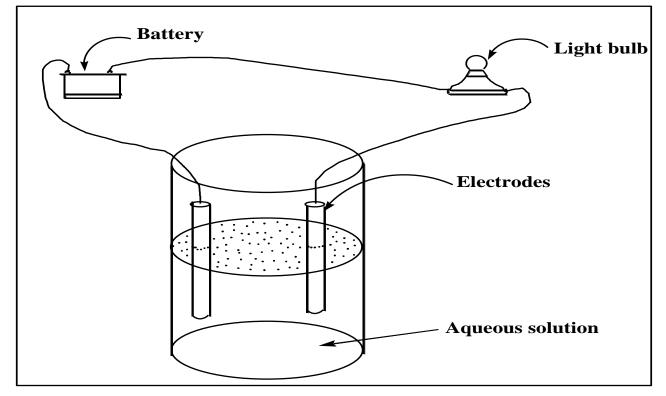
# <u>Lec:(5)</u>

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

An electrical circuit can also contain aqueous solution as shown in following figure.



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

-The two electrode are oppositely charged.

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

-The solution must be able to conduct electricity. Glowing light bulb indicates that electricity is flow through circuit.

Aqueous solutions either conduct electricity or they do not. One that conducts electricity is called an *electrolytic solution*; one that dose not is called *a nonelectrolytic solution*.

	•	ť	
Electrolytes		Nonelectrolytes	
NaCl	sodium chloride	$C_{12}H_{22}O_{11}$	sucrose
KI	potassium iodide	$C_2H_5OH$	Ethyl alcohol
LiBr	Lithium bromide	C <sub>3</sub> H <sub>6</sub> O	Acetone
Na <sub>2</sub> SO	4 sodium sulfate	$CH_4$	Methane
KNO <sub>3</sub>	potassium nitrate	$N_2$	Nitrogen
$CaCl_2$	Calcium chloride	$O_2$	Oxygen
LiF	Lithium floride	ĊŌ	Carbon monoxide

**Electrolytes and Nonelectrolytes** 

**Electrolyte:** A solute that forms an aqueous electrolytic solution.

**Nonelectrolyte:** A solute that forms an aqueous nonelectrolytic solution.

**Hydration:** is a close association of water molecule with an ion, we say that ion is hydrated. Thus according to **Arrhenius theory**, one mole of sodium chloride forms one mole of sodium ions and 1 mole of chloride ion when dissolved in water.

\*Aqueous solution of electrolytes are really solutions of hydrated ions.

\*The total number of ions formed per mole of electrolyte depends on the chemical formula of the electrolyte as shown in following Table. **Ex:** 1 mole of calcium chloride dissolved in water forms 1 mole of hydrated calcium ions and 2 moles of hydrated chloride ions.

rumber of fons formed per more of electrolyte				
chemical	ions formed in	Number of ions in 1 mol		
formula	aqueous solution	of electrolyte		
NaCl	Na <sup>+</sup> Cl <sup>-</sup>	$2 \times 6.02 \times 10^{23}$		
LiBr	$Li^+$ Br <sup>-</sup>	$2 \times 6.02 \times 10^{23}$		
KNO <sub>3</sub>	$K^+ NO_3^-$	$2 \times 6.02 \times 10^{23}$		
CaCl <sub>2</sub>	Ca <sup>+</sup> Cl <sup>-</sup> Cl <sup>-</sup>	$3 \times 6.02 \times 10^{23}$		
Na <sub>2</sub> SO <sub>4</sub>	Na <sup>+</sup> Na <sup>+</sup> SO <sub>4</sub> <sup>-2</sup>	$3 \times 6.02 \times 10^{23}$		
Na <sub>3</sub> PO <sub>4</sub>	Na <sup>+</sup> Na <sup>+</sup> Na <sup>+</sup> PO <sub>4</sub> <sup>-3</sup>	$4 \times 6.02 \times 10^{23}$		

Number of ions formed per mole of electrolyte

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

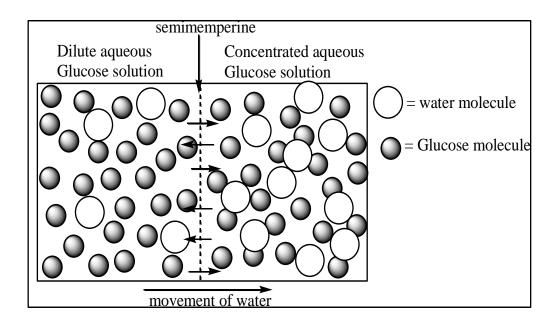
### **OSMOSIS AND OSMOTIC PRESSURE**

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

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

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

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



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

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

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

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

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

**\*Hypotonic:** One of the two solutions that has the lower

osmotic pressure than the other, for example, 1M NaCl solution has a lower osmotic pressure than a 2M LiBr solution.

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

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

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

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

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

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

**-Colloidal dispersion:** A uniform dispersion of a colloid in water.

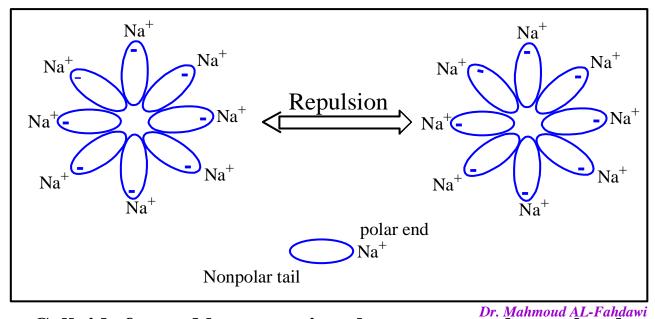
<u>-Dispersion substance</u>: the colloid in a colloidal dispersion

<u>-Dispersing substance</u>: The continuous matter in which the colloid is dispersed.

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

Dispersed	Dispersing	Example
substance	substance	
Liquid	Gas	Fog, clouds
Solid	Gas	Smoke
Gas	Liquid	Foams, whipped cream
Liquid	Liquid	Milk, butter
Solid	Liquid	Paints, glue
Gas	Solid	Foam, rubber, pumice
Liquid	Solid	Jellies, cheese
Solid	Solid	Colored glass, gems

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



**Colloids formed by attractions between complex molecules** 

**Emulsifying agent**: A Compound or substance that stabilized a colloidal dispersion for example (Soap) in mixture of oil and water.

Water is immiscible with water, if we add soap to mixture the oil is emulsified by the soap.

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

**Dailysis:** The selective passage of small molecules and ions in either direction by dialyzing membrane. Dialysis differ from osmosis in that osmotic membrane allow only solvent molecules to pass.

\*The kidneys are an example of organs in the body that use dialysis to maintain the solute and electrolyte balance of the blood.

The main purpose of the kidneys are to clean the blood by removing the waste products of metabolism and control the concentration of electrolyte.

\*The efficient kidneys purified 180L of blood in a 68kg (150 Ib) adult.

# Lec:(6) VVVVVVVVVV Dr.Mahmoud S. Muter

# Chemical reactions in aqueous solutions

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

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

a. compound insoluble in water, called a precipitate. b. Gas.

c. compound that is soluble in water but dose not as ions, called an un-ionized compound.

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

#### $LiCl + NaNO_3 \rightarrow LiNO_3 + NaCl$

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

The products lithium nitrate and sodium chloride, also exist as ions in solution. This means that an aqueous solution of the two salts is a mixture of the four ions,  $Li^+$ ,  $Na^+$ ,  $NO_3^-$ ,

and Cl<sup>-</sup>. No precipitate, no gas, no un-ionized compound is formed as product product. therefore, no chemical reaction has taken place.

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

**NaCl** + AgNO<sub>3</sub> ------ NaNO<sub>3</sub> + AgCl The salts sodium chloride, silver nitrate are all electrolytes. In contrast, silver chloride is insoluble in water (precipitate). therefore, chemical reaction is ionic reaction.

# *Ions in living systems*

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

Cations	Anions
Na <sup>+</sup>	Cl
<b>k</b> <sup>+</sup>	HCO <sub>3</sub>
$Mg^{+2}$	$H_2PO_4$
$Ca^{+2}$	HPO <sub>4</sub> <sup>-2</sup>
$Fe^{+2}$	_
Fe <sup>+3</sup>	_

-Na<sup>+</sup>, Ca<sup>+2</sup> : in intercellular fluid (fluid between cells). Calcium ions are needed for healthy bones and teeth, for blood clotting, and for regulation of the heartbeat. - $\mathbf{K}^+$  Mn<sup>+2</sup> : in cellular fluid, the Mn<sup>+2</sup> ions assist enzymes in

-K<sup>+</sup>, Mn<sup>+2</sup>: in cellular fluid, the Mn<sup>+2</sup> ions assist enzymes in their biological roles.

**-Fe<sup>+2</sup>**, **Fe<sup>+3</sup>**: part of cytochrome system involved in oxidative phosphorylation and the hemoglobin contain Fe<sup>+2</sup>that play very important role in the transport of oxygen and carbon dioxide.

-Cu<sup>+2</sup>, Zn<sup>+2</sup>, Co<sup>+2</sup> and Mn<sup>+2</sup>: assist enzymes in their biological role.

-Hg<sup>+2</sup>: Extensive damage to brain and nervous system.

-**Pd**<sup>+2</sup> : Toxic effect on kidney and nerve damage.

-O<sub>2</sub>: carried in blood stream to cells as part of molecule Oxyhemoglobine.

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

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

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

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

### **Chemical Equilibrium**

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

### $N_2 + 3H_2 \longrightarrow 2NH_3$

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

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

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

### $N_2 + 3H_2 \longrightarrow 2NH_3$

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

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

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

$2SO_2 + O_2 \longrightarrow 2SO_3$	$\mathbf{K} = \frac{[\mathbf{SO}_3]^2}{[\mathbf{SO}_2]^2[\mathbf{O}_2]}$
$30_2 \implies 20_3$	$\mathbf{K} = \frac{\left[\mathbf{O}_3\right]^2}{\left[\mathbf{O}_2\right]^3}$
$Cl_2 + 2HBr \implies Br_2 + 2HCl$	$\mathbf{K} = \frac{[\mathbf{Br}]^2 [\mathbf{HCl}]^2}{[\mathbf{Cl}] [\mathbf{HBr}]^2}$

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

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

Many example of this principle are found in living systems:

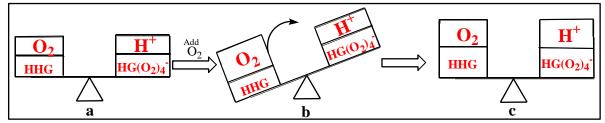
\*Oxygen needed by the body is carried in the blood stream to the cells as part of the molecule oxyhemoglobin. This molecule is formed in the blood by the reaction between dissolved oxygen gas obtained from air and hemoglobin in the red blood cells. This reaction is reversible. In the cells, oxyhemoglobin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

#### Hemoglobin + $4O_2 \implies Oxyhemoglobin$

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

### HHG + $4O_2 \implies HG(O_2)_4 + H^+$

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



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

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

$$\begin{array}{rcl} \mathbf{G-1-P} & \xrightarrow{\text{Enzyme}} & \mathbf{G-6-P} \\ \mathbf{K} = \frac{[\mathbf{G-6-P}]}{[\mathbf{G-1-P}]} = & \mathbf{20.0} \end{array}$$

We know from many experiments that the equilibrium constant for this reaction is 20.0 at body temperature (37 °C). This means that concentration of G-6-P is 1.00M and the

concentration of G-1-P is  $0.0500\mathrm{M}$  . this is an equilibrium mixture of the two compounds.

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

### **IONIZATION OF WATER**

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

 $2H_2O \Longrightarrow H_3O^+ + OH^- \dots (1)$ 

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

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

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

# $\mathbf{K} = \frac{[\mathbf{H}_{3}\mathbf{O}^{+}][\mathbf{O}\mathbf{H}^{-}]}{[\mathbf{H}_{2}\mathbf{O}]^{2}}$

The concentration of water molecules is essentially constant. Thus:

The ionization of water is often written simply as:

 $H_2O \implies H^+ + OH^- \dots (2)$ 

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

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

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

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

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

-An aqueous solution in which [H<sup>+</sup>] is grater than [OH<sup>-</sup>] is called *acidic solution*. While in *basic solution* [OH<sup>-</sup>] is grater than [H<sup>+</sup>].

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

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

```
K_{w} = [H^{+}][OH^{-}] = 1x10^{-14}
(a) [OH^{-}] = \frac{1x \ 10^{-14}}{[H^{+}]} = \frac{1x \ 10^{-14}}{1x \ 10^{-5}} = 1X \ 10^{-9}M
(b) [OH] = 1x10^{-4}
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**Exercise:**Decide whether each of the following solutions is acidic, basic or neutral.

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

**PH scale:** Molar concentration is used to express the concentration of H<sup>+</sup> and OH<sup>-</sup> ions, another way is PH. P= function= -log[con.] to express very low concentrate.

PH =  $0 \longrightarrow 7 \longrightarrow 14$ acidic neutral basic PH= -log[H<sup>+</sup>] [H<sup>+</sup>]= 1x 10<sup>-PH</sup> [H<sup>+</sup>] for pure water is 1x 10<sup>-7</sup>M [H<sup>+</sup>]= 1x 10<sup>-7</sup>M = 10<sup>-PH</sup> PH= 7

In same way: POH = 7

Kw=  $(1x 10^{-PH}) x (1x 10^{-PH}) = 1x 10^{-14}$ PH+POH=14 so POH= 14-PH

#### **Example:**

(1) calculate PH and POH of solution its  $[H^+]$  1.5 x 10<sup>-3</sup> PH= -log $[H^+]$ = -log  $[1.5 \times 10^{-3}]$ = -log 1.5 - log 10<sup>-3</sup> PH= -log1.5 + 3= 2.82 POH= 14- PH = 14 - 2.82 = 11.18 (2) calculate  $[H^+]$  conc. Of solution that its PH= 5.25. PH= -log  $[H^+]$ LogH<sup>+</sup>= -PH= -5.2 Auti log = 5.62 x 10<sup>-6</sup> \*Body fluid differ in (1) their acidity (2) range of acidity. -Stomach :  $PH = 1 \longrightarrow 3$ -Urine :  $PH = 4.8 \longrightarrow 7 \longrightarrow 8.4$ 

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

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

# Lec:(7)

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

**\*Bronsted (1923):** defined an acid as any compound or ion that donate proton (H<sup>+</sup>), and a base any compound or ion that accepts a proton.

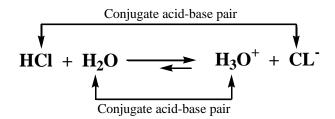
\*Lewis (1930): defined an acid as any compound or ion accept one pair of electron, and a base any compound or ion donate one pair of electron.

\*Arrhenius (1887): define an acid as any compound that ionize in water to form  $[H_3O^+]$ , and a base any compound that ionize in water to form  $[OH^-]$ .

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

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

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

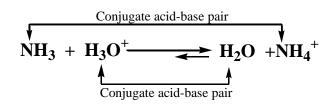


**Exercise** : Identify the two conjugate acid-base pair in each of the following equation:

- (a) HBr +H<sub>2</sub>O  $\longrightarrow$  H<sub>3</sub>O<sup>+</sup> + Br<sup>-</sup>
- (b)  $H_2SO_4 + H_2O \longrightarrow HSO_4 + H_3O^+$
- (c)  $H_3O^+ + OH^- \longrightarrow H_2O + H_2O$
- (d)  $OH^{-} + C_2H_3O_2H \longrightarrow H_2O + C_2H_3O_2^{-}$

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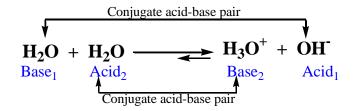
Ammonia reacts with a proton (hydrogen ion) to form an ammonium ion according to the following equation:



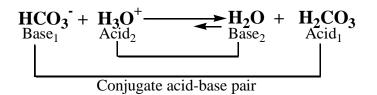
 $NH_3$  is a Bronsted base, but it dosent fit the Arrhenius definition of base.

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

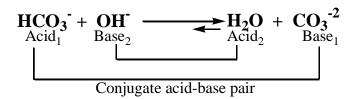
One water molecule donates a proton to another molecule of water to form a hydronium ion and a hydroxide ion. One water molecule acts as an acid and the other acts as a base, as shown in the following equation:



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



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



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

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

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

> $\frac{\text{HCl}}{\text{Hydrogen}} + \frac{\text{H}_2\text{O}}{\text{Water}} \longrightarrow \frac{\text{H}_3\text{O}^+}{\text{Hydrogen}} + \frac{\text{CL}^-}{\text{Chloride}}$ chloride ion ion

Other compounds that are strong acids are (HBr, HClO<sub>4</sub>, HI, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HF, HCN, H<sub>2</sub>CO<sub>3</sub>,C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>H).

- Bases are also called alkaline substances. Some bases exist as ions in aqueous solution and are called **strong bases**. Sodium hydroxide (NaOH) is an example of a strong base. When dissolved in water, hydrated sodium ions (Na<sup>+</sup>) and hydroxide ions (OH<sup>-</sup>) are formed, as shown in the following equation:

NaOH  $\longrightarrow$  Na<sup>+</sup> + OH<sup>-</sup>

Other common bases are potassium hydroxide (KOH),

calcium hydroxide (Ca(OH)<sub>2</sub>), and magnesium hydroxide (Mg(OH)<sub>2</sub>), these bases all exist as ions in aqueous solution.

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

**Ex**: Acetic acid ionization:

 $C_{2}H_{3}O_{2}H + H_{2}O \longrightarrow H_{3}O^{+} + C_{2}H_{3}O_{2}^{-}$  $K = \frac{[H_{3}O^{+}] [C_{2}H_{3}O_{2}^{-}]}{[H_{2}O] [C_{2}H_{3}O_{2}H]} \longrightarrow K \times [H_{2}O] = \frac{[H^{+}] [C_{2}H_{3}O_{2}]}{[C_{2}H_{3}O_{2}H]}$ 

Diprotic acids ionize in two steps:

$$H_{2}CO_{3} + H_{2}O \implies H_{3}O^{+} + HCO_{3}^{-} \implies K_{a1} = \frac{[H^{+}][HCO_{3}]}{[H_{2}CO_{3}]}$$
$$HCO_{3}^{-} + H_{2}O \implies H_{3}O^{+} + CO_{2}^{-} \implies K_{a2} = \frac{[H^{+}][HCO_{3}]}{[H_{2}CO_{3}]}$$
$$PK_{a} = -logK_{a}$$

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

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

 $\mathbf{NH}_{3} + \mathbf{H}_{2}\mathbf{O} \longrightarrow \mathbf{NH}_{4}^{+} + \mathbf{OH}^{-}$  $\mathbf{K} = \frac{[\mathbf{NH}_{4}^{+}][\mathbf{OH}^{-}]}{[\mathbf{H}_{2}\mathbf{O}][\mathbf{NH}_{3}]} \longrightarrow \mathbf{K} \times [\mathbf{H}_{2}\mathbf{O}] = \mathbf{K}_{b} = \frac{[\mathbf{NH}_{4}^{+}][\mathbf{OH}^{-}]}{[\mathbf{NH}_{3}]}$ 

 $\mathbf{PK}_{\mathbf{b}} = -\mathbf{log}\mathbf{K}_{\mathbf{b}}$ 

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

**Example:** Which is the stronger acid, HCN ( $K_a$ =4.93x 10<sup>-10</sup>) or HF ( $K_a$ = 3.53 x 10<sup>-4</sup>)?

Ans: Decide which value of K is smaller.

4.93x 10<sup>-10</sup> is smaller than 3.53 x 10<sup>-4</sup> therefore, HCN is the weaker acid.

#### **Problems:**

1. Calculate the PH of a 0.025M solution of HCl (log2=0.3). HCl  $\longrightarrow$  H<sup>+</sup> + Cl<sup>-</sup>

 $[H^+] = 0.025M$ PH= -log2.5 x 10<sup>-2</sup>, log 2.5= 0.4 = -log(10<sup>0.4</sup> x 10<sup>-2</sup>) = -log10<sup>-1.6</sup> =-(-1.6)=1.6

2. Find the PH of 0.1M  $NH_4OH$  (K<sub>b</sub>=2 x 10<sup>-5</sup>)

NH<sub>4</sub>OH 
$$\leftarrow \rightarrow$$
 OH<sup>-</sup> +NH<sub>4</sub><sup>+</sup>  
[OH<sup>-</sup>]=  $\sqrt{\text{Kb x C}}$  C= Conc. of weak base  
 $= \sqrt{2x \ 10^{-5}x} \ 10^{-1} = 1.42x \ 10^{-3}$   
POH= 2.85  
PH + POH= 14  
PH=11.15

# Neutralization

An acid reacts with a base to form water and a salt. For example, aqueous solutions of sodium hydroxide and hydrochloric acid react to form water and sodium chloride, as the following equation :  $NaOH + HCl \rightarrow H_2O + NaCl$ 

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

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

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

### ACID BASE TITRATION

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

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

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

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

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

### **BUFFER SOLUTIONS**

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

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

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

 $C_2H_3O_2 + H_3O - C_2H_3O_2H + H_2O$ Weaker base

Most of the added H<sup>+</sup> ions are removed from the solution and PH hardly changed.

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

 $\mathbf{OH} + \mathbf{C}_2\mathbf{H}_3\mathbf{O}_2\mathbf{H} \longrightarrow \mathbf{C}_2\mathbf{H}_3\mathbf{O}_2^{-} + \mathbf{H}_2\mathbf{O}$ 

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

# $\mathbf{PH} = \mathbf{PK}_{\mathbf{a}} + \log \frac{[\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{O}_{2}^{-}]}{[\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{O}_{2}\mathbf{H}]}$

A buffer solution has a limited ability to react with acids and bases without changing its PH. It acts as buffer because it contains both members of a conjugate acid-base pair.

Removal of one of these two by chemical or physical process destroys the buffer action of the solution. Buffer solutions are important in the body because they maintain the acidbase balance in the blood.

# **Acid-base balance in blood:**

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

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

 $HPO_4^{-2} + H^+ \longrightarrow H_2PO_4^{-1} + H_2O$ 

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

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

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

 $CO_2 + H_2O \implies H_2CO_3 \implies HCO_3 + H^+$ 

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

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

The PH of the blood becomes more basic when the ratio  $HCO_3^-/H_2CO_3$  becomes greater than than 20/1. the alkaline condition of the blood signified by a PH greater than 7.45 is called *alkalimia*.

Death occurs if the PH of the blood is more acidic than 6.8 or more basic than 7.8 .

-Let us consider how the body uses the carbonic acidbicarbonate ion buffer system to cope with an increase in either the acid or the base concentration in the blood.

<u>First</u>: *acidosis* (the physiological processes causing academia) occur in a patient who has illness that causes an increase in the concentration of acidic products in the blood. The acidic products react with  $HCO_3$  to produce  $H_2CO_3$ ; this causes a decrease in the ratio  $HCO_3^-/H_2CO_3$ .

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

### $H_2CO_3 \longrightarrow H_2O + CO_2^{\uparrow}$

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

<u>Second</u>: **Alkalosis**: (the physiological processes causing alkalemia) occur in a patient who has an illness that causes an increase in the concentration of bacic products in the blood. These basic products react with  $H_2CO_3$  to produce  $HCO_3^-$  ions; this causes an increase in the ratio  $HCO_3^-/H_2CO_3$ . to prevent this ratiofrom increasing is to conserve the  $CO_2$  in the body and use it to produce more  $H_2CO_3$ . to do this, loss of  $CO_2$  through lungs is minimized by slower breathing. This process called *hypoventilation*. As before,

the kidneys can help if needed by removing  $HCO_{3}^{-}$  and addition of H<sup>+</sup> ions to blood. Thus, the lungs and kidneys can function to maintain the PH of the blood within its normal range of 7.35 to 7.45.