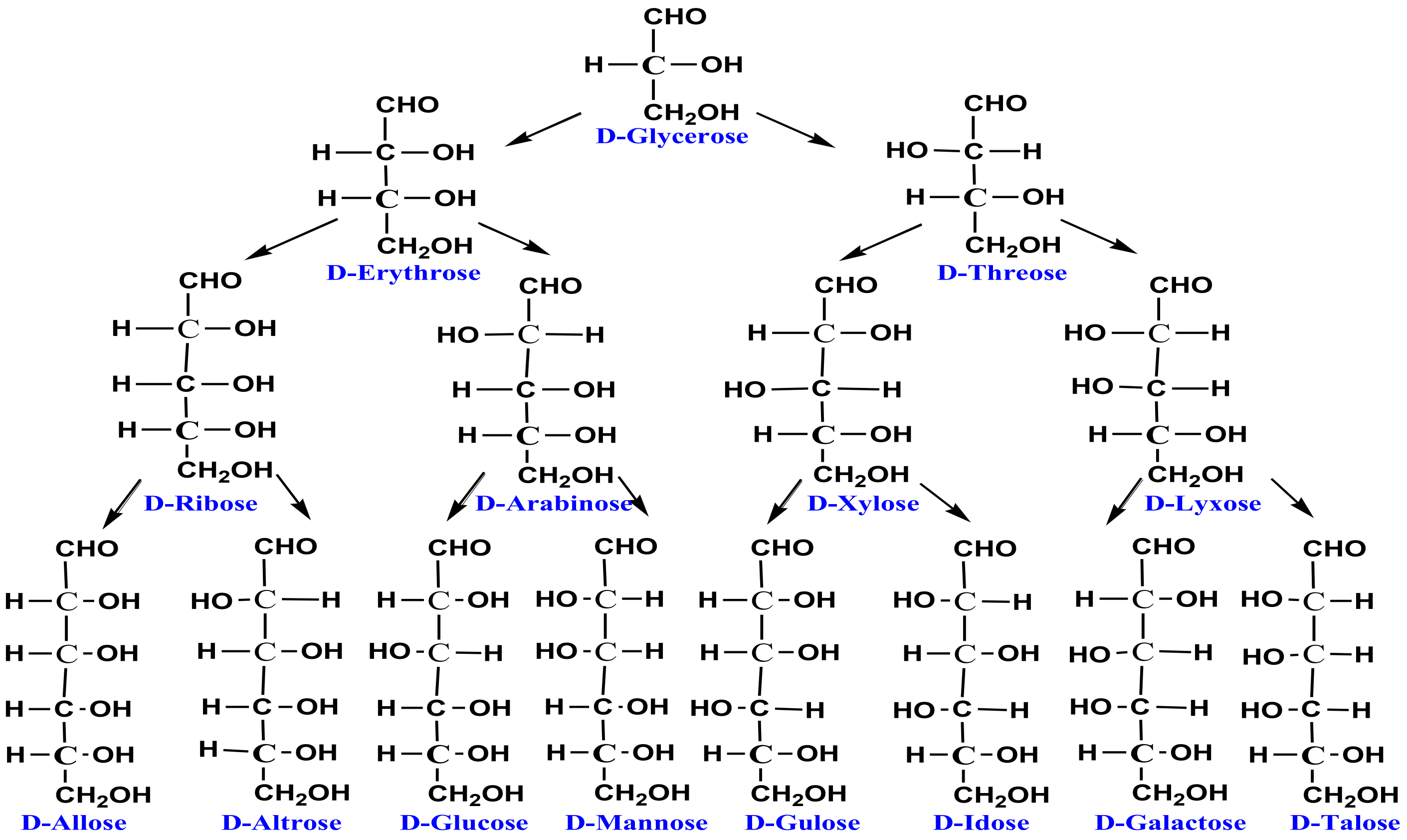
N. of C atoms	Generic name	Example
3	**Trioses**	**Glyceraldehyde**
4	**Tetroses**	**Erythrose**
5	**Pentoses**	**Ribose**
6	**Hexose**	**Glucose**
7	**Heptoses**	**Sedoheptulose**
9	**Nonoses**	**Neuraminic acid**

2. Disaccharides: Product from condensation two monosaccharide units. ex:
-maltose = Glucose + Glucose.
-sucrose= Glucos + Fructose.
-Lactose= Glucose + Galactose.
3. Oligosaccharides: Product from condensation of two to ten monosaccharide units. ex:
-Maltotriose = three α-glucose residues.
4. Polysaccharides: Product from condensation more than ten molecules of monosaccharide. Ex:
-Starch : linear Polysaccharides
-Dextrin: branched Polysaccharides.

Isomers and epimers: compounds that have the same chemical formula but have different structures are called isomers, ex: fructose, glucose, mannose and galactose are all isomers of each other, having the same chemical formula ($C_6H_{12}O_6$).

If two monosaccharides differ in configuration around only one specific carbon atom (exeption of the carbonyl carbon), they are defined as epimers of each other. (of course they are also isomers).

Ex: glucose and galactose are C-4 epimers –their structures differ only in the position of the -OH group at carbon 4.

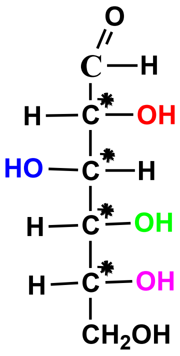


Stereochemistry of monosaccharides:

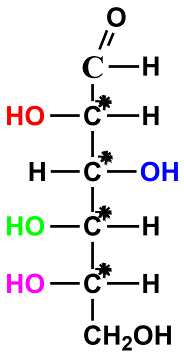
Presence of asymmetrical carbon atoms (carbon atoms attached to 4 different atoms or groups), also called kiral center. The orientation of the H and OH groups around the carbon atom adjacent to the terminal primary alcohol carbon (ex: carbon no.5 in glucose), determines whether the sugar belongs to the **D** (Dextrorotary, rotate the light plane to the right) or **L** (levorotary, rotate the light plane to the left), this called **optical activity**. The number of possible isomers of a compounds depends on the number of asymmetric carbon atoms (n) equal $\mathbf{2^n}$ (2=D and L).

Ex: glucose with 4 As carbon atoms, therefore has 16 isomers.

Most of the monosaccharides occurring in mammals are of the D configuration and enzyme responsible for their metabolism are a specific for this configuration.



D-Glucose



L-Glucose

Structure of D-Glucose:

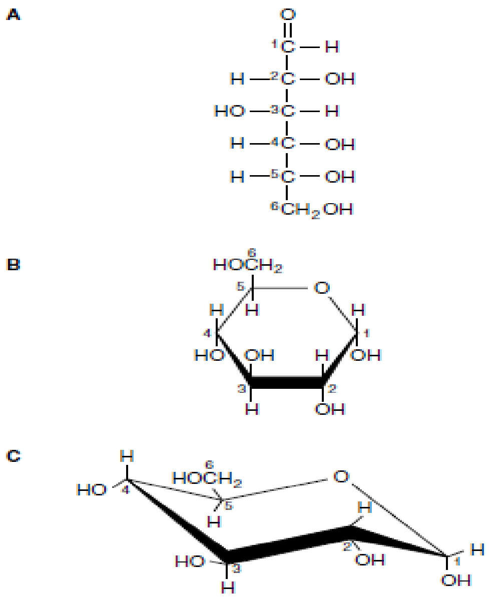


Figure 13–1. D-Glucose. A: straight chain form. B: α-D-glucose; Haworth projection. C: α-D-glucose; chair form.

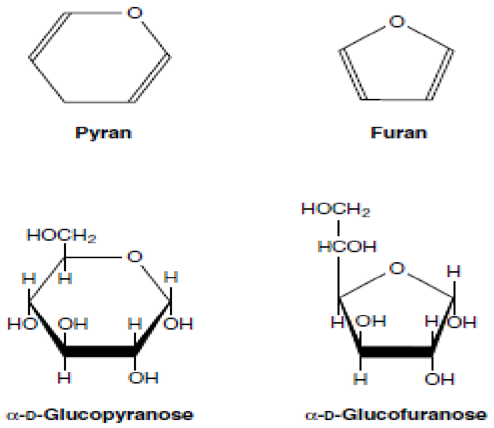
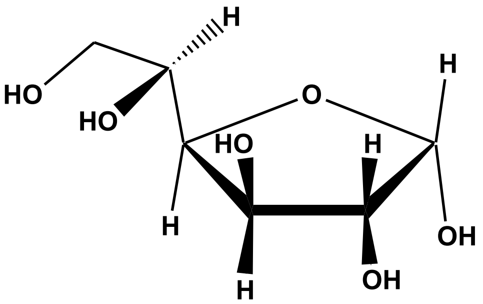


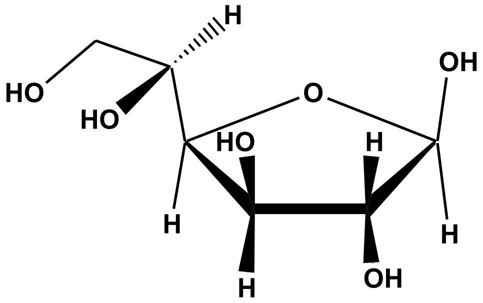
Figure 13–3. Pyranose and furanose forms of glucose.

Anomeric carbon: Formation of a ring results in the creation of an anomeric carbon at carbon 1 of an aldose or at carbon 2 of a ketose. These structures are designated the **α** or **β** configurations of the suger, for example: α-D-glucose and β-D-glucose. These two sugars are both glucose, but they are **anomers** of each other. Enzyme are able to distinguish between these two structures and use one or the other preferentially.

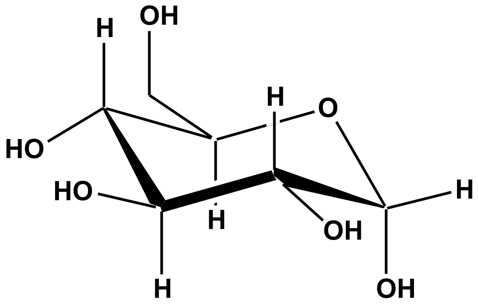
Ex: glycogen is synthesized from α-D-glucopyranose, while cellulose is synthesized from β-D-glucopyranose. The cyclic α and β anomers of a sugar in solution are in equilibrium with each other, and may be spontaneously interconverted, this called **mutarotation** .



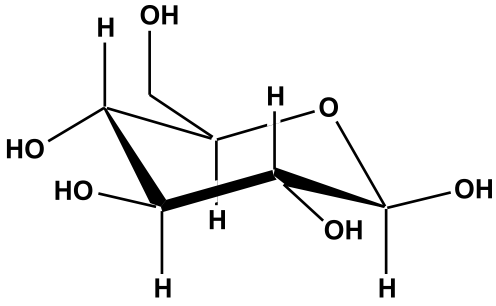
∝-D-Glucofuranose



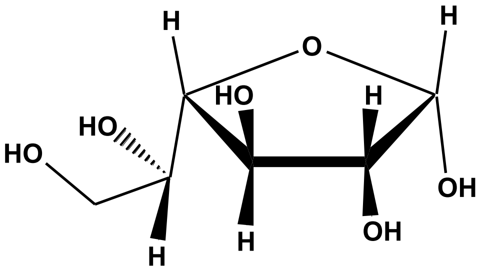
β-D-Glucofuranose



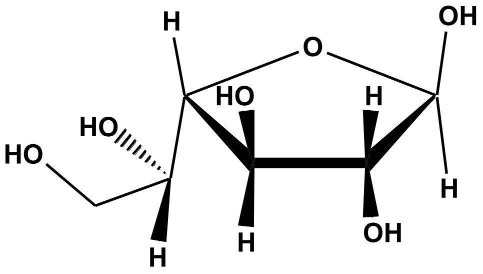
∝-D-Glucopyranose



β-D-Glucopyranose



∝-D-Galactofuranose



β-D-Galactofuranose

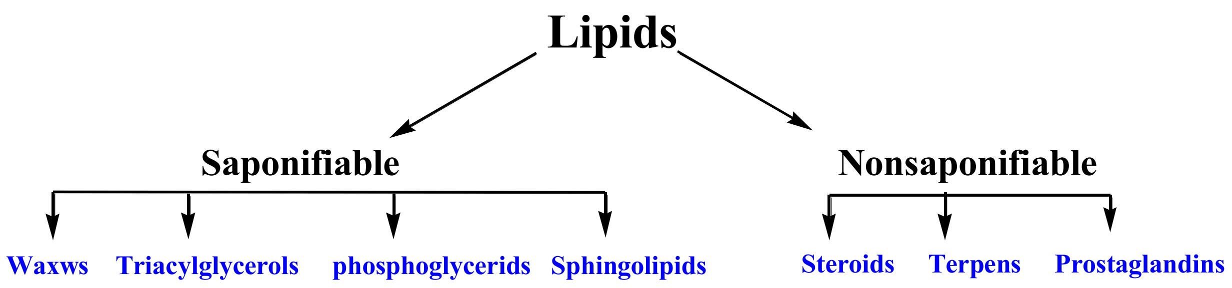
Lipids

Class of compounds of living systems, that contain one or more carboxylic groups (COOH). Lipids are classified according to their solubility. Lipids are readily in non polar organic solvents and soluble in organic solvent such as diethyl ether, chloroform, or benzene but are insoluble in water, because the water is polar. when animal or plant material is crushed and mixed with these solvents, the compounds that dissolve are classified as lipids. This is one difference between lipids and the other two major classes of compounds of living systems, carbohydrates and proteins, which are insoluble in organic solvents because of their highly polar structure. Fats, vegetable oils, and waxes are examples of lipids that are familiar to everyone.

- The important function of lipids in living systems:

1. Main energy reserve for living systems
2. Form part of cell membranes
3. Regulate the activities of cells and tissues

Saponification: one way for classified of lipid is according to whether or not they undergo saponification. Lipids that undergo alkaline hydrolysis are called ***saponifiable lipids***. Lipids that do not undergo such a reaction are called ***nonsaponifiable lipids***.



Fatty acids: Fatty acids are named for the fact that they are the major component of fats. They are carboxylic acids in which a long straight hydrocarbon chain is attached to the carboxyl group.

Fatty acids differ in chain length and in the number and positions of double bonds in the hydrocarbon chain. The hydrocarbon chain of fatty acid that contain one or more double bonds are called *unsaturated fatty acids*, while those don't contain double bonds are called *saturated fatty acids*. Only traces of free fatty acids are found in the cells.

Naming of fatty acids: we have two ways to indicate the double bond:

(1) by using Δ^9 this indicate the double bond between C no. 9 and C no. 10 starting from carboxylic end:

$$C\text{-}C\text{-}C\ldots\ldots C_{10}= C_9\ldots\ldots C_1OOH$$

(2) by using W^9 this mean the double bond between C no. 9 and C no. 10 starting from another end:

$$C_1\text{-}C_2\text{-}C_3\ldots\ldots C_9= C_{10}\ldots\ldots COOH$$

(3) by x:y:z numbers where:
x= no of carbons atoms
y= no. of double bonds
z= no. carbon atom that contain double bonds

Example: Oleic acid (one C=C) 18:1:9 or $\Delta^9$18:1 or $w^9$18:1

$$CH_3(CH_2)_7\text{-}HC{=}CH(CH_2)_7\text{-}COOH$$

The mammals can not synthesis fatty acid that cantain more than a double bond. Because the mammals don't have a enzymes to synthesis this F.A this F.A called essential F.A like (linoleic, linolenic acid).

CH_3-$(CH_2)_4$- HC=CH- CH_2- HC=CH $(CH_2)_7$ –COOH

Linoleic acid : (18: 2, $\Delta^{9,12}$) and may be cis or trans.

Some important structure of fatty acids

1. linolenic acid (18:3, $\Delta^{9,12,15}$)

CH_3CH_2-CH=CH-CH_2HC=CHCH_2- HC=CH $(CH_2)_7$ –COOH

IUPAC Name: cis,cis,cis-9,12-Octadecatrienoic acid

2. Oleic acid (18:1, Δ^{9})

CH_3-$(CH_2)_6$- CH_2- HC=CH $(CH_2)_7$ –COOH

IUPAC Name: cis-9,12-Octadecenoic acid

3. palmitic acid $CH_3(CH_2)_{14}COOH$ **Hexadecanoic acid**

4. palmitoleic acid (16:1, Δ^{9})

CH_3-$(CH_2)_5$-HC=CH $(CH_2)_7$ –COOH

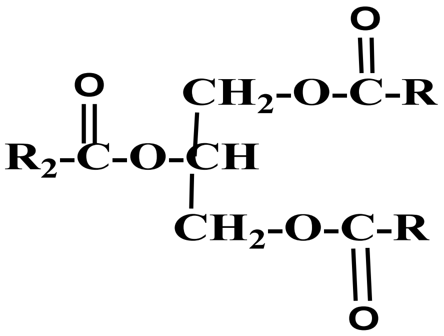
IUPAC Name: cis-9,12-Hexadecenoic acid

5. Lauric acid $CH_3(CH_2)_{10}COOH$ **Dodecanoic acid**

-Fats are solid in room temperature due to their containt of saturated f.a while oils is liquid in room temperature because it composed of unsaturated f.a.

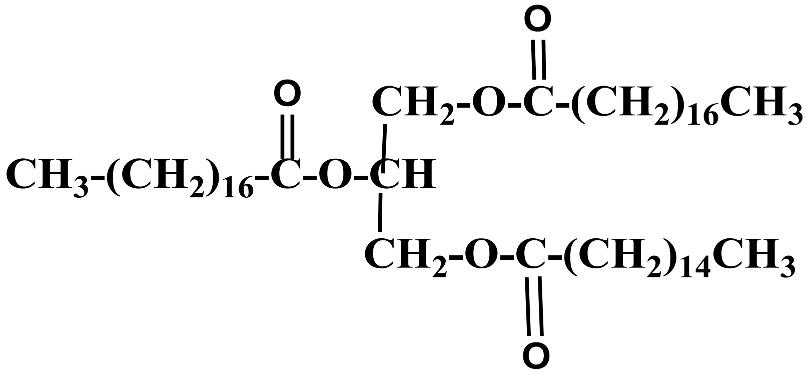
-most of lipids in living systems are Triacylglycerol (T.G) (ester of f.a and alcohol glycerol) because the main energy reserved are stored as T.G in cell and tissues of living system.

-Oil can be converted to fat by process called hydrogenation.



Triacylglycerol

EXAMPLE: 1,2- distearyl-3-palmityl glycerol



Chemical properties of T.G:

T.G Compound that containing f.a with glycerol combine by ester linkage. So their chemical properties depend on f. a by :

a. Saturation or unsaturation.

b. long of the chain (number of c atom).

The greater number of the C=C in molecule cause more unsaturated T.G and more liquid . we can measure the degree of unsaturation by iodine number.

Iodine number: is the number of I_2 in gm that would be add to 100gm of substance (lipid) for saturated f. a.

No. of I_2 =0 because is no double bonds so we don't add I_2.

EX:

Oleic acid = 90

Linoleic acid = 131

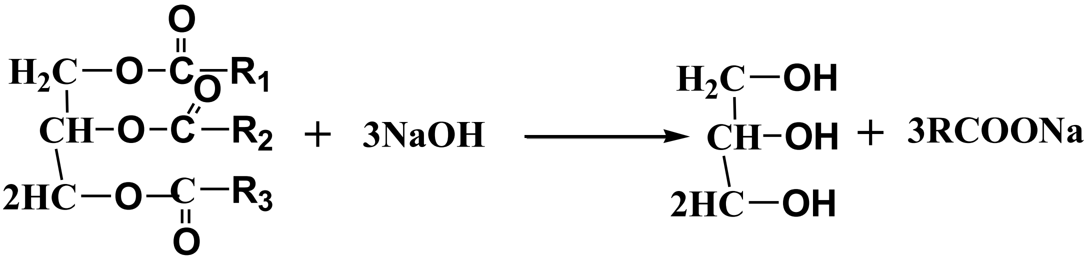
Linolenic acid = 274

T.G can be hydrolysis to give 3 f. a + glycerol, this by action of an enzyme called lipase.

$$\mathbf{T.G} \xrightarrow{\text{lipase}} \mathbf{3\ F.\ a + glycerol}$$

Note: in small intestine the first step of hydrolysis occur by lipase secreted by pencrease.

Saponification of T.G (formation of soap) reaction of T.G with a strong base like NaOH or KOH to form 3 salt (Na or K salts) + glycerol.



T. G

Glycerol

F. A. S

The normal range of T.G in human serum is 40- 165 mg/100ml over this range cause hyperlipidemia.

Q1/ Why the T.G is a good energy source ?
Ans :

1. The complete oxide of T.G give 9 calari/gm while in case of CHO or Proteins we obtained 4 Cal/ gm .
2. T.G is very nonpolar compound so they stored nearly unhydrous (with out water), while CHO and proteins are less polar so they are highly hydrate and stored with water (each gm of glycogen with 2 gm of water).

Classification of lipids:

1. Simple lipids: means that they are esters of f. a with various alcohols.

a. Fats: ester of fatty acid with glycerol . fat in the liquid state is known as an oil.

b. Waxes: are esters of f.a with higher molecular weight monohydroxy alcohols .

2. Complex lipids : it is ester of fatty acid.

a. glycolipids: this contain the sphingosine fatty acid combination with one or more suger molecule.

b. phospholipids:

- glycerophospholipids (phosphotidyl choline)
- sphingophospholipids (alchohol sphingosine)

c. Other complex lipids such as susulpholipids, aminolipid and lipoproteins

3. derived lipids: this including :

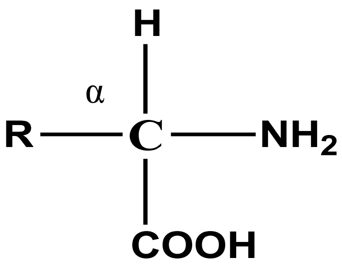
a. fatty acid (saturated and unsaturated)
b. glycerol
c. steroids
d. alcohols
e. fatty aldehyde
f. ketone bodies.

First -dentistry-SECOND SEMISTE

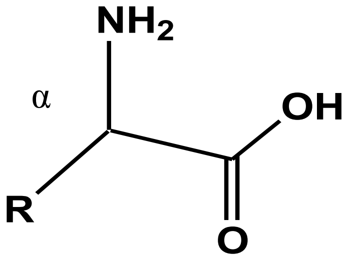
Lecture (8) 2022-2023 Dr. Mahmoud

AMINO ACIDS & PROTEINS

There are 20 amino acids, that are incorporated in proteins, these are standard amino acids. Proteins are high molecular weight polypeptides, may also contain substances in addition to amino acids (heme, carbohydrate, lipid), play very important role in living systems. The metabolism of amino acids gives rise to many compounds of biomedical importance. All amino acids contain both amino and carboxylic acid functional groups. In an α– amino acid, both are attached to the same (α) carbon atom, and different in side chain (R), (except glycine because side chain is H atoms). These groups exhibit all the expected reactions of these functions.



$$\overset{\alpha}{} R-\underset{COOH}{\overset{H}{C}}-NH_2$$



Classification of amino acids

Amino acids or side chains of them can be classified to different classes, depending on their chemical features like:

- hydrophobic or hydrophilic character
- polar or non polar nuture
- aliphatic or aromatic
- according the reaction
- according the nutrition

classified nutritionally in to three groups:

1. **Essential A. Ac.**

There are 8 amino acids they are don't synthesized in the body and must be taken in diet in amount adequate to support the infant growth or to maintain health in adults like: (Valine, Leucine, Isoleucine, Phenylalanine, Tryptophan, Lycine, Threonine, Methionine)

2. **Non-Essential A. Ac**. They can be synthesized by the body. (12 Amino acids).

3. **Semi- Essential A. Ac**. These are growth promoting factors since they are not synthesized in sufficient quantity during growth. This type include only 2 standard amino acids (Arginin, Histidine). They become essential in growing, pregnancy, and lacting women.

Amino acid are classified in to three groups depending on their reactions:

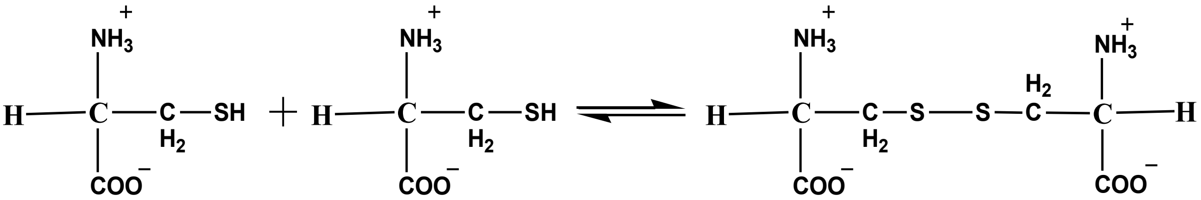
1. **Neutral**: they amino acid are aliphatic, aromatic, and cyclic structures, or containing of hydroxyl or sulfur group. (Ala, Val, Gly, Leu, Ile, Phe, Trp, Ser, Thr, Cys, Met, Pro).
2. **Acidic**: This class contain 4 standard A. Ac. (Asp, Asn, Gly, Gln).
3. **Basic:** This class contain only 3 standard A. Ac. (His, Lys, Arg).

20 A.A called ((standard amino acid)) occurs in almost all proteins and are coded in DNA. Some amino acid may become chemically modified after being assembled in proteins, which called (**unusual L-α-amino acids**) by the processes occurs after formation of the poly peptides back bone, which forms by post processing:

- Oxidation
- Phosphorylation
- methylation
- carboxylation
- formylation
- acetylation.

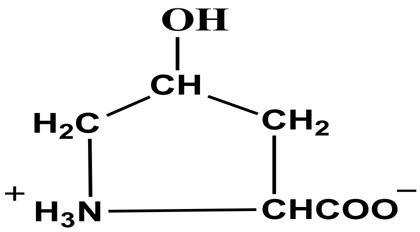
These modification are important for protein function and structures for examples:

a. **Cystine** : which formed by oxidation of the SH groups of the two Cysteines to form (- s—s-) disulfide bond :

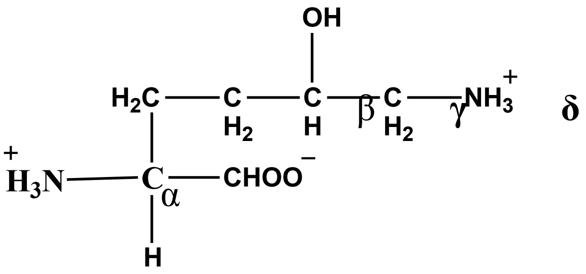


Cysteines Cystine

b. **4-Hydroxyproline:** This amino acid is important for collagen structure.



c. δ-hydroxylysine: is important for the cross-link in the elastin where highly elastic fibers are needed.



d. δ-N-methyl lysine: is the constituent of myosin, a contractive protein of muscle.

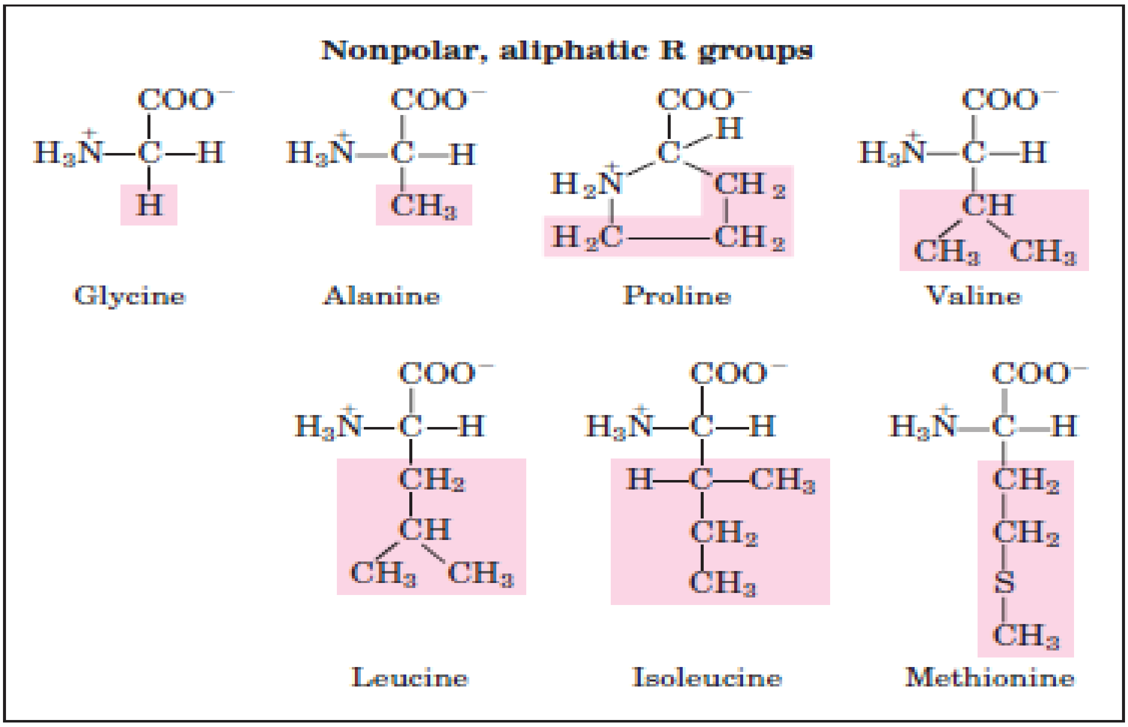
Function of amino acids

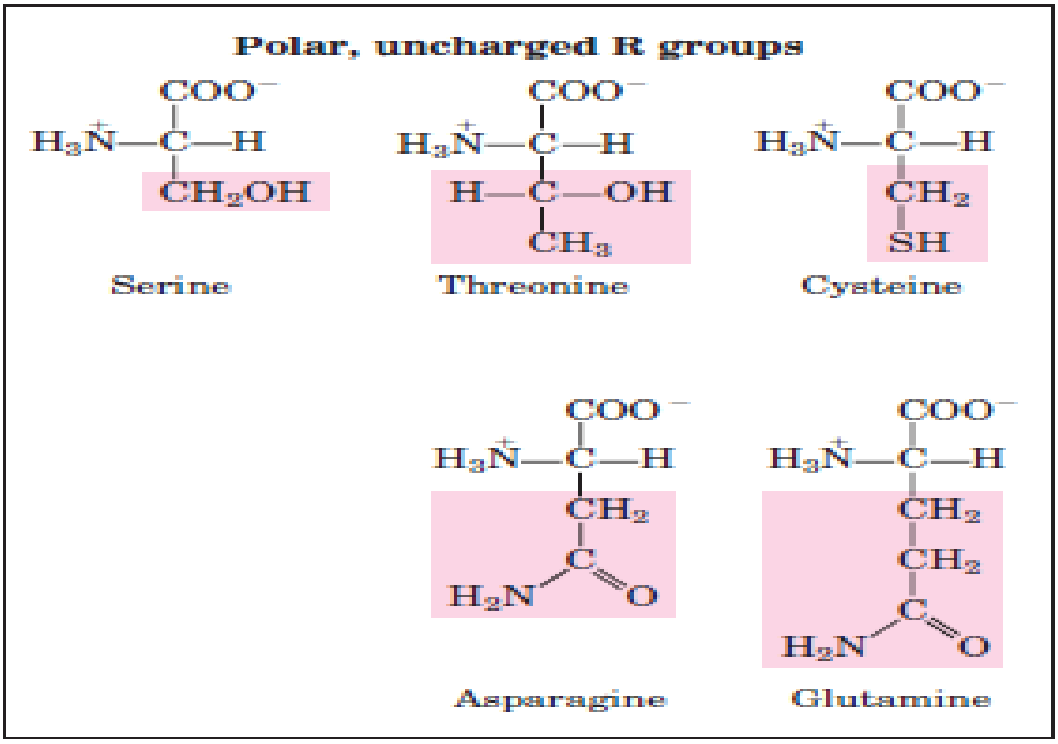
Amino acids build and form the structures of proteins, enzymes, hormones and most biological molecules in living system. It is coded for genetic material by formation structure of DNA. Amino acids induced to transport the defects of A. As. In the cells by excretion of these A. AC. In urine. This process called **Amino acid uriase.** In addition to their roles in proteins, amino acids and their derivatives participate in intracellular functions as :

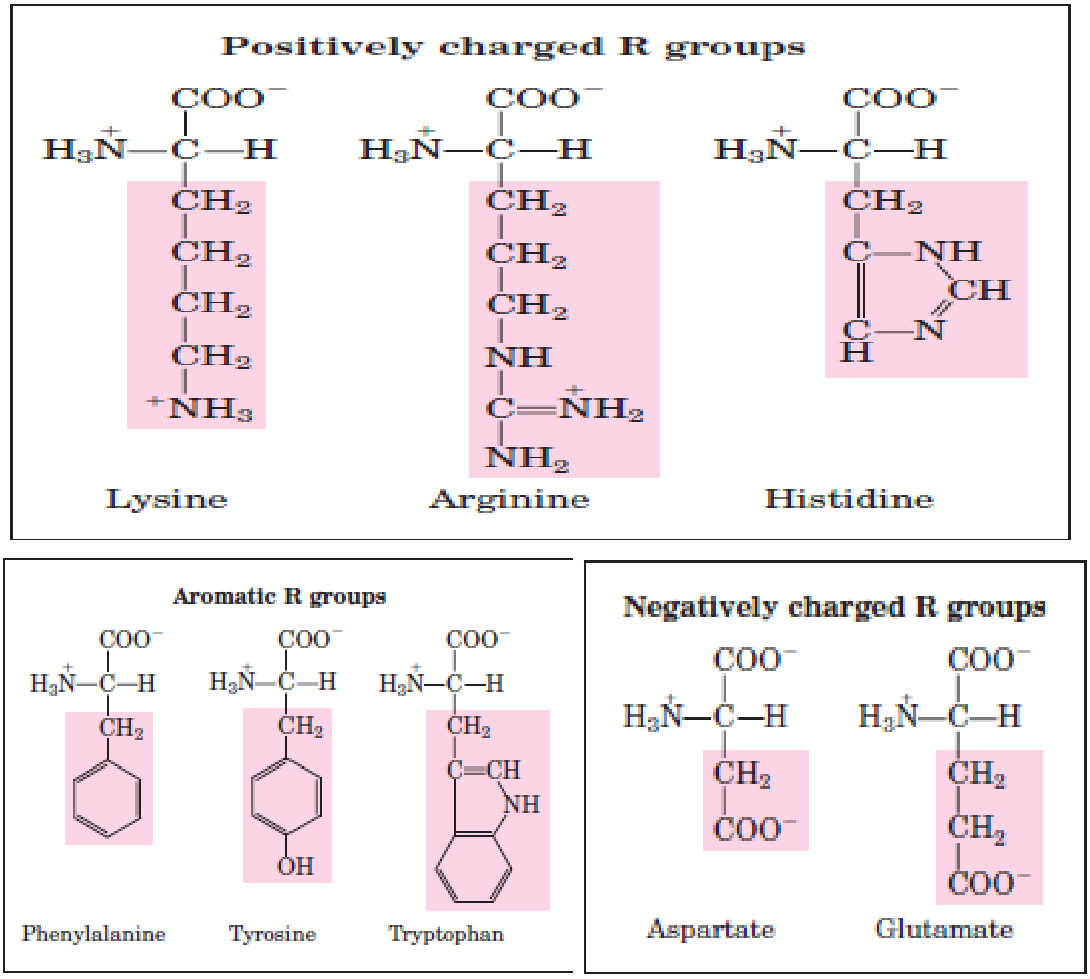
(A) Some A. As are converted to carbohydrates and are called **glycogenic amino acid**, and this can be converted to glucose when it needed in a process know as **gluconeogeneses** such as (Asp, Ala, Cys, Thr). Another A. Ac can be converted to glucose and ketone bodies by **ketogenic** such as (Leu and Lys). Exclusively converted to acetyl Co-A.
Another A. Ac can be converted to glucose and ketonebodies such as (Tyr, Ile, Phe and Trp).

(B) Specific A. Ac give rise to specialized:
1. Tyrosine: forms hormones such as thyroid hormones (T_3, T_4), epinephrine, norepinephrine and melanin pigment.
2. Tryptophan: can synthesized a niacin vitamin.
3. Glycine, Arginine and Methionine synthesize creatine.
4. Glycine and Cysteine help in synthesize Bile salts.
5. Glutamate, Cysteine and Glycine synthesize Glutathaion (GSH) which is important for several enzyme.
6. Histidine : changes to Histamine.
7. Glycine is used for synthesis of heme prophyrins.
8. pyrimidins and Purins used several A. Ac for their synthesis such as ((Asp, Glu) for pyrimidine and (Gly, Asp , Gln, Ser) for purine synthesis.
9. Methionine act as active methionine (δ-adenosyl- methionine) to transfer methyl group to various substances by transmethelation.

10. Cys and Met are sources of sulfur for the sulfur compound in the body.





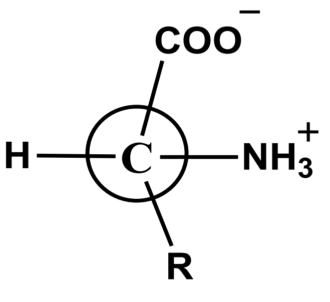


The 20 common amino acids of proteins.

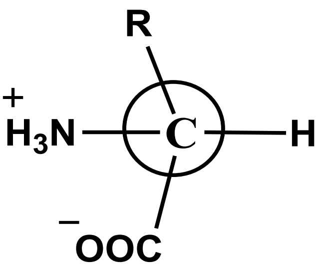
Physical and chemical properties of amino acids

1. Optical isomerism

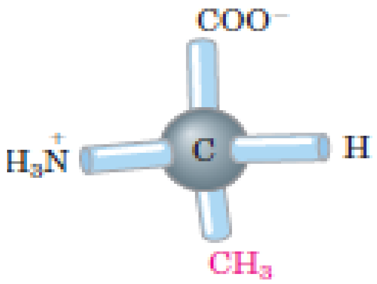
All amino acids except Gly have optical activities and rotate the plane of polarized light and exist as Levo (L) or Dextro (D) isomers. These proper due to cheral center of α-carbon atom.



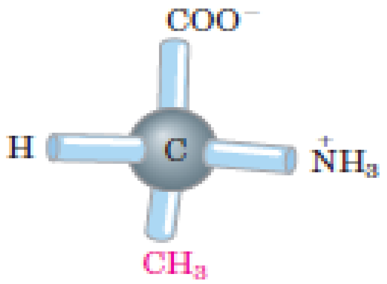
D



L



L-Alanine



D-Alanine

Optical activity depend on the PH and side chain (R).

- Few amino acids like (Thr) and (Ile) have an additional asymmetric carbon in their structure.

2. Ultra Violet absorption

Aromatic A.A which are (Tyr, Trp, Phe) can absorb Uv-light in the region around 280nm, because they have aromatic rings. This absorption is frequently used for the analytical detection of proteins.

3. Amphoteric nature (Buffers)

Amino acids solution resists change in PH following the addition of an acid or base. A buffer can be created by mixing a weak acid (HA) with its conjugate base (A^-). If an acid such as HCl is added to such a solution, A- can neutralize it, in the process being converted to HA. If a base is added, HA can neutralize it in the process being converted to A-. Maximum buffering capacity occurs at a PH equal to the PK_a, but a conjugate acid/base pair can still serve as an effective buffer when the PH of a solution is within approximately $-^{+}$ 1 PH unit of the PK_a.

$$\underset{\text{weak acid}}{\mathbf{HA}} \rightleftharpoons \underset{\text{proton}}{\mathbf{H}^{+}} + \underset{\text{conjugate base}}{\mathbf{A}^{-}}$$

The dissociation constant of the acid is:

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

$$\boxed{PH = pk_a + \log \frac{[A-]}{[HA]}}$$

We can obtain of PH by Henderson equation:
The –NH2 group, -COOH group and charged side chains of A. A are ionized depending on the PH of solution. These groups act as proton donors (acids) or as proton acceptors (bases). This property is called ampholytes. All specific PH A.Ac can varies both, changes in equal number, this PH is called Isoelectric PH and The PH at which the net charge on A. A is zero is called **Isoelectric point** (PI).

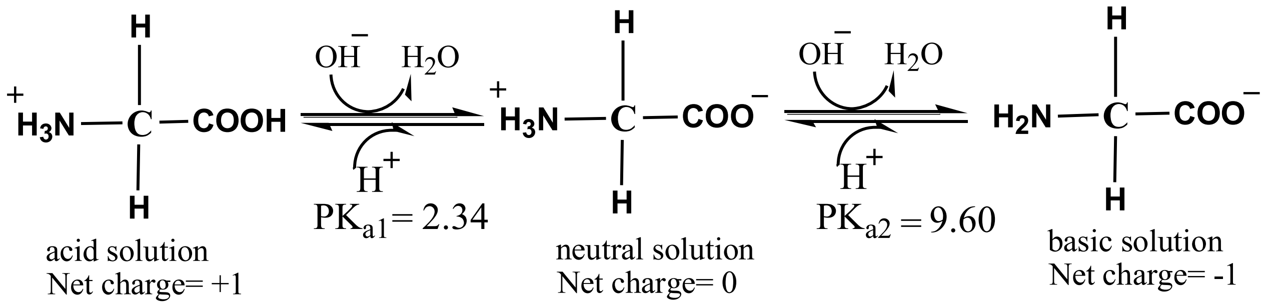
$$\mathbf{PI} = \frac{\mathbf{PKa1 + PKa2}}{\mathbf{2}}$$

In this point become : $[A^-] = [HA]$

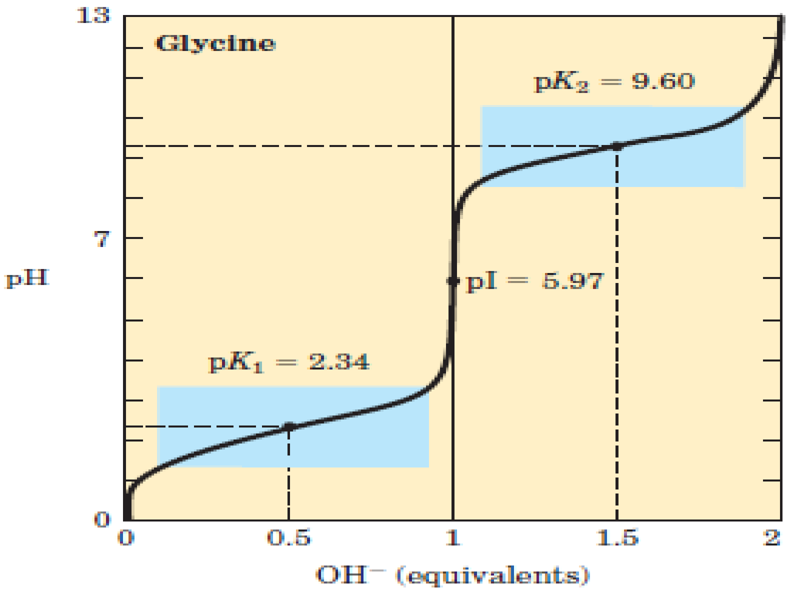
And due to : $\mathbf{PH = pk_a + \log 1}$

due to : $\boxed{\mathbf{PH = pk_a}}$

Amino acids can be titrated potentiometrically and give titration curve, for **example**: Ionic forms of **Glycine** in basic solution ;

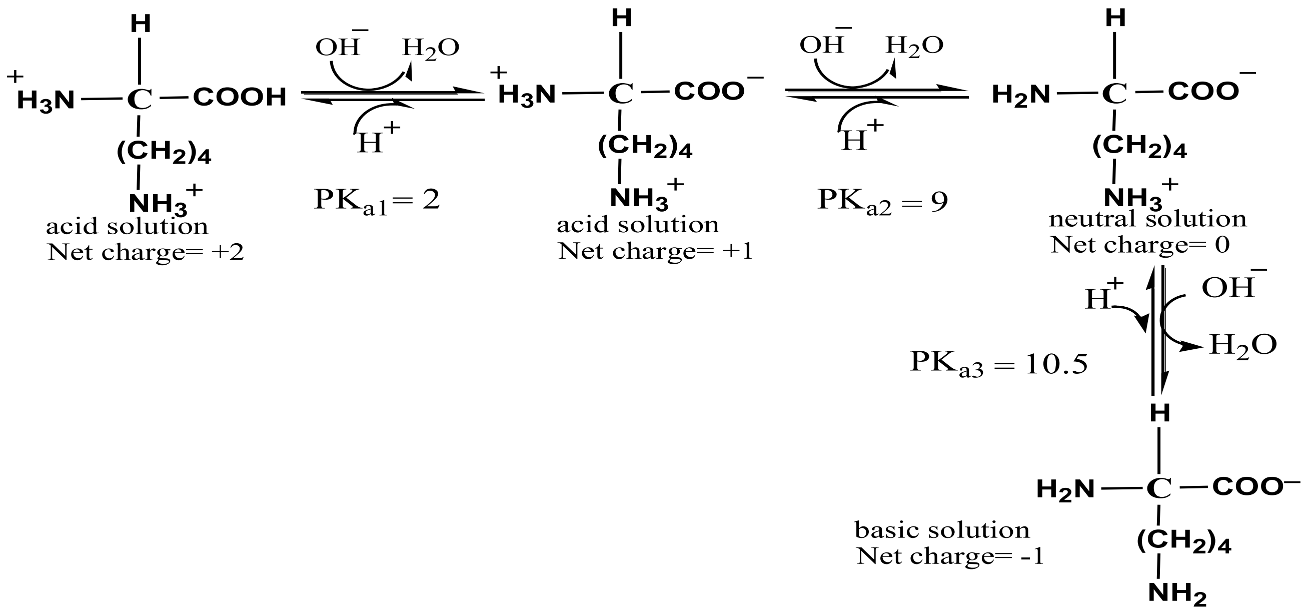


Isoelectric point: $$\mathbf{PI} = \frac{\mathbf{PKa_1 + PKa_2}}{\mathbf{2}} = \frac{\mathbf{2.34 + 9.60}}{\mathbf{2}} = \mathbf{5.97}$$



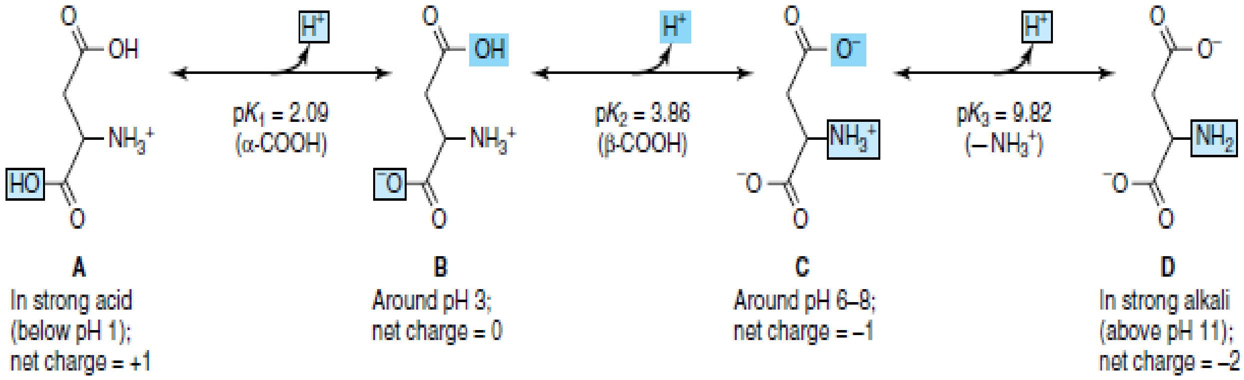
Neutral A.Ac are treated as diprotic acids (Gly, Ala, Thr). While acidic A. AS (Asp, Glu) and basic A. As (Lys, His, Arg) are treated as triprotic acids.

Ex: Titration curve of **Lys**:



$$\mathbf{PI} = \frac{\mathbf{PKa2 + PKa3}}{\mathbf{2}} = \frac{\mathbf{9 + 10.5}}{\mathbf{2}} = \mathbf{9.7}$$

Ex: Titration curve of **Asp**:



The calculation of PI from PK values on either side of the isoelecteric AA° structure. The calculation of PI is of value in the clinical laboratory to estimated the mobility of compounds in electrical fields and to select appropriate buffer for separation and also to separate A. Ac on charge resin like DEAE cellulose , CM cellulose or Dowex resin.

Q1/ Two amino acids with PI values of 6 and 8 . can you separated these two A.AS at a buffer with PH 7.08?
Q2/ Write the equilibrium equation for His. Draw the structure of His each ionization state, and calculate isoelectric point, (when pk= ?

Nucleic acids

Nucleic acids consist from nucleotides which are the monomers or the building units of Nucleic acids . Nucleotides form apart of many coenzymes and serve as donors of phosphoryl groups (e.g. ATP & GTP) . Nucleotides consist from : nitrogen base , pentose , and phosphoric acid .

1. Nitrogen base : The nucleotides include two types of nitrogen bases , purine (Adenine,Guanine) and pyrimidine (Thymine,Cytosine,Uracil). purine and Pyrimidine are nitrogen- containing heterocycles cyclic compounds whose rings contain both carbon and other elements .

¤ There are two common purine bases in nucleic acids :

-Adenine: is found in DNA & RNA .

-Guanine: is found in DNA & RNA .

¤ There are three common pyrimidin bases in nucleic acids :

_ Cytosine : is found in DNA & RNA .

_ Thymine : is found in DNA only.

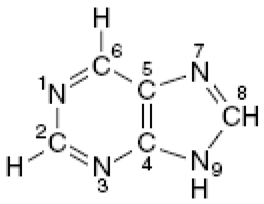
_ Uracil : is found in RNA only.

RNA : ribonucleic acid .

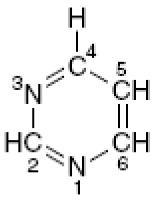
DNA : deoxyribonucleic acid .

In addition to the pyrimidine bases mentioned above the nucleic acids include small amounts of other bases like 5-methyl cytosine , 5-hydroxy methyl cytosine and dihydrouracil .

In addition to there are other purine bases like 1-methyl guanine , 2-methyl adenine and dimethyl guanine .



Purine



Pyrimidine

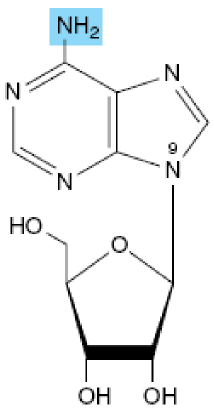
The conjugated double bonds of purine and pyrimidine derivatives absorb ultraviolet light . the mutagenic effect of ultraviolet light results from its absorption by nucleotides in DNA with accompany chemical changes . While spectra are PH dependent, at PH 7.0 all the common nucleotides absorb light at a wavelength close to 260 nm . the concentration of nucleotides , and nucleic acids thus often is expressed in term of " absorbance at 260 nm. "

2. Pentose : there are two types of pentose in the nucleotides , the first one is ribose which is found in the nucleotides that are derivated from RNA , while the second is deoxy ribose which is found in the nucleotides that are derivated from DNA .

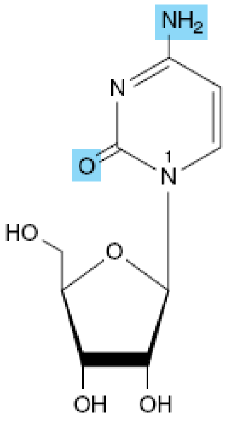
Nucleosides

Nucleosides are derivatatives of purines and pyrimidines that have a sugar linked to a ring nitrogen of heterocyclic . the sugar in ribonucleosides is D-_ribose and in deoxyribonucleosides it is deoxy-D-ribose . The sugar is linked to the heterocyclic base via a ß-N-glycosidic bond to N-1 of pyrimidine or to N-9 of purine .

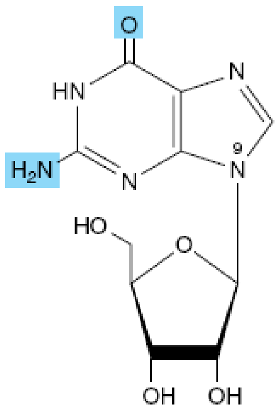
This means that : nitrogen base + ribose = Nucleoside . Like : adenosine , cytidine , guanosine , and uridine .



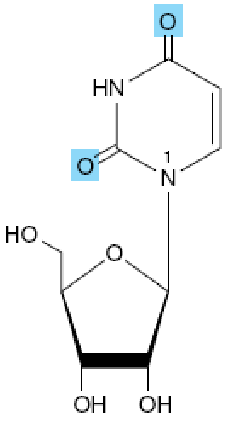
Adenosine



Cytidine



Guanosine



Uridine

Nucleosides + phosphoryl group = mononucleotide .

Additional phosphoryl groups linked to the phosphoryl group of mononucleotides form nucleoside diphosphate and and triphosphate.

Mononucleotide + add. Phosphoryl group = nucleoside di or tri phosphate .

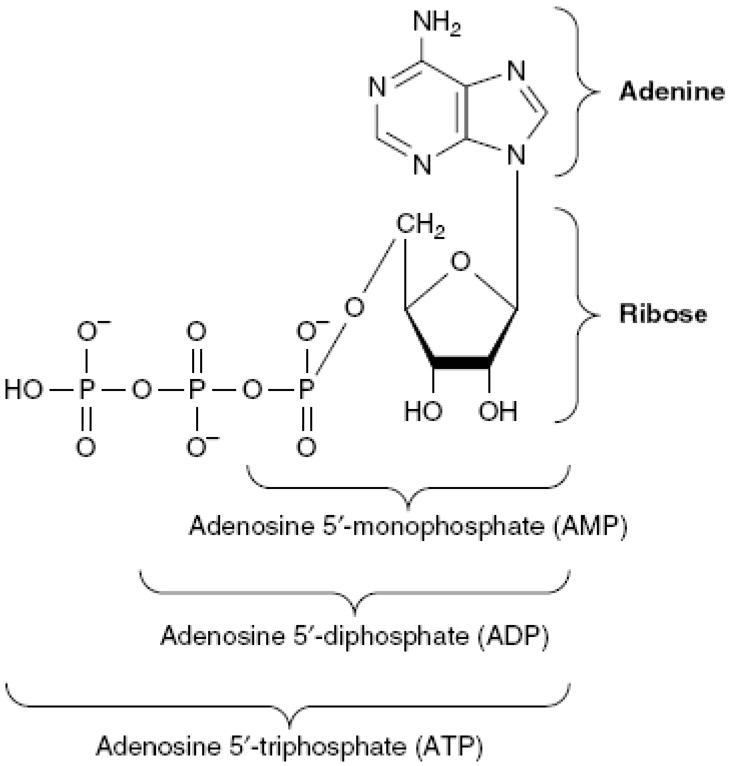


Figure 33–4. ATP, its diphosphate, and its monophosphate.

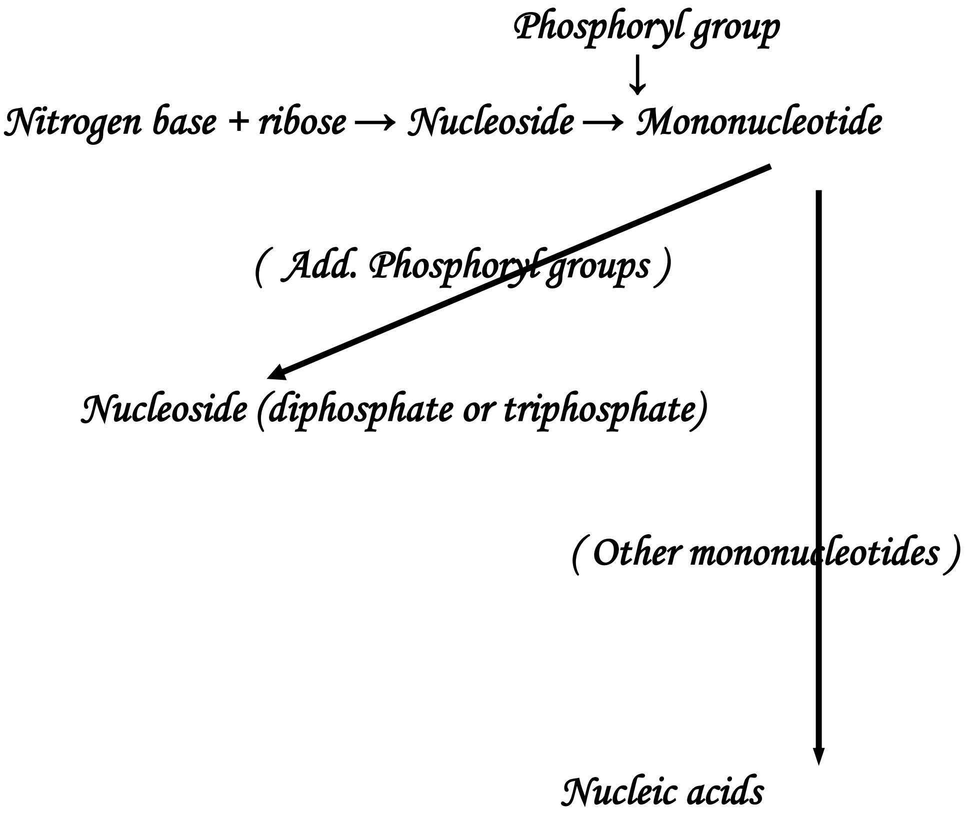


Illustration diagram of nucleic acid component .

Functions of some nucleosides tri or di and monophosphates :

- Function as group transfer agents , like ATP which is the principal carier of chemical energy in the cell . ATP transfers phosphate group from the process which produces energy to other needs . In spite of the (ATP , ADP , AMP) is the principal nucleoside mono , di , and tri phosphate for phosphate group transport , GTP and UTP participate in the transport of phosphate group and energy .
- Precursors of nucleic acids .
- GTP serves as an allosteric and as energy source for protein synthesis .
- cGMP serves as second second messenger during relaxation of smooth muscle .
- UDP participate in biosynthesis of glycogen .
- CTP participates in biosynthesis of phosphoglycerides .

Nucleotides and chemotherapy

Synthetic nucleotide analogs are used in chemotherapy . synthetic analogs of purine , pyrimidine , nucleosides , and nucleotides altered in either the heterocyclic ring or the sugar moiety have numerous applications in clinical medicine . Their toxic effects reflects either inhibition of enzymes essential for nucleic acids synthesis or their incorporation into nucleic acids .

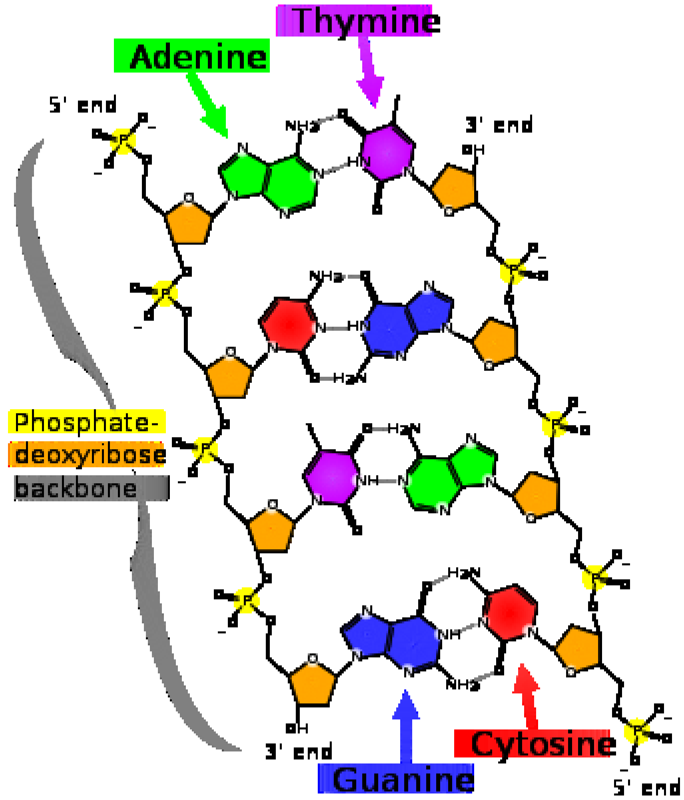
Examples :

- Oncologists employ 5-fluoro or 5-iodo uracil , 3- deoxyuridine , 6-thioguanine , and 6-mercaptopurine which are incorporated into DNA .
- The purine analog allopurinol , used in treatment of hyperuricemia and gout , inhibits purine synthesis and xanthine oxidase activity .
- Cytarabine is used in chemotherapy of cancer .
- Azathioprine which is catabolized to 6-mercaptopurine , is employed during organ transplantation to suppress immunologic rejection .

DNA:

DNA consists from four types of monomeric deoxynucleotide units: deoxyadenylate , deoxyguanylate , deoxycytidylate , and thymidylate . these monomeric units of DNA are held in a polymeric form by 3,5 phosphodiester bridges constituting a single strand . The informational content of DNA (the genetic code) resides in the sequence of the four bases along the backbone of DNA molecule .

Backbone made of sugars and phosphate groups joined by ester bonds .



Chemical structure of DNA

The polymer possesses a polarity , one end has a 5-hydroxyl or phosphate terminal while the other has 3-phosphate or hydroxyl terminal . In DNA molecules the concentration of deoxynucleotide (A) equals that of thymidine (T) , (A = T) , (G = C) .

DNA molecules consist from two strands of polydeoxynucleotides that are complementary to each other in a form of double helix . the double stranded structure of DNA can be separated into two component strands in solution by increasing the temperature and these separated of DNA renature when a physiologic temperatures are achieved .

The two strands of this double stranded helix are held in register by hydrogen bonds between purine and pyrimidine bases . The pairings between purine and pyrimidine on the opposite strands are very specific and are dependent upon the hydrogen binding of A with T , and G with C .

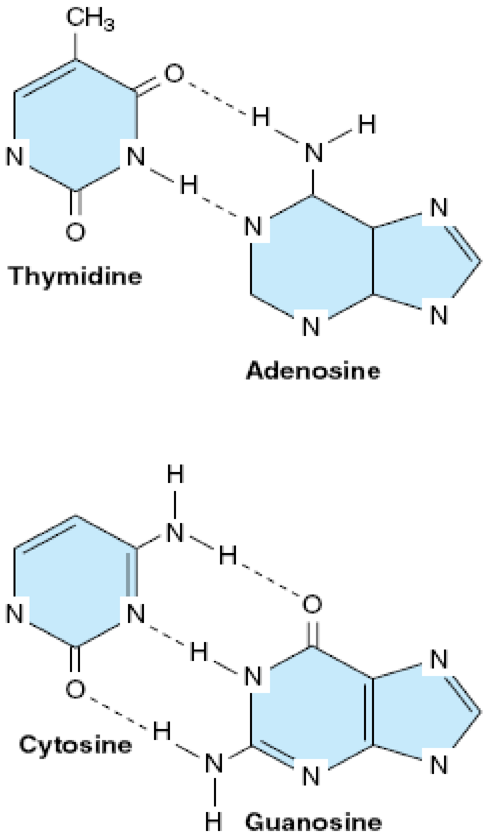


Figure 35–3. Base pairing between deoxyadenosine and thymidine involves the formation of two hydrogen bonds. Three such bonds form between deoxycytidine and deoxyguanosine. The broken lines represent hydrogen bonds.

This base pairing explains that in double stranded DNA molecules the content of A equals that of T and the content of G equals that of C . The two strands of the double helical molecule are antiparallel , one strand runs into 5 to 3 direction and the other in the 3 to 5 direction . In the double stranded DNA molecules the genetic information resides in the sequence of nucleotides on one strand , the template strand , this is the strand of DNA that is copied during RNA synthesis .

The double stranded of DNA can be separated (melted) into two component strands in solutions by increasing temperature and these separated of DNA renature when a physiologic temperature are achieved .

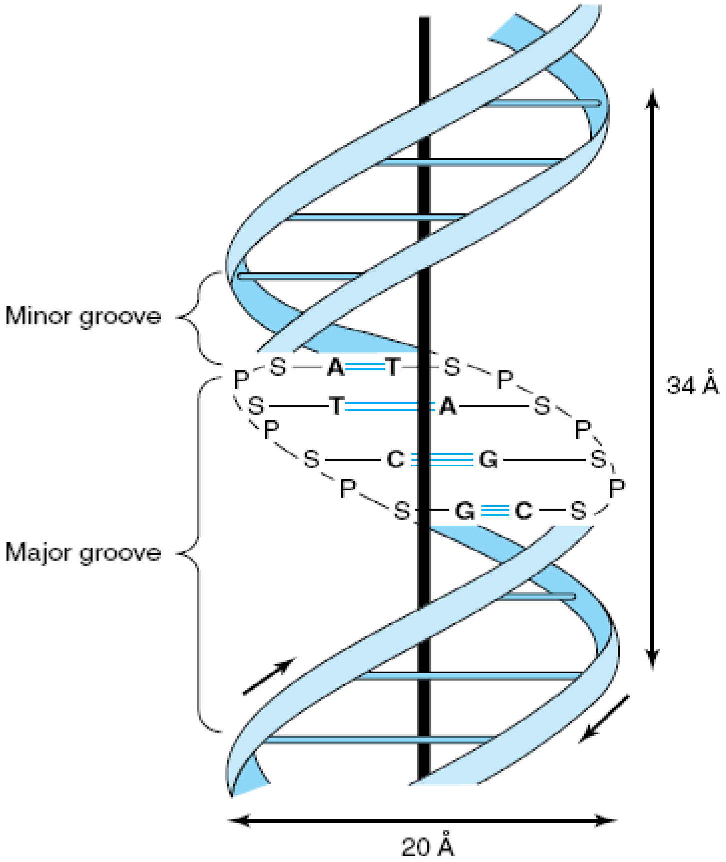


Figure 35–2. A diagrammatic representation of the Watson and Crick model of the double-helical structure of the B form of DNA. The horizontal arrow indicates the width of the double helix (20 Å), and the vertical arrow indicates the distance spanned by one complete turn of the double helix (34 Å). One turn of B-DNA includes ten base pairs (bp), so the rise is 3.4 Å per bp. The central axis of the double helix is indicated by the vertical rod. The short arrows designate the polarity of the antiparallel strands. The major and minor grooves are depicted. (A, adenine; C, cytosine; G, guanine; T, thymine; P, phosphate; S, sugar [deoxyribose].)

Enzymatic hydrolysis of nucleic acid

Specific nucleases digest nucleic acids . These nuclease can be classified in several ways . Those which exhibit specificity for deoxyribonucleic acid are referred to as deoxyribonucleases . Those which specifically hydrolyze ribonucleic acids are ribonucleases within both of these classes are enzymes capable of cleaving internal phosphodiester bonds to produce either 3-hydroxyl and 5-phosphoryl terminal or 5-hydroxyl and 3-phosphoryl terminal and these are referred to endonucleases .

Some are capable of hydrolyzing both strands of a double stranded molecule , whereas others can only cleave single strands of nucleic acids . Some nucleases can hydrolyze only unpaired single strands , while others are capable of hydrolyzing single strands participating in the formation of double stranded molecule . Some nucleases are capable of hydrolyzing a nucleotide only when it is present at a terminal of a molecule , these are referred to as exonucleases . Exonucleases act in one direction (3 – 5 or 5 – 3) only .

These enzymes which attack the phosphodiester bridges in DNA and RNA are grouped into a and b enzymes or (3 and 5) according to side of bridge attacking .

A enzymes hydrolyze the ester bond between the phosphate group and carbon atom (number 3) the most common example of is the enzyme phosphodiesterase which is present in the rattlesnake poison which hydrolyze the third carbon bonds in DNA and RNA to produces nucleoside phosphate . This enzyme needs for free hydroxyl group in the terminal of (3 carbon atom) .

B enzymes hydrolyze the ester bond between phosphate group and carbon atom (number 5) .

The enzymatic hydrolysis of nucleic acid is important in the determination of nucleotide sequence in the nucleic acids .

RNA:

Ribonucleic acid (RNA) is a polymer of purine and pyrimidine ribonucleotides linked together by 3,5- phosphodiester bridges analogous to those in DNA .

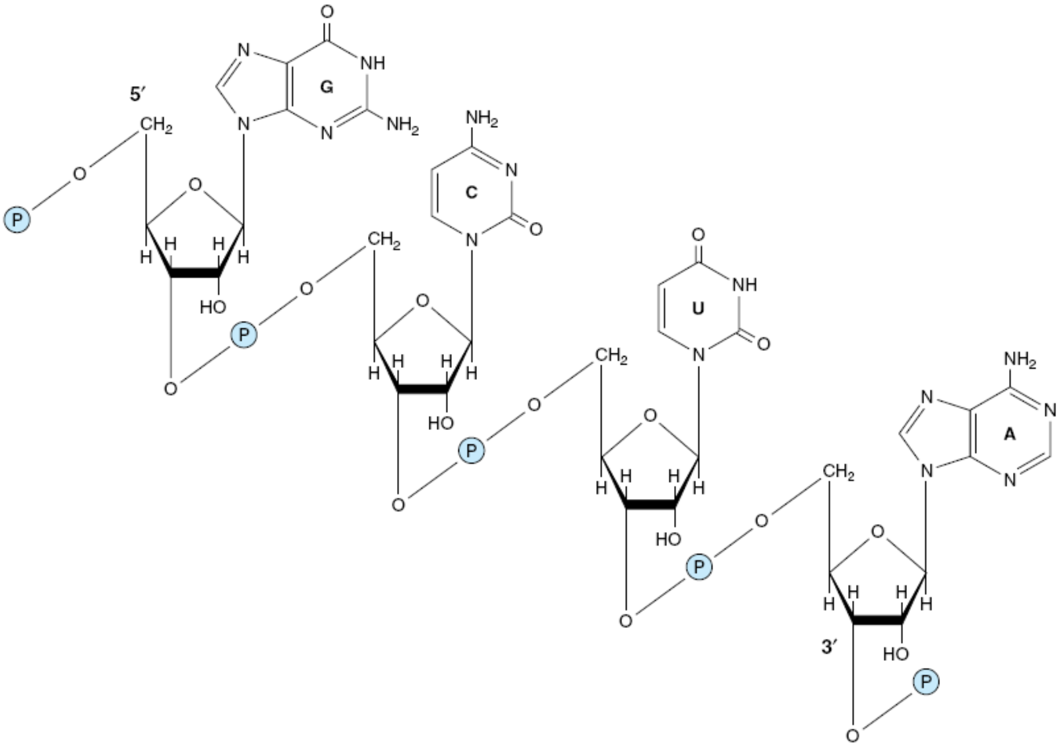


Figure of RNA

Although sharing many features with DNA , RNA prossesses several specific differences :

1. In RNA , the sugar moiety is ribose rather than deoxyribose of DNA .
2. The pyrimidine components of RNA differ from those of DNA . Although RNA contains the ribonucleotides of adenine , guanine , and cytosine it does not possess thymine except in the rare case . Instead of thymine RNA contains the ribonucleotide of uracil .
3. RNA exists as a single strand , whereas DNA exists as a double stranded helical molecule . The single strand of RNA is capable of folding back on its self like a hairpin and thus acquiring double stranded characteristics .
4. Since the RNA molecule is a single strand complementary to only one of the tow strands of a gene , its guanine content does not necessarily equal its cytosine content , nor does its adenine content necessarily equal its uracil content .

Information of within single strand of RNA is contained in its sequence of purine and pyrimidine nucleotides within the polymer, the sequence is complementary to template strand of the gene from which it was transcribed . Because of this complementarity , an RNA molecule can bind specifically by base pairing rules to its template DNA strand , it will not bind with other (coding) strand of its gene . The sequence of the RNA molecule (except for U replacing T) is the same as that of the coding strand of the gene

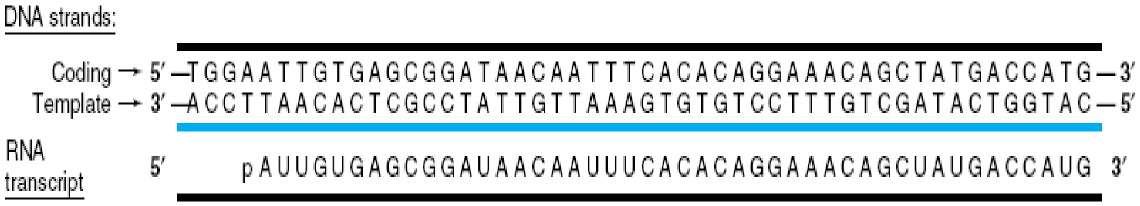


Fig. of : The relationship between the sequences of RNA transcript and its gene

There are three main classes of RNA molecules : messenger RNA (mRNA) , transfer RNA (tRNA) , and ribosomal RNA (rRNA) . Each differs from the others by size , function , and general stability .

mRNA :- This class is the most heterogeneous in size and stability . All members of this class function as messengers conveying the information in gene to the protein synthesizing machinery , where each serves as template on which a specific sequence of amino acids is polymerized to form a specific protein molecule .

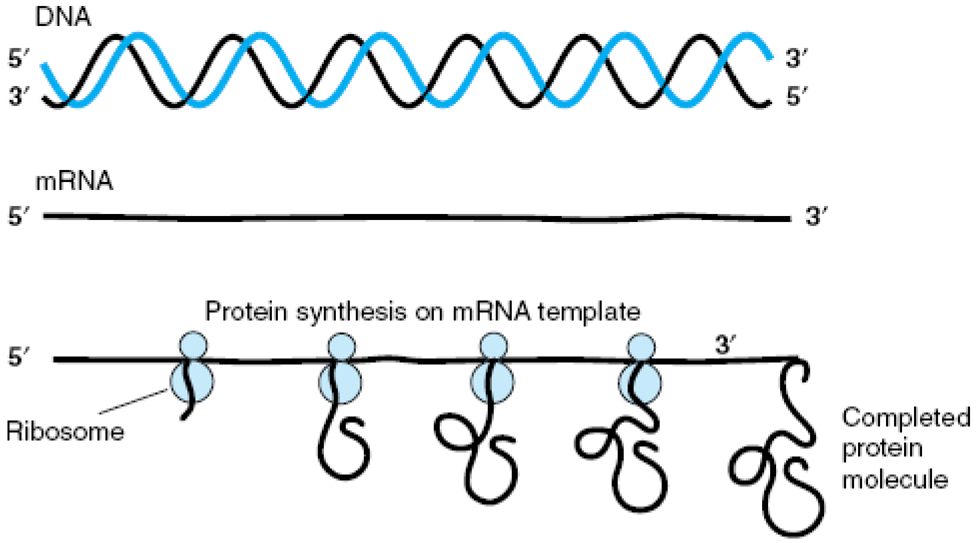


Fig. of : The expression of genetic information in DNA into the form of an mRNA transcript

This means that mRNA carries information from DNA to the ribosome , the site of protein synthesis in the cell . The coding sequence of the mRNA determines the amino acid sequence in the protein that is produced .

mRNA contains the cardinal four bases only (A , G , C , and U) , and is created in the nucleus during the DNA transcription therefore the sequence of mRNA bases is complementary with the sequence of one transcripted strand of DNA . After its synthesis in nucleus mRNA crosses the to the cytoplasm to be template for amino acid sequence during the protein synthesis .

tRNA :- tRNA molecules vary in length from 74 – 95 nucleotides that transfer a specific amino acid to a growing polypeptide chain at the ribosomal site of protein synthesis during translation . It has sites for amino acid attachment and anticodon region for codon recognition that binds to a specific sequence on the mRNA chain through hydrogen bond . There are at least 20 species of tRNA molecules in every cell , at least one corresponding to each of the 20 amino acid required for protein synthesis . tRNA molecules have intrastrand complementary to generate structure that appears in two dimensions like a cloverleaf .

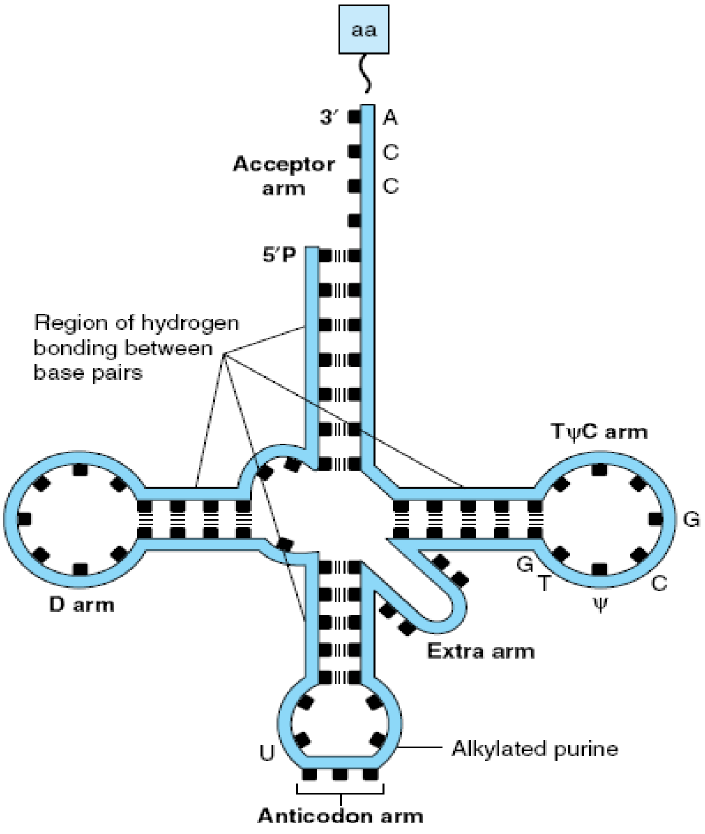


Fig. of : Typical aminoacyl tRNA

All tRNA molecules contain four main arms . The acceptor arm terminates in the nucleotides CCAoh the amino acid is attached or charged onto the 3OH group of the A moiety of the acceptor arm .

Anticodon : This region contains three nucleotides , and it is complementary with the nucleotides of codon which are present on the mRNA . Each codon determines the amino acid which will added to the sequence of amino acid in the protein synthesis .

Ribosomal RNA (rRNA) : - A ribosome is a cytoplasmic nucleoprotein structure called ribonucleoprotein that acts as the machinery for the synthesis of protein from mRNA template . On ribosome the mRNA and tRNA molecules interact to translate into a specific protein molecule information transcribed from the gene . Many ribosomes are associated with an mRNA to form which is called polysome . There are three types of rRNA according to the sedimentation velocity (Svedberg units) . The functions of the rRNA are not fully understood , but they are necessary for ribosomal assembly and seem to play key roles in the biding of mRNA to ribosomes and its translation .

Small RNA :- A large number of discrete and highly conserved RNA species are found in eukaryotic cells . Most of these are complexed with protein to form ribonucleoprotein and are distributed in the nucleus , in the cytoplasm , or in both . Small RNA includes : - Small nuclear RNAs (snRNAs) .

- Micro RNA .
- Small interfering RNA .

snRNAs are involved in mRNA processing and gene regulation .
miRNA and snRNA play important roles in gene regulation .
Certain RNA molecules acts as catalysts and called (ribozyme) .

Metabolism of purine and pyrimidine nucleotides

Introduction

The biosynthesis of purines and pyrimidines is regulated by feed back mechanisms that ensure their production in quantities and at times appropriate to varying physiologic demand . Genetic disease of purine metabolism include , gout , Lesch-Nyhan syndrome , adenosine deaminase deficiency , and purine nucleoside phosphoyrlase deficiency . Human tissues each synthesize purines and pyrimidines therefore the ingested nucleic acids and nucleotides are dietary non essential and are degraded in the intestinal tract to mononucleotides , which may be absorbed or converted to purine and pyrimidine bases . The purine bases are then oxidized to uric acid which may be absorbed and excreted in the urine .

Biosynthesis of purine nucleotides

Introduction

Purine and pyrimidine nucleotides are synthesized in vivo at rates consistent with physiologic need . The nucleotides are synthesized by two different pathways , the first one is de novo pathway which synthesizes purine and pyrimidine cycle from low molecular weight precursors by sequence reactions , these precursors (ribose , phosphate , many amino acids , CO2 ,and ammonia) incorporate to form nucleotides .

The cells are capable to use the free bases or nucleosides which are made from nucleic acid destruction in the synthesis of nucleotides , this pathway is the second and is called salvage pathway .

The de novo pathway is the most common in the most cells , but in the cells which lack to the enzymes that are participate in the de novo pathway , the salvage pathway will be the responsible for nucleotides formation .

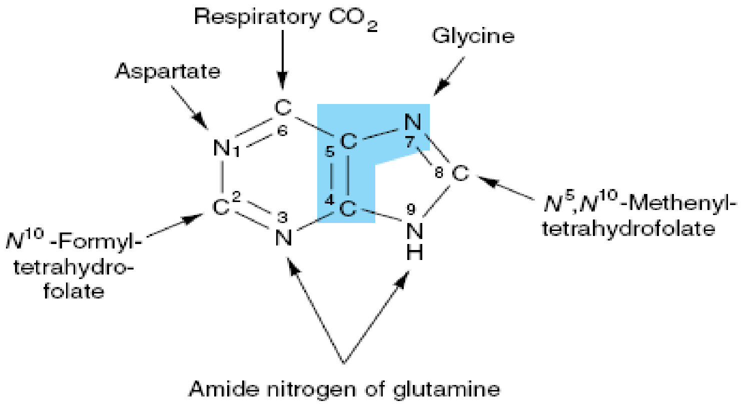


Figure 34–1. Sources of the nitrogen and carbon atoms of the purine ring. Atoms 4, 5, and 7 (shaded) derive from glycine.

Three processes contribute to purine nucleotide biosynthesis , these are in order of decreasing importance :

1. De novo pathway .
2. Phosphoribosylation of purines .
3. Phsphorylation of purine nucleosides .

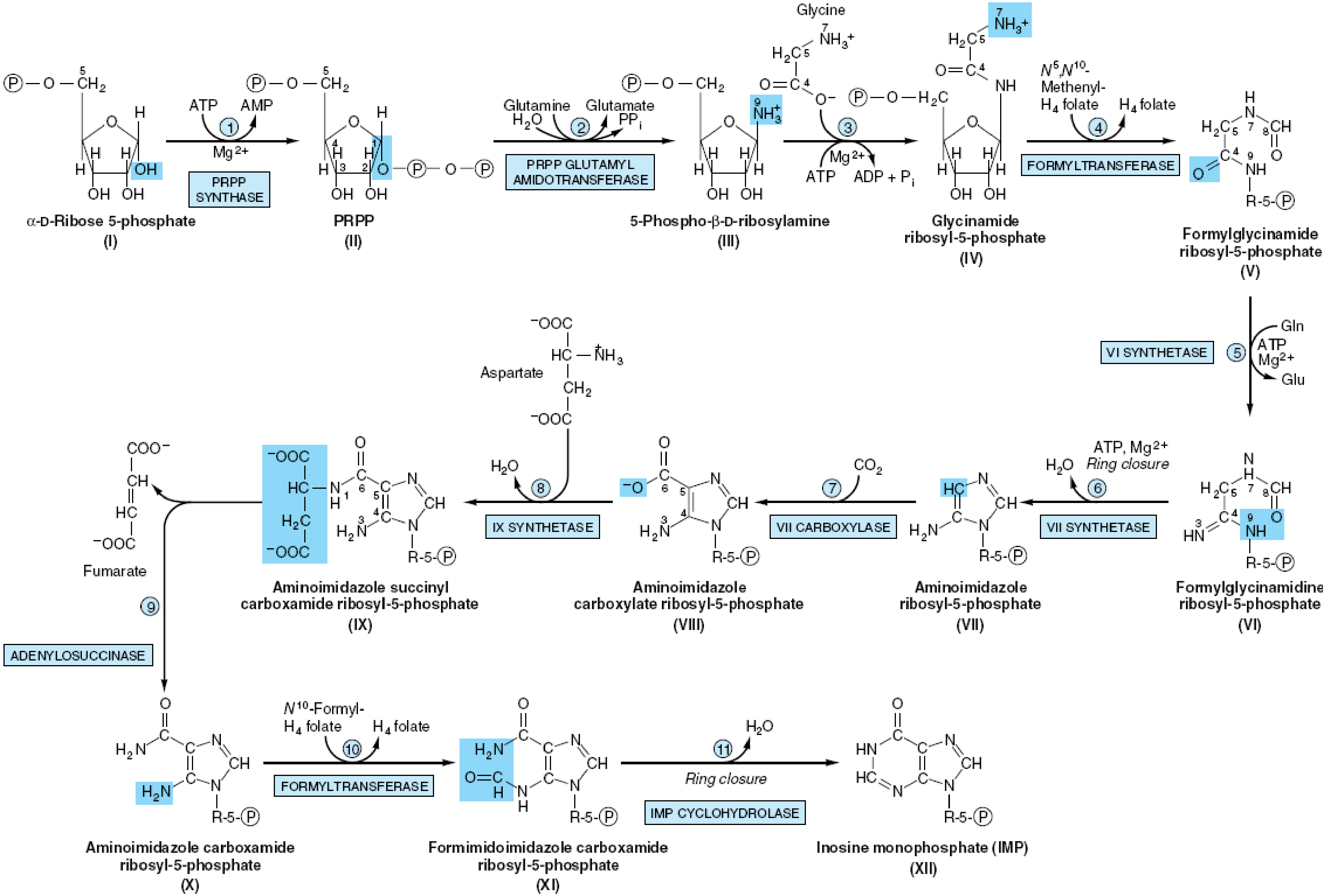


Figure 34–2. Purine biosynthesis from ribose 5-phosphate and ATP. See text for explanations. (Ⓟ, PO_3^{2-} or PO_2^-.)

The carbons added in reaction 4 and 10 are contributed by derivatives of tetrahydrofolate . Purine deficiency occurs with folic acid deficiency , therefore antifolate drugs block purine nucleotides biosynthesis . Inhibitory compounds and the reaction they inhibit include azaserine (reaction 5) , diazanorleucine (reaction 2) , 6-mercaptopurine (reaction 13 and 14) , and sulfonamide (reaction 10) and mycophenolic acid (reaction 14 fig. 34-3) .
Azaserine which is made from special types of streptomyces inhibits the enzymatic transport of amide group from glutamine by competitive inhibition because that the structure of glutamine resembles the structure of azaserine .
Sulfonamide which is used as antibacterial affects indirectly in the step of the addition of formyl group to aminoimidazol because sulfonamides resembles p-aminobezoic acid which is the building unit of folic acid therefore sulfonamide inhibits the step in which the folic acid is the responsible .
The major determinant of the rate of de novo purine nucleotide biosynthesis is the concentration of PRPP . The rate of PRPP synthesis depends on the availability of ribose 5-phosphate and on the activity of PRPP synthase , an enzyme sensitive to feedback inhibition by AMP , ADP , GDP , and GMP . PRPP synthase is feedback inhibited by both purine and pyrimidine nucleotides .

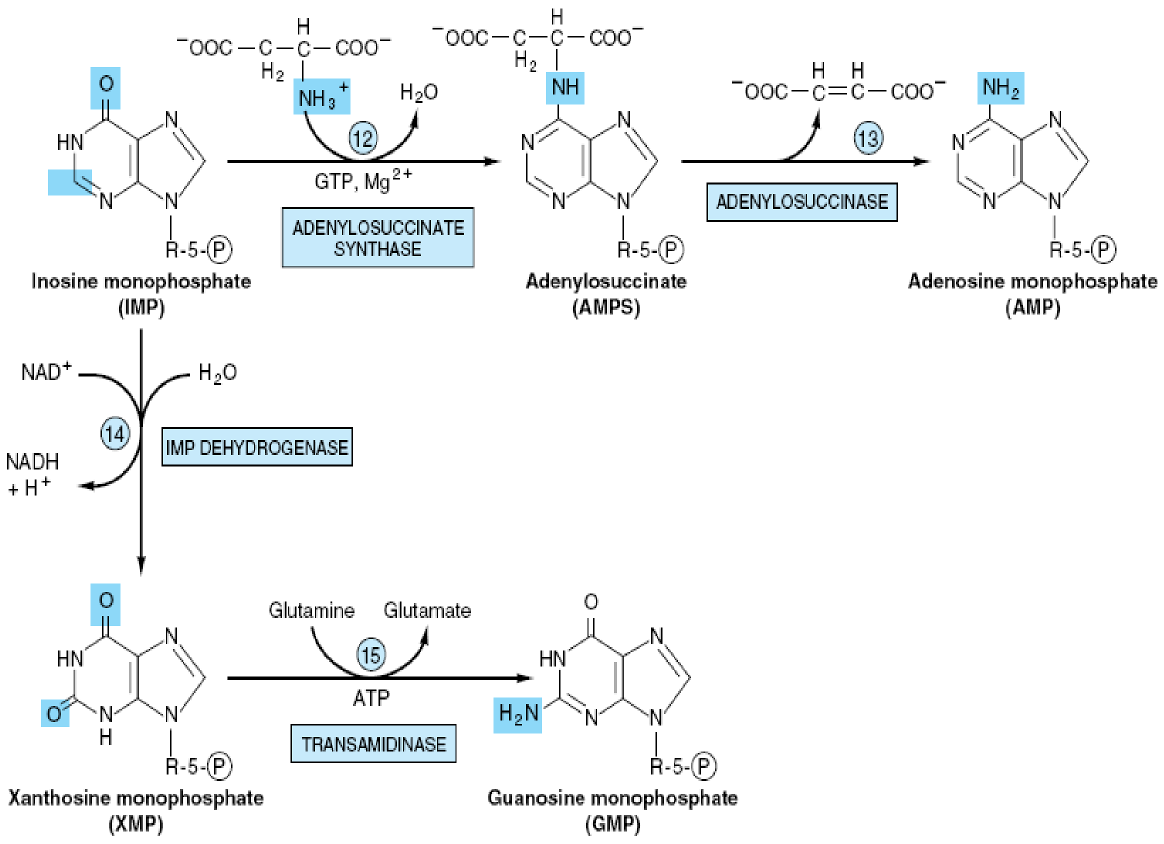


Figure 34–3. Conversion of IMP to AMP and GMP.

Tow mechanisms regulate conversion of IMP to GMP and AMP. AMP and GMP feedback inhibit adenylosuccinate synthase and IMP dehydrogenase respectively (reaction 12 and 14 fig. 34-3) . GMP feedback inhibits PRPP glutamyl amidotransferase (reaction 2 fig. 34-2) .

Pyrimidine biosynthesis

The fig 34-7 illustrates the intermediates and enzymes of pyrimidine nucleotides biosynthesis . This cycle also called orotate pathway . The uridine MP is main end product of this cycle and the other pyrimidine nucleotides derived from it .

Methotrexate blocks reduction of dihydrofolate . Reaction 12 of fig33-7 requires tetrahydrofolate . For further pyrimidine biosynthesis to occur , dihydrofolate must be reduced back to tetrahydrofolate , a reaction is catalyzed by dihydrofolate reductase which is inhibited by inhibitors such as the anticancer drug methotrexate .

نقص رسم ٣٤-٧ صـ ٣٠٦

Regulation of pyrimidine nucleotides biosynthesis .

The activities of the first and second enzymes of pyrimidine nucleotide biosynthesis are controlled by allosteric regulation .
Carbamoyl phosphate synthase II (reaction 1) is inhibited by UTP but activated by PRPP .
Aspartate transcarbamoylase (reaction 2) is inhibited by CTP but activated by ATP .

Disorders of purine metabolism

Humans convert adenosine and guanosine to uric acid (fig.33-8) . Adenosine is first converted to inosine by adenosine deaminase . In mammals uricase converts uric acid to the water soluble product . While humans lack uricase , therefore the end products of purine catabolism is uric acid .

نقص رسم ٣٣-٨ صـ ٣٠٧

☻Uric acid present in plasma as sodium urate which is more soluble at a pH near neutrality (fig. ----) . An elevated in serum urate concentration is known as hyperuricemia . Uric acid and urate are relatively insoluble molecules that readily precipitate out of aqueous solutions such as urine or synovial fluid .

☻ Formation of urate

Urate is formed in three ways : 1 / metabolism of DNA , RNA , and other purines . 2 / by the breakdown of dietary nucleic acid .

☻ Excretion of urate

Urate is excreted by two ways :

1/ Via the kidney : urate is excreted via the kidney . It is filtered at the glomerulus but 99% is is reabsorbed in the tubule .

2/ Via the gut : smaller amount of urates are excreted into the gut where it is broken down by bacteria , this process is called uricolysis .

☻Urate concentrations in serum are higher in men than women.

☻ High serum urate may arise from : Increased urate production or decreased urate excretion .

☻ 90% of cases are due to decreased excretion of urate .

☻ 10% of cases are due to increased production of urate .

Gout

Gout is a clinical syndrome that is characterized by hyperuricemia and acute arthritis . Acute gout is triggered by the tissue deposition of urate crystals that cause an inflammatory response . Thus when serum urate level exceed the normal concentration , sodium urate crystallizes in soft tissues and joints . However most causes of gout reflect abnormalities in renal handling of uric acid .

Gout is exacerbated by alcohol because that :

- Ethanol increases the turnover of ATP and urate production .
- Ethanol in excess may cause the accumulation of organic acids that compete with the tubular secretion of uric acid .

Treatment

- The symptom of acute gout respond to anti inflammatory drugs such as indometacine but these drugs have no direct effect on the serum urate level .
- Low dose aspirin should be avoided as it inhibits renal urate excretion .
- Treatment must be directed at the hyperuricemia .
- Drugs such as probenecid , which promote urate excretion can be used prophylactically .
- A diet that is low in purines and alcohol may be prescribed in an effort to reduce the plasma urate concentrations .
- Allopurinol , a specific inhibitor of the enzyme xanthine oxidase that catalyzes the oxidation of hypoxanthine to xanthine and uric acid .

Lesch – Nyhan syndrome

A clinical syndrome that is characterized by hyperuricemia , and caused by a deficiency hypoxanthine – guanine phosphoribosyl transferase which is involved in salvaging purine bases for resynthesis to purine nucleotides .

The syndrome is characterized clinically by excessive uric acid production , hyperuricemia , and neurological problems that include mental retardation .

Von – Gierks disease

This disease occurs as a result of glucose-6-phosphate deficiency and is characterized by hyperuricemia . an associated lactic acidosis elevates the renal threshold for urate , elevating total body urate .

Hypouricemia

Hpouricemia and increased excretion of hypoxanthine and xanthine are associated with xanthine oxidase deficiency due to genetic defect or to sever liver damage .

Renal disease and hyperuricemia

The most common renal disease is urate nephropathy which is caused by the deposition of urate crystals in renal tissues or the urinary tract to form urate stones . This may be associated with chronic hyperuricemia . Acute renal failure can be caused the rapid precipitation of uric acid crystals that commonly occurs during treatment of patient with leukaemias . In the acute tumor nucleic acids are released as a result of tumor cell breakdown and are rapidly metabolized to uric acid .

Chromosome

A chromosome is an organized structure of DNA and protein that is found in cells. Chromosomes contain DNA-bound proteins, which serve to package the DNA and control its functions. The word *chromosome* comes from the Greek (*chroma*, color) and (*soma*, body) due to their property of being very strongly stained by particular dyes.

Diagram of a duplicated chromosome. (1) Chromatid – one of the two identical parts of the chromosome . 2) Centromere – the point where the two chromatids touch . (3) Short arm. (4) Long arm.

Chromosomes vary widely between different organisms. The DNA molecule may be circular or linear, and can be composed of 10,000 to 1,000,000,000[1] nucleotides in a long chain . In eukaryotes (cell with nuclei) , nuclear chromosomes are packaged by proteins into a condensed structure called chromatin. This allows the very long DNA molecules to fit into the cell nucleus. Chromosomes are the essential unit for cellular division and must be replicated, divided, and passed successfully to their daughter cells so as to ensure the genetic diversity and survival of their progeny.
Mammalian chromosomes possess a twofold symmetry with identical duplicated sister chromatides connected at a centromere . Chromosomes contain two short arms and two long arms . Human cells have 23 pairs of large linear nuclear chromosome giving a total of 46 per cell .

Chromosomal aberrations

Chromosomal aberrations are disruptions in the normal chromosomal content of a cell, and are a major cause of genetic conditions in humans, such as Down syndrome. Some chromosome abnormalities do not cause disease in carriers, such as chromosomal inversions, although they may lead to a higher chance of birthing a child with a chromosome disorder. Abnormal numbers of chromosomes may be lethal or give rise to genetic disorders.

The gain or loss of DNA from chromosomes can lead to a variety of genetic disorders. Human examples include:

- Cri du chat, which is caused by the deletion of part of the short arm of chromosome 5. "Cri du chat" means "cry of the cat" in French, and the condition was so-named because affected babies cry in a sound like those of a cat. Affected individuals have wide-set eyes,

a small head and jaw, and are moderately to severely mentally retarded and very short .
- Wolf-Hirschhorn syndrome, which is caused by partial deletion of the short arm of chromosome 4. It is characterized by severe growth retardation and severe to profound mental retardation.
- Klinefelter's syndrome (XXY). Men with Klinefelter syndrome are usually sterile, and tend to have longer arms and legs and to be taller than their peers. Boys with the syndrome are often shy and quiet .
- Triple-X syndrome (XXX). XXX girls tend to be tall and thin. They have a higher incidence of dyslexia.

Terms illustration

- Deletion – loss of part of a chromosome
- Duplication – extra copies of a part of a chromosome
- Inversion – reverse the direction of a part of a chromosome
- Translocation – part of a chromosome breaks off and attaches to another chromosome .

Chromatin

Chromatin is the complex combination of DNA and protein that makes up chromosomes. It is found inside the nuclei of eukaryotic cells. The major components of chromatin are DNA (Genetic Formula) and histone proteins . The functions of chromatin are to package DNA into a smaller volume to fit in the cell, to strengthen the DNA to allow mitosis and meiosis, and to serve as a mechanism to control expression and DNA replication . Changes in chromatin structure are affected by chemical modifications of histone proteins such as methylation (DNA and proteins) and acetylation (proteins), and by non-histone, DNA-binding proteins.

***chromatin* definition:** The DNA double helix in the cell nucleus is packaged by special proteins termed histones. The formed protein/DNA complex is called chromatin. The structural entity of chromatin is the nucleosome.

Electron microscopic studies of chromatin have demonstrated dense spherical particles called nucleosomes , which are approximately 10 nm in diameter and connected by DNA filament .