Electrolyte Solutions
Acid-Base Equilibrium

LECTURE 3

1. *The Bronsted-Lowry Theory*
2. *The Lewis Theory*
3. *Buffer Solutions*
4. *Buffer Systems of Blood*

Acid-Base Equilibrium

- Acids and bases form a particularly important class of electrolytes
- The precise balance of their concentrations or pH in our bodies is necessary for the proper function of enzymes, maintenance of osmotic pressure

1. The Bronsted-Lowry Theory

Protolytic theory of acids and bases

- In 1923, an English scientist, T.M.Lowry, and a Danish scientist, J.N.Bronsted independently proposed that

An acid is a proton (hydrogen ion) donor

A base is a proton (hydrogen ion) acceptor

- Any acid-base reaction is described as:

acid + base → conjugate base + conjugate acid

The conjugate base of an acid is the remainder of the acid after the proton transfer

acid → conjugate base + H^+

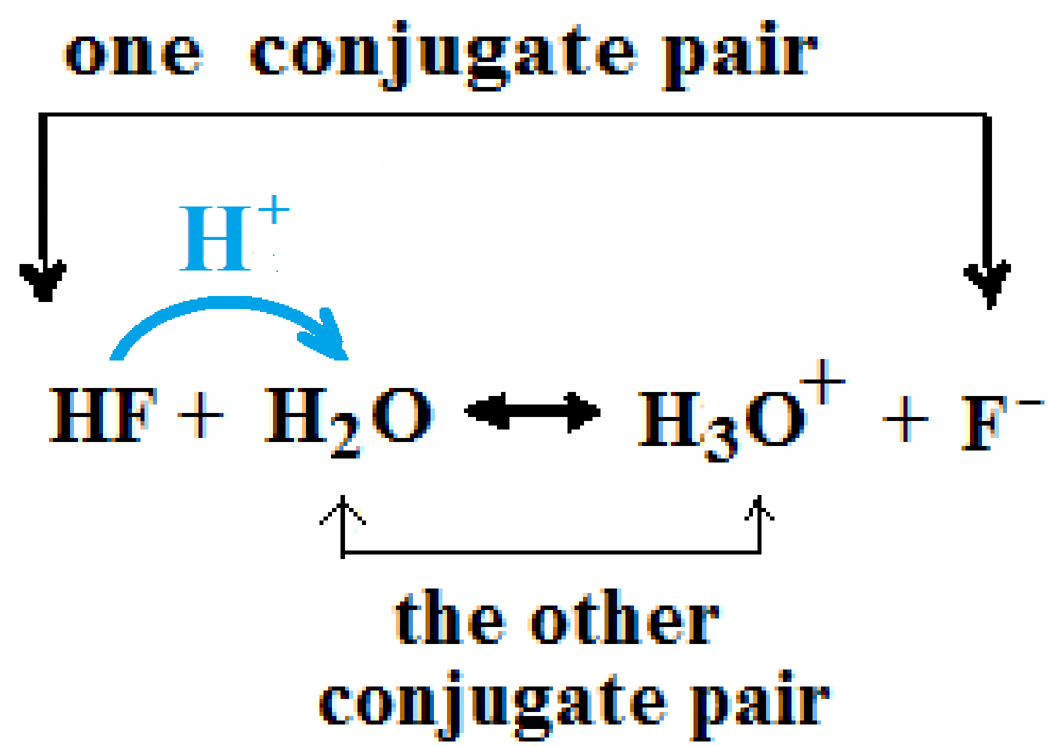
H^+

acid + base → conjugate base + conjugate acid

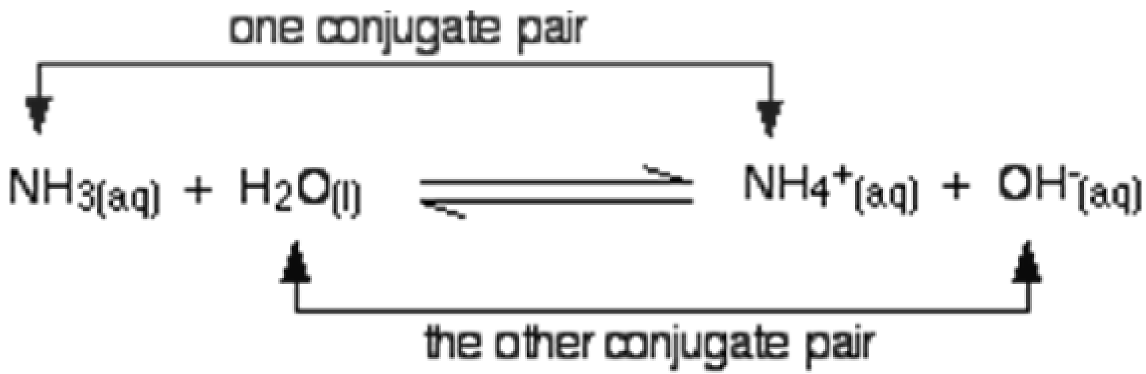
- ***The conjugate acid*** of a base is formed when the base acquires a proton from the acid

base + H^+ → conjugate acid

For example, interaction of an acid with water can be represented as



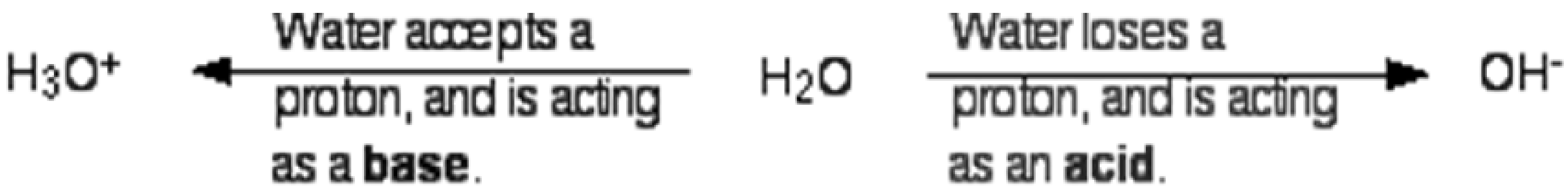
The reaction between ammonia and water also involves two conjugate pairs:



- **Ammonia is a base because it accepts hydrogen ions from the water**
- **The ammonium ion is its conjugate acid - it can release that hydrogen ion again to reform the ammonia**

A substance which can act as either an acid or a base is described as being amphoteric

- For example water is acting as a base in one case whereas in the other one it is acting as an acid:



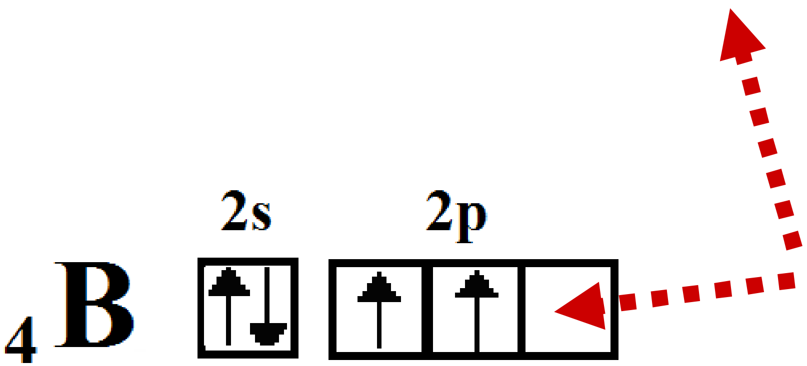
2. The Lewis Theory

- In 1923, the same year that Bronsted and Lowry proposed their theories, Gilbert Newton Lewis, an American chemist, proposed an broader definition of acids and bases
  - **an acid is an electron pair acceptor**
    - **a base is an electron pair donor**

- Lewis focused on electron but not on proton transfer
- His definition is more inclusive than the previous, and applies to reactions which do not even involve hydrogen ions

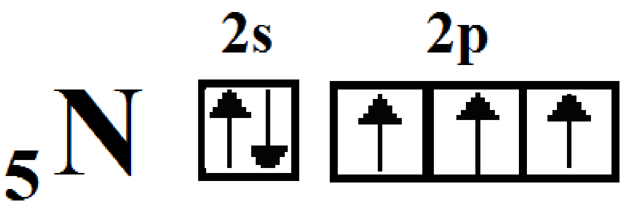
- Consider the reaction between ammonia and boron trifluoride:

$$H_3N \quad + \quad \square BF_3 \rightarrow$$

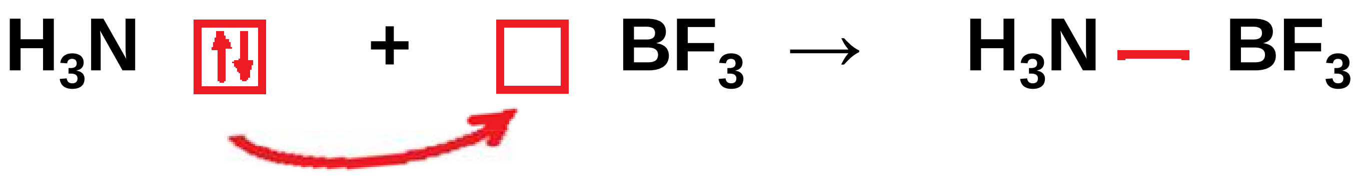


Note that boron has an empty orbital, and can accept electrons in its valence level

H_3N ⇅ + □ BF_3 →



- Note that the nitrogen atom has an unshared electron pair



- Since boron trifluoride ***BF_3*** can accept an electron pair, it is ***a Lewis acid***

- Ammonia **NH_3** is ***a Lewis base***, because it can donate an electron pair

- The Bronsted-Lowry theory classifies ammonia NH_3 as a base because it accepts a proton H^+
- The Lewis theory classifies NH_3 as a base because it donates an electron pair

From the point of view of protolytic theory of acids and bases determine in which of the reactions water plays the role of a base:

a) $NH_3 + HOH \rightleftarrows NH_4^+ + OH^-$

b) $CH_3COOH + HOH \rightleftarrows CH_3COO^- + H_3O^+$

c) $R-NH_2 + HOH \rightleftarrows [R-NH_3]^+ + OH^-$

d) $PO_4^{3-} + HOH \rightleftarrows HPO_4^{2-} + OH^-$

3. Buffer Solutions

- ***Buffer solutions or buffers*** are solutions, which have an ability to resist in case of pH change upon the addition of small quantities of acids and bases

- Each buffer solution contains **a conjugate pair**, which is responsible for a solution ability to neutralize acids and bases added to it

a) $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

acid — conjugate base

b) $H_2CO_3 \leftrightarrow HCO_3^- + H^+$

acid — conjugate base

c) $NH_4^+ \leftrightarrow NH_3 + H^+$

acid — conjugate base

An acid is a proton donor

A conjugate base is a proton acceptor

Classification of buffer solutions

1. The buffer solution consists of weak acid and its salt

Acetate buffer system: CH_3COOH/CH_3COONa

2. Weak base and its salt

Ammonia buffer system: NH_3/NH_4Cl

3. Two acid salts

Hydro phosphate buffer system: NaH_2PO_4/Na_2HPO_4

4. Acid salt and neutral salt

Carbonate buffer system: $NaHCO_3/Na_2CO_3$

Henderson-Hasselbach equation

- ***Buffer solutions*** have an ability to resist pH
- pH of a buffer solution may be calculated by Henderson-Hasselbach equation:

$$pH = pK + \log \frac{[conjugatebase]}{[acid]}$$

where $pK = -\log K_{acid}$ or $pK = -\log K_{base}$

Acetate buffer system

CH_3COOH/CH_3COONa

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

CH_3COONa ® $CH_3COO^- + Na^+$

n $$pH = pK_a + lg \frac{[conjugatebase]}{[acid]}$$

n $$pH = pK_a + lg \frac{[CH_3COONa]}{[CH_3COOH]}$$

Poblem . We add 49,2 g of CH_3COONa to 2 L of 0,1 M of CH_3COOH solution. Calculate the pH of the obtained buffer solution, K_a (CH_3COOH) = $1{,}75 \times 10^{-5}$

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

$$CH_3COONa \text{ ® } CH_3COO^- + Na^+$$

1. The concentration of sodium acetate in the solution:

$$C_M(CH_3COONa) = m/(M \times V) = 49{,}2 / (82 \times 2) = 0{,}3 \text{ mol/L}$$

2. The pH of acetate buffer solution:

$$pH = -\lg Ka + \lg \frac{[CH_3COONa]}{[CH_3COOH]} =$$

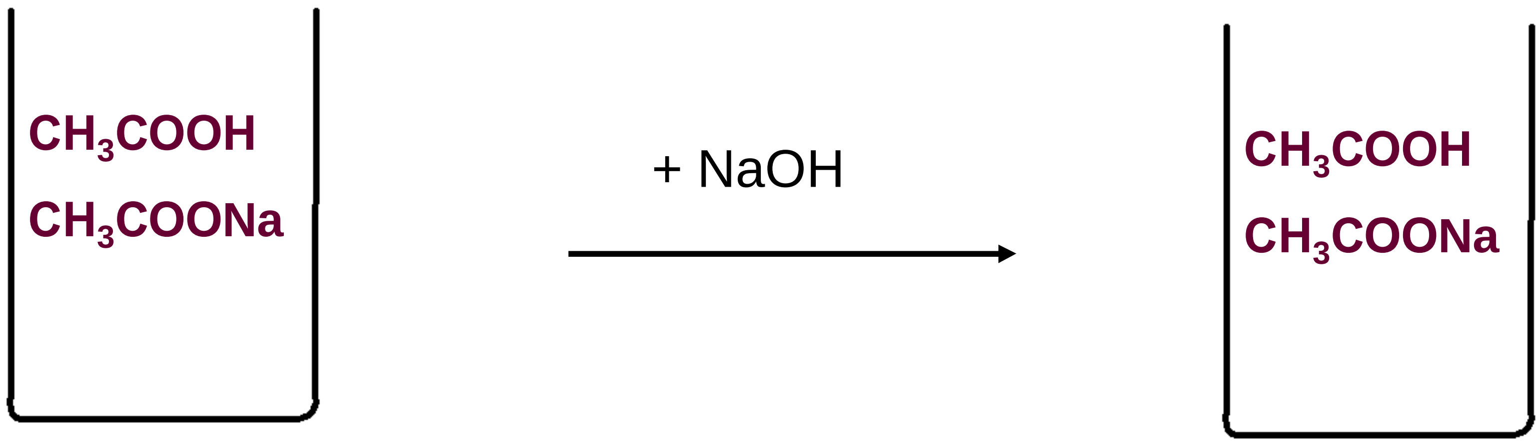
$$= -\lg 1{,}75 \cdot 10^{-5} + \lg \frac{0{,}3}{0{,}1} = 4{,}75 + 0{,}48 = 5{,}23$$

CH_3COOH/CH_3COONa

- An ability to resist pH – **buffer action** – a solution ability to neutralize acids and bases added to it

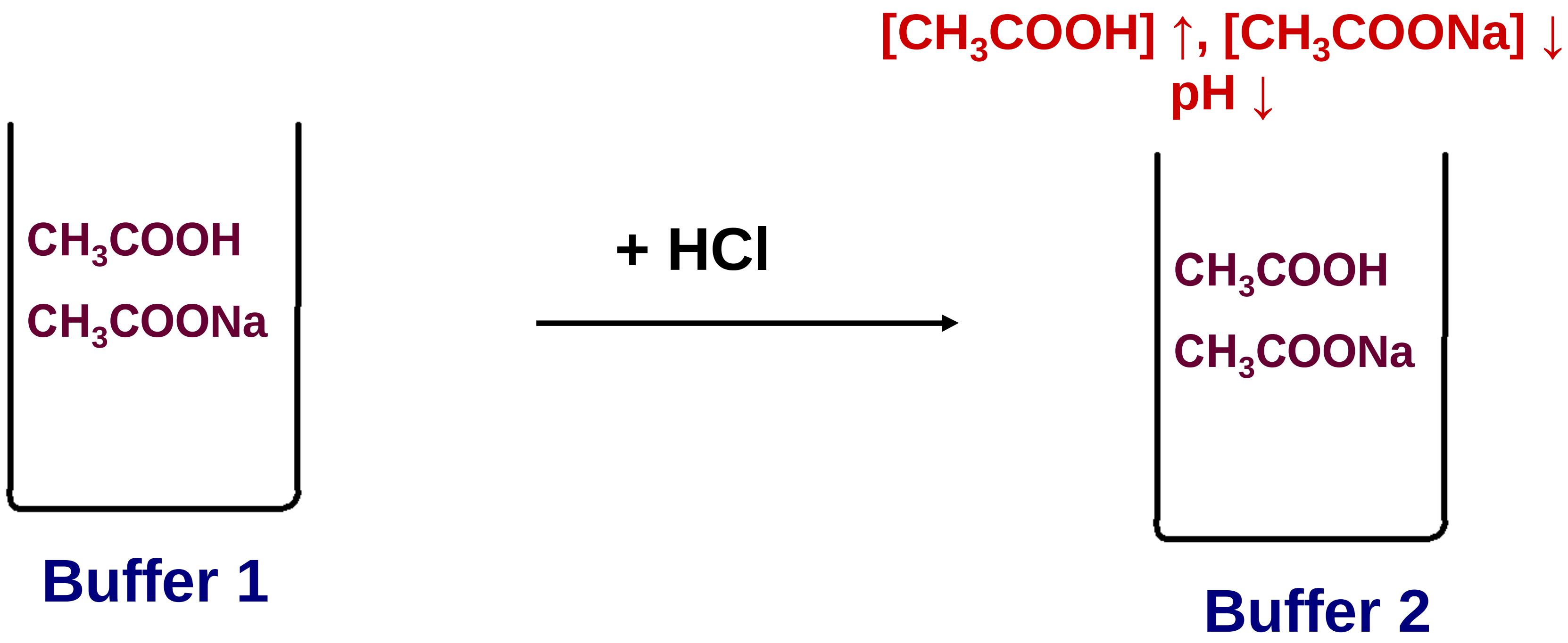
$[CH_3COOH]\downarrow$, $[CH_3COONa]\uparrow$

pH $\uparrow$



Buffer 1 **Buffer 2**

$$\mathbf{NaOH + CH_3COOH \leftrightarrow CH_3COONa + H_2O}$$



$$HCl + CH_3COONa \leftrightarrow CH_3COOH + NaCl$$

CH_3COOH/CH_3COONa

- *Nentralization of an added acid*

$HCl + CH_3COONa \leftrightarrow CH_3COOH + NaCl$

- *Neutralization of an added base*
- $NaOH + CH_3COOH \leftrightarrow CH_3COONa + H_2O$

The zone of effective action of a buffer system is determined by the ratio: $\Delta pH = pK \pm 1$

$K_a (CH_3COOH) = 1,75 \cdot 10^{-5}$

$pK_a = -\log K_a = 4,75$

ΔpH = from (4,75 -1) to (4,75 +1) =

from 3,75 to 5,75

Ammonia buffer system

NH_3/NH_4Cl

- Mechanism of buffer activity is the following:

$HCl + NH_3 \leftrightarrow NH_4Cl$

Neutralization of an added acid

$NaOH + NH_4Cl \leftrightarrow NH_3 + NaCl + H_2O$

Neutralization of an added base

- $pOH = pK_b(NH_4OH) + \lg \dfrac{[NH_4Cl]}{[NH_4OH]}$

$$pH = 14 – pOH = 14 - pK(NH_4OH) – \lg \frac{[NH_4Cl]}{[NH_4OH]}$$

- For the ammonia buffer solution pK_b = 4.75 and the zone of effective buffer action lies in the interval of the **pOH = 5.75 ¸ 3.75**
- the interval of the **pH = (14-5.75) ¸ (14-3.75) =**

  = 8.25 ¸ 10.25

Hydro phosphate buffer system NaH_2PO_4/Na_2HPO_4

- Mechanism of buffer activity:

$HCl + Na_2HPO_4 \leftrightarrow NaH_2PO_4 + NaCl$

Neutralization of an added acid

$NaOH + NaH_2PO_4 \leftrightarrow Na_2HPO_4 + H_2O$

Neutralization of an added base

$$pH = pK_a(H_2PO_4^-) + \lg \frac{[Na_2HPO_4]}{[NaH_2PO_4]}$$

- **Which buffer solution can effectively maintain the constant pH of the medium for the solution, pH of which is 9:**

a) acetate buffer, pK(CH_3COOH) = 4,75;

b) ammonia buffer, pK(NH_4OH) = 4,75;

c) phosphate buffer, pK($H_2PO_4^-$) = 6,8;

d) formate buffer , pK(HCOOH) = 3,75.

- **Poblem.** We've added 40 ml 0,04 M of NaH_2PO_4 solution into 16 ml 0,1 M of Na_2HPO_4 solution. Determine:
- **a)** pH of the obtained buffer solution

  $К_a (H_2PO_4^-) = 6,2 \cdot 10^{-8}$
- **b)** how will pH of this solution change when adding of 6 ml 0,1M of HCl solution

Solution

In the phosphate buffer solution the role of an acid is performed by ion dissociating on the following scheme: $\mathbf{H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}}$

$$pH = -\lg K_a\,(H_2PO_4^-) + \lg \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

- It is necessary to take into account that at mixing of two solutions the initial concentrations of components change. New concentrations can be calculated on the formula:

$$\mathbf{C_{init} \times V_{init} = C_{final} \times V_{final}}$$

$$[NaH_2PO_4] = \frac{C\ (NaH_2PO_4)_{init} \cdot V(\text{solution } NaH_2PO_4)}{V(\text{buffer solution})}$$

$$[Na_2HPO_4] = \frac{C\ (Na_2HPO_4)_{init} \cdot V(\text{solution } Na_2HPO_4)}{V(\text{buffer solution})}$$

$C\ (NaH_2PO_4)_{init} \times V(\text{of } NaH_2PO_4 \text{ solution}) = n\ (NaH_2PO_4)$

$C\ (Na_2HPO_4)_{init} \times V(\text{of } Na_2HPO_4 \text{ solution}) = n\ (Na_2HPO_4)$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{n(Na_2HPO_4)\cdot V(\text{buffer sol.})}{n(NaH_2PO_4)\cdot V(\text{buffer sol.})} = \frac{n(Na_2HPO_4)}{n(NaH_2PO_4)}$$

$$\mathbf{pH = -\lg 6{,}2 \times 10^{-8} + \lg} \frac{n(Na_2HPO_4)}{n(NaH_2PO_4)} \mathbf{= 7{,}21 + \lg} \frac{0{,}0016}{0{,}0016} =$$

$$\mathbf{= 7{,}21 + \lg 1 = 7{,}21}$$

b) Let's calculate the pH change at adding HCl solution to the buffer solution.

At adding 6 mL 0,1 M of HCl solution (which is 0,0006 mole), the added acid will react with 0,0006 mole of Na_2HPO_4 with the formation of 0,0006 mole of NaH_2PO_4:

$$Na_2HPO_4 + HCl = NaH_2PO_4 + NaCl$$

The amount of Na_2HPO_4 will decrease in 0,0006 mole:

n (Na_2HPO_4) = 0,0016 – 0,0006 = 0,0010 mol

And the amount of NaH_2PO_4 will increase in 0,0006 mole: n (NaH_2PO_4) = 0,0016 + 0,0006 = 0,0022 mol

Hence: $pH = -\lg 6{,}2 \cdot 10^{-8} + \lg \dfrac{n(Na_2HPO_4)}{n(NaH_2PO_4)} =$

$= 7{,}21 + \lg \dfrac{0{,}0010}{0{,}0022} = 6{,}86$

Preparation of buffer system

- **Choose the pairs of aqueous solutions of substances, at pouring out of which buffer systems will be formed (pay attention to the reaction products):**

1) 200 mL 0,2M of NH_4OH solution

a) 200 mL 0,3M of NH_4Cl solution;

b) 100 mL 0,3M of HCl solution;

c) 100 mL 0,1M of HCl solution;

d) 200 mL 0,1M of NaCl solution.

Ammonia buffer system:
NH_3/NH_4Cl

or NH_4OH/NH_4Cl

1) **200 mL 0,2M of NH_4OH solution +**

a) 200 mL 0,3M of NH_4Cl solution

1) **200 mL 0,2M of NH_4OH solution +**

c) 100 mL 0,1M of HCl solution

0,04 mole 0,01 mole

$$NH_4OH \quad + \quad HCl \rightarrow NH_4Cl + H_2O$$

Buffer capacity

- *Buffer capacity* of a solution (B, mmol/L) is the amount of added acids or bases the buffer solution can tolerate without exceeding a specified pH range

$$B = \frac{C_N \times V}{\Delta pH \times V_{BS}}$$

where C_N – normality of added strong acid or strong base, mol/L

V – a volume of an added acid or base, L

ΔpH – change in pH

V_{BS} – a volume of a buffer solution, L

Buffer capacity depends upon:

- **Concentration:** the higher the concentration, the greater is buffer capacity of a solution
- **The ratio of components' concentration**

$$\text{B max when } \frac{[\text{component }1]}{[\text{component }2]} = 1$$

- Biological buffer systems are characterized by:

  B_A – buffer acids capacity

  B_B – buffer bases capacity

- Usually $B_A > B_B$, because the amount of acidic metabolites generated in a human body is much greater than amount of basic metabolites

Buffer Systems of Blood

- The most powerful biological buffer systems are contained in blood. They are subdivided into two categories:
  - buffers of plasma
  - buffers of erythrocytes

BUFFER SYSTEMS of BLOOD

Plasma | **Erythrocytes**

Hydrocarbonic

Hydrophosphoric

Proteins (albumins, globulins)

Hemoglobin - Oxy hemoglobin

- The pH of blood plasma is maintained at 7.4 by several buffer systems, the most important of which is the **HCO_3^-/H_2CO_3**

- In the erythrocyte, where pH is 7.25, the principal buffer systems are **HCO_3^-/H_2CO_3 and hemoglobin**

Hydrocarbonic buffer system

- Weak carbonic acid and bicarbonate anion: H_2CO_3/HCO_3^-
- The formation of a buffer in biological fluids is represented as:

carbonic anhydrase

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

The mechanism of buffer activity

(a) Neutralization of acids:

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3$$

(b) Neutralization of bases:

$$OH^- + H_2CO_3 \leftrightarrow HCO_3^- + H_2O$$

- In blood plasma the ratio of H_2CO_3 and HCO_3^- concentrations is

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{40}{1}$$

- The excess of bicarbonate anion maintaines ***the base reservoir of blood***
- buffer capacity by acids is much greater than buffer capacity by bases:

B_A = 40 mmol/L; B_B = 1-2 mmol/L

- Hydrocarbonic buffer system is contained in all biological fluids of a human body

- HCO_3^- analysis in blood is an important diagnostical test which signals about respiratory and metabolic diseases

A hydro phosphoric buffer system

- It is composed of anions of phosphoric acid $H_2PO_4^-/HPO_4^{2-}$

Mechanism of buffer activity:

$$H^+ + HPO_4^{2-} \leftrightarrow H_2PO_4^-$$

Neutralization of an added acid

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

Neutralization of an added base

A hydro phosphoric buffer system

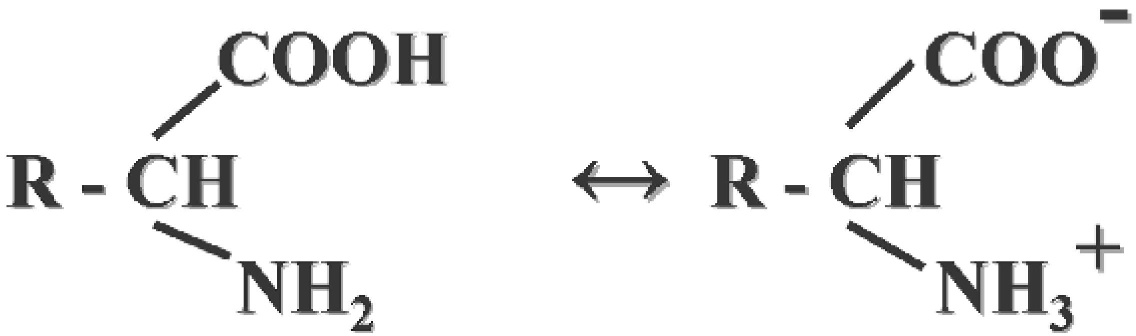
- This buffer exhibits low capacity in blood is due to low concentration of its components:

B_A = 1– 2 mmol/L and B_B = 0.5 mmol/L

- But hydro phosphoric buffer system is crucial in urea, intracellular fluids and other biological liquids.

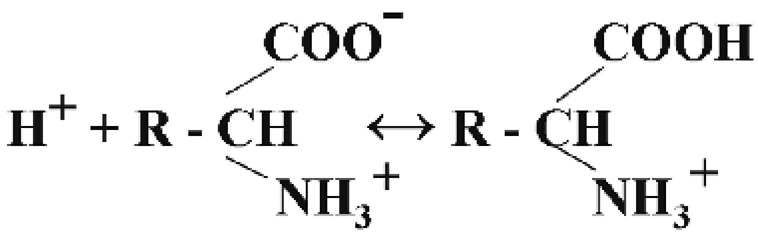
Protein buffer system (albumins, globulins)

- Strong buffer which presents in blood plasma but not in erythrocytes.
- Proteins are amphiprotic polyelectrolytes which exist as bipolar ions:

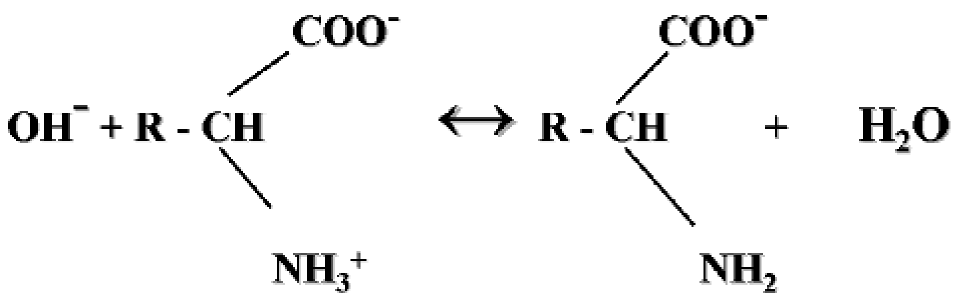


Protein buffer system

- The mechanism of buffer activity is:
- (a) Neutralization of acids:



- (b) Neutralization of bases:



- Protein buffer systems are contained not only in blood plasma, but in all biological fluids of a body. Their buffer capacities in blood plasma are:
- B_A (albumins) = 10 mmol/L and B_A (globulins) = 3 mmol/L respectively.

A hemoglobin-oxyhemoglobin buffer

- Buffer system presents in erythrocytes and is responsible for 75% of blood buffer capacity.
- Hemoglobin (HHb) and oxyhemoglobin ($HHbO_2$), formed by the combination of oxygen and with hemoglobin in the lungs according to the reaction

$$HHb + O_2 \leftrightarrow HHbO_2$$

- $HHb \leftrightarrow H^+ + Hb^-$

  weak *acid* *conjugate base*

- $HHbO_2 \leftrightarrow H^+ + HbO^-$

  weak *acid* *conjugate base*

The mechanism of their buffer activity

- Neutralization of acids:

$$H^+ + Hb^- \leftrightarrow HHb$$

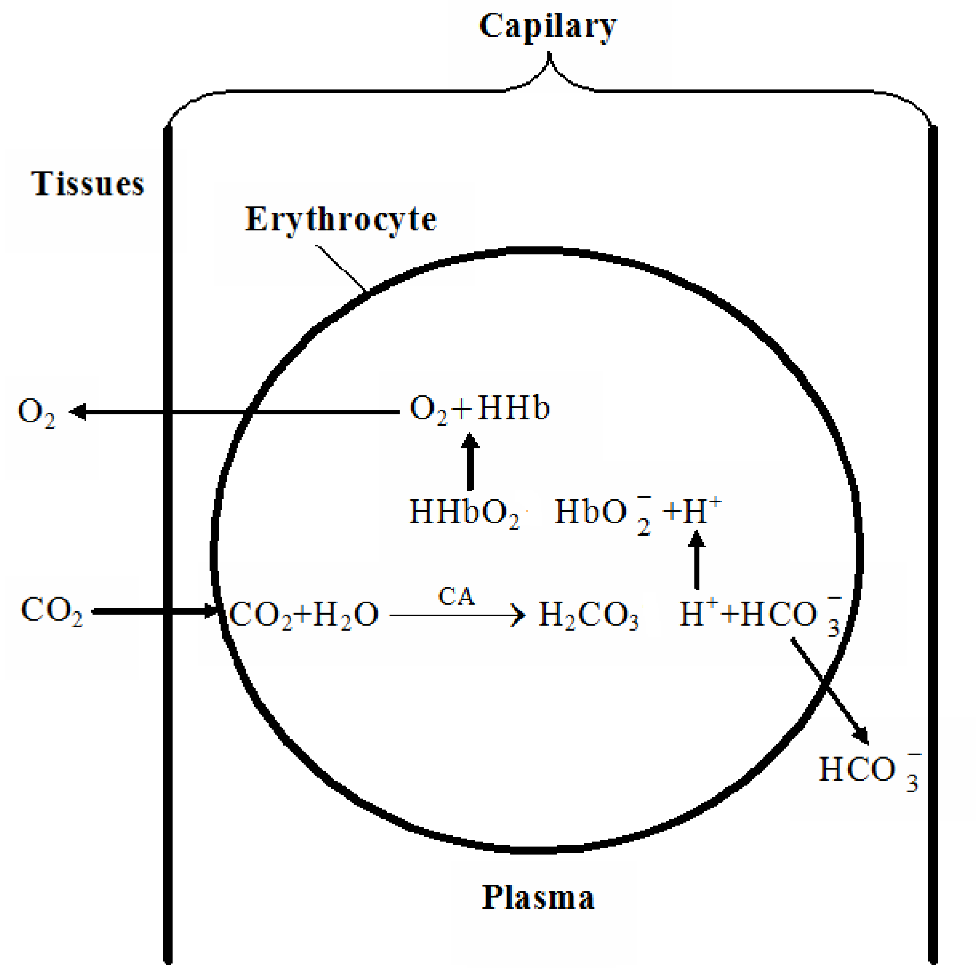
$$H^+ + HbO^- \leftrightarrow HHbO_2$$

- (b) Neutralization of bases:

$$OH^- + HHb \leftrightarrow Hb^- + H_2O$$

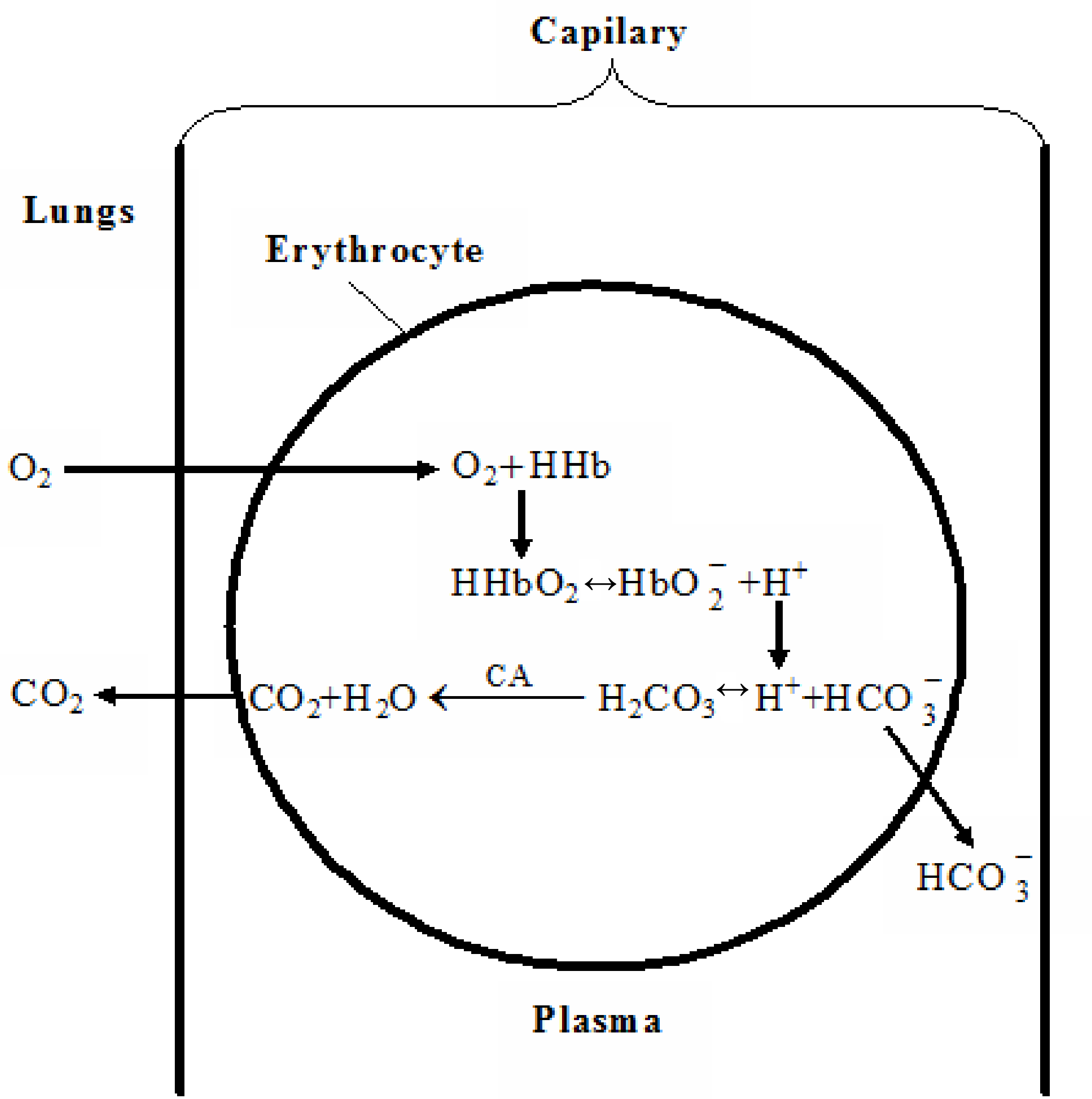
$$OH^- + HHbO_2 \leftrightarrow HbO^- + H_2O$$

- Hemoglobin and hydrocarbonic buffer systems are working together to deliver oxygen to tissues and to remove carbon dioxide out of tissues.



Capilary
Tissues
Erythrocyte
O_2
O_2+HHb
$HHbO_2$
HbO_2^- +H^+
CO_2
CO_2+H_2O
CA
H_2CO_3
H^++HCO_3^-
HCO_3^-
Plasma

(a)


Capilary
Lungs
Erythrocyte
O2
O2+HHb
HHbO2↔HbO2− +H+
CO2
CO2+H2O
CA
H2CO3↔H++HCO3−
HCO3−
Plasma

(b)

- A disturbance of acid-base status is rather dangerous for people’s health since pH deviation may cause:
- Decrease in hormone and enzyme activity
- Change in osmotic pressure
- Alteration in rates of biochemical reactions catalyzed by protons

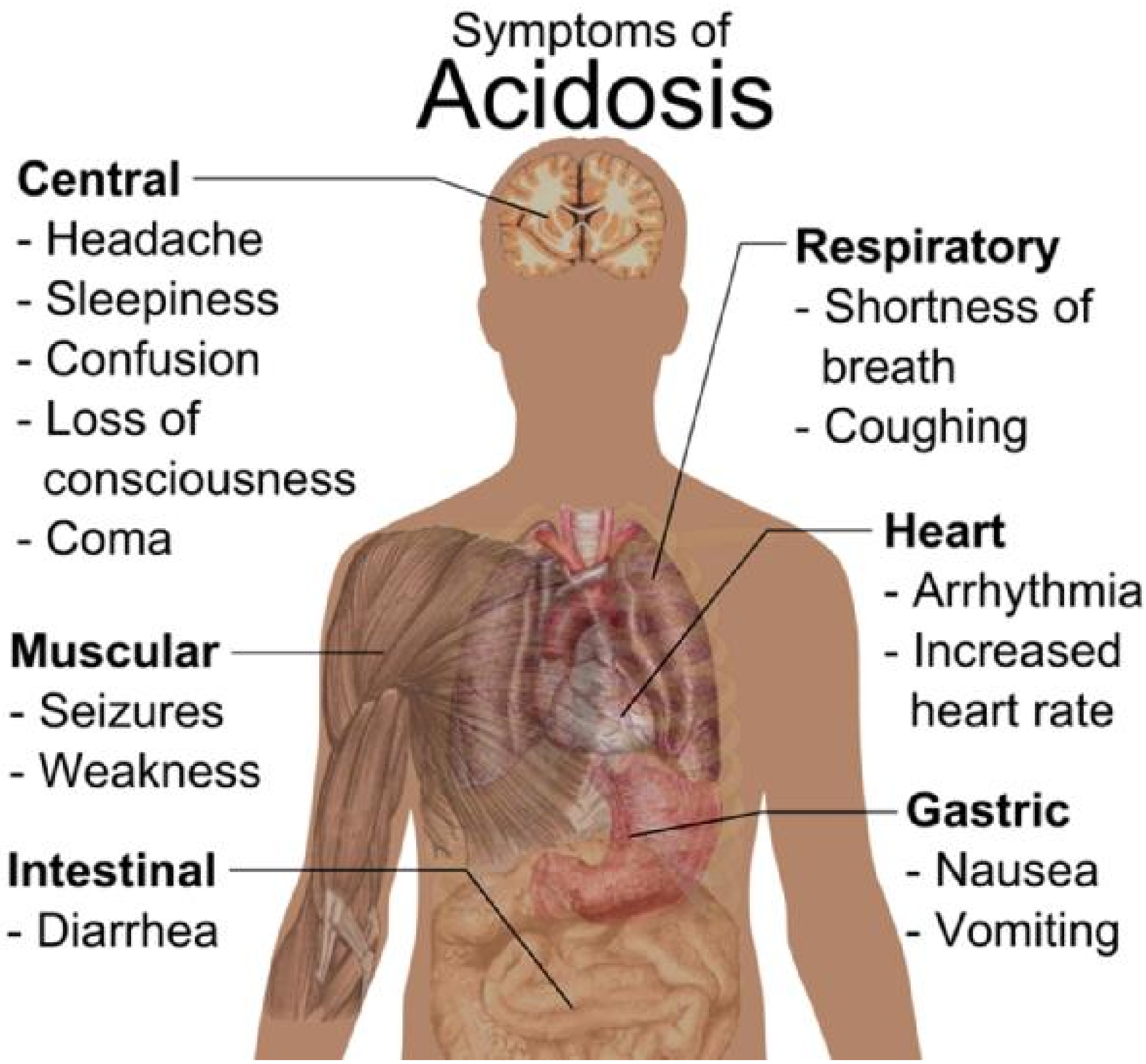
- Even 0.4 pH units deviation from the normal pH value in blood may cause coma or even death of a patient
- For babies even 0.1 pH deviations is also very dangerous

- The most dangerous types of acid-base disturbance in blood are:
- acidosis – increase in blood acidity and other body tissue
- alkalosis –increase in blood basicity

Blood plasma pH =7.36

•The term acidemia describes the state of low blood pH

•Alkalemia -…



Symptoms of
Acidosis
Central
- Headache
- Sleepiness
- Confusion
- Loss of consciousness
- Coma
Muscular
- Seizures
- Weakness
Intestinal
- Diarrhea
Respiratory
- Shortness of breath
- Coughing
Heart
- Arrhythmia
- Increased heart rate
Gastric
- Nausea
- Vomiting

- Two main types of acidosis can be distinguished:

(a) Respiratory, caused by hypoventilation of lungs and accumulation of carbonic acid in blood: $CO_2 + H_2O \leftrightarrow H_2CO_3$

(b) Metabolic, caused by Diabetes Mellitus and some other diseases responsible for extra production of acids

- Acidosis correction done by intravenous injection of 4% $NaHCO_3$ solution:

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3$$

- Soda and another antacidic (hypocidic) drugs are substances which reduce acidity of biological fluids

- Alkalosis is initiated by:

(a) Hyperventilation of lungs (for example, neurotic paroxysm) - respiratory alkalosis

(b) The excess of food products with high basicity - metabolic alkalosis

Respiratory alkalosis. Symptoms

- Symptoms of respiratory alkalosis are related to the decreased blood carbon dioxide levels, the alkalosis may disrupt calcium ion balance, and cause the symptoms of hypocalcaemia (such as fainting)

- Alkalosis correction is achieved by injection of 5-15% ascorbic acid solutions

- Respiratory alkalosis is a medical condition in which increased respiration (hyperventilation) elevates the blood pH
- Alkalosis refers to a high pH in tissue.
- Alkalemia refers to a high pH in the blood.