Chapter 1: *Structure of Matter*

CHAPTER OUTLINE: The student will be able to:-

- **The atom-*size; weight***
- **Inside the atom**
- **Fundamentals particles**
- **Atomic weight**
- **Atomic number**
- **Mass number**
- **Numbers of neutrons in the nucleus**
- **Isotopes**
- **The periodic table**

The Atom:

The smallest portion of an element that retains all of the properties of the element.

Consider a bar of iron. Iron is an element. It has certain properties. Cutting the bar in half produces two pieces of iron. Both pieces have the same properties as the original bar. Continued cutting produces smaller and smaller pieces, all with identical properties. In time, we could theoretically arrive at the smallest piece of iron attainable. This smallest piece of iron is an atom-an atom of iron.

A piece of iron is made up of many atoms of iron, a piece of copper of many atoms of copper, and a piece of silver of many atoms of silver. The atoms of one element differ from those of another and so give characteristic properties of each element.

Size: An atom has a diameter of approximately (1/ 100, 000,000 cm).
Weight: An atom weights very little.

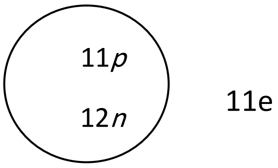
Fundamental particles:

Atoms are considered to be made of three fundamental particles, the proton, the neutron, and the electron. The proton (p) has a charge of positive one (+1) and mass (weight) of approximately one atomic mass unit (amu $\approx 1.6605 \times 10^{-24}$ g.). Protons are located inside the nucleus of the atom. The electron (e) has a negative charge (-1) and a mass (weight) of 1/1837 amu. Electrons are located outside the nucleus. The neutron (n) has no charge; it is neutral. It has a mass (weight) of approximately 1 amu. Neutrons are located inside the nucleus (see table 1-1).

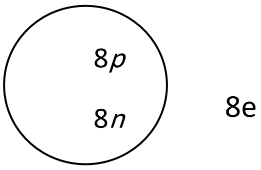
particle	Symbol & charge	Weight amu	Location in the atom
Proton	p or P^+	1	Inside nucleus
Electron	e or e^-	1/1837	Outside nucleus
Neutron	n or n^0	1	Inside nucleus

Atomic weight: The relative weight of an atom. The chemist uses atomic weights rather than exact weight. What does the term relative weight mean? The chemist has given the carbon-12, sodium-23, oxygen-16…..and so on.

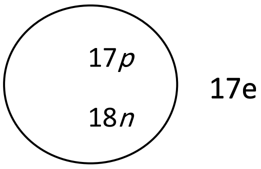
Na=23



O=16



Cl=35



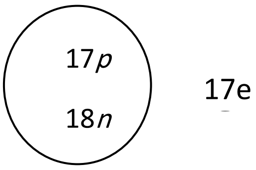
The atomic weight of carbon is 12, that of oxygen is 16, and that of sodium is 23. For precise, however, the exact atomic weights must be used. The atomic weights of all the elements are listed in the periodic table.

The atomic number: It indicates the number of protons in the nucleus of an atom of that element. However, since all atoms are electrically neutral. Therefore, the atomic number also tells the number of electrons in the atom, these electrons being located outside the nucleus. [why the atoms are neutral? There must be as many electrons (negative charge) as protons (positive charge)].

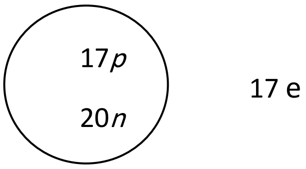
Mass number: The mass number of a nucleus is equal to the total number of protons and neutrons in that nucleus.

Number of the neutrons in the nucleus: The number of neutrons can be found by subtracting the atomic number of an element from its mass number. Knowing that each neutron weights 1 amu.

Isotopes: Are defined as atoms of an element having the same atomic numbers but different mass numbers. The first isotope of chlorine (Cl)-atomic number 17 and mass number 35-has 17 protons in its nucleus, 17 electrons outside its nucleus, and 18 neutrons (35-17) in its nucleus. The second isotope of chlorine-atomic number 17 and mass number 37-has 17 protons in its nucleus, 17 electrons outside its nucleus, and 20 neutrons (37-17) in its nucleus.



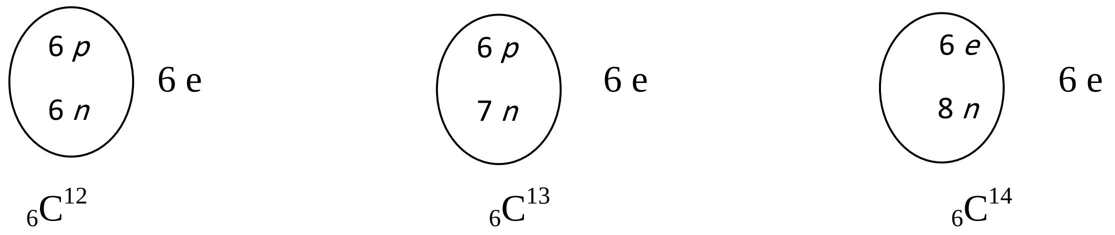
$_{17}\mathbf{Cl}^{35}$



$_{17}\mathbf{Cl}^{37}$

The atomic weight is the average weight of all the isotopes: If the two isotopes of chlorine , mass number (atomic weight) 35 and 37, were present in equal amounts, the atomic (average) weight would be 36. However, since the atomic weight is listed as 35.5 must be *predominant* one *because the atomic weight is closer to 35 than to 37*.

The element carbon-atomic number 6 has three isotopes. Their mass number are 12, 13, and 14. They all have atomic number 6, which means that they all have 6 protons in their nucleus and 6 electrons outside their nucleus. The isotope of mass number 12 has 6 neutrons in its nucleus; the isotope of mass number 13 has 7 neutrons in its nucleus; and the isotope of mass number 14 has 8 neutrons in its nucleus. The carbon-12 is the most *abundant* *since the atomic weight of carbon is 12.011*, indicating small amounts of the other isotopes.



Three isotopes of carbon

Isotopes have been defined as atoms of an element having the same atomic number but different mass number; therefore isotopes of an element must have the same number of protons and electrons but different number of neutrons. In general, isotopes have identical chemical properties because they contain the same number of electrons as well as protons. However, isotopes have different physical properties.

Radioactive: **Substance like uranium that spontaneously give off radiation**. ***Radioactivity:*** **is the property that causes an element to emit radiation. This radiation comes from the nucleus of the atom**. Radiations produced by a radioactive element are *alpha, beta (electrons)* , and *gamma(neutrons).*

Radioisotopes: The isotopes produced artificially by bombardment with one of the various particles (radioactive isotopes or radioisotopes). Some radioisotopes used in medicine and in biochemistry ^{131}I, ^{60}Co, ^{99}Tc, ^{14}C, and ^{59}Fe.

Biologic effects of radiation: Externally, alpha and beta particles are relatively harmless to humans since they have slight penetrating power. Gamma rays, with their great penetrating power, have a very definite effect upon the body. If a radioactive substance is taken inside the body, it is the alpha particles that are most harmful. **protection by** shielding, distance, and limiting exposure are the only effective preventative methods against radiation exposure.

Alpha rays

_Alpha rays are the larger rays between the previous two types.

_Its radiation length is short compared to the length of beta and gamma rays without a barrier.

_Alpha particles are the nucleus of a helium atom.

_ Its danger lies when it enters the human body, since its ***heavy mass is sufficient to destroy all tissues that stand in its way.***

Sources of radiation: The body receives radiation externally from three principal sources: *natural background radiation, medical radiation, and fallout and radioactive waste*. Background radiation comes from space and from radioactive material present in the soil, in the air, in the water, and in the building materials of the our houses.

Chapter 2- *Chemical Bonding*

CHAPTER OUTLINE: The student will be able to:-

Molecules	**Covalent bonds**
Stability of the atoms	**Oxidation numbers**
Symbols and formulas	**Molecular weight**
Formation of ions	
Ionic bonds	

Molecules: It is a combination of two or more atoms. These atoms may be the same elements, as in the oxygen molecule (O_2), or of different elements, as in the hydrogen chloride molecule (HCl). A more complicated molecule is that of glucose, $C_6H_{12}O_6$. Atoms are held together by bonds that may be classified into two main types-ionic and covalent bond.

Stability of atoms: Most atoms are considered stable (nonreactive) when their highest (outer) energy level is filled to eight (electrons). The noble gases-neon, argon, krypton, xenon, and radon-all have eight electrons in their highest energy level. They are stable.

Atoms that do not have eight outer electrons may lose, gain, or share their valence electrons with other atoms in order to reach a more stable structure with lower chemical potential energy. **This process of rearrangement of the *valence electrons* is responsible of chemical reactions between atoms.**

Symbols and Formulas:

A symbol not only identifies an element but also represents one atom of that element. Thus, the symbol Cu designates the element copper and also indicates one atom of copper (two atoms of copper are designated as 2Cu). [2O, 2Cl….].

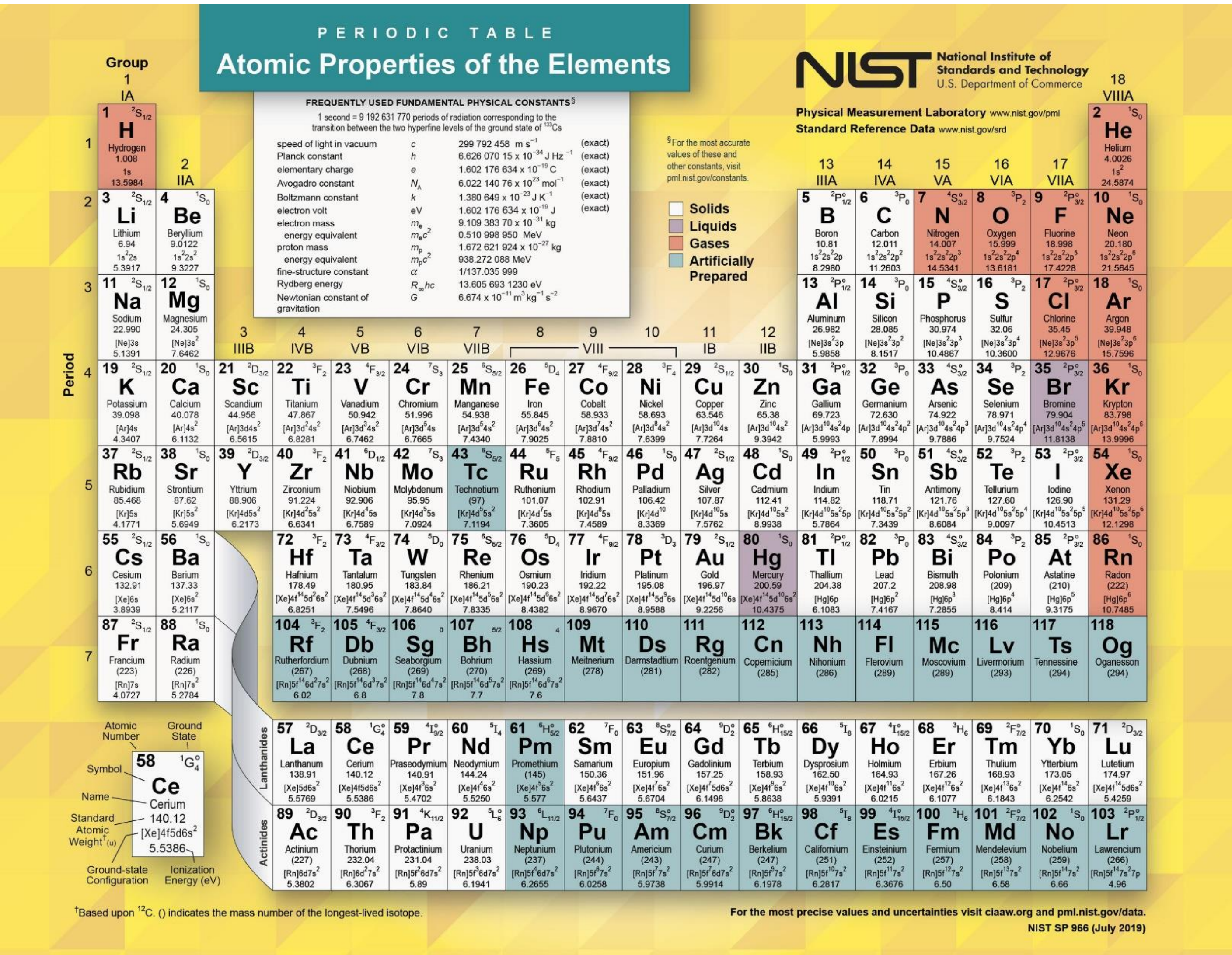
A formula consists of a group of symbols that represents the elements present in a substance. It also indicates one molecule of that substance. Thus the formula NaCl indicates that the compound (sodium chloride) consists of one atom of sodium (Na) and one atom of chlorine (Cl). In the compound HNO_3 (nitric acid) there is one atom of hydrogen (H), one atom of nitrogen (N), and three atoms of oxygen (3O). [$K_2Cr_2O_7$ Potassium dichromate]. ***To designate more than one molecule of that substance*** $2HNO_3$, $6K_2Cr_2O_7$, **a number (a coefficient)** is placed in front of the formula for that substance.

Diatomic molecules: O_2, H_2, N_2, Cl_2, Br_2, and I_2.

Formation of ions:

Table 2-1 Electron-dot structures of the first 18 elements

^{1}H.							^{2}He:
^{3}Li.	^{4}Be:	^{5}B…	• • ^{6}C • •	• • ^{7}N • • •	:^{8}O : • •	• : ^{9}F : • •	• • : ^{10}Ne : • •
^{11}Na•	^{12}Mg:	^{13}Al…	• •^{14}Si • •	• • ^{15}P • • •	:^{16}S : ••	• : ^{17}Cl : ••	•• :^{18}Ar: ••



FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS§

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.626 070 15 x 10^{-34} J Hz^{-1}	(exact)
elementary charge	e	1.602 176 634 x 10^{-19} C	(exact)
Avogadro constant	N_A	6.022 140 76 x 10^{23} mol^{-1}	(exact)
Boltzmann constant	k	1.380 649 x 10^{-23} J K^{-1}	(exact)
electron volt	eV	1.602 176 634 x 10^{-19} J	(exact)
electron mass	m_e	9.109 383 70 x 10^{-31} kg	
energy equivalent	m_ec^2	0.510 998 950 MeV	
proton mass	m_p	1.672 621 924 x 10^{-27} kg	
energy equivalent	m_pc^2	938.272 088 MeV	
fine-structure constant	α	1/137.035 999	
Rydberg energy	$R_\infty hc$	13.605 693 1230 eV	
Newtonian constant of gravitation	G	6.674 x 10^{-11} m^3 kg^{-1} s^{-2}	

§For the most accurate values of these and other constants, visit pml.nist.gov/constants.

†Based upon ^{12}C. () indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit ciaaw.org and pml.nist.gov/data.

NIST SP 966 (July 2019)

Table 2-1 indicates the electron-dot structures of the elements in the first three periods of the periodic chart.

Consider the sodium ion with the electron structure 2e) 8e) 1e). if the sodium atom **<u>loses</u>** its one outer electron, it will reach a noble gas structure of eight electrons in its outer energy level. Such a noble gas structure has great stability. When a sodium atom loses an electron, it becomes a positively charged particle called a sodium ion. this reaction may be written as

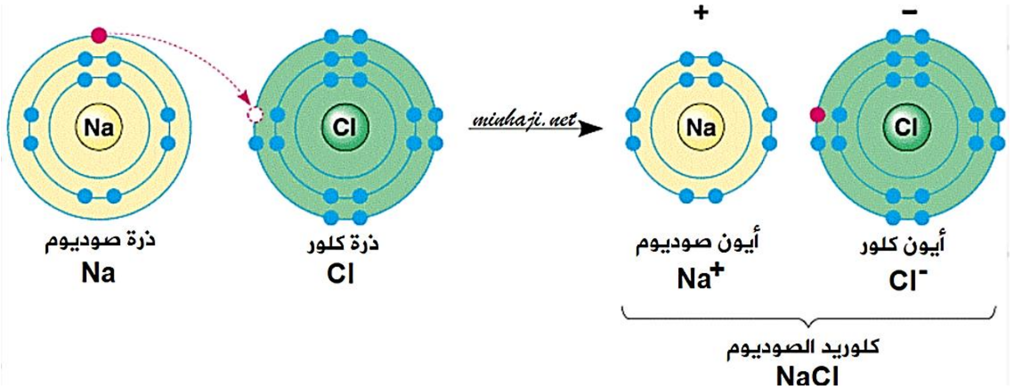
$$Na^{\bullet} - 1e \longrightarrow Na^{+}$$

Or, with the electron-dot being understood,

$$Na - 1e \longrightarrow Na^{+}$$

Consider the element chlorine, 2e) 8e) 7e). the electron atom will tend to gain one electron to fill its outer energy level to eight, reaching a stable (noble gas) structure. Chlorine will thus form an ion with a charge of (-1), or omitting the dots,

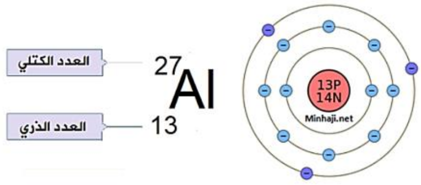
$$Cl + 1e \longrightarrow Cl^{-}$$



Where the positive sign indicates a charge of (+ 1) on the sodium ion. (note that the number 1 is understood and not written.) **The charge on the sodium ion is positive <u>because the sodium ion still has (11) protons in its nucleus but now has only (10) electrons outside that nucleus</u>**.

Likewise, the aluminum atom, which has the electron structure of 2e) 8e) 3e), **<u>loses</u>** all three outer electrons when it forms an aluminum ion with a charge of (+3) [written above the symbol as 3+].

$$Al\vdots - 3e \longrightarrow Al^{3+} \quad \text{or simply} \quad Al - 3e \longrightarrow Al^{3+}$$

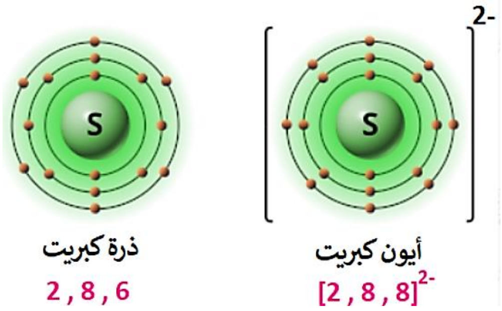


<u>A **metal**</u> that has one valence electron forms an ion with a (*1+ charge*); a metal with two valence electrons forms an ion with a (*2+ charge*), and so on. The positive charge on a metallic ion is equal to the number of electrons lost by the metal.

Elements that have (6 or 7) outer electrons tend to **<u>gain</u>** electrons to each a stable noble gas of eight. Such element are called **<u>nonmetals</u>**. Most elements having 4 or 5 outer electrons are also **nonmetals**.

Since the ion has one more electron that the atom, it will have a charge of (-1), again with the 1 being understood and not written. Likewise, the sulfur atom, 2e) 8e) 6e), can gain 2 electrons to form an ion with a charge of (-2).

$$S + 2e \longrightarrow S^{2-}$$



The S^{2-} ion has a **full outer energy level**, reaching a **noble gas** structure.

An atom that has either lost or gained in its outer energy level is called ions. Ions formed from a **metal** will have a **positive charge** equal to the number of **electrons lost**. Ions formed from **nonmetal** will have a negative charge equal to the number of **electrons gained**.

Positive ions are attracted toward a negatively charged electrode called a **cathode**. Such ions are called **cations**. Likewise, **negative ions** are attracted toward a positively charged electrode, called an **anode**. These ions are called **anions**. Common cations in body fluids are the sodium ion, Na^+, the potassium ion, K^+, and the calcium ion, Ca^{2+}. **The chloride ion, Cl^-, is the most common anion in the body fluids.**

Ionic Bonds: When a sodium atom (Na) combines with a chlorine atom (Cl) to form a sodium chloride molecule (NaCl), the sodium atom loses one electron to form a positively charged sodium ion (Na^+). At the same time the chlorine atom gains that one electron to form a negatively charged chloride ion (Cl^-). The reaction is

$$\mathrm{Na}^{\bullet} + {}^{\bullet}\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{Cl}}}: \longrightarrow\ :\overset{\bullet\bullet}{\underset{\bullet\bullet}{\mathrm{Cl}}}:^{-} + \mathrm{Na}^{+} \quad \text{or} \quad \mathrm{Na} + \mathrm{Cl} \longrightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$

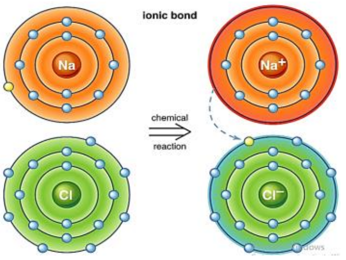
Another example of a transfer of electrons from a metal to a nonmetal is in the reaction between magnesium (Mg) and chlorine (Cl_2, here written as 2Cl):

$$\mathrm{Mg}: + \begin{matrix}\mathrm{Cl}^{7-}\\ \\ \mathrm{Cl}^{7-}\end{matrix} \longrightarrow \mathrm{Mg}^{2+} + \begin{matrix}\mathrm{Cl}^{8-}\\ \\ \mathrm{Cl}^{8-}\end{matrix} \quad \text{or} \quad \mathrm{Mg} + 2\mathrm{Cl} \longrightarrow \mathrm{Mg}^{2+} + 2\mathrm{Cl}^{-} = \mathrm{MgCl_2}$$

Again each ion has a completed outer energy level of eight.

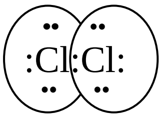
The positively charged of metal ion (sodium ion, magnesium ion) and the negatively charged (chloride ion) will be attracted to each other and will be held together by electrostatic attraction of their charges (opposite charges attract each other). This type of bonding is called an **ionic bond.** Ionic compounds or electrolytes are acids, bases, and salts.

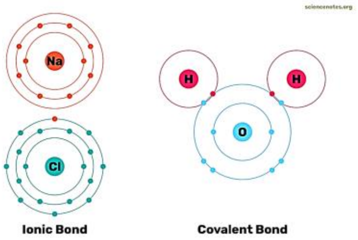
Ionic bond, **type of linkage formed from the electrostatic attraction between oppositely charged ions in a chemical compound.**



Covalent Bonds*:** ***Ionic bonding results from the loss or gain of electrons. However, there is another method by which atoms can be bonded together. ***This is by sharing of electrons*** (**covalent bonding)**. Involve the sharing of a pair of valence electrons by two atoms.

In the chlorine molecule, Cl_2, each of the chlorine atoms has seven outer electrons. In this case both atoms will share electrons so that each will have a completed outer energy level of eight electrons.





Cl-Cl, O=C=O, N≡N or Cl:Cl, O::C::O, N:⁝N

Note that in CO_2 and in N_2 there are eight electrons around each atom.

Oxidation numbers:

For ionic compounds, the oxidation number, sometimes called the *charge* of an element, is equal to the of electrons lost or gained and so is the same as the charge on the ion. that is, in sodium chloride, Na^+Cl^-, the oxidation number of sodium is +1, and that of chlorine -1. In the compound $MgBr_2$, where the magnesium ion has a charge of 2+ and each bromide ion a charge of 1-, the oxidation number of magnesium is +2 and that of each bromine -1.

For covalent compounds, where electrons are shared and not transferred, oxidation numbers are assigned to elements using the following rules:

1. All elements in their free state have an **oxidation number of zero**.
2. The oxidation number of oxygen is **-2** (except in peroxide where it is **-1**).
3. The oxidation number of hydrogen is **+1**.
4. The sum of oxidation number in all compounds **must equal zero**. (That is, all compounds are **electrically neutral**).
5. All elements in group **1A** have an oxidation number of **+1**.

Table 2-2 indicates the oxidation numbers of various elements.

? -2=0 +1 +? +4(-2)= 0 ? + 3 (-2)= 0
Zn O , K Mn O_4 , As_2 S_3

In order for the sum of oxidation numbers to be zero, the number of **Mn** must be **+7**, of **As** **+6** applies to two **As** atoms, so that the oxidation of each **As** is **+3**.

Table 2-2. Oxidation Numbers of Elements

Positive oxidation number			Negative oxidation number		
Name and Symbol		Oxidation Number	Name and Symbol		Oxidation Number
Hydrogen	H^+	+1	Chloride	Cl^-	-1
Sodium	Na^+	+1	Bromide	Br^-	-1
Potassium	K^+	+1	Iodide	I^-	-1
Silver	Ag^+	+1	Sulfide	S^{2-}	-2
Calcium	Ca^{2+}	+2	Oxide	O^{2-}	-2
Magnesium	Mg^{2+}	+2			
Aluminum	Al^{3+}	+3			
Ammonium	NH^+	+1			
Iron	$Fe^{2+}$and Fe^{3+}	+2 and +3			
Copper	$Cu^+$and Cu^{2+}	+1 and +2			
Tin	$Sn^{2+}$and Sn^{4+}	+2 and + 4			

Molecular weight: The molecular weight of any compound is the sum of the **atomic weights** of all of the atoms present in the molecule of that compound. Examples:

NaBr = (23+80)= 123; H_2O= (2×1 + 16) =18; $C_6H_{12}O_6$ =(6×12 + 12×1 + 6×16)= 180;

$Ca_3(PO_4)_2$ = (3×40 + 2×31+ 8×16) = 310

Percentage Composition: The percentage composition of a compound can be calculated **from the relative atomic weights of the elements present in the compound**. Consider the compound $Ca_3(PO_4)_2$, calcium phosphate whose molecular weight was found to be 310. Of this weight, calculate the percentage of Ca, P, and O in the upper compound.

$$\% \text{ Ca} = \frac{\text{Weight of calcium in compound}}{\text{Weight of compound}} \times 100 = \frac{120}{310} = 38.7\ \%;$$

$$\% \text{ P} = \frac{62}{310} = 20.0\ \%;$$

$$\% \text{ O} = \frac{128}{310} = 41.3\ \%$$

Chapter 3- ***Liquid Mixture-Solutions***

CHAPTER OUTLINE: The student will be able to:-

Solutions	**percentage**
Preparation of Standards units	**Formal solution**
Concentration	**Molar solution**
	Normal solution

Solutions: *A solution is a homogenous mixture of two or more substances evenly distributed in each other*.

Solubility: The quantity of **solute** that will dissolve in a definite quantity of **solvent**, the solubility of a substance is measured by ***the concentration of its saturated solution***.

***Preparation of standard solution unit*:**

Standard solution: *is one whose concentration (the quantity of reagent in a given volume) is known*. The concentration of a standard solution is usually expressed in grammes or equivalents of the active constituent in each liter of the solution. The process by which the concentration of a solution is determined is called **standardization**

***Requirements of a primary standard substance*:**

1. It must be of highest purity.
2. A primary standard substance should be stable, it should not be attracted by constituent of the atmosphere.
3. It should be readily available and not too expensive.
4. It should not be hygroscopic.
5. Finally, it should have a reasonably high equivalent weight. *A high equivalent weight tend to minimize weighing errors*.

Preparation a standard solution is always prepared by dissolving the standard material in a small volume. Generally, the standard substance is weighed directly on to a clock-glass, or if hygroscopic, in a weighing bottle, and then transferred to the graduated flask. the volume is carefully adjusted to the mark, and the stopper flask is inverted 30-40 times to sure mixing of the contents.

Factors affecting solubility of a solute:

1. Temperature:

Most solid solutes are more soluble in hot water than in cold water. There is variation of solubility of various substances in a water as a function of temperature.

For example-KNO_3 becomes much more soluble with an increase of temperature; however $Ce_2(SO_4)_3$, gases such as HCl and SO_2 become less soluble with increasing temperature, and NaCl shows little change in solubility. The solubility of Br_2, a liquid, is practically unaffected by temperature.

2. Pressure:

The pressure will affect the solubility of a gaseous solute. ***The greater the pressure, the greater the solubility of a gas in a liquid.***

3. Surface area:

It does affect the rate of dissolution. ***The greater the amount of surface area, the quicker a solute will dissolve in a solvent.***

4. Stirring:

The rate at which solute dissolves can also be increased by stirring the mixture. The process of stirring brings fresh solvent in contact with solute and so ***permits more rapid solution.***

5. Nature of solvent:

In general, polar liquids ***dissolve*** polar compounds, and non-polar liquids ***dissolve*** non-polar compounds. Some polar liquids (H_2O, CH_3OH, and C_2H_5OH) . Some non-polar liquids (benzene, carbon tetrachloride (CCl_4), and ether).

Importance of solutions:

During digestion, foods are changed to soluble substances so that they may pass into the bloodstream and be carried to all parts of the body. At the same time the waste products of the body are dissolved in the blood and carried to other parts of the body where they can be eliminated. Plants obtain minerals from the groundwater in which those minerals have dissolved.

Many chemical reactions take place in solution. ***This reaction occurs because the ions in the solution are free to move and react with other ions.***

$$AgNO_3 + NaCl \longrightarrow Ag^+ + Cl^- + Na^+ + NO_3^-$$

Many medications are administered orally, subcutaneously, or intravenously as solutions. Drugs must be in solution before they can be absorbed from the gastrointestinal (GI) tract. As you might expect, when drugs are taken in solution, such as syrups and elixirs, they are absorbed more rapidly than drugs in a solid form, such as tablets and capsules.

Strength of Solutions:

when a few crystals of sugar are placed in a beaker of water, a ***dilute*** sugar solution is produced (solvent more than solute). As more and more sugar is added to the water, the solution becomes more ***concentrated*** (solute more than solvent). However, both dilute and concentrated are *relative terms.* A dilute sugar solution may contain 5 g of sugar per 100 ml of solution, whereas 5 g (the same amount) of boric acid per 100 ml of solution will produce a concentrated boric acid solution. That is, the term dilute and concentrated usually have no specific quantitative meaning and so are not generally used for medical applications. Dilution law C_1V_1 X C_2V_2

Concentration Expressions:

Table 3-1: **CONCENTRATION EXPRESSIONS**

Expression	***symbol***	**Definition**
Molarity	*M,c*	Moles (gram molecular weights) of solute in 1 liter of sol.
Normality	*N*	Gram equivalent weights of solute in 1 liter of solution
Molality	*m*	Moles of solute in 1000 g of solvent
Mole fraction	*X*	Ratio of the moles of one constituent (e.g., the solute) of a solution to the total moles of all constituents (solute & solvent
Mole percent		Moles of one constituent in 100 moles of solution; mole percent is obtained by multiplying mole fraction by 100
Percent by weight	% w/w	Grams of solute in 100 g of solution
Percent by volume	% v/v	Milliliter of solute in 100 mL of solution
Percent weight-in-volume	% w/v	Grams of solute in 100 mL of solution
Milligram percent	—	Milligrams of solute in 100 mL of solution

The concentration of a solution can be expressed either in terms of the quantity of solute in a definite *volume of solution* or as the quantity of solute in a definite *mass of solvent or solution.*

Percentage solution: The weight-volume method express *the weight of solute in a given volume of solvent, usually water*. A 10 percent glucose solution will contain 10 g glucose per 100 ml of solution. A 0.9 percent saline solution will contain 0.9 g sodium chloride per 100 ml of solution. The **percentage** ***indicates the number of grams of solute per 100 ml of solution (% w/v).***

Ex1: prepare 500 ml of 2 percent citric acid solution.

500 ml X 2 (g citric acid) / 100 ml = 10 g citric acid

1. Weight out exactly 10 g citric acid.
2. Dissolve 10 g citric acid in a small amount of water contained in a 500-ml graduated cylinder.
3. Add water to the 500-ml mark and stir.

Ex2: a patient is given 1000 ml 0.9 percent NaCl intravenously. How many grams of NaCl did the patient receive?

0.9 % means 0.9 g NaCl/100 ml solution

1000 ml X 0.9 g NaCl / 100 ml = 9 g NaCl

In clinical work involving dilute solutions, concentrations sometimes expressed in terms of milligrams percent **(mg %)**, *which indicates the number of milligrams of solute per 100 ml of solution.* Milligrams percent is also referred to as milligrams per deciliter (mg/dl). The values of blood components in these units. Hint (1 dL = 100 mL).

Parts per Million (ppm): low concentration may be expressed in units *milligrams per liter* (mg/L). Another method of expressing low concentration is parts per million (ppm). *One part per million is equivalent to (1 mg/L).* that is, if a solution has a concentration of 40 mg/L, its concentration may be expressed as 40 ppm.

$$c_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$$

ppm = wt of solute / wt of solution X 1000.000

Ratio Solutions: Another method of expressing concentration is a ratio solution . A 1:1000 merthiolate solution contains 1 g in 1000 ml solution. A 1:10.000 $KMnO_4$ solution contains 1 g in 10.000 ml solution.

Molar Solutions (molarity): *Moles (gram molecular weights) of solute in 1 liter of solution*. Molar used the symbol (M). A 1 molar (1M) solution of glucose ($C_6H_{12}O_6$) will contain 1 mol glucose (180 g) in 1L solution. (M = moles of solute per 1 liter of solution)

$$M = \frac{\text{Moles of solute}}{\text{Liters of solution}} = \frac{\text{Weight of solute}}{\text{Molecular weight of solute}} \text{ X } \frac{1000}{\text{Volume of solution (ml)}}$$

Ex3: Prepare 3L of 2M (2molar) KCl (molecular weight 74.5).
M = wt/m.wt X 1000/vol. of solution (ml)
2 = wt/74.5 X 1000/3000 = 447 g KCl

Ex4: Prepare 500 ml 0.1 M NaOH (m.wt, 40).
M = wt/ m.wt X 1000/vol. of solution (ml)

0.1 = wt/40 X 1000/500 = 2 g NaOH (Thus, we should dissolve 2 g NaOH in water and dilute to 500 ml.)

Ex5: How many grams of glucose are present in 0.5L of 2.0 M of glucose solution?

2.0 M = wt/180 X 1000/500 (ml) = 180 g glucose

Ex6: What is the molarity (molar concentration) of sodium carbonate (m.wt, 106), in which the % w/v 0.85.?
%w/v is the number of grams of solute in 100 ml of solution.
$M = 0.85/106 \text{ X } 1000/100 = 0.08\ M$

Molality: *is the number of moles of solute per 1000 grams of solvent (water).*The **molal** contains 1 g molecular weight (mole) dissolve in 1000 g of water.

$$\text{Molality } (m) = \text{moles of solute/kg of solvent}$$

Ex7: what are the molality of KOH solution, if dissolve 23 g of KOH in 500 g water.

Normal solution: *Gram equivalent weights of solute in 1 liter of solution*_(symbol *N*). A 1 normal (1*N*) solution contains one gram equivalent weight of solute per liter of solution. **The gram equivalent weight is represent the molecular weight of atoms or molecules to the *valence* of atoms or molecules**.

$$\text{Equivalent weight (g/Eq)} = \frac{\text{Atomic weight}}{\text{Number of equivalents (valence)}} \qquad \textit{for atom}$$

$$\text{Equivalent weight (g/Eq)} = \frac{\text{Molecular weight (g/mole)}}{\text{Equivalent/mole}} \qquad \textit{for molecules}$$

The valence (oxidation number) for hydrogen 1; potassium K, 1; sodium Na, 1; fluorine F, 1; calcium Ca, 2; magnesium Mg, 2; oxygen O, 2; aluminum Al, 3;….and so on.
The equivalent weight of F, H, K, and Na; is identical to the molecular weight, according to the upper equation for atom. Therefore, the valence for Ca, Mg, and O, are 2 and its equivalent weight one half of its atomic weight, aluminum is 3 and its equivalent weight is one third of its atomic weight, or 27/3 = 9 g/Eq.

Equivalent weight of acid: *The gram equivalent weight of an acid can be calculated by dividing the weight of 1 mol of that acid by the number of replaceable hydrogen that it contains*. For example, hydrochloric acid HCl, contains one replaceable H. the grams equivalent weight is the weight of 1 mol (36.5 g) divided by 1. The gram equivalent weight of sulfuric acid H_2SO_4, is the weight of 1 mol of H_2SO_4 (98 g) divided by 2, or 49 g.

Equivalent weight of base: *The gram equivalent weight of a base can be calculated by dividing the weight of 1 mol of that base by the number of* OH^- *groups it contains*. The gram equivalent weight of sodium hydroxide (NaOH), is the weight of 1 mol of NaOH (40 g) divided by 1, or 40 g. the gram equivalent of calcium hydroxide $Ca(OH)_2$ (74 g), is the weight of 1 mol of $Ca(OH)_2$ divided by 2, or 37 g.

Equivalent weight of salt: The equivalent weight of sodium chloride (NaCl) is identical to its molecular weight, 58.5 g/Eq. that is, the equivalent weights of NaCl is the sum of the equivalent weights of sodium (23 g) and chlorine (35.5 g), or 58.5 g/Eq. The g/Eq of NaCl is identical to its molecular weight, 58.5 g, because the valence of sodium and chlorine is each1in the compound. The Eq of Na_2CO_3 is numerically half of its molecular weight. The valence of the carbonate ion, CO_3^{2-}, is 2 and its equivalent weight is 60/2 = 30 g/Eq. although the valence of sodium is 1, two atoms are present in Na_2CO_3. Providing a weight of 2 x 23 g = 46 g ; its equivalent weight is one half of this, or 23 g/Eq. the equivalent weight of sodium carbonate is therefore 30 + 23 = 53 g, which is one the molecular weight.

Eq for salt = m. wt of salt / oxidation of salt

Eq for reducing and oxidizing agent = m.wt / no. of electrons gained or lost

$$N = \frac{\text{Weight of solute}}{\text{Equivalent weight}} \times \frac{1000}{\text{Volume of solution (ml)}}$$

Ex8: Prepare 2L of 1.5 *N* H_2SO_4.

N = wt/Eq. wt X 1000/vol. (ml)

Equivalent weight of H_2SO_4 = 98 / 2 = 49 g/Eq

1.5 = wt/49 X 1000/ 2000 = 147 g dissolve it in water, and dilute to a total of 2 L.

Ex9: Prepare 100 ml of 0.2 *N* NaOH (Na:23 ; O: 16; H: 1).
Molecular weight of sodium hydroxide = 23 + 16 + 1 = 40
Equivalent weight (g/Eq) for NaOH = m. wt/equivalent = 40/1 = 40
N = wt/equivalent X 1000/vol. (ml)
0.2 = wt/40 X 1000/100
Wt = 0.8 g NaOH thus we should dissolve 0.8 g NaOH in water and dilute to 100 ml.

Ex12: Prepare 250 ml of 0.1 *N* sodium carbonate solution. (Na:23; C: 12; O: 16) Results: wt: 1.325 gm.

Ex13: Dissolve 5.3 gm of sodium carbonate in water, then complete the volume of the solution to ¼ liter. Compute molarity of solution. (Na: 23; C: 12; O: 16). Results: 0.2 mol/liter.

Ex14: Compute the molarity of 100 milliliter of solution of 0.001 mol of KOH.

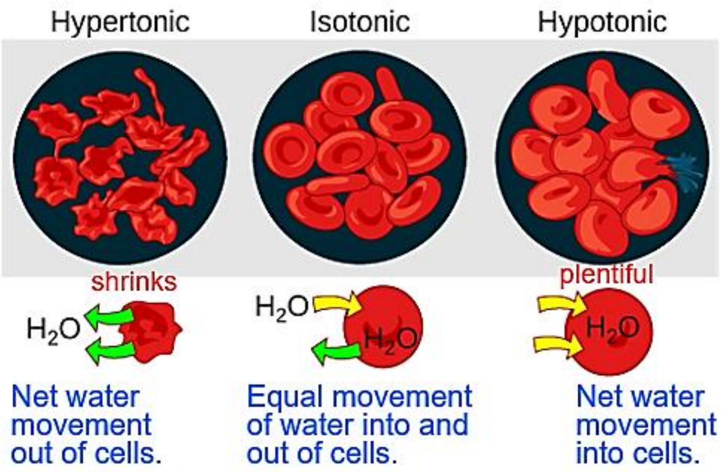
M = moles/liter = 0.001/ (100/1000) = 0.01 *M*

Some definitions:

Diffusion: The movement of solute into a solvent or through a solution.
Osmosis: The flow of solvent through a semipermeable membrane.
Osmotic pressure: The pressure exerted during osmosis. Osmotic pressure is expressed in terms of the **osmolarity** of the solution.
Isotonic solution: Solution has the same salt concentration as the salt concentration of blood and is used for transfusion.

Hypotonic solution: Solution has a solute concentration less than that sodium chloride of the blood. If injected into the bloodstream, a **hypotonic solution** can cause hemolysis- the bursting RBC.

Hypertonic solution: Solution has a solute concentration greater than that salt concentration of the blood. If injected into the bloodstream, a **hypertonic solution** may cause crenation or plasmolysis-the shrinking of the RBC.



Osmotic pressure changes the shape of red blood cells in hypertonic, isotonic, and hypotonic solutions.

Questions and Problems:

A. Preparation of Liquid - Liquid Solutions

General method for preparation of diluted acid solution

The normality of concentrated acid can be calculated from the information written on the bottle (percentage % w/w , specific gravity , equivalent weight) according to the equation:-

$$N = \frac{\% \times sp.gr \times 1000}{eq.wt}$$

To calculate the volume of conc. acid that should be taken (diluted) to prepare a specific volume of diluted acid in the selected normality we have to use the equation below:

$$N_1 \times V_1 = N_2 \times V_2$$

of conc. acid of dilute acid

Notes

1.Dilution is usually carried out by a factor of ten exactly.

2.Density and Specific Gravity

Density = mass/volume (The units are usually grams/mL).

Specific Gravity = (mass of substance)/(mass of equal volume water)

= (Density of substance)/Density of water)

Note that the temperature must be specified for specific gravity. Specific gravity is a unit less ratio (i.e., it doesn't matter what the units are so long the same units are used for the substance and water). **Specific gravity** is more often used in commerce and commercial reagent labeling than **density**.

Procedure

Transfer (x) mL of concentrated acid into volumetric flask (x) mL using cylinder or pipette, complete to the mark with distilled water and mix well.

A. *Preparation of Approximately 0.1 N Hydrochloric acid*

For HCl

$\% = 37\%$ $Sp.gr = 1.18$ $eq.wt = 36.5$

So that

Normality = 1.18 × 0.37 × 1000 / 36.5 = 11.96 N ~ 12N

To calculate the volume of conc. HCl that should be taken to prepare (250) mL of (0.1) N HCl

$$12N \times V_1 = 0.1N \times 250\ mL$$

So

V_1 = 2.08 mL should be diluted with distilled water in 250 mL volumetric flask to obtain 0.1N HCl.

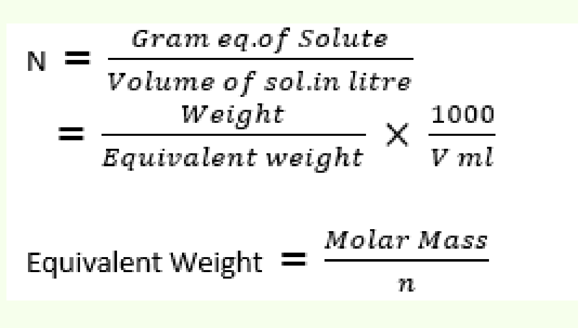
B. Preparation of Solid - Liquid Solutions

We can expressed the concentration of solution prepared by dissolving a specific amount of solid substance in a specific volume of solution, in two ways **formal concentration**, and **normal concentration**.

$$\mathbf{M} = \frac{\mathbf{wt\ (g)}}{\mathbf{M.wt\ (\frac{g}{mol})}} \times \frac{\mathbf{1000}}{\mathbf{V\ (mL)}} \qquad normality = \frac{no.of\ equivalents}{1liter\ of\ solution}$$

To calculate the weight need to prepare any one of these concentration in specific volume of solvent we use the equations:

The normality of a solution is the gram equivalent weight of a solute per liter of solution. It may also be called the **equivalent concentration**. It is indicated using the symbol N.



$$N = \frac{Gram\ eq.of\ Solute}{Volume\ of\ sol.in\ litre}$$

$$= \frac{Weight}{Equivalent\ weight} \times \frac{1000}{V\ ml}$$

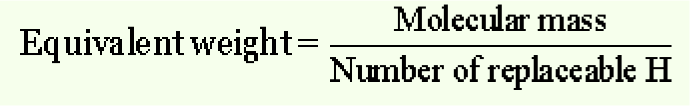
$$\text{Equivalent Weight} = \frac{Molar\ Mass}{n}$$

1-Acids :

The molecular formula of sulfuric acid is H_2SO_4.

Its molecular mass is =(1×2)+32+(16×4)=2+32+64=98

The expression for the equivalent weight of an acid is as given below.



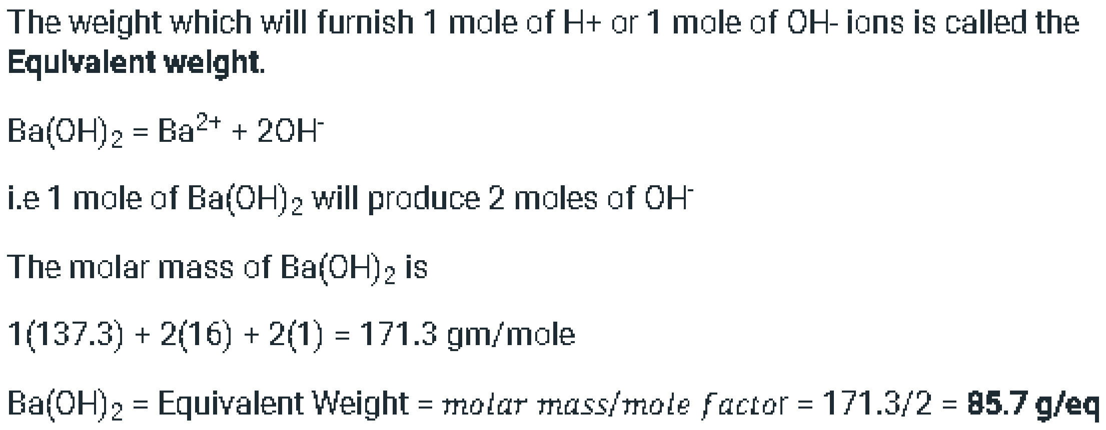
$$\text{Equivalent weight} = \frac{\text{Molecular mass}}{\text{Number of replaceable H}}$$

sulfuric acid contains two replaceable hydrogens.

Substitute values in the above expression.

Equivalent weight =98/2=49

2-Bases :



The weight which will furnish 1 mole of H+ or 1 mole of OH- ions is called the **Equivalent weight**.

$Ba(OH)_2 = Ba^{2+} + 2OH^-$

i.e 1 mole of $Ba(OH)_2$ will produce 2 moles of OH^-

The molar mass of $Ba(OH)_2$ is

1(137.3) + 2(16) + 2(1) = 171.3 gm/mole

$Ba(OH)_2$ = Equivalent Weight = $molar\ mass/mole\ factor$ = 171.3/2 = **85.7 g/eq**

3- Salts:

$$\text{Equivalent weight of salt} = \frac{\text{Molecular weight of salt}}{\text{Charge present on ionic form}}$$

$$\text{Molecular weight of } Na_2CO_3 = 106$$

$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$$

$$\text{Charge} = 2$$

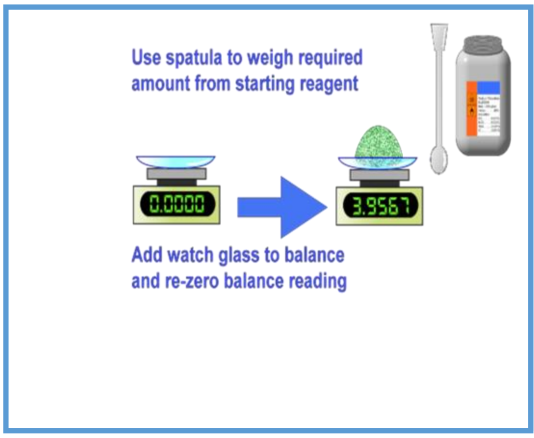
$$\text{Eq. Wt.} = \frac{106}{2} = 53 \text{ g/eq}$$

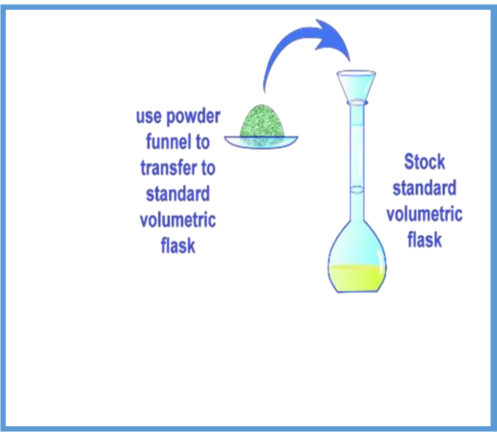
$$\mathbf{wt} = \frac{\mathbf{M} \times \boldsymbol{Mwt} \times \mathbf{V}(\boldsymbol{mL})}{\mathbf{1000}}$$ For formal concentration

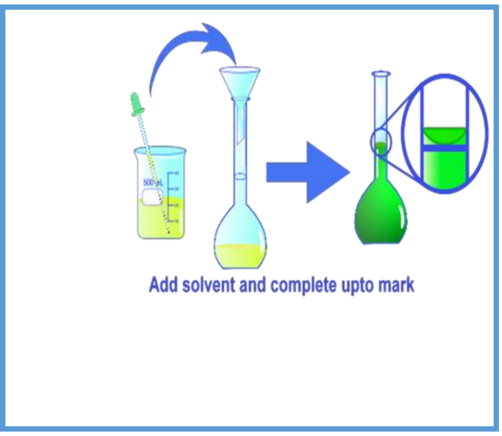
$$Weight = \frac{eq.wt \times N \times v(mL)}{1000}$$ For normal concentration

Procedure

Dissolve (x) gm of solid substance into a small beaker with distilled water and transfer the solution after dissolution into the volumetric flask (x) mL , washing the beaker many times and adding the washing into the volumetric flask for quantitative transferring of the solution, complete to the mark and mix well.





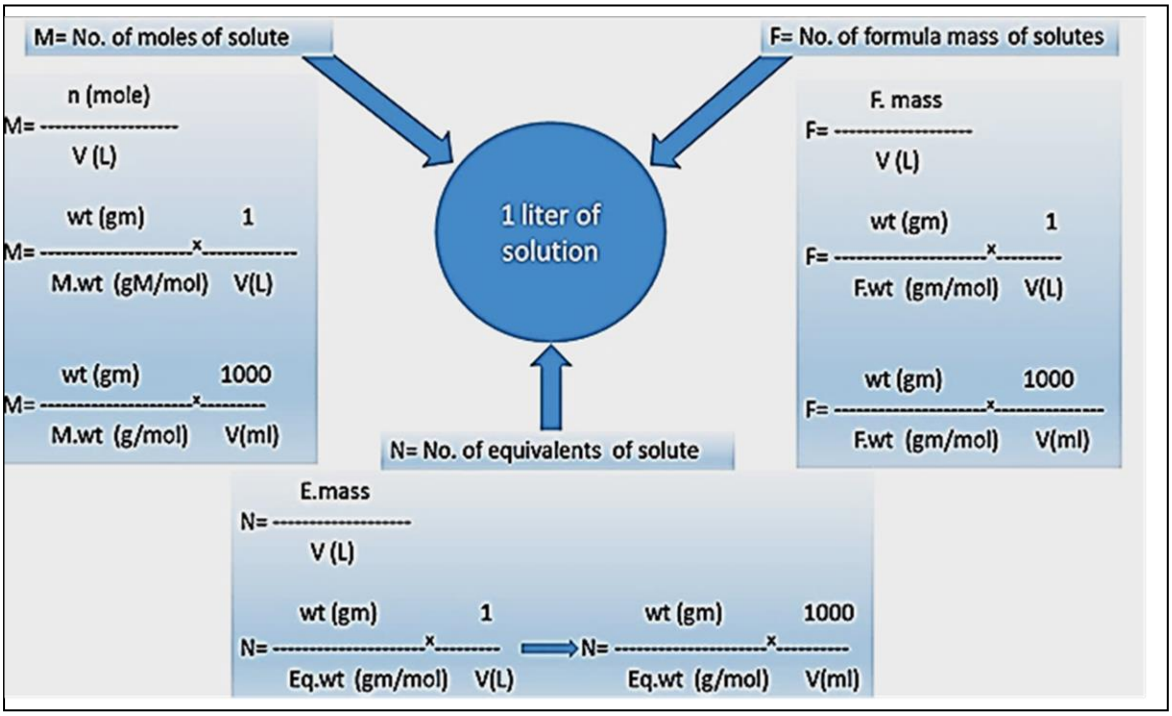


Methods of Expressing the Concentration of a Solution

The concentration of a solution can be expresses in a number of ways. The important methods are:

1- Molarity: is the number of moles of a solute dissolved in a liter of solution.

2- Normality : is the number of equivalents of a solute dissolved in a liter of solution.



Q/ what are the molarity of (125 ml) solution containing of 0.050 moles of HCl ?

A/ before anything : convert ml to L

125ml/1000 = 0.125 L

M= n(mole) / V(L)

M= 0.050 / 0.125= 0.40 mol/L

Q/ you dissolve 152.5 gm of $CuCl_2$ in water to make solution with final volume of 2.25 L what is the molarity ?

A/ M.wt ($CuCl_2$)= 63.55 + (2×35.44)= 134.45 gm/mol

n= wt/M.wt

n=152.5 / 134.45= 1.134 mol M= n/v

(L) = 1.134 / 2.25

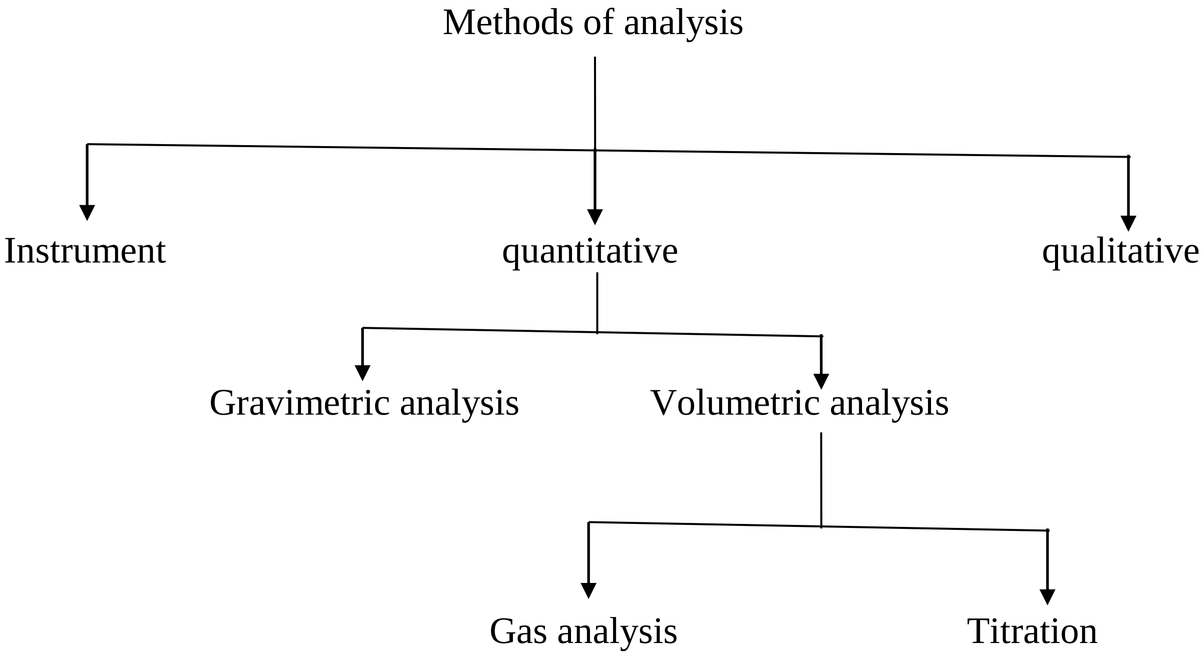
M= 0.504 mol/L

Chapter 4 - *Methods of Analysis*

CHAPTER OUTLINE: The student will be able to:-

1. Know that we mean by Gravimetric analysis.
2. Know that we mean by precipitation reaction.
3. Know the types of indicators.

Methods of analysis:



Volumetric (Titrimetric) Analysis:

General principles: in titrimetric analysis volumetrically measures the amount of reagent, often called a titrant, required to complete a chemical reaction with the analyte. A generic chemical reaction for titrimetric analysis is

$$aA + tT \longrightarrow Products$$

where (*a*) moles of analyte *A* contained in the sample reacts with(*t*) moles of the titrant T in the titrant solution.

The raction is generally carried out in a flask containing the the liquid or dissolved sample. Titrant solution is volumetrically delivered to the reaction flask using a burette. Delivery of the titrant is called a titration. The titration is complete when sufficient titrant has been added with all the analyte. this is called equivalent point.

An indicator is often added to the reaction flask to signal when all of the analyte has reacted. The titrant volume where the signal is generated is called the end point. The equivalence and end points are rarely the same.

Successful titrimetric analysis: A few rules of thumb for designing a successful titration are:

1. The titrant should either be a standard or should be standardized.
2. The reaction should proceed to a stable and well defined equivalence point.
3. The equivalence point must be able to be detected.
4. The titrant's and sample's volume or mass must be accurately known.
5. The reaction must proceed by a definite chemistry. There should be complicating side reactions.
6. The reaction should be nearly complete at the equivalence point . in other words, chemical equilibrium favors products.
7. The reaction rate should be fast enough to be practical.

Volumetric analysis: any method of quantitative chemical analysis in which the amount of a substance is determined by measuring the volume that is occupied or, in broader usage, the volume of a second substance that combines with the first is known proportions, more corrected called titrimetric analysis.

The technique of volumetric analysis uses the reaction between a solution of known concentration with a solution of unknown concentration. The most common reaction are between acids and bases. Although many other reactions can be used as the basis of a volumetric method.

Titration (titrimtry): method of quantitative chemical analysis that is used to determine the unknown concentration of an identified analyte since volume measurements play a key role in titration. It is also known as *volumetric analysis*. A reagent called the *titrant* is prepared as a standard solution. A known concentration and volume of titrant reacts with a solution of *analyte* to determine concentration.

Procedure: A typical titration begins with a beaker or conical flask containing a very precise volume of the analyte and a small amount of indicator placed underneath a calibrated burette or chemistry pipe ting syringe containing the titrant small volumes of the titrant are then added to the analyte and indicator until the indicator changes, reflecting arrival at the endpoint of the titration.

Depending on the endpoint desired, single drops or less than a single drop of the titrant can make the difference between a permanent and temporary change in the indicator. When the endpoint of the reaction is reached, the volume of reactant consumed is measured and used to calculate the concentration of analyte by:

$$M_1 \times V_1 = M_2 \times V_2$$

Types of titration: there are many types of titrations with different procedures and goals. The most common types of qualitative titrations are acid-base titration and redox titrarion. The types of titration are:

Acid-base titration; Redox-titration; Gas phase titration; complexometric titration; Zeta potential titration; Assay.

Acid-base titration: depends on the neutralization between an acid and a base when mixed in solution. In addition to the sample an appropriate indicator is added to the titration chamber, reflecting the pH range of the equivalence point. The acid-base indicator indicates the endpoint of the titration by changing color. The endpoint and the equivalence point are not exactly the same because the equivalence point is determined by the stoichiometry of the reaction while the endpoint is just the color change from the indicator. Thus, a careful selection of the indicator will reduce the indicator error. For example, if the equivalence point is at a pH of 8.4, then the phenolphthalein indicator would be used instead of Alizarin yellow because phenolphthalein would reduce the indicator error. When the reagents are a weak acid and a weak base, a *pH meter* or a conductance meter are used.

Indicator	Color on acidic side	Range of color change	Color on basic side
Methyl violet	Yellow	0.0-1.6	Violet
Bromophenol blue	Yellow	3.0-4.6	Blue
Methyl orange	Red	3.1-4.4	Yellow
Methyl red	Red	4.4-6.3	Yellow
Litmus	Red	5.0-8.0	Blue
Bromothymol	Yellow	6.0-7.6	Blue

blue			
Phenolphthalein	Colorless	8.3-10.0	Pink
Alizarin yellow	Yellow	10.1-12.0	Red

Methods of acid-base titration: Before starting the titration a suitable pH indicator must be chosen. The equivalence point of the reaction, the point at which equivalent amounts of the reactants have reacted, will have a pH dependent on the relative strengths of the acid and base used. The pH of the equivalence point can be estimated using the following rules

1. *A strong acid will react with a strong base to form a neutral (pH = 7) solution*. Titrate 25 ml portions of the approximately 0.1 N solution of sodium hydroxide with the approximately 0.1 N hydrochloric acid. Use methyl orange, methyl red, bromothymol blue and phenolphthalein as indicators.
2. *A strong acid will react with a weak base to form an acidic (pH < 7) solution*. Titrate 25 ml portions of the approximately 0.1 N solution of ammonia with the standard 0.1 N hydrochloric acid. Use methyl red and phenolphthalein as indicators.
3. *A weak acid will react with a strong base to form a basic (pH > 7) solution. A strong acid will react with a weak base to form an acidic (pH < 7) solution*. Titrate 25 ml portions of the approximately 0.1 N solution of acetic acid with the standard solution of 0.1 N sodium hydroxide. Use methyl red and phenolphthalein as indicators.
4. *A weak acid will react with a weak base to form a neutral (pH = 7) solution*. Titrate 25 ml portions of the approximately 0.1 N solution of ammonia with the approximately 0.1 N solution of acetic acid. In the presence of using 2-3 drops of screened neutral red-methylene blue indicator. The color change at pH 7.0 is from green to blue violet. The titration must be carried out carefully, especially near the endpoint.

Redox titration: Redox titration are based on a reduction-oxidation reaction_between an oxidizing agent and a reducing agent. A potentiometer_or redox indicator_is usually used to determine the endpoint of the titration.

Definition of various terms used in volumetric analysis:

Volumetric analysis: is to determine the volume of a solution of know concentration require to react quantitavely with a solution of substance to be analyzed.
Titrate: substance to be analyzed or to be determined.
Titrant: reagent of know concentration.
Titration: the process of determining the volume.
Equivalence point: the point at which complete chemical reaction takes place and equivalent quantity of reagent is used.
Endpoint: the point at which the indicator changes its color.
Indicator: auxiliary agents used to determine the end point of titration.

Importance of volumetric analysis:

1. High precision is obtained.
2. Simple apparatus is required.
3. Easy process and fast result.
4. Different methods for different types of substance.

Gravimetric analysis: which by definition is based upon the measurement of mass, can be generalized into two types; precipitation and volatilization.

The quantitative determination of a substance by the precipitation method of gravimetric analysis *involves isolation of an ion in solution by a precipitation reaction*,

1. Filtering.
2. washing the precipitate free of contaminants.
3. Conversion of the precipitate to a product of known composition.
4. Finely weighing the precipitate and determining its mass by difference. From the mass and known composition of the precipitate, the amount of the original ion can be determined.

Calculation: The weight of the precipitate multiplied by a factor known as the gravimetric conversion factor *gives the amount of the desired constituent in the precipitate*. The factor can be easily calculated from the atomic or molecular weights of the constituent sought and the weighing form.

Thus, if the chloride content of sample of sodium chloride were determined gravimetrically as silver chloride, the percentage of chloride would be represented by

$$\boxed{\% \text{ Cl} = \frac{\text{Wt. of AgCl x factor x 100}}{\text{Wt. of sample}}}$$

$$\boxed{\text{Factor} = \frac{\text{Atomic weight of Cl (or ion)}}{\text{Mol. Wt. of AgCl (or sample)}}}$$

$$\boxed{\text{Percent of Cl (or ion)} = \text{factor x 100} = 24.737}$$

$$\boxed{\% \text{ of ion} = \frac{\text{Wt. of precipitate (g)}}{\text{Wt. of sample (g)}} \text{ x log percent}}$$

The successful determination the following criteria must be met: The desired substance must be completely precipitated. In most determinations the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the " common ion " effect, this further reduces the solubility of the precipitate. When Cl^- is precipitated out by addition of Ag^+.

$$Ag + Cl^- \longrightarrow AgCl$$

The low solubility of AgCl is reduced still further by the excess of Ag^+ which is added, pushing the equilibrium to the right. We can further decrease the solubility by decreasing the temperature of the solution by using an ice bath. The weight form should be of known composition. The product should be "pure" and easily filtered. it is usually difficult to obtain a product which is "pure", i.e. on which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.

Definition of gravimetric analysis (GA): is a part of quantitative analysis is defines as the process of weighing an element or a definite compound of the element in as pure form as possible. Methods used in GA precipitation, filtration, washing, drying or ignition, and weighing.

Precipitation method: is a process of weighing an element in form of precipitates which is separated by filtration from solution.

Factors affecting on precipitation method:

1. Precipitates must be free from soluble impurities.
2. Precipitate must be insoluble in solution.
3. Precipitate must be readily separated from the solution by filtration.
4. Precipitation must be convertible into a pure compound by ignition or by simple evaporation.

Example: GA of a sulphate or halides, iron, aluminum, magnesium, calcium, sodium, potassium, nickel, phosphorus, etc.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$
$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + NaCl$$

Photometric analysis: *The set of methods of quantitative analysis based on the relationship between the concentration of a substance in a solution or gas and the absorption of radiation*. For monochromatic radiation, this relationship is expressed by the **Bouguer-Lambert-Beer** law. *Photometric analysis* includes measurements in the visible, ultraviolet, and infrared regions of spectrum. It generally involves comparison of the intensity of radiation passing through a sample of the material being analyzed with the initial intensity or the intensity of a reference sample. The method of photometric analysis that uses visible light is called *colorimetry*. Photometric analysis in which the intensity of the monochromatic components of transmitted radiation are scanned is called spectrophotometry. Methods similar to photometric analysis include atomic absorption analysis, turbidimetric analysis, and nephelometric analysis.

Colorimetric analysis: is defined as the color of a solution containing the constituent to be determined against the color of standard solutions containing known quantities of the constituent. (Used visible light)

Absorption spectrophotometry: when radiation in the infrared, visible or ultraviolet region of the electromagnetic spectrum passed through a solution and the amount of radiation absorbed in a particular waveband is measured by instruments, the technique is generally known as "absorption spectrophotometry".

The both techniques are branches of photometric analysis, which is based on the measurement of radiation.

Absorption spectrophotometry is usually subdivided according to the wavelength of the radiation used:
Infrared spectrophotometer for radiation of 1 to 15 µm (micrometer),
visible spectrophotometer for radiation of 350 to 800 nm (nanometer),
ultraviolet spectrophotometer for radiation of 200 to 350 nm.
[10^3 nm = 1 µm = 10^{-6} meter]; [1 Angstrom (Å) = 0.1 nm].
A large number of inorganic and organic materials may be determined by photometric analysis. The inorganic quantitative analysis is based on the elemental analysis [determines the compositions of elements (ions)], and functional group analysis [determines the content of functional (reactive) atoms or groups in the object (organic material) being analyzed].

Ex1: A 0.25 g sample of pure NaCl is titrated by 40.0 ml $AgNO_3$ solution. What is the Cl^- titer of the solution?
One ml $AgNO_3$ titration X 250 mg NaCl / 40 ml $AgNO_3$ = 6.250 mg
In 6.250 mg NaCl (m. wt = 58.46)
Therefore, 6.250 X 35.46 / 58.46 = 3.971 mg (Cl^- m. wt = 35.46)
So, the Cl^- titer is 3.971 mg / ml

Ex2: A 0.300 g sample is analyzed by titration with 45.0 ml of the $AgNO_3$ solution. What is the percent % of Cl^- in the sample?
Weight Cl^- in milligrams = 45.0 x 3.791 mg = 170.6 mg . ml
% Cl^- = 170.6 / 300.0 x 100 = 56.87 % of Cl^-

- THIS LECTURE JUST FOR PATHOLOGICAL ANALYSES DEPARTMENT.

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1. Quantitative inorganic analysis, Belcher & Nutten's, 3th ed., 1970.

Chapter 4: *Oxidation-Reduction*

CHAPTER OUTLINE: The student will be able to:-

Oxidation-reduction
Oxidizing agents & reducing agents
Importance of oxidation-reduction: *cleaner Effects, Effects on hair protein, and Stain removal*

Oxidation: May be defined as "a loss of electrons". Consider the electron-dot structures in reaction 4-1. The sodium atom has one outer electron. When the sodium atom loses this one electron, it forms a sodium ion with a +1 charge: **This loss of an electron is defined as oxidation**. Therefore, the sodium atom was oxidized.

$$Na\bullet + \bullet Cl: \longrightarrow Na^+ + :\ddot{\underset{..}{Cl}}:^- \qquad (4\text{-}1)$$

A second definition of **oxidation** states that it is **an increase in oxidation number**. Consider reaction 4-2.

$$2Na + Cl_2 \longrightarrow 2NaCl \qquad (4\text{-}2)$$

An uncombined element has an oxidation number of zero. The oxidation number of sodium in sodium chloride (NaCl) is +1 and that of chlorine -1. Therefore, reaction 4-2 may be written as follows.

$$\overset{0}{2Na} + \overset{0}{Cl_2} \longrightarrow \overset{+1}{2Na} + \overset{-1}{2Cl}$$

The sodium has changed in oxidation number from zero to +1, This is oxidation. The sodium atom was oxidized. The cells in the body burn glucose producing carbon dioxide (CO_2), water, and energy.

$$\underset{\text{glucose}}{\overset{0}{C_6H_{12}O_6}} + \overset{0}{6O_2} \longrightarrow \overset{+4}{6CO_2} + 6H_2O + \overset{-2}{\text{energy}}$$

The oxidation number of each carbon atom in glucose is zero. The oxidation number of the carbon atom in carbon dioxide is +4. † Therefore, the carbon atom increased in oxidation number. A gain in oxidation number is oxidation; therefore, the carbon atom in glucose was oxidized, or it can be said that the glucose, which contain the carbon atom, was oxidized.

A third definition of **oxidation** is “**addition of oxygen**.” Consider reaction 4-3, which involves the oxidation of formaldehyde to formic acid.

$$\underset{\text{Formaldehyde}}{HCHO} + [O] \longrightarrow \underset{\text{formic acid}}{HCOOH} \qquad (4\text{-}3)$$

Note that this reaction involves the addition of oxygen.

A fourth definition of **oxidation** involves the “**removal of hydrogen**” in reaction 4-4

$$\underset{\text{ethanol}}{CH_3CH_2OH} + [O] \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O \qquad (4\text{-}4)$$

The following oxidation reactions take place in the body.

$$\text{Carbohydrate} + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$$

$$\text{fat} + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$$

$$\text{protein} + O_2 \longrightarrow CO_2 + H_2O + \text{urea} + \text{energy}$$

Thus, oxidation may be defined as

1. A loss of electrons
2. An increase in oxidation number
3. A gain of oxygen
4. A loss of hydrogen

Reduction: reduction is the opposite of oxidation;

1. A gain of electrons
2. A decrease in oxidation number
3. A loss of oxygen
4. A gain of hydrogen

$$\underset{\text{acetic acid}}{CH_3COOH} + H_2 \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + H_2O \qquad (4\text{-}5)$$

$$\underset{\text{acetone}}{CH_3COCH_3} + H_2 \longrightarrow \underset{\text{isopropyl alcohol}}{CH_3CH(OH)CH_3} \qquad (4\text{-}6)$$

- Oxidation is when there is an increase in oxidation number; Reduction is when there is a decrease in oxidation number.

Oxidizing agents & Reducing agents:

Reducing agent- The substance that causes the reduction of an element or compound.
Oxidizing agent- The substance that causes the oxidation of an element or compound.

$$\overset{0}{H_2} + \overset{+2\ -2}{PbO} \longrightarrow \overset{0}{Pb} + \overset{2(+1)-2}{H_2O}$$

$$\underset{\substack{\text{oxidized}\\ \text{reducing agent}}}{H_2} + \underset{\substack{\text{reduced}\\ \text{oxidizing agent}}}{PbO} \longrightarrow Pb + H_2O$$

Oxidation and reduction reactions produce the energy the body needs to carry out its normal functions. Oxidation-reduction in the body involves either oxygen or hydrogen, or both.

Enzymes involved in oxidation-reduction reactions in the body is called **oxidoreductases**. Many of these enzymes are present in the mitochondria. These enzymes are responsible for the production of heat and energy.

Importance of oxidation-reduction:

Antiseptic effects- Because they are oxidizing agents, many antiseptics have the property of killing bacteria. Among these is *chlorine*, which oxidizes organic matter and bacteria and so is used in the treatment of water to make it potable. *Calciumhypochlorite* $Ca(OCl)_2$, another commonly used oxidizing agent and bleaching powder, is used as disinfectant for clothes and hospital beds. Tab. 4-1 lists some of the common antiseptics that are oxidizing agents.

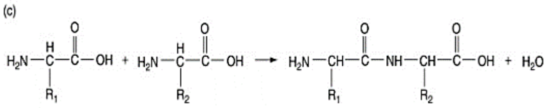
Table 4-1, Antiseptic agents

Formula	Name	Use

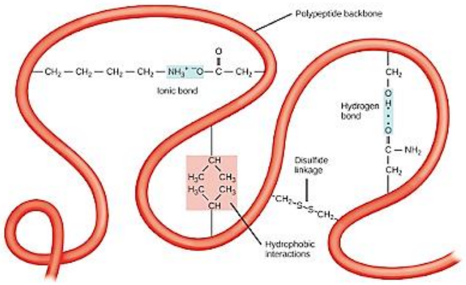
$3\%H_2O_2$	Hydrogen peroxide	More cuts and scratches
$KMnO_4$	Potassium permanganate	Treatment of infection in urethra & bladder
$KClO_3$	Potassium chlorate	Treatment of sore throat
I_2 in H_2O	Lugol's solution	Treatment of minor cuts
NaOCl	Sodium hypochlorite (Dakin's solution)	Treatment of wounds

Formaldehyde and sulfur dioxide are two reducing agents used in disinfecting rooms formerly occupied by patients with contagious diseases.

Effects on hair protein- Oxidizing and reducing agents denature protein by affecting the disulfide bonds of the amino acid cysteine.



$$H_2N-\underset{R_1}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH + H_2N-\underset{R_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH \rightarrow H_2N-\underset{R_1}{CH}-\overset{O}{\overset{\|}{C}}-NH-\underset{R_2}{CH}-\overset{O}{\overset{\|}{C}}-OH + H_2O$$



Stain removal-Oxidizing and reducing agents are used to remove most stains that cannot otherwise be removed. Common stain removers and indicates where they may be used safely (H_2O_2, $KMnO_4$, and sodium hypochlorite, NaOCl;) are oxidizing agent. ($Na_2S_2O_3$), sodium thiosulfate and oxalic acid $[COOH]_2$ are reducing agent.

Redox Reactions in Biology

What is the purpose of redox reactions in the cell?

Many biological processes involve redox reactions, such as in cellular respiration and photosynthesis.

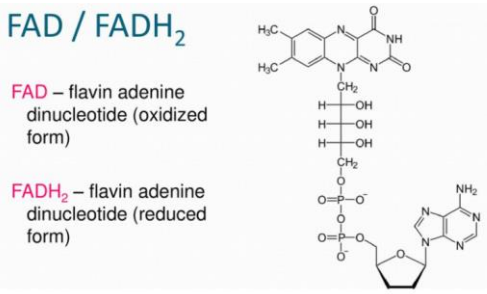
Cellular respiration

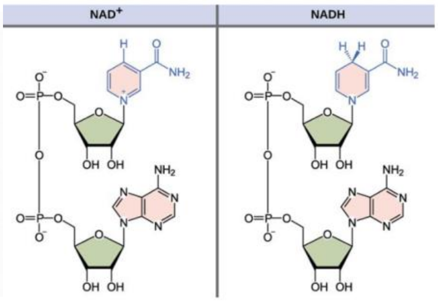
Cellular respiration ($C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$) is the oxidation

of glucose into carbon dioxide (CO2) and reduction of oxygen (O2) to water (H2O).

The method of cellular respiration redox is related to the reduction and oxidation of NAD+ into NADH and vice versa. Below is a schematic diagram of cellular respiration. schematic diagram of cellular respiration.

(NADH) nicotinamide adenine dinucleotide





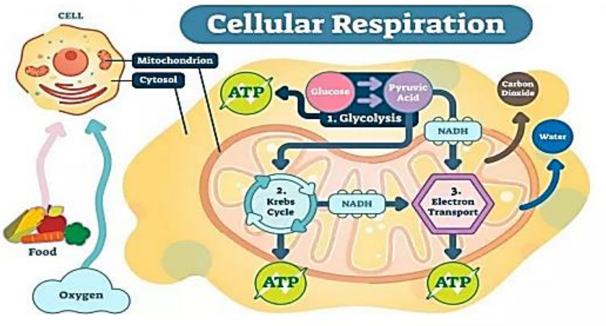


Figure 1: Schematic diagram of aerobic respiration as a form of cellular

Respiration. There are many instances where in redox occurs in this biological process. An example is the oxidation of glucose during glycolysis where NAD+ is reduced, thereby, producing NADH. This is is reduced, thereby, producing NADH. This is also, what occurs involving the other electron carriers, such as FAD producing FADH2. And the steps of the citric acid cycle are, in fact, a series of redox reactions.

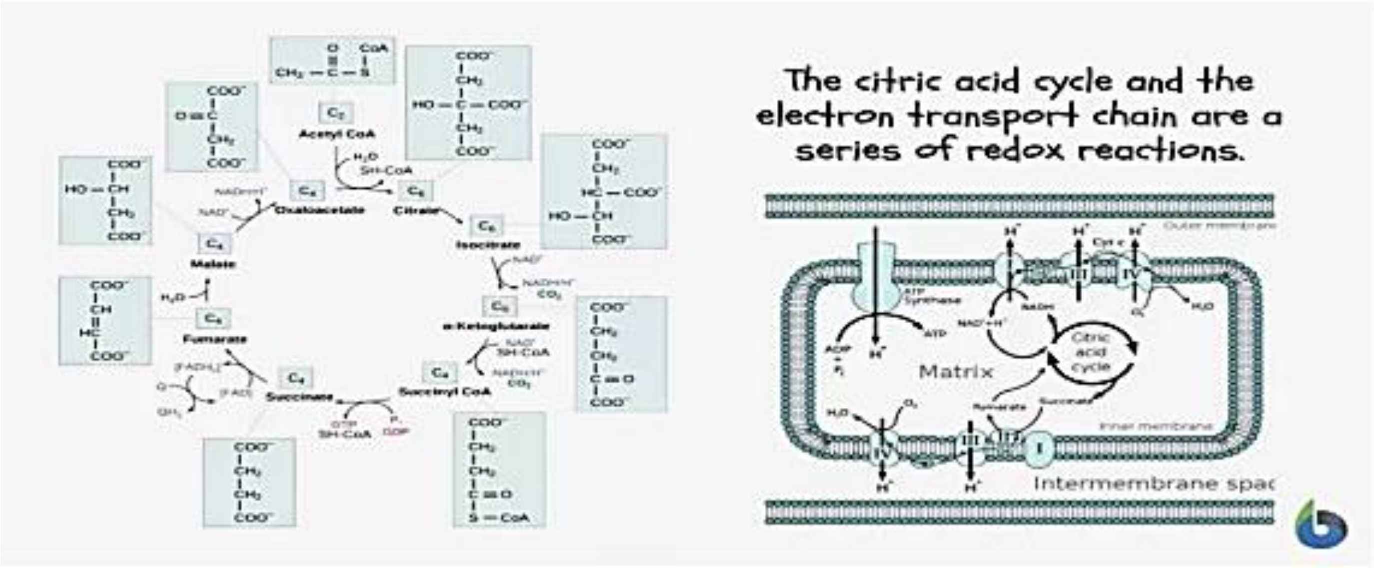


Figure 2: Citric acid cycle (left) and electron transport chain (right) are

shown to illustrate redox reactions. Photosynthesis In redox reactions in photosynthesis

($6\ CO_2 + 6\ H_2O$ + light energy → $C_6H_{12}O_6 + 6\ O_2$),

Carbon dioxide is reduced into sugar and water oxidation gives molecular oxygen. The number of electrons in oxygen is 8. Although cellular respiration and photosynthesis appear like opposite reactions, these two processes are not reverse of each other.

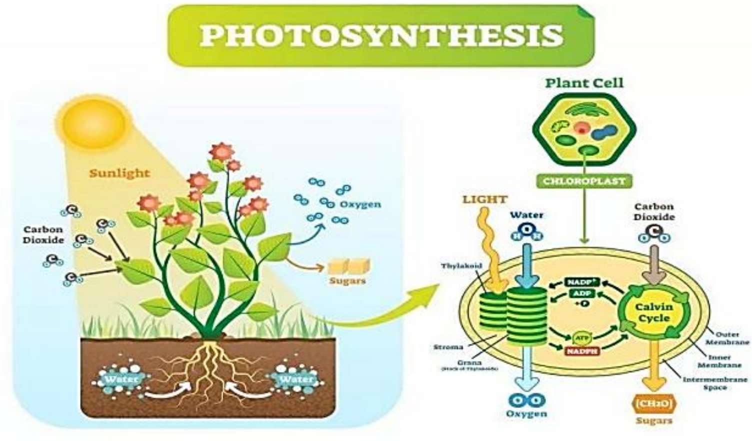


Figure 3: Photosynthesis involves the losing and gaining of electrons, which unlike in cellular respiration, is driven by light (photon)

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1. Dickson, T. R. *introduction to chemistry*, 4th ed. John Wiley & Sons, Int., New York, 1983, chapter 13.
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3. Chemistry for the Health Sciences, George, 5th ed., 1985.

Chapter 5 - *Statistical Treatment of Analytical Data*

CHAPTER OUTLINE: The student will be able to: -

1. **The types of errors**
2. **The definition of accuracy, mean value, precision, deviation, standard deviation, absolute error, and relative error.**
3. **The types of rejection of measurement result.**

Statistical: Statistical techniques must be never applied unless adequate data have been collected. Nevertheless the results obtained in the investigation of a new method should be set out in such a way that another chemist or statistician can use them.

Error: may be defined as a deviation from the absolute value or from the true average of a large number of results. Two types of errors are recognized *determinate* (constant) and *indeterminate* (random or accidental).

Types of errors:

1. Gross careless errors.
2. Random errors (indeterminate errors or accidental errors)
3. Systematic errors (determinate errors or constant errors)

Gross careless errors: are those due to mistakes that are not likely to be repeated in similar determinations. Examples, are the spilling of apportion of sample recording the wrong value for one of weights used, reading the wrong number for the volume of liquid in a burette…..etc. when a series of careful measurement contains one result that differs widely from the others of errors has occurred.

Random (indeterminate) errors: are due to (a) inherent limitations of the equipment (b) to limitations of observations, and (c) to lack of care in making the measurement.
They can minimized by using high grade equipment and by careful work with this equipment, but these can never be completely eliminated.

Systematic (determinate) errors: can never be detected from the results of a single series of measurements, but only by comparing results of separate measurements using different instruments or method.

Chemical analysis are often subject to systematic errors. The use of impure materials for standardization of solutions, incorrect weights, in properly calibrated volumetric apparatus, even inadequate methods of analysis— all these and many other factors may lead to systematic errors.

Many of the possible systematic errors of analysis may be avoided by certain routine precautions, such as calibration of measuring apparatus, determination of a blank, performing an analysis by two or more independent methods, and testing a method by a control analysis on a sample of known composition.

Types of systematic errors: (a) personal errors,(b) operative errors,(c) instrumental errors and (d) methodic.

The Mean $\overline{X}$ **:** The mean, arithmetic mean, and average are refer to the numerical value of the various measurements and dividing the total by number *N* of the measurements. In mathematical notation, the arithmetic mean for a small group of values expressed as:

$$\overline{X} = \frac{\sum (X_i)}{N}$$

For example: we have these numerical value-31.60, 31.60, 31.70, 31.76, 31.71, 31.53, 31.62, 31.47, 31.64. the total divided by the number of individual results.

$$\bar{X} = 31.60 + 31.60 + 31.70 \ldots\ldots\ldots + 31.64/9 = 31.67$$

Precision: *is a measure of the agreement among the values in a group of data*. That have been made in identical fashion.

Accuracy: *is the agreement between the data* (mean value) *and the true value*.

Indeterminate or chance errors influence the precision of the results, and the measurement of the precision is accomplished best by statistical mean. Determinate or constant errors affect the accuracy of data.

Indeterminate errors obey the laws of probability, both positive or negative errors being equally probable, and larger errors being less probable than smaller ones.

Presentation of data: There is no standard method of presenting data. The criteria must be that the data sufficient, the statistics legitimate and the definitions clear enough to be understood by another analyst. Terms such as (mean error, relative error, and error) are ambiguous. For a series of results it is desirable to give the following data:

Precision data (1) Arithmetic mean.
(2) Range, i.e. the difference between the highest and lowest results.
(3) Average deviation, i.e. the average difference, without regard to sign, of each result in the series from the mean.
(4) Standard deviation, i.e. the square root of the sum of the squares of the differences of each result from the mean after division by one less than the total number of results.

Accuracy data (5) Average difference, i.e. the average difference with regard to sign of each result in the series from the 'true' result.
(6) Average recovery, i.e. the mean of series of results as a percentage of the 'true' result.

Accuracy data are not statistical measures and need only be calculated if it is suspected that the method under examination has a ***systematic bias***. The actual systematic bias of any method can often only be found after collaborative, or inter laboratory studies, for the results of a single worker may have a bias owing to, e.g. an inaccurate standard solution. An example may help to clarify the methods involved.

Strength of sulfuric acid method: Titration with N sodium hydroxide.

The following series were carried out at different times by one chemist, but conditions for each series were the same. All results are expressed as percent by weight.

Series	1	2	3	4
	98.44	98.49	98.54	98.53
	98.51	98.49	98.51	98.49

	98.49	98.51	98.51	98.49
Mean of Series . . $\bar{x}$	98.48	98.497	98.52	98.503
Precision data				
Range w	0.07	0.02	0.03	0.04
Mean Range $\bar{w}$ = 0.04				
Average Deviation	0.026	0.009	0.013	0.018
Standard Deviation . . s	0.036	0.012	0.017	0.023
Accuracy Data. The ‘true’ value found by a large number of collaborating laboratories was 98.05				
Average Difference				
with regard to sign	+0.43	+0.447	+0.47	+0.45

Absolute errors (E): The absolute error can be defined as E = O ─ A, where the error E is the difference between the observed value (O) and the accepted value or true value (A). suppose that the accepted value for the percentage chloride in sample is 24.34 percent . E = 24.29 ─ 24.34 = - 0.5 percent. Here, we ordinarily retain the sign of the error to indicate whether the result is high or low.

Mean Error: The difference between the sample arithmetic mean and the true value gives a measure of the accuracy of an operation; is known as *mean error*. Example, if the arithmetic mean is 0.90 and the true value is 1. The mean error in this case is

$$1.00-0.90 = 0.10 \text{ g}$$

Relative Error: Is obtained by dividing the mean error by the true value. It can be expressed as a percentage by multiplying by 100, or in parts per thousand by multiplying by 1000. It is easier to compare several sets of results by using relative error rather than the absolute mean error. The relative error in the case just cited is

$$0.10/1.00 \text{ X } 100 = 10\%$$

Deviation (D): Is the numerical difference without regard to sign between an experimental value and the mean or average for a set of data that includes that value.

To illustrate, suppose that the following results were obtained for chloride analysis.

Sample	Percent Cl	Deviation from mean

1	24.39	0.10
2	24.20	0.09
3	24.28	0.01

The mean value is 24.29 percent and the first result has a deviation from the mean of 0.10 percent. the set exhibits an average deviation from the mean of 0.07.

Mean (average) Deviation: The *mean deviation d* for a sample, that is, the deviation of an individual observation from the arithmetic mean of the sample, is obtained by taking the difference between each individual value X_i and the arithmetic mean $\bar{X}$, (adding the differences without regard to the algebraic signs), and dividing by the sum of the number of values to obtain the average . the mean deviation of a sample is expressed as:

$$d = \frac{\sum (X_i - \bar{X})}{N}$$

Standard Deviation(s): The *standard deviation σ* (sigma) is the square root of the mean of the squares of the deviations. This parameter is used to measure the dispersion or variability of a large number of measurements, for example, the weights of contents of several million capsules. This set of items or measurements approximates the *population* or the *universe*, and *σ* is therefore called the *standard deviation of the universe*. The standard deviation of the population is known as the *sample standard deviation* and is designed by the letter *s*. In which $\sum \left| X_i - \bar{X} \right|$ is the sum of the absolute deviations from the mean. The formula is written as: (the *s* for very large number of measurements).

Population mean deviation = δ

For large number of measurements $S = \sqrt{\dfrac{\sum (X_i - \bar{X})^2}{N}}$

Universe standard deviation = σ

For small number of measurements $S = \sqrt{\dfrac{\sum (X_i - \bar{X})^2}{N-1}}$

The number $N-1$ is known as the *number of degrees of freedom*. It replaces *N* to reduce the bias of the standard deviation *s*, which on the average is lower than the universe standard deviation .

The difference between the arithmetic mean and the *true* or *absolute* value express the *error* that can often be used as a measure of *accuracy* of the method.

Ex1: Consider the following sets of data

31.60	31.76	31.62
31.60	31.71	31.47
31.71	31.53	31.64

Calculate mean, deviation- average deviation, and standard deviation.

Rejection of measurement result:

1. Q-test

Q critic [90 percent confidence], Q %

Q 90%	Number of observation
0.94	3
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

Q critic value = (the outlying result— its nearest) / (larger number— smaller number)

If the observed Q is as large as the one of the table, the value id discarded and the mean of the remaining values is reported.

1. rule of 4d:

Ex2: in titration acid against base the following data were obtained (10.95, 11.12, 11.40, 11.02)

Fined the rejection value $\bar{X}$ = 11.02 + 11.12 + 10.95 /3 = 11.03

$$d = \frac{\sum(\bar{X}_i - X)}{N} = (11.12-11.03) + (11.02-11.03) + (10.95-11.03)/3 = 0.06$$

11.40 — 11.03 = 0.37

4d = 4 X 0.06 = 0.24 so that, 0.37 larger than 0.24 thus the value 11.40 is discarded.

Statistical Analysis Of Divided Powder Compounding Technique

Weight of powder contents (g)	Deviation (sign ignord $\lvert X_i - \bar{X} \rvert$	Square of the deviation $(X_i - \bar{X})^2$
1.00	0.02	0.0004
0.98	0.00	0.0000
1.00	0.02	0.0004
1.05	0.07	0.0049
0.81	0.17	0.0289
0.98	0.00	0.0000
1.02	0.04	0.0016
Total $\sum = 6.84$	$\sum = 0.32$	$\sum = 0.0362$
Average = 0.98	0.046	

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- THIS LECTURE JUST FOR PATHOLOGICAL ANALYSES DEPARTMENT.

Chapter 6 – *Chemical Reactions*

CHAPTER OUTLINE: The student will be able to:-

1. Know what we mean by chemical reaction

2. Definition of chemical equation equilibrium
3. Know the factor affection on reaction rate
4. Know what we mean by ionization ad theory of ionization
5. Definition the solubility & solubility product
6. Calculate the solubility product

Chemical reaction: In a physical change, the appearance of a substance is altered, but no to its composition, where liquid water becomes a gas or freezes to a solid, it is still water
In a chemical change, the reading substances change into new substances that have different formulas and different properties. A chemical reaction always involves chemical change becomes atoms of the reacting substances, form new combination with new properties. A chemical equation uses symbols & formulas to represent a chemical reaction. The substances on the left side of the equation are called reactants, & those on the right side are called products.

Types of chemical reaction: chemical reactions can be divided into 1. *Combination reaction*, 2. *Decomposition reaction*, 3. *Single replacement* or *substitution reactions*, 4. and *Double displacement*. These are illustrated in table 4-1.

Table 4-1. Chemical reactions

Type	General equation	Example
Combination	$A + B \longrightarrow AB$	$C + O_2 \longrightarrow CO_2$ $2S + 3O_2 \longrightarrow 2SO_3$
Decomposition	$AB \longrightarrow A + B$	$2HgO \longrightarrow 2Hg + O_2\uparrow$ $2KClO_3 \longrightarrow 2KCl + 3O_2\uparrow$
Single replacement	$A + BC \longrightarrow AC + B$ or $A + BC \longrightarrow BA + C$	$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$ $Cl_2 + 2NaBr \longrightarrow 2NaCl + Br_2$
Double displacement	$AB + CD \longrightarrow AD + CB$	$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4\downarrow$ $\uparrow$ $FeS + 2HCl \longrightarrow FeCl_2 + H_2S$

Equilibrium reactions: Many times when two or more reactants are unite to form a certain number of products, these products themselves unite to reform the original reactants. Reaction of this type is called ***reversible reactions***. They are indicated by a double arrows $\rightleftarrows$ showing that the reaction may proceed in either direction depending upon the conditions that exist.

If we start with a mixture of N_2 and H_2. At a given *temperature* and *pressure* (with a *catalyst*) we will soon have some NH_3 formed. As more NH_3 is formed, it will begin to decompose into N_2 and H_2, or $N_2 + 3H_2 \rightleftarrows 2NH_3$.

When the rates of formation and decomposition become equal, **a chemical *equilibrium*** exists. An equilibrium may be-

defined as ***a dynamic state in which the rate of the forward reaction is equal to the rate of the reverse reaction***.

Two examples of equilibrium reactions in the body are

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

and

$$\text{hemoglobin} + \text{oxygen} \rightleftarrows \text{oxyhemoglobin}$$

equilibrium constant (***law of mass action***): Consider the following general equilibrium reaction.

$$A + B \rightleftarrows C + D$$

The **law of mass action** states that the rate of a chemical reaction is proportional to the concentration of the reacting substances. So, for the above reaction, rate forward equal to the = $k_1[A][B]$ where k_1 is proportionality constant and the brackets, [ ], indicate concentrations in the units **moles/liter** .likewise, the rate of the reverse reaction = $k_2[C][D]$where k_2 another proportionality constant.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, so

$$K_1 \text{ x } [A] \text{ x } [B] = k_2 \text{ x } [C] \text{ x } [D]$$

Whence

$$\frac{[C] \text{ x } [D]}{[A] \text{ x } [B]} = \frac{k_1}{k_2} = k_{eq}$$

In general, the equilibrium constant, K_{eq}, equals the product of the products concentration divided by the product of the reactants concentration, each concentration raised to the power indicated by *its coefficient* in the equation. So. For the reaction as follows:

$$4A + 3C \rightleftarrows 2D + F$$

$$K_{eq} = \frac{[D]^2[F]}{[A]^4[C]^3}$$

Ex1: In the conversion of glucose to vitamin C, the following reaction take place.

$$C_5H_{11}O_5COO\,H \rightleftharpoons H^+ + C_5H_{11}O_5COO^-$$

gluconic acid hydrogen ion gluconate ion

In the equilibrium concentrations in moles per liter are $C_5H_{11}O_5COOH$, 0.10; H^+, 3.7×10^{-3}; $C_5H_{11}O_5COO^-$, 3.7×10^{-3}, calculate the value of K_{eq}.

$$K_{eq} = [H^+] \times [C_5H_{11}O_5COO^-] / [C_5H_{11}O_5COOH]$$

$$K_{eq} = (3.7 \times 10^{-3}) \times (3.7 \times 10^{-3}) / 0.10 = 1.4 \times 10^{-4}$$

Ex2:In manufacturing of wood alcohol , the following equilibrium reaction occurs; $CO + 2H_2 \rightleftharpoons CH_3OH$. At equilibrium the concentrations in moles per liter are CO, 0.025 ; H_2 0.050; CH_3OH, 0.12; calculate the value of K_{eq}.

$$K_{eq} = [CH_3OH] / [CO] \times [H_2]^2 = (0.12) / (0.025) \times (0.050)^2 = 1.9 \times 10^3$$

In general, a large value of K_{eq} indicates an equilibrium that has been shifted far to the right, whereas a small value indicates one shifted to the left.

Le Chatelier's Principle: Le Chatelier's principle states that *if a stress is applied to a reaction at equilibrium, the equilibrium will be displaced in such a direction as to relieve the stress*. Stresses are 1. Effect of concentration 2. Effect of temperature 3. Effect of a catalyst.
A catalyst: Any substance that increase the speed of a reaction without itself being changed chemically is called **catalyst**. Those catalysts present in the body called **enzymes**. During digestion, for example, the foods undergo many chemical changes, each under the influence of a specific enzyme. There are also **inhibitors** that slow down rather than speed up chemical reactions.

Reaction Rates: Some chemical reactions proceed at a slow rate. Iron, for example, rusts very slowly. Wood takes years to decay. On the other hand, some chemical reactions proceed more rapidly. Coal burns steadily and quickly. Concrete begins to set within a few hours. Some chemical reactions not only occur rapidly, they take place almost instantaneously. Consider the violent explosion of dynamite. Within a fraction of a second, the complete reaction has take place.

What determines the speed of a chemical reaction? The speed of a chemical reaction depends upon several factors: (1) the nature of the reacting substances, (2) the temp.,

(3) the concentration of the reacting substances, (4) the presence of a catalyst, and (5) the surface area.

Temperature: A patient who has a fever of only a few degrees has an increased pulse rate and also an increased respiratory rate. Reactions taking place throughout the body proceed at an accelerated rate.

When the temperature of the human body drops, the various metabolic processes slow down. This fact is of great importance, for example, during open-heart surgery.

Solubility and solubility product: When slightly soluble electrolytes are dissolved to form saturated solutions, the solubility is described by a special constant, known as the *solubility product*, K_{sp}, of the compound .

Silver chloride is an example of such a slightly soluble salt. The equation

$$AgCl_{solid} \rightleftharpoons Ag^{+} + Cl^{-}$$

The equilibrium expression can be written in terms of concentrations instead of activities:

$$K = \frac{[Ag^{+}] \text{ x } [Cl^{-}]}{[AgCl_{solid}]}$$

Moreover, because the concentration of the solid phase is essentially constant,

$$K_{sp} = [Ag^{+}] \text{ x } [Cl^{-}]$$

As in the case of other equilibrium expressions, the concentration of each ion is raised to power equal to the number of ions appearing in the formula. Thus, for aluminum hydroxide, $Al(OH)_3$,

$$Al(OH)_{3solid} \rightleftharpoons Al^{+3} + 3OH^{-}$$

$$K_{SP} = [Al^{3+}] \text{ x } [OH^{-}]^{3}$$

Ex3: **Solubility of silver chloride**

The measured solubility of the silver chloride in water at $20^{0}C$ is $1.12 \text{ x } 10^{-5}$ mole/liter. This is also the concentration of the silver ion and the chloride ion because silver chloride, as a strong electrolyte, is nearly completely dissociated. Calculate the solubility product of this salt. We have

$$K_{SP} = (1.12 \text{ x } 10^{-5}) \text{ x } (1.12 \text{ x } 10^{-5}) = 1.25 \text{ x } 10^{-10}$$

Ex4: The solubility magnesium hydroxide, $Mg(OH)_2$in water at $18^{0}C$. is $1.7 \text{ x } 10^{-4}$ mole/ liter . find the solubility product of magnesium hydroxide.

$$Mg(OH)_{2solid} \rightleftharpoons \underset{1 \text{ mole}}{Mg^{+2}} + \underset{2 \text{ mole}}{2OH^{-}}$$

$$K_{SP} = [Mg^{+2}] \text{ x } [OH^{-}]^{2}$$

$$K_{SP} = (1.7 \text{ x } 10^{-4}) \text{ x } (3.4 \text{ x } 10^{-4})^{2} = 1.96 \text{ x } 10^{-11}$$

Ionization: it can be shown experimentally that the only water solution that conduct electricity are those of acids, bases, and salts. *The substances whose water solutions conduct electricity are called* ***electrolytes***. *Substances whose water solutions does not conduct* *electricity are called* ***non-electrolytes***. Pure water is a non electrolyte, as is alcohol, sugar solutions are also non-electrolytes.

Electrolytes have unusual effect on the boiling point and the freezing point of a solution. This effect is due to the presence of ions.

Theory of Ionization: Arrhenius proposed a theory to explain the behavior of electrolytes in a solution.

1. The ionization is the formation of ions.
2. Some of the ions have a positive charge, others a negative charge.
3. The sum of the +ve charges is equal to the sum of –ve charges
4. The conductance of electricity by solutions of electrolytes is due to the presence. of ions. Non-electrolytes do not conduct electricity. because of the absence of ions.
5. The effect of electrolytes on the boiling point and on the freezing point of a solution is due to the increased the number of particles (ions) present in the solution.

The modern theory of ionization considers that ions are already present in a crystalline salt and that these ions are released to move about when that substance is placed in solution.

Most salts are strong electrolytes because they are completely (strongly) ionized. Acids and bases that are strong electrolytes are highly ionized. Acids and bases that are poor electrolytes are weakly ionized.

The presence of ions is of a great importance in the body in the maintenance of the electrolyte balance of the body fluids.

Consider a 1*M* solution of an electrolyte such as sodium chloride and a *M* solution of a non-electrolyte such as a sugar. The increase in the boiling point of the water containing the electrolyte sodium chloride will be approximately twice that for water containing,
non-electrolyte sugar. Likewise, the freezing point of the sodium chloride solution will be lowered approximately twice as much as that of the sugar solution.

Why do electrolytes conduct electricity? Why do they have an effect on the boiling point and freezing point of the solution?

Table 4-2. Ions found in body-necessary as a part of the blood buffer system.

Calcium ion	Ca^{2+}	Necessary for clotting of the blood, for formation of bones and teeth; for action of muscle, including heart.
Iron ion	Fe^{2+}	Used for formation of hemoglobin and cytochromes.
Sodium ion	Na+	Principal extracellular positive ion.
Potassium ion	K^+	Principal intracellular positive ion.
Chloride ion	Cl^-	Intracellular and extracellular negative ion.
Bicarbonate ion	HCO_3^-	Extracellular negative ion.
Iodide ion	I^-	Present in thyroid hormones.
Ammonium ion	NH_4^+	Acid-base balance.

Phosphate ion	PO_4^{3-}	Used in the formation of bones and teeth.
Magnesium ion	Mg^{2+}	An important activator for many enzymes systems.

References:

1. Fundamentals of analytical chemistry, Skoage, 2nd ed., 1969.
2. General, org. & biological chemistry, Karen, C. Timber, 2nd ed., 2007
3. Chemistry for the Health Sciences, George, 5th ed., 1985.
4. Physical Pharmacy and Pharmaceutical Sciences, 5th ed. Martin's. 2006.

Carbon Oxides and Nitric oxide in Eye

1- Nitric oxide in eye

Nitric oxide (NO) was first discovered in the 1770s by Joseph Priestly in England . NO's medicinal benefit was essentially ignored until the early 1900s, as it was believed to be an air pollutant . Then, medicine began using nitrates (e.g., nitroglycerin) for angina, and pharmacologists started to outline the physiologic responses of various tissues to these compounds, specifically in the cardiovascular field, where the improvement of angina pectoris and reversal of ischemia were reported.

NO and the Eye

NO is produced pre- and post-synaptically in the nervous system, and while beyond the scope of this review, it behooves mentioning that NO physiologically influences the visual system posterior to the eye at the lateral geniculate nucleus (LGN) and in the primary visual cortex .

Within the ocular globe, NO plays an important role in both the anterior and posterior segments.

NO in Ocular Surface Cells:

The main sources of NO in ocular surface tissue are the corneal epithelium, fibroblast, endothelium and inflammatory cells .

NO in the Retina:

NO in retinal cells acts as a light response modulator by activating specific ion conductors in rods, cones and bipolar and ganglion cells. Other studies have demonstrated that NO acts as a vascular endothelial relaxant involved in normal retinal blood flow control, as well as related to several ocular diseases associated with oxidative stress, including retinitis pigmentosa, diabetic retinopathy, glaucoma and macular degeneration (AMD).

NO for the Treatment of Corneal Wound Healing:

The wound-healing effects of NO are well-known. One study showed that a topical treatment with $NaNO_2$ (10 μM) enhanced the corneal epithelial recovery, as well as decreased corneal opacity, in a murine corneal alkali burn created by modulating inflammatory cytokines .

NO and Intraocular Pressure (IOP):

NO has shown to be an IOP regulator. IOP is a balance between aqueous humor production and outflow through the uveoscleral network and the pressure-dependent trabecular meshwork pathway . NO and its messenger cGMP directly act on trabecular meshwork cells to help increase the outflow. Studies have exhibited similarities between trabecular cells and smooth muscle cells, and both are very reactive to NO .

NO for the Treatment of Glaucoma:

Many existing therapies for IOP reduction are beneficial for a period of time, after which individuals require additional drugs to prevent the progression of nerve death . One of the challenges to create therapies including NO is its short half-life in tissues of two seconds and only two milliseconds in blood . A way to overcome this is to utilize known effective drugs for lowering IOP combined with NO-donor substances that are metabolized inside the eye and then release NO in the targeted tissue .

What is IOP reduction?

Intraocular pressure (IOP) reduction is key to controlling primary open-angle glaucoma (POAG), the second-leading cause of blindness worldwide.

NO and AMD:

Oxidative stress has been implicated in many chronic disease processes, such as AMD. Reduced NO levels were detected in the plasma of patients with AMD as compared with the control subjects . The impaired availability of NO is also associated with the enhanced synthesis of endothelin-1 (ET-1), which is a potent vasoconstrictor agent .

AMD pathology: is characterized by degeneration involving the retinal photoreceptors, retinal pigment epithelium, and Bruch's membrane, as well as, in some cases, alterations in choroidal capillaries.

NO and Myopia:

Research has shown that exposure to outdoor light, which affects light receptors and the natural circadian rhythm, is the best natural way to stimulate dopamine . There is a lot of data supporting the hypothesis that dopamine is one of the neurotransmitters in the retina signaling eye growth in infancy and childhood. Evidence suggests that dopamine stimulates the synthesis and release of NO. NO operates with the enzyme group NOS to regulate eye growth.

Carbon dioxide and oxygen are commonly used in the treatment of central retinal artery obstruction to improve retinal oxygenation. While oxygen alone causes retinal vasoconstriction, it is thought that the carbon dioxide balances this effect, even causing a net vasodilatation.

ENVIRONMENTAL POLLUTION:

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Tropospheric Pollution Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

1. **Gaseous air pollutants:** These are oxides of sulphur, nitrogen and carbon, hydrogen supplied, hydrocarbons, ozone and other oxidants.
2. **Particulate pollutants:** These are dust, mist, fumes, smoke, smog etc.

Oxides of Nitrogen: Dinitrogen and dioxygen are the main constituents of air. These gases do not react with each other at a normal temperature. At high altitudes when lightning strikes, they combine to form oxides of nitrogen. NO_2 is oxidized to nitrate ion, NO_3 − which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:

$N_2 (g) + O_2 (g) \rightarrow 1483K + 2NO (g)$

Hydrocarbons: Hydrocarbons are composed of hydrogen and carbon only and are formed by incomplete combustion of fuel used in automobiles. Hydrocarbons are carcinogenic, i.e., they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

2- Oxides of Carbon

(i) Carbon monoxide: Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon. Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc. The number of vehicles has been increasing over the years all over the world. Many vehicles are poorly maintained and several have inadequate pollution control equipments resulting in the release of greater amount of carbon monoxide and other polluting gases. Do you know why carbon monoxide is poisonous? It binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3–4 per cent, the oxygen carrying capacity of blood is greatly reduced. This oxygen deficiency, results into headache, weak eyesight, nervousness and cardiovascular disorder. This is the reason why people are advised not to smoke. In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(ii) Carbon dioxide: Carbon dioxide (CO_2) is released into the atmosphere by respiration, burning of fossil fuels for energy, and by decomposition of limestone during the manufacture of cement. It is also emitted during volcanic eruptions. Carbon dioxide gas is confined to troposphere only. Normally it forms about 0.03 per cent by volume of the atmosphere.

Refrence:

ERDINEST, Nir, et al. Nitric oxide interaction with the eye. *Vision*, 2021, 5.2: 29.

DEUTSCH, Thomas A., et al. Effects of oxygen and carbon dioxide on the retinal vasculature in humans. *Archives of Ophthalmology*, 1983, 101.8: 1278-1280.

Chapter 7: *Neutralization-Acids & Bases*

CHAPTER OUTLINE: The student will be able to:-

1. Know properties of acids & bases.
2. Know the degree of ionization of acids and bases.
3. Know what mean by oxidation-reduction equilibrium.
4. Definition of pH, buffer solution.

Acids: *Acids may be defined as compounds that yield or donate hydrogen ions* (H^+) *in a water solution.* it is the hydrogen ions that are responsible for the properties of acids.

Common acids: solid acids; boric acid and citric acid, liquids are; HCl, H_2SO_4, HNO_3, carbonic acid (H_2CO_3), Phosphoric acid (H_3PO_4), acetic acids (CH_3COOH).

Properties of acids:

1. Acids yield hydrogen ions when placed in water solution.
2. Strong acids are completely ionized in solution whereas weak acids are partially ionized.
3. Solutions of acids have a sour taste-acetic acid taste or lactic acid taste for sour milk.
4. When acids react with certain compounds, these compounds change in color. Due to the presence of *indicator*. One of the most common indicators for acids litmus paper.
5. Acids react with metal oxides or hydroxides to form water and a salt.

$$MgO + 2HCl \longrightarrow H_2O + MgCl_2$$

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

Neutralization: *The reaction of acids with certain metal hydroxides* (called bases). That is, acids neutralize bases to form water and a salt.

Uses of acids: a. Commercial **antacids** are available to react with the excess stomach acid. Among these are:

1. Tums─ which contains calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and magnesium trisilicate ($Mg_2Si_3O_8$).
2. Maalox─ which contains magnesium hydroxide [$Mg(OH)_2$], and aluminum [$Al(OH)_3$] in suspension.

b. Hydrochloric acid, normally found in the gastric, is necessary for the proper digestion of protein in the stomach. Patients who have a lower than normal amount of HCl in the stomach, a condition called ***hypoacidity***, are given dilute hydrochloric acid orally before meals to overcome this deficiency.

c. Nitric acid is used to test for the presence of albumin in urine because it will coagulate protein.

d. Nitric acid, dichloroacetic acid, and trichloroacetic acid have been used to remove warts.

Bases: *bases are be defined as substances that yield hydroxide (OH^-) ions in a water solution*.

That is, bases increase the hydroxide ion concentration in water.A more general definition of a base is that of Bronsted: **a base is a substance that accepts protons**.C_2H_5OH (ethyl alcohol) is not a base because it does not accept a proton. It does not ionize in water.

Common bases: they consist of a metal ion ionically bonded to an OH^- ion. the only exception to this rule is the base ammonium hydroxide. NH_4OH, in which the ammonium ion, NH_4^+ is considered to act as a metal ion. for example to bases: sodium hydroxide, potassium hydroxide, calcium hydroxide [$Ca(OH)_2$], and magnesium hydroxide [$Mg(OH)_2$].

Properties of bases:

1. Have bitter taste.
2. Bases neutralize acids to form water and a salt.

$$Ca(OH)_2 + H_2SO_4 \longrightarrow 2H_2O + CaSO_4$$

3. Bases also react with indicators. Bases turn red litmus to blue.
4. Strong bases react with certain metals to produce hydrogen gas.
5. They have a corrosive effect on tissue because of their ability to react with proteins and fats. And may cause burn to the skin when is spilled on the skin.

Uses of bases:

1. Sodium hydroxide (lye) is used to remove fats and grease from clogged drains. and used in the conversion of fat to soap.

2. Calcium hydroxide to overcome excess acidity in the stomach. It is also used medicinally as an antidote for poisoning because it reacts with it to form an insoluble compound.

3. Magnesium hydroxide is used as a laxative, and as antacid.

4. Spirits of ammonia, which contains (NH_4OH and ammonium carbonate $[(NH_4)_2CO_3]$, is used as a heart and respiratory stimulant.

Acid-base titration: when an acid reacts with a base, a salt and water are produced. This reaction is called ***titration***. An indicator is used with this reaction. *The indicator is one that will change in color when the acid are reacted with all of the base present. This is called* ***end-point***. Or equivalence point of titration.

$$\text{Volume}_{\text{acid}} \times \text{Normality}_{\text{acid}} = \text{Volume}_{\text{base}} \times \text{Normality}_{\text{base}}$$

Ionization of weak acid: In general, the acidity constant for an uncharged weak acid HB can be expressed by

$$HB + H_2O \rightleftharpoons H_3O^+ + B^-$$

The law of mass action is applied to give the equilibrium as expressed

$$K_a = \frac{[H_3O^+][B^-]}{[HB]} \qquad (6\text{-}1)$$

Ionization of weak base: In general, for an anionic base B^-.

$$B^- + H_2O \rightleftharpoons OH^- + HB$$

$$K_b = \frac{[OH^-][HB]}{[B^-]} \qquad (6\text{-}2)$$

The ionization of water: One molecule of water can be thought of as a weak electrolyte solute that reacts with another molecule water as solvent. The *autoproteolytic* reaction is represented as

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

The law of mass action is applied to give the equilibrium as expressed

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad (6\text{-}3)$$

Because molecular water exists in great excess relative to the concentration of hydrogen and hydroxyl ions, $[H_2O]^2$ is considered as constant and is combined with K to give a new constant, K_w, known as the *dissociation constant*, or the *autoprotolysis constant*, or the *ion product* of water: $K_w = K[H_2O]^2$ the value of the ion product is approximately 1×10^{-14} at 25^0C; it depends on temperature.

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$$

Ex1: A quantity of HCl (1×10^{-3}) is added to water at 25^0C to increase the hydrogen ion concentration from 1×10^{-7} to 1.5×10^{-3} mole/liter. What is the new OH^- ion conc.

$$[OH^-] = 1 \times 10^{-14} / 1.5 \times 10^{-3} = 6.7 \times 10^{-12} \text{ mole/liter}$$

***Relation between K_a* and *K_b*:**

$$K_a \times K_b = [H_3O^+][OH^-] = K_w$$

Ex2: Ammonia has a K_b of 1.74×10^{-5} at 25^0C. Calculate K_a for its conjugate acid, NH_4^+. We have

$$K_a = K_w / K_b = 1 \times 10^{-14} / 1.74 \times 10^{-5} = 5.75 \times 10^{-10}$$

Sorensen's pH: He is suggested simplified method of expressing hydrogen ion concentration in term *pH*, which was originally written as

$$\text{pH} = -\log[H_3O^+]$$

Ex3: The hydronium ion concentration of a 0.05 *M* solution of HCl is 0.05 *M*. What is the pH of this solution?

$$\text{pH} = -\log(5.0 \times 10^{-2}) = -\log 10^{-2} - \log 5.0 = 2 - 0.70 = 1.30$$

Table 6-1. pH values

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Strength of acid (H^+ in mol/L)	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-}										10^{-14}
Strength of base (OH^- in mol/L	10^{-14}	10^{-13}	10^{-12}	10^{-11}											10^0

Buffer solutions: The pH of pure water (a neutral solution) is 7.0 if an acid added to water, the pH goes down. How far below 7.0 it goes depends on how much acid and how strong an acid is added. When a base is added to pure water, the pH rises above 7.0.

A buffer solution: is defined as *a solution will resist changes in pH upon the addition of small amounts of either acid or base*. Buffer solutions, or buffers, are found in all body fluids and are responsible for helping maintain the proper pH of those fluids. The normal range of the blood is 7.35 to 7.45. Even a slight change in pH can cause a very definite pathologic condition. When the pH falls below 7.35, can cause ***acidosis. Alkalosis*** the blood pH rises above 7.45.

What does a buffer solution consist of and how does it work? A buffer system consists of (1) a weak acid and its salt, such as , acetic acid and sodium acetate. carbonic acid and its salt sodium bicarbonate ($NaHCO_3$) presents in the blood as buffer solution.

(2) Abase and its salt, for example, a solution of ephedrine and ephedrine hydrochloride.

It work: if the strong acid is added to 0.01 *M* solution containing equal quantities of acetic acid and sodium acetate, the pH is changed only 0.09 pH units because the base Ac^- ties up the hydrogen ions according to the reaction

$$Ac^- + H_3O^+ \rightleftharpoons HAc + H_2O$$

If a strong base, sodium hydroxide (NaOH), is added to the buffer mixture of acid and its salt, acetic acid neutralizes the hydroxyl ions as follows:

$$HAc + OH^- \rightleftharpoons H_2O + Ac^-$$

References:
1. Chemistry for the Health Sciences, George, 5th ed., 1985.
2. Physical Pharmacy and Pharmaceutical Sciences, 5th ed. Martin's. 2006.

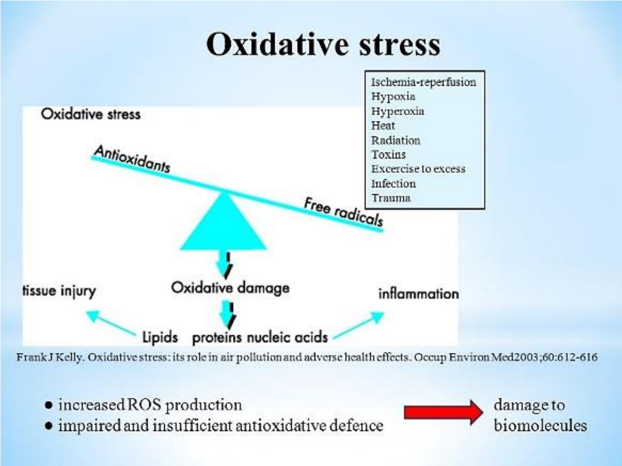
Oxidation stress in the eye

What is oxidative stress?

- Oxygen is necessary for life. Our bodies constantly react with oxygen as we breathe and our cells produce energy, resulting in the production of free radicals such as Reactive Oxygen Species (ROS)and Reactive Nitrogen Species (RNS).
- Free radicals are "live wires" and interact with other molecules inside cells, harming cells if the interactions are uncontrolled.
- Oxidative stress occurs during normal respiration, digestion, and metabolism, and is necessary for living cells to survive.
- It also drives critical signaling pathways that create normal tissues,heal wounds, and allow adaptation to stress and disease.
- There is no way to avoid oxidative stress because it is a normal process occurring

during routine living and aging, from exposure to UV (ultraviolet) light, and from normal cellular metabolism.

- In healthy tissues, the body balances the normal oxidative stress of daily living by using antioxidants (such as grapeseed extract and omega 3 fatty acids) to control and balance free radicals.
- Damage and disease occur when this balance is lost. The formation of unbalanced free radicals from oxidative stress can set off a chain reaction that damages DNA or cell membranes, often causing cell death.
- Many antioxidants, such as vitamin C and green tea extract, are well-proven to provide protection against oxidative stress.



Oxidative stress

Frank J Kelly. Oxidative stress: its role in air pollution and adverse health effects. Occup Environ Med2003;60:612-616

- increased ROS production
- impaired and insufficient antioxidative defence

damage to biomolecules

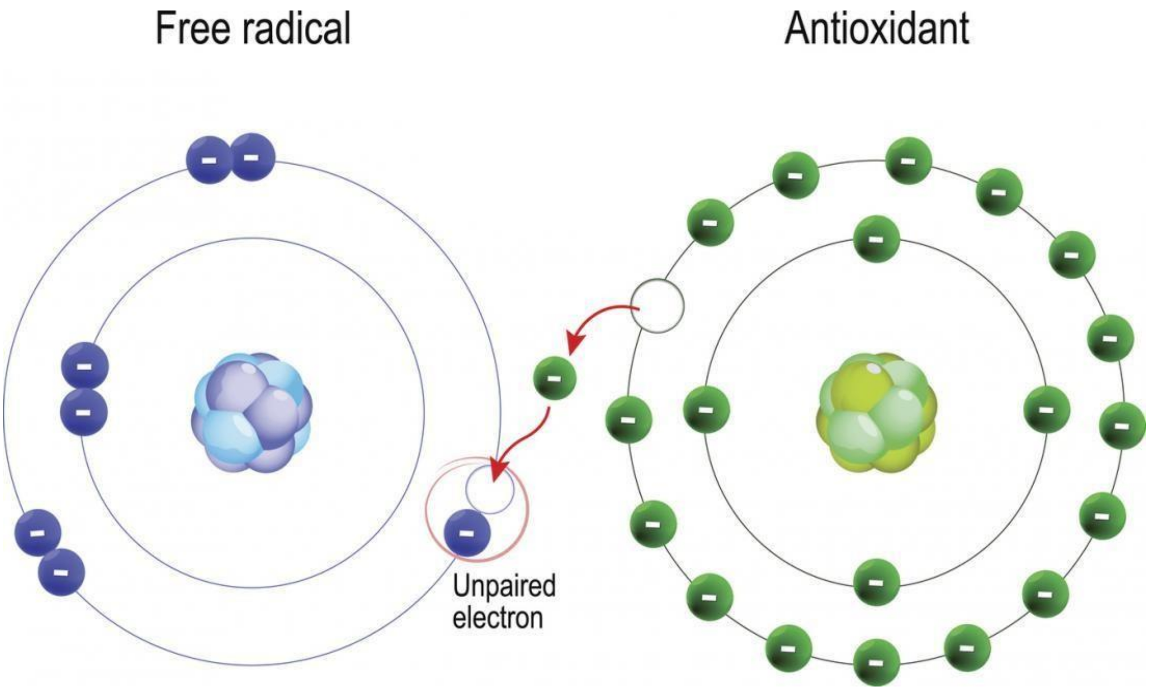
Free radical

A free radical is a molecule or molecular fragment that contains one or more unpaired electrons in its outer orbital .

Free radical is generally represented by a superscript dot, (R•).

Oxidation reactions ensure that molecular oxygen is completely reduced to water.

The products of partial reduction of oxygen are highly reactive and create havoc in the living systems. Hence, they are also called Reactive oxygen species or ROS.

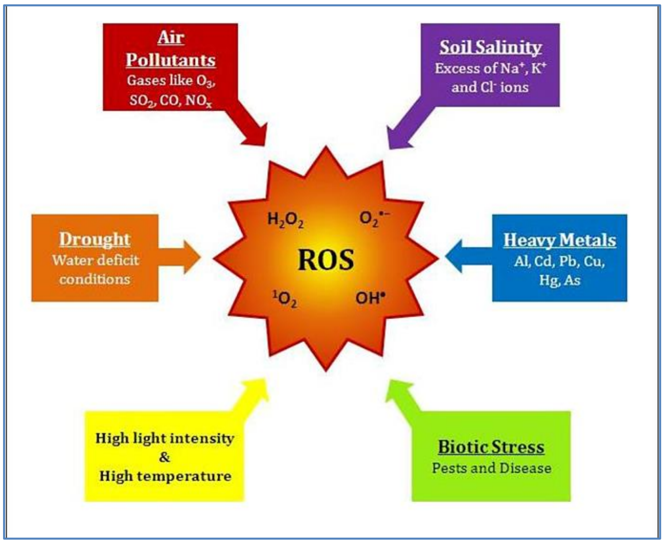


Formation of Free Radicals

- By Reduction-Oxidation reactions during normal metabolicprocess.
- Primary source is our body during energy production
- Enzymatic Metabolism of exogenous chemicals and drugs.
- During Inflammation.
- Prolonged low blood flow states (atherosclerosis, heart attacks &stroke)
- Environmental contaminants
- Tobacco (Smoking) is a major oxidative stress, that is a source ofmutagens.
- Absorption of Radiation energy
- Diet (fatty and processed foods)
- Low levels of antioxidants

The following are members of this group:

1. Superoxide anion radical (O2 --•)
2. Hydroperoxyl radical (HOO•)
3. Hydrogen peroxide (H2O2)
4. Hydroxyl radical (OH•) Lipid peroxide radical (ROO•)
5. Singlet oxygen (1O2)
6. Nitric oxide (NO•)
7. Peroxy nitrite (ONOO--•).


Air Pollutants
Gases like O_3, SO_2, CO, NO_x
Soil Salinity
Excess of Na^+, K^+ and Cl^- ions
Drought
Water deficit conditions
H_2O_2
$O_2^{\bullet-}$
ROS
$^1O_2$
$OH^\bullet$
Heavy Metals
Al, Cd, Pb, Cu, Hg, As
High light intensity & High temperature
Biotic Stress
Pests and Disease

- **What is the main cause of oxidative stress?**

Oxidative stress is a phenomenon caused by an imbalance between production and accumulation of oxygen reactive species (ROS) in cells and tissues and the ability of a biological system to detoxify these reactive products.

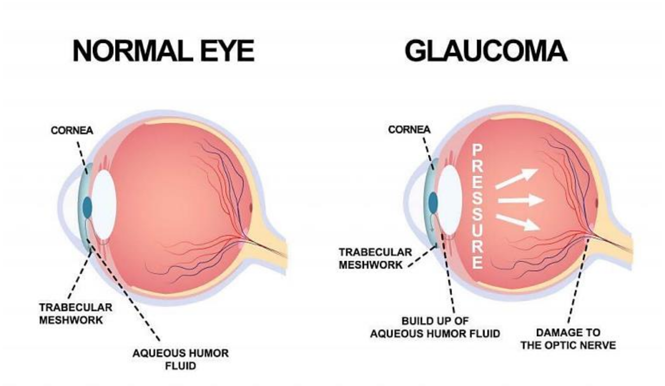
- Oxidative Stress • It is imbalance between free radicals and antioxidants in the body.

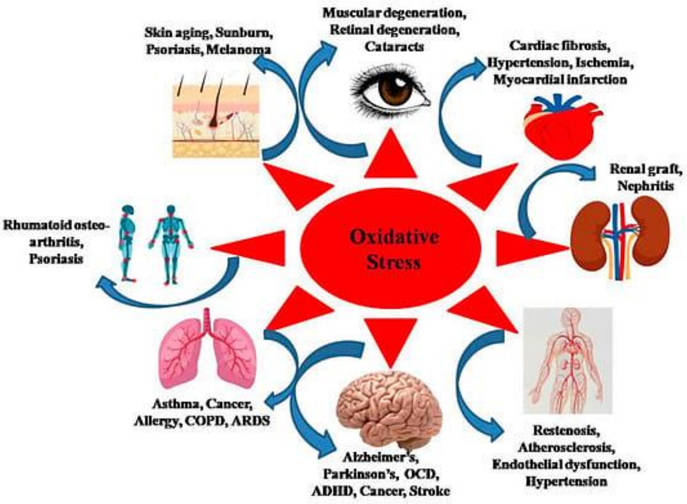
  • Under normal conditions, cells are able to balance the production of oxidants and antioxidants. Oxidative stress occurs when cells aresubjected to excess levels of ROS or as a result of antioxidant depletion.

  • It is harmful because ROS attack biological molecules such as lipids, proteins, and DNA that involved in the pathogenesis oflifestyle-related diseases.

- **Risks and consequences of oxidative stress**.

The eye is an organ that is predisposed to great levels of oxidative stress. The eye is constantly exposed to factors such as radiation, chemicals, oxygen, drugs, which induce the formation of reactive oxygen species (ROS) that can ultimately damage cells.


NORMAL EYE
GLAUCOMA
CORNEA
TRABECULAR MESHWORK
AQUEOUS HUMOR FLUID
CORNEA
PRESSURE
TRABECULAR MESHWORK
BUILD UP OF AQUEOUS HUMOR FLUID
DAMAGE TO THE OPTIC NERVE


Oxidative Stress
Muscular degeneration, Retinal degeneration, Cataracts
Skin aging, Sunburn, Psoriasis, Melanoma
Cardiac fibrosis, Hypertension, Ischemia, Myocardial infarction
Renal graft, Nephritis
Rhumatoid osteo-arthritis, Psoriasis
Asthma, Cancer, Allergy, COPD, ARDS
Alzheimer's, Parkinson's, OCD, ADHD, Cancer, Stroke
Restenosis, Atherosclerosis, Endothelial dysfunction, Hypertension

What are the symptoms of oxidative stress?

Why is it a problem?

- Fatigue.
- Memory loss and/or brain fog.
- Muscle and/or joint pain.
- Decreased eye sight.
- Headaches and sensitivity to noise.
- Susceptibility to infections.

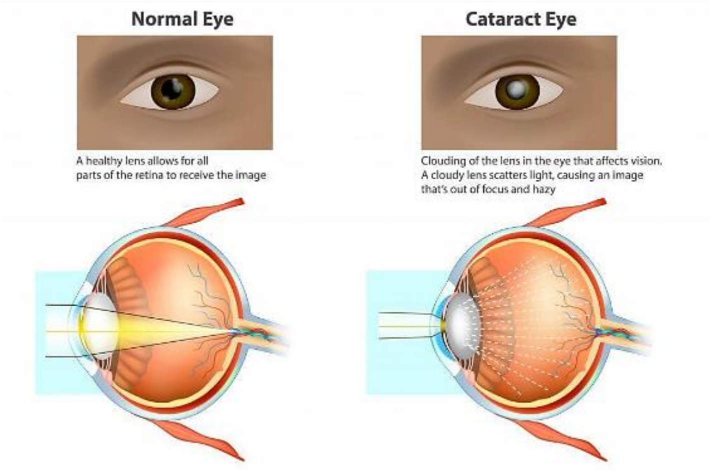
Does oxidative stress cause glaucoma?

These findings suggest that intraocular pressure increase, which characterizes most glaucomas, is related to oxidative and degenerative processes affecting the more specifically, its endothelial cells.

This supports the theory that glaucomatous damage is the pathophysiological consequence of oxidative stress.

Does oxidative stress cause cataracts?

Cataracts are the leading cause of blindness . Opacity of the lens is a direct result of oxidative stress. Cataracts occur primarily due to age, but also are common in diabetes where superoxide in the mitochondria is elevated as a result of hyperglycemia.



Cataracts are a clouding of the lens. Medical illustration of a normal eye and an eye with a cataract, clouded lens

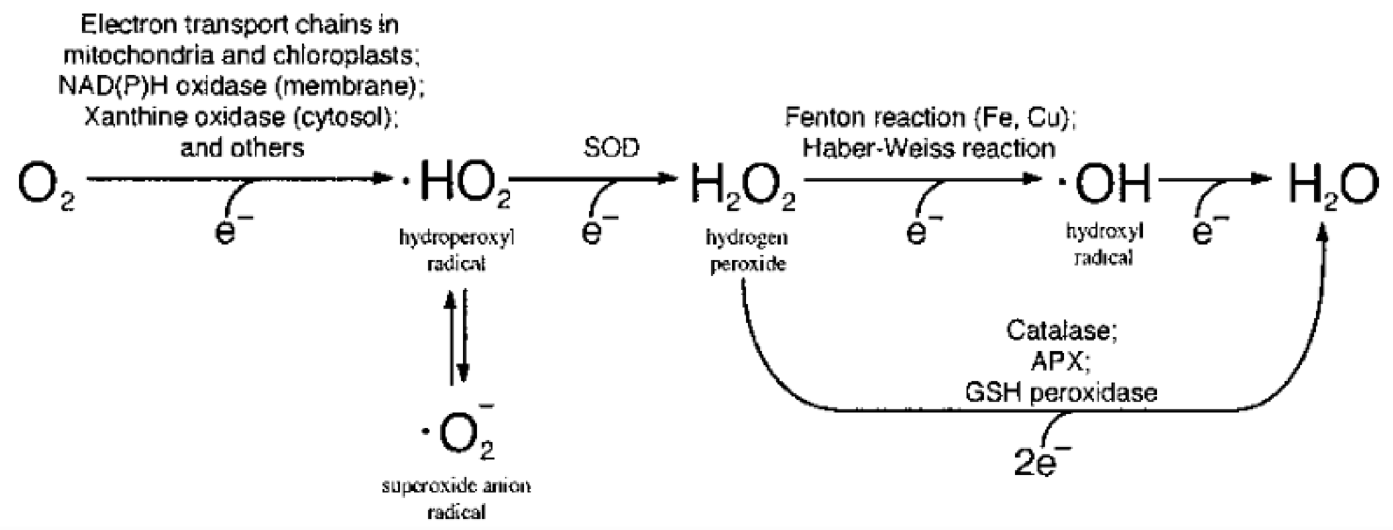
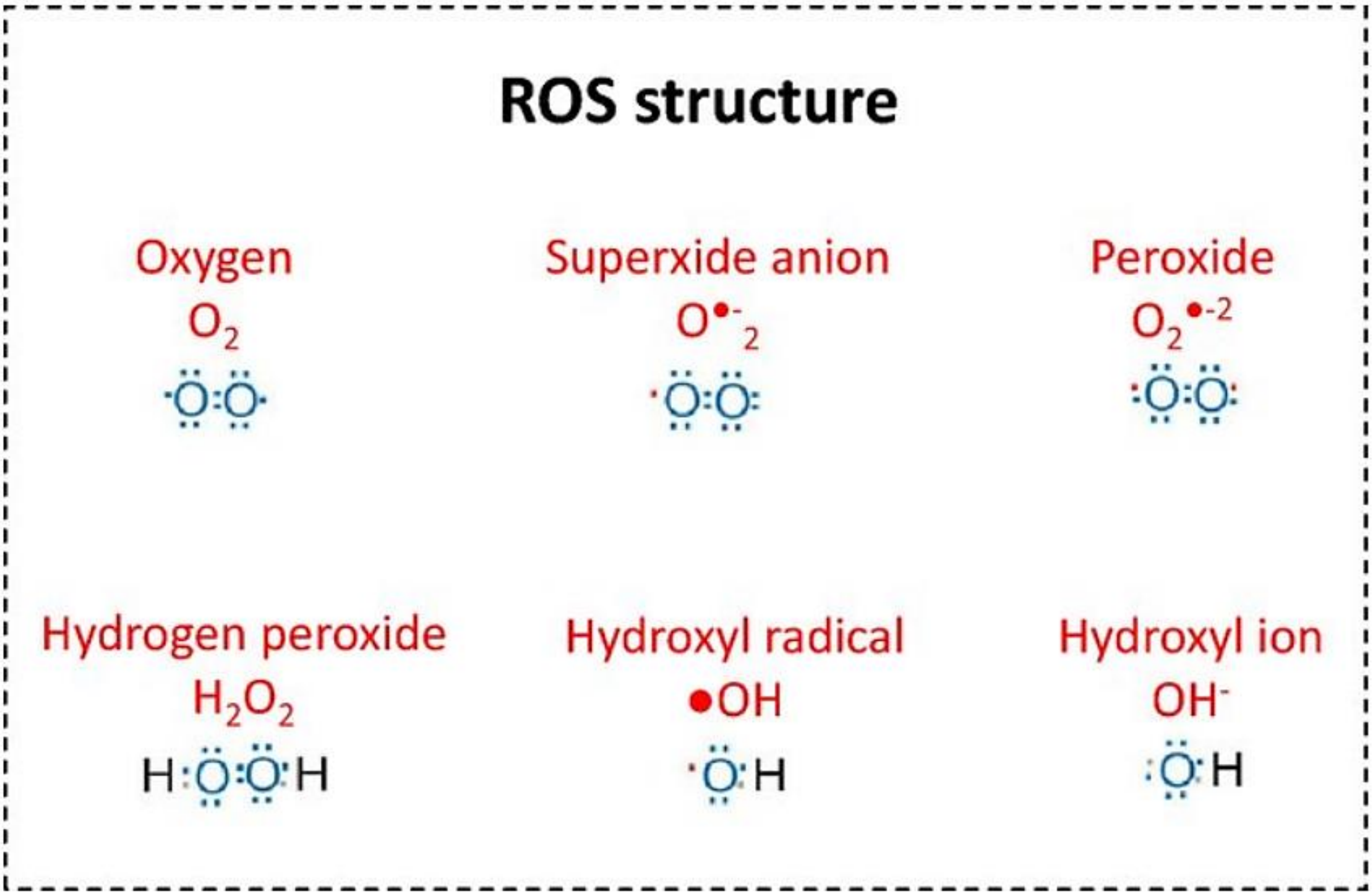


Figure 1. Metabolic pathways of reactive oxygen species in plants. Some of the important enzymes in reactive oxygen species metabolic pathways are illustrated. APX, ascorbate peroxidase; GSH, glutathione; SOD... Expand

Published in 2004

Update on Reactive Oxygen Species Activation of Ca 2 1 Channels Reactive Oxygen Species Activation of Plant Ca 2 1 Channels . A Signaling Mechanism in Polar Growth , Hormone Transduction , Stress Signaling , and Hypothetically Mechanotransduction 1



Chapter 8- *The Gaseous State- Air Pollution*

CHAPTER OUTLINE: The student will be able to:-

Know the gas laws, Boyles law, Charles law, Pressure-Temperature relationship, combined gas law, Daltons law, Grahams law, Henrys law and, molar gas volumes and air pollution.

General properties: The gases have no definite shape, no definite volume, and a low density.
Boyle’s Law: The relationship between the volume of a given quantity of a gas and its pressure. *Volume inversely proportional to the pressure at constant temperature.*

The increased volume in the lungs causes the pressure in the lungs to drop slightly. Since air always flows from an area of high pressure to one of lower pressure. Air flows into the lung. And vice versa. Another application of Boyles law in the use of a sphygmomanometer, a device used to measure blood pressure. When the rubber bulb is squeezed, the volume of air in that bulb is decreased and its pressure is increased. This increased pressure transmitted to the cuff.

Charles’ Law: *The volume is directly proportional to its Kelvin temperature, at constant pressure.*

A direct application of Charles law may be seen as in incubator. When air comes in contact with the heating element, it expands and becomes lighter. This lighter air rises, causing a circulation of warm air throughout the incubator.

Pressure temperature relationship: Another relationship may be expressed between the pressure exerted by a gas and its temperature. *These two factors are directly propor-tional, at constant volume*.

A common application of this relationship is the autoclave, a device used in hospitals for sterilization. The normal temperature of a steam is 100^0C, but in an autoclave it may rise as high as 120^0C because of the increased pressure. This higher temperature is sufficient to destroy any microorganisms that may exist in material being autoclaved.

Combined gas law: $P_1 V_1 / T_1 = P_2 V_2 / T_2$

Dalton's law: Dalton's law states that, in a mixture of gases, each gas exerts a partial pressure proportional to its concentration.

Gases law flow from an area of higher partial pressure to one of lower partial pressure. An example of diffusion of gases caused by a difference in partial pressure is

found in our own bodies (see fig 8-1). The partial pressure of oxygen in the inspired air is 158 mm. the partial pressure of oxygen in the alveoli is 104 mm. therefore, oxygen passes from the lungs into the alveoli (from a higher partial pressure to a lower partial pressure). From the alveoli the oxygen diffuses into the venous blood (from a partial pressure of 104 mm to one of 40 mm). This diffusion of oxygen into the venous blood in the lungs changes venous blood into arterial blood, in which the partial pressure of oxygen of 95. When the arterial blood reaches the tissues, where the partial pressure of oxygen is 40 mm, oxygen diffuses to those tissues (again from a higher partial pressure to a lower one). When the arterial blood loses oxygen to the tissues, its oxygen partial pressure drops to 40 mm and it becomes venous blood, which returns to the lungs to begin the cycle a new.

Conversely, in the tissues the partial pressure of the carbon dioxide is 50 mm and in the arterial blood it is 40 mm, so that the CO_2 diffuses out of the tissues into the blood. When the arterial blood picks up CO_2 (and at the same time loses oxygen) it becomes venous blood with a carbon dioxide partial pressure of 45 mm. this venous blood, in turn, loses CO_2 to the alveoli where the carbon dioxide partial pressure is 40 mm.

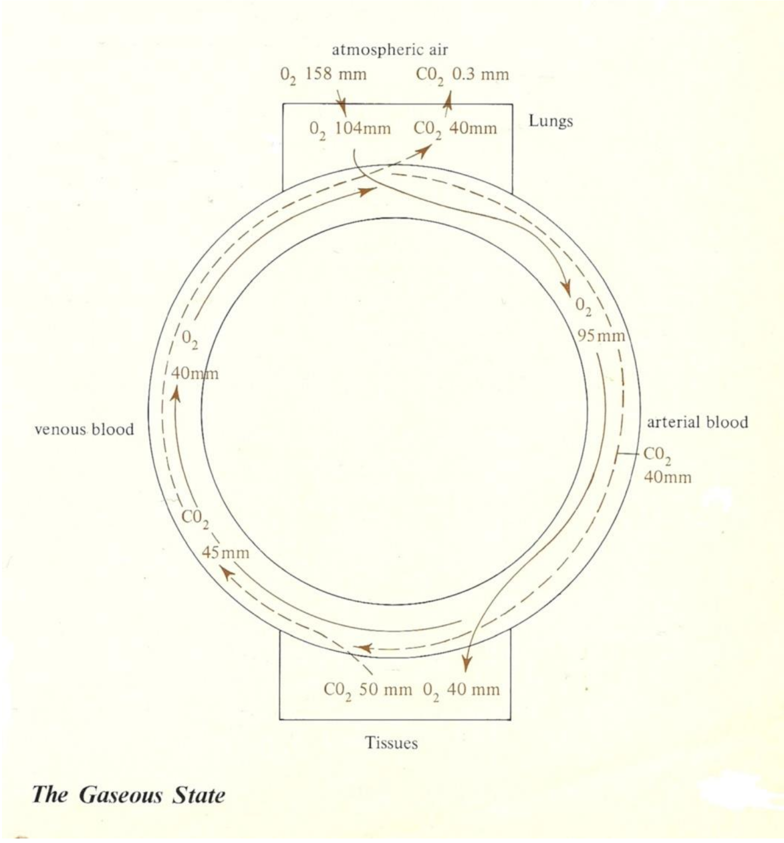


Fig 8-1: diagram showing O_2 & CO_2 flow and partial pressures in body

From the alveoli the carbon dioxide passes into the lungs (from a partial pressure of 40 mm to one of 0.3 mm) and then is exhaled.

Uses of Dalton's law in the intermittent partial pressure breathing apparatus, which fills the patient's lung by increasing the partial pressure of the gas being inhaled.

Graham's law: *The rates of diffusion of gases inversely proportional to the square roots of the molecular weight* (**or inversely proportional to the square roots of their densi-ties).** If a container of ammonia and a container of ether are opened simultaneously, a person standing at the far end of the room will notice the odor of ammonia before that of the ether. Both gases will diffuse through the air but ammonia has a molecular weight of 17 and ether a molecular weight of 74. Lighter molecules diffuse faster than heavier one. This relationship was stated by Graham.

$$\frac{\text{rate of diffusion gas}_1}{\text{rate of diffusion gas}_2} = \sqrt{\frac{\text{molecular weight gas}_2}{\text{molecular weight gas}_1}}$$

Henry's law: *The solubility of a gas in a liquid at a given temperature is proportional to the pressure of the gas.* That is, more gas dissolves at higher pressures and less at lower pressures. Carbonated drinks are made by dissolving carbon dioxide, under pressure, in a given liquid. When the container is opened, the pressure is released and bubbles of CO_2 escape.

Molar gas volume: The volume occupied by 1 mol of any gas at STP (standard temperature and pressure, 0^0C and 760 mm Hg) is 22.4 L. however, this volume may be used only at STP.

Air pollution: The principal sources of air pollution are ***automobiles***, ***tobacco smoke***, and the ***burning of fossil fuel***. Concentration of pollutants in the air are expressed as parts per million (ppm), **where 1 ppm corresponds to 1 part pollutant to 1 million parts air.**

Concentration of pollutants at level far below 1 ppm can have an adverse effect upon human life. For example, 0.2 ppm sulfur dioxide in the atmosphere leads to an increased death rate and 0.02 ppm of peroxybenzoyl nitrate (a constituent of smoke) causes severe eye irritation.

Automobile: Is the principal source of CO, hydrocarbons, and nitrogen oxides, which is also the source of such particulate matter in the air as asbestos (from brake lining) and lead aerosols (from leaded gasoline).

Tobacco smoke: Is a source of CO as well as particulate matter (ash). It is one of the most dangerous types of air pollution. Smokers inhale large amounts of CO_2, tars, and , Particulate matter. Peoples around smokers are also exposed to these same pollutants. Evidence has shown that expectant mothers who smoke have smaller babies who have a higher infant mortality rate than those of nonsmokers. Smokers also have a greater chance of developing lung cancer, emphysema, and cardiovascular disease.

Fossil–fuel- powered electrical generating stations: are also a major source of air pollutants such as sulfur dioxide.

Ozone: Is formed by the action of sunlight on oxygen and is normally present in the atmosphere in small amounts. Ozone reacts with hydrocarbons emissions and with oxides of nitrogen to form peroxyacyl nitrates, which are the eye irritants of smoke. The levels of the ozone in the air are usually lower at night than during the day.

References:

1. Chemistry for the Health Sciences, George, 5th ed., 1985.

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Chapter 9: *Oxidation-Reduction*

CHAPTER OUTLINE: The student will be able to:-

Oxidation-reduction
Oxidizing agents & reducing agents
Importance of oxidation-reduction: *Antiseptic Effects, Effects on hair protein, and Stain removal*

Oxidation: May be defined as "a loss of electrons". Consider the electron-dot structures in reaction 9-1. The sodium atom has one outer electron. When the sodium atom loses this one electron, it forms a sodium ion with a + 1 charge: **This loss of an electron is defined as oxidation**. Therefore, the sodium atom was oxidized.

$$\mathrm{Na}\bullet \ + \ \bullet\mathrm{Cl}: \longrightarrow \ \mathrm{Na}^{+} \ + \ :\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:^{-} \qquad (9\text{-}1)$$

A second definition of **oxidation** states that it is **an increase in oxidation number**. Consider reaction 9-2.

$$2\mathrm{Na} \ + \ \mathrm{Cl}_2 \longrightarrow \ 2\mathrm{NaCl} \qquad (9\text{-}2)$$

An uncombined element has an oxidation number of zero. The oxidation number of sodium in sodium chloride (NaCl) is +1 and that of chlorine -1. Therefore, reaction 9-2 may be written as follows.

$$2\overset{0}{\mathrm{Na}} \ + \ \overset{0}{\mathrm{Cl}_2} \longrightarrow \ 2\overset{+1}{\mathrm{Na}} \ + \ 2\overset{-1}{\mathrm{Cl}}$$

The sodium has changed in oxidation number from zero to +1, This is oxidation. The sodium atom was oxidized. The cells in the body burn glucose producing carbon dioxide (CO_2), water, and energy.

$$\overset{0}{C_6H_{12}O_6} + 6\overset{0}{O_2} \longrightarrow 6\overset{+4}{CO_2} + 6H_2O + \overset{-2}{\text{energy}}$$

glucose

The oxidation number of each carbon atom in glucose is zero. The oxidation number of the carbon atom in carbon dioxide is +4. † Therefore, the carbon atom increased in oxidation number. A gain in oxidation number is oxidation; therefore, the carbon atom in glucose was oxidized, or it can be said that the glucose, which contain the carbon atom, was oxidized.

A third definition of **oxidation** is "**addition of oxygen**." Consider reaction 9-3, which involves the oxidation of formaldehyde to formic acid.

$$\underset{\text{Formaldehyde}}{HCHO} + [O] \longrightarrow \underset{\text{formic acid}}{HCOOH} \qquad (9\text{-}3)$$

Note that this reaction involves the addition of oxygen.

A fourth definition of **oxidation** involves the "**removal of hydrogen**" in reaction 9-4

$$\underset{\text{ethanol}}{CH_3CH_2OH} + [O] \longrightarrow \underset{\text{acetaldehyde}}{CH_3CHO} + H_2O \qquad (9\text{-}4)$$

The following oxidation reactions take place in the body.

$$\text{carbohydrate} + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$$

$$\text{fat} + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$$

$$\text{protein} + O_2 \longrightarrow CO_2 + H_2O + \text{urea} + \text{energy}$$

Thus, oxidation may be defined as

5. A loss of electrons
6. An increase in oxidation number
7. A gain of oxygen
8. A loss of hydrogen

Reduction: reduction is the opposite of oxidation;

5. A gain of electrons
6. A decrease in oxidation number
7. A loss of oxygen
8. A gain of hydrogen

$$\underset{\text{acetic acid}}{CH_3COOH} + H_2 \longrightarrow \underset{\text{ethanol}}{CH_3CHO} + H_2O \qquad (9\text{-}5)$$

$$\underset{\text{acetone}}{CH_3COCH_3} + H_2 \longrightarrow \underset{\text{isopropyl alcohol}}{CH_3CH(OH)CH_3} \qquad (9\text{-}6)$$

Oxidizing agents & Reducing agents:

Reducing agent- The substance that causes the reduction of an element or compound.
Oxidizing agent- The substance that causes the oxidation of some element or compound.

$$\overset{0}{H_2} + Pb\overset{+2\ -2}{O} \longrightarrow \overset{0}{Pb} + H_2\overset{2(+1)-2}{O}$$

$$\underset{\substack{\text{oxidized} \\ \text{reducing agent}}}{H_2} \quad + \quad \underset{\substack{\text{reduced} \\ \text{oxidizing agent}}}{PbO} \quad \longrightarrow \quad Pb + H_2O$$

Oxidation and reduction reactions produce the energy the body needs to carry out its normal functions. Oxidation-reduction in the body involves either oxygen or hydrogen, or both.

Enzymes involved in oxidation-reduction reactions in the body is called **oxidoreductases**. Many of these enzymes are present in the mitochondria. These enzymes are responsible for the production of heat and energy.

Importance of oxidation-reduction:

Antiseptic effects- Because they are oxidizing agents, many antiseptics have the property of killing bacteria. Among these is *chlorine*, which oxidizes organic matter and bacteria and so is used in the treatment of water to make it potable. *Calciumhypochlorite* $Ca(OCl)_2$, another commonly used oxidizing agent and bleaching powder, is used as disinfectant for clothes and hospital beds. Tab. 9-1 lists some of the common antiseptics that are oxidizing agents.

Table 9-1, Antiseptic agents

Formula	Name	Use
$3\%H_2O_2$	Hydrogen peroxide	More cuts and scratches
$KMnO_4$	Potassium permanganate	Treatment of infection in urethra & bladder
$KClO_3$	Potassium chlorate	Treatment of sore throat
I_2 in H_2O	Lugol᾽s solution	Treatment of minor cuts
NaOCl	Sodium hypochlorite (Dakin᾽s solution)	Treatment of wounds

Formaldehyde and sulfur dioxide are two reducing agents used in disinfecting rooms formerly occupied by patients with contagious diseases.

Effects on hair protein- Oxidizing and reducing agents denature protein by affecting the disulfide bonds of the amino acid cysteine.

Stain removal-Oxidizing and reducing agents are used to remove most stains that cannot otherwise be removed. Common stain removers and indicates where they may be used safely (H_2O_2, $KMnO_4$, and sodium hypochlorite, $NaOCl$;) are oxidizing agent. ($Na_2S_2O_3$), sodium thiosulfate and oxalic acid $[COOH]_2$ are reducing agent.

References:

4. Dickson, T. R. *introduction to chemistry*, 4th ed. John Wiley & Sons, Int., New York, 1983, chapter 13.
5. McQUARRIE, DONALD A. and Peter A. Rock. *General chemistry* , W. H. Freeman and Company, New York, 1984, chapter 24.
6. Chemistry for the Health Sciences, George, 5th ed., 1985.

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