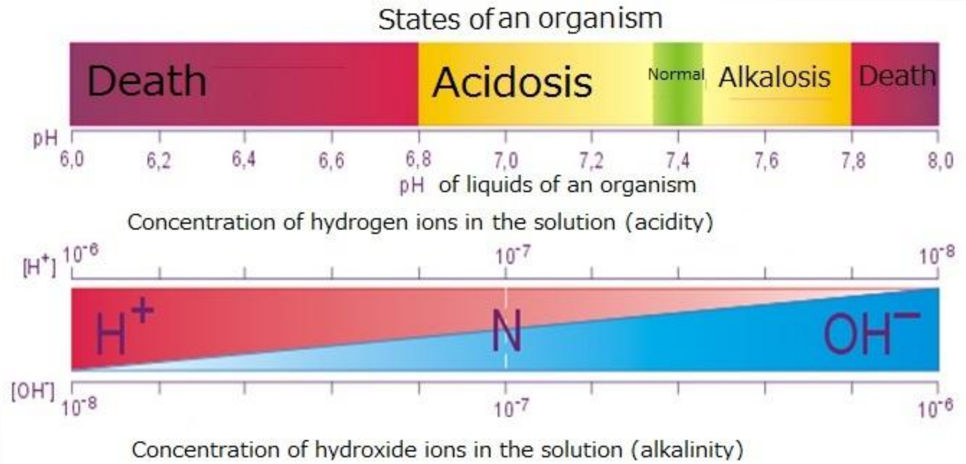
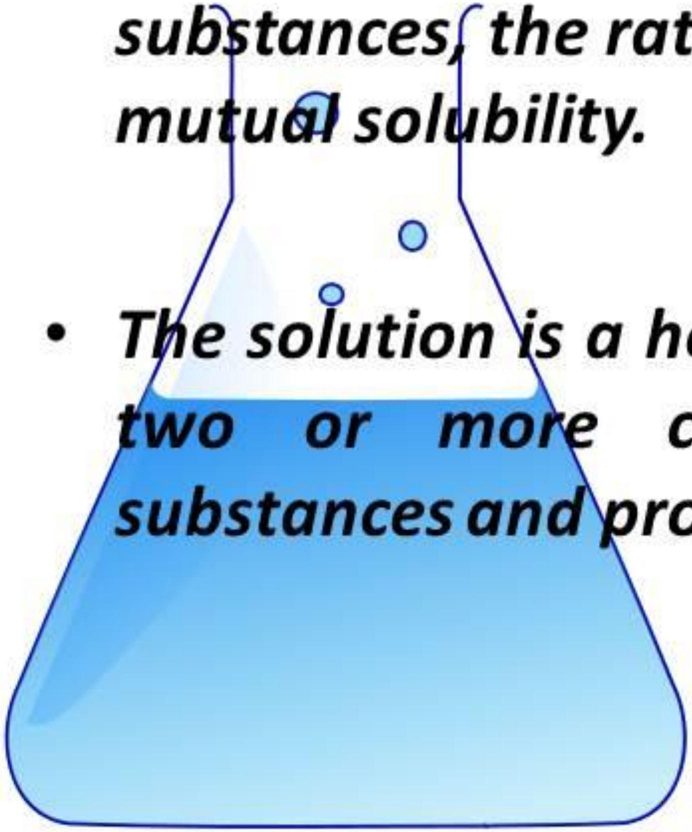
Solutions. Acid–base equilibrium in biological systems



Plan

- 0. Solutions and their colligative properties
- 1. The theory of electrolytic dissociation. Dissociation of bases, acides and salts in water solutions.Strong and weak electrolytes
- 2. Protolytic theory.
- 3. Dissociation of water. Hydrogen ion exponent.
- The homeostasis.
- 4. The importancy of pH maintenance in human body. 5. The concept of buffer solutions.
- 6. Hydrocarbonate buffer system
- 7. Phosphate buffer system
- 8. Protein buffer systems
- 9. Hemoglobin buffer system
- 10. Acidosis and alkalosis. Treatment of acidosis and alkalosis.

Definitions and Concepts



- ***Solutions are thermodynamically stable homogeneous systems consisting of 2 or more substances, the ratio of which is determined by their mutual solubility.***

- ***The solution is a homogeneous system consisting of two or more components: solvent, dissolved substances and products of their interactions.***

Solubility

Solubility (S) is quantitatively expressed by the ratio of weight (g) by the volume or mass of solvent (l).

P=m(substance)/V(solvent)

According to solubility the substances are divided into:

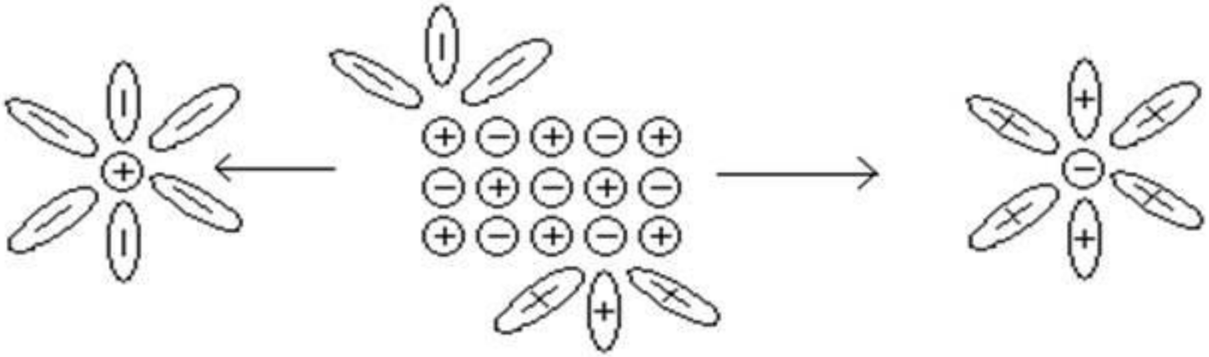
1. **Soluble;**
2. **Slightly soluble;**
3. **Insoluble.**

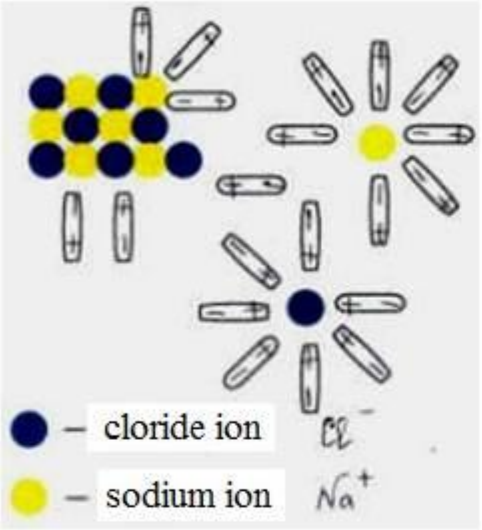
Physical theory of solution’s formation.

The founders of this theory are the Arrhenius, Ostwald and van't Hoff. These scientists considered the process of dissolution as gomogenious mechanical distribution of solute particles all over the solvent volume.

Chemical theory of solution's formation

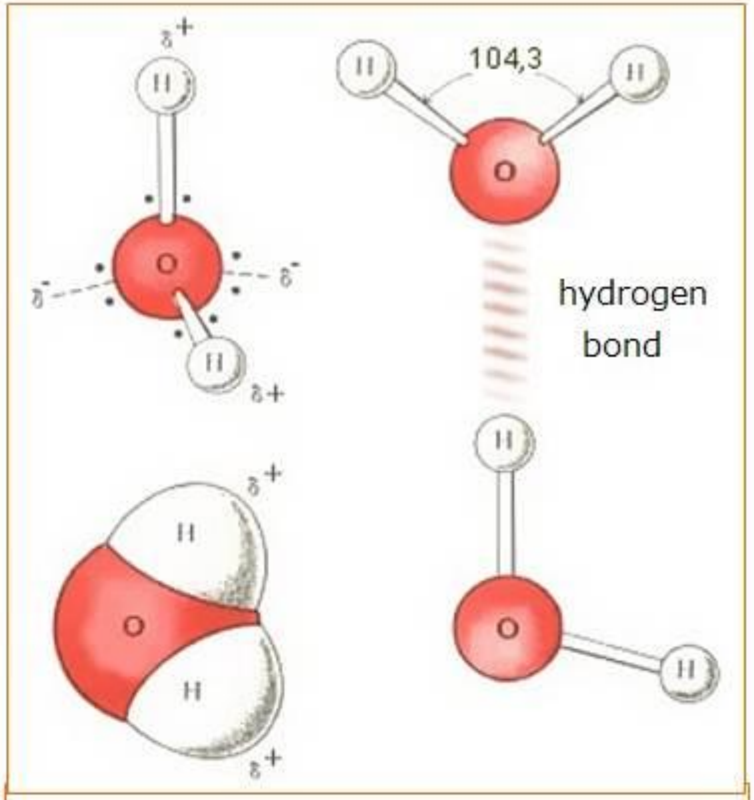
Hydrates (solvates) are not formed by formation of chemical bonds. They are formed by Van der Waals forces or hydrogen bonds. Energy of these bonds is small so the resulting compounds are not very strong and can easily break down. When substances of ionic structure are dissolved the solvent molecules around an ion are held by ion-dipole interaction.

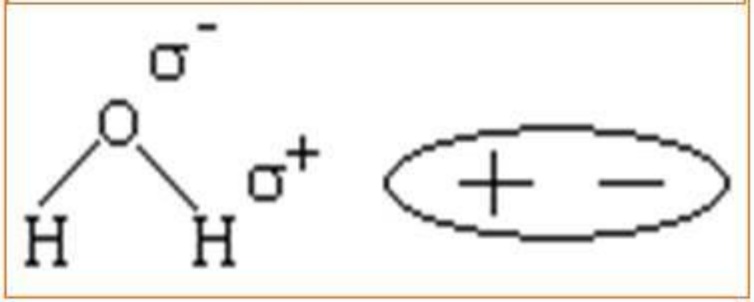




Chemical theory of solution's formation

Solvates (hydrates) are formed due to the dipole-dipole interaction when substances with molecular structure dissolved. Dipoles of dissolved substances can be permanent (from substances with polar molecules) or induced, i.e. induced influence of solvent (from substances with non-polar molecules).





The modern theory of solution's formation

- Stage of hydration is exothermic and stage of dissolution is endothermic. Overall heat effect of the process consists of the sum of two thermal effects:

ΔHtot=ΔHst. hydrat.+ΔHst. dissolution

- If **ΔHst. hydrat.>ΔHst. dissolution**, then the solution of such substances in water generates heat.

  For example: dissolving the sulfuric acid in water.
- If **ΔHst. hydrat.<ΔHst. dissolution**, then dissolution of such substances in water must expend energy.

  For example: the dissolution of sodium thiosulfate in the water, the dissolution of sucrose in the water.
- If **ΔHst. hydrat.≈ΔHst. dissolution**, then the dissolution of such substances, the temperature factor is almost not affected.

Solubility of gases

- The temperature and pressure affects on the solubility of gases in liquids.
- Dependence of the solubility of gases from pressure is expressed by Henry's law:

- ***The mass of gas that dissolves at a constant temperature in a particular volume of a substance is directly proportional to the gas partial pressure***

- $m=kp$,

- *where m-mass dissolved gas, p – pressure, k – the coefficient of proportionality (Henry's constant)*

Ways of expressing concentration

1. Mass fraction of W - is the ratio of the mass of the solute (m subst.) to the weight of the solution (m solut.)

$$W = \frac{m\ \text{subst.}}{m\ \text{solut.}} 100\% \qquad (\%)$$

Molar fraction Wm - is ratio of the amount of solute (n) to the total amount all the substances in solution (Σn).

$$Wm = \frac{n_{sol.}}{\sum n_{subst.}} \cdot 100\%$$

Ways of expressing concentration

3. The molar concentration (C_M) indicates the quantity of substance (n) that is dissolved in 1 liter of the solution (V)

$$C_M = \frac{n}{V} = \frac{m}{MV} \text{ (mole/l)}$$

4. Equivalent molar concentration (C_H) indicates how many mole equivalents (n_{eq}) of solute is contained in one liter of solution

$$C_H = \frac{n_{eq}}{V} = mole / L$$

Ways of expressing concentration

5. Molality (Cm) shows how much of the substance (n) corresponds to 1 kg of solvent (m solv.)

$$Cm = \frac{n}{m(solv.)} = \frac{m(subst.)}{M \cdot m(solv.)} = \frac{mole}{kg}$$

6. The titer (T) indicates the number of grams of the substance (m subst.) dissolved in 1 mL of a solution (V solut.)

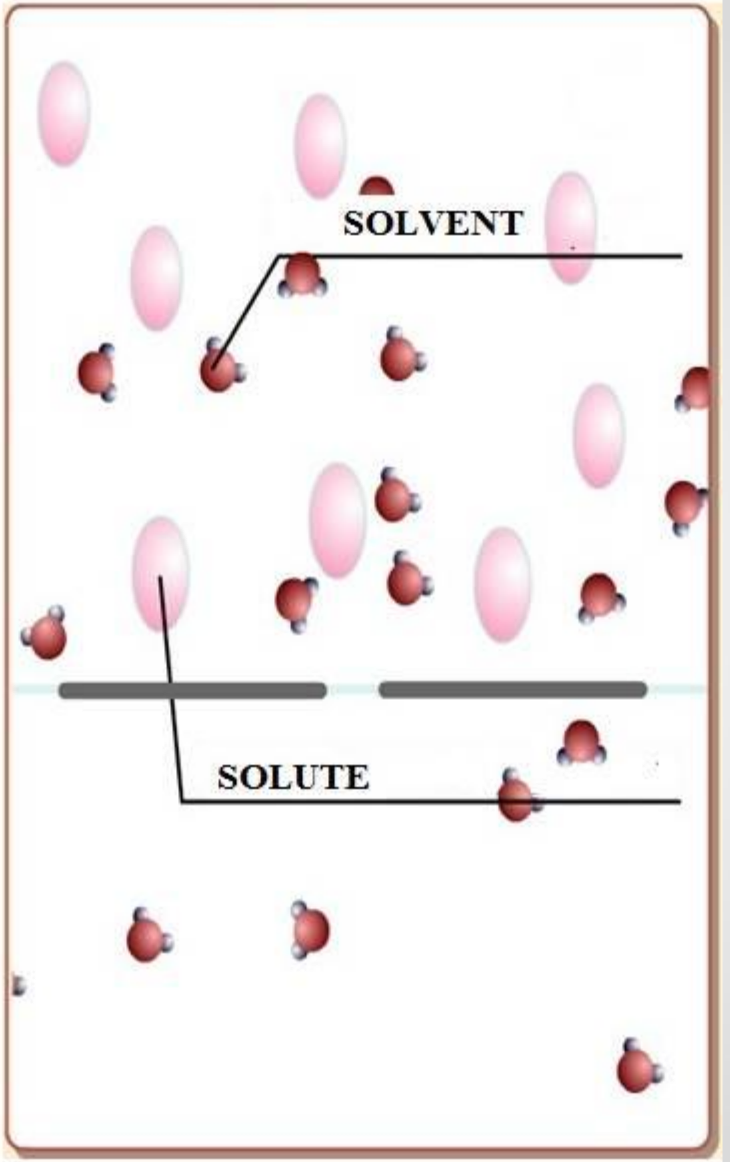
$$T = \frac{m_{(\text{ subst.})}}{V_{(\text{ solut.})}}$$

Ideal solutions

The solution consists of a dissolved substance (A) and solvent (B)

There is an interaction between the same molecules and between the molecules of dissimilar substances,

Ideal solutions are solutions in which the forces of interaction between the similar and dissimilar particles are equal and can be neglected.



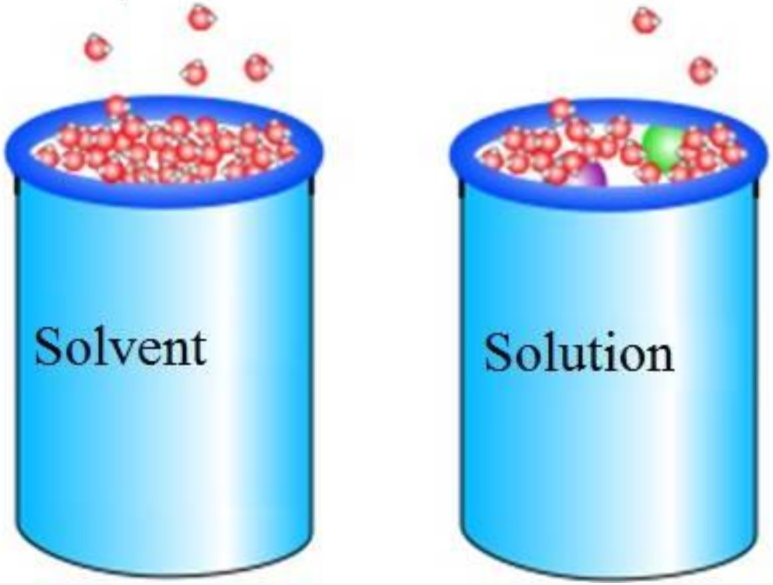
The Raul' Law. Colligative properties of solutions.

F.Raul found that:

For ideal (dilute) solutions saturated vapor pressure of the solvent over a solution p_1 is proportional to its mole fraction in the solution x_1

$$P_1 = P_1^0 X_1$$

, where P_1^0 - Vapor pressure of the pure solvent



Colligative properties of solutions. Ebullioscopy.

Colligative properties of solutions are not typical for the electrolytes. These properties are also increasing the boiling point and the lowering of the freezing point of the solution osmotic pressure.

The boiling point of the solution of non-volatile substances is always higher than the boiling point of the solvent.

$\Delta T_{bol.} = Em$, where m- molality, E – ebullioscopic constant

Ebullioscopic constant numerically equal to the boiling temperature of 1 mole solution.

The law of the Van’t Hoff-Pfeffer

Osmotic pressure of a solution is the same as the pressure that would be that of dissolved substance if it was in the gaseous state and occupied the same volume of solution at a particular temperature .

Calculation of the osmotic pressure is carried by the formula:

$P=cRT$, where c - the molar concentration of solution (g / mole)

The law of the Van’t Hoff-Pfeffer

In electrolyte solutions, the number of particles per unit volume of solution is larger, since each molecule of the substance dissociates into a certain number of ions.

Calculation of the osmotic pressure of the electrolyte solutions was conducted as follows:

$\mathbf{P=icRT}$, where **i** - isotonic coefficient depends on the degree of dissociation of the electrolyte α and the number of ions n.

$$\mathbf{i = 1+\alpha(n-1)}$$

Cryoscopy

Reducing saturated vapor pressure above the solution lowers the freezing temperature thereof. In other words, the freezing point of the solvent is always higher than the freezing point of the solution.

$\Delta T_{freez.} = Km$, where m - molality, К - cryoscopic constant

Cryoscopic constant is numerically equal to the freezing temperature 1 mole solution.

1. Theory of electrolytic dissociation (Arrhenius’ theory).
2. Protolytic theory (Bronsted – Lowry’ theory).
3. Electronic theory (Lewis’ theory).

The theory of electrolytic dissociation

Substances	
Electrolytes	Non- electrolytes
solutions or melts conduct electric current	

Electrolytic dissociation – process of decomposition of solutes in the solvent into ions.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$KOH \rightleftharpoons K^+ + OH^-$$

- 1) Substances dissociating in solutions or melts into positively charged Cat^+(cations) and negatively charged An^- (anions). The latter include acids, bases and salts.
  2) In electric field Cat^+ move to cathode, An^- move to anode.
  3) Electrolytes decompose into ions in different degree.
  4) Dissociation depend of:
  a) nature of electrolyte;
  b) nature of solvent;
  c) concentration;
  d) temperature.

Dissociation of bases, acides and salts in water solutions

Acides are compounds dissociating in aqueous solutions with the formation of positive ions of one species – hydrogen ions.
$HCl \rightarrow H^+ + Cl^-$
Bases are compounds dissociating in aqueous solutions with the formation of negative ions of one species – hydroxide ions OH^-.
$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$
Medium salts dissociate to form metal cations and anion of acid radical.

Strong and weak electrolytes

Degree of dissociation α

$$\alpha = \frac{N_i}{N_{tot}} \qquad \alpha = \frac{N_i}{N_{tot}} \cdot 100\%$$

N_i - the number of molecules, dissociating into ions;

N_{tot} – the total number of dissolved molecules.

Classification of electrolytes

weak	medium	strong
$\alpha<3\%$	$3\%< \alpha<30\%$	$\alpha>30\%$

Strong electrolytes

Majority of salts.

Some acids (HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4).

Alkalis (LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$)

Weak electrolytes

Majority of acids and bases (H_2S, H_2CO_3, $Al(OH)_3$, NH_4OH).

The dissociation of weak electrolytes is a reversible process

$$\mathrm{CatAn} \rightleftharpoons \mathrm{Cat}^{+} + \mathrm{An}^{-}$$

The equilibrium constant K is called the dissociation (ionization) constant

$$K = \frac{C_{Cat^+} \cdot C_{An^-}}{C_{CatAn}}$$

Ostwald dilution law

$$Kd = \frac{\alpha^2 \cdot C_M}{1-\alpha}$$

Because in solutions of weak electrolytes, degree of dissociation of a very small quantity, 1-α = 1, then

$$Kd = \alpha^2 \cdot C_M$$

Dissociation constant, Kd, and the degree of dissociation, M is the molar concentration of the solution. Very often, instead of the dissociation constants are in their common logarithms:

$$pK = -\lg Kd$$

Acidity and basicity constants

- The dissociation constants of acids and bases, respectively called acidity constants (KA) and major (KB).
- Product constant acidity and basicity constants, with the acid conjugate base is the ion product of water:

$$Ka \cdot K\text{в} = Kw$$

$$pKa + pK\text{в} = 14$$

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-$$

$$K_a = \frac{[\mathrm{H}^+]\,[\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{[\mathrm{H}^+]^2}{C-[\mathrm{H}^+]} \approx \frac{[\mathrm{H}^+]^2}{C} \qquad \mathrm{pH} \approx \frac{1}{2}(\mathrm{p}K_a - \lg C)$$

$$\mathrm{p}K_a = -\lg K_a$$

pH=1/2pKa-1/2lgCa

the degree of dissociation $\alpha = \frac{[\mathrm{H}^+]}{C}$

$$K_a = \frac{\alpha^2}{1-\alpha}C \approx \alpha^2 C \qquad \alpha \approx \sqrt{\frac{K}{C}}$$

$$\mathrm{BOH} \rightleftarrows \mathrm{B}^+ + \mathrm{OH}^-$$

$$K_b = \frac{[\mathrm{B}^+]\,[\mathrm{OH}^-]}{[\mathrm{BOH}]} = \frac{[\mathrm{OH}^-]^2}{C-[\mathrm{OH}^-]} \approx \frac{[\mathrm{OH}^-]^2}{C} \qquad \mathrm{pH} \approx 14 - \frac{1}{2}(\mathrm{p}K_b - \lg C)$$

$$\mathrm{p}K_b = -\lg K_b$$

pH=7+1/2pka+1/2lgCb

Dissociation of water

$H_2C \rightleftharpoons H^+ + OH^-$

$$K = \frac{C_{H^+} \cdot C_{OH^-}}{C_{H_2O}}$$

$$K_w = K \cdot C_{H_2O} = C_{H^+} \cdot C_{OH^-} = 10^{-14}$$

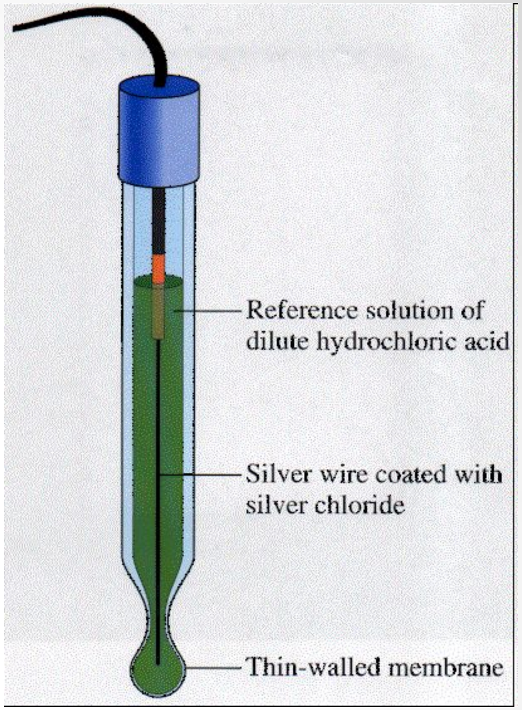
Kw is constant, ion product of water.

Hydrogen ion exponent

$$pH = -\lg [H+]$$

pH Measurement

- indicators
- pH - meters



Acidity of the solution

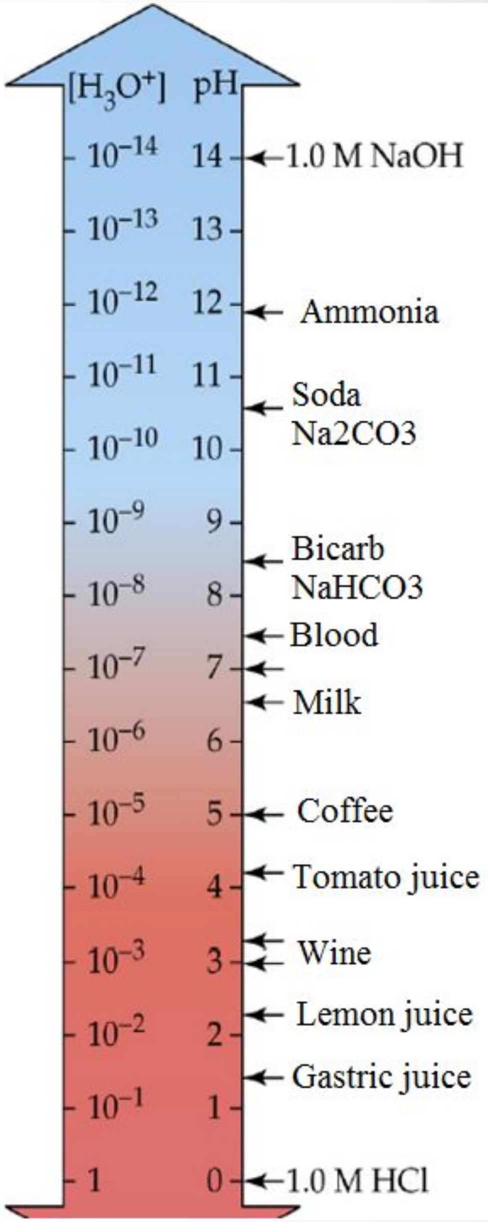
The pH of solutions of acids, bases and salts with a concentration of 0.1 mole/l

The class of compounds		Substance	pH
Acid	Strong	HCl	1,0
	Weak	CH_3COOH	2,9
		H_2S	4,1
Salts		$AlCl_3$	3,0
		KNO_3	7,0
		Na_2CO_3	11,6
		Na_3PO_4	12,5
Base	Weak	$NH_3 \cdot H_2O$	11,1
	Strong	NaOH	13,0

$$\overset{0.1}{NaOH} \rightarrow Na^+ + \overset{0.1}{OH^-}$$

$$pOH = -\lg 0.1 = 1$$

$$pH = 14 - pOH = 13$$



Protolytic theory

- Danish physicist and chemist Johannes Brønsted and the English chemist Thomas Lowry in 1928-1929 was offered Protolytic (protonic) theory of acids and bases, according to which:

- **Base -** **a substance (particle) that can attach proton (i.e. base - proton acceptor).**
- **Acid- a substance (particle) that can donate proton (i.e. acid – proton donor)**
- **In the general form:**

$$A \rightleftharpoons H^{+} + B^{-}$$

A-(acid); B-(base).

Such a system, consisting of acids and bases called protolytic conjugate pair of acid and base, offsetting or appropriate

Salt - the reaction product of acid and base

- Example:

$$HO_4 \rightleftharpoons H^+ + O_4^-$$

Conjugated acid

Conjugated base

$$NH_3 + H \rightleftharpoons NH_4^+$$

Conjugated base

Conjugated acid

By this theory, acids and bases may be both neutral molecules and ions (cations and anions).

The homeostasis. The importancy of pH maintenance in human body

The human body has mechanisms of coordination of physiological and biochemical processes proceeding inside it and maintenance constancy of internal medium (optimal value of pH, levels of different substances, temperature, blood preassure). This coordination and mantanance are called *homeostasis*.

concentration is one of important constant of internal medium of organism, because:

1) Hydrogen ions have catalytic effect on many biochemical processes;
2) Enzymes and hormones exhibit biological activity only at a specific range of pH values;
3) Small changes of pH in blood and interstitial fluids affect the value of the osmotic pressure in this fluids.

pH values of different biological fluids and tissues of the human body

Biological fluid	**pH (normal)**
Blood plasma	7.40±0.04
Saliva	6.35-6.85
Gastric juice	0.9-1.1
Urine	4.8-7.5
Cerebrospinal liquor	7.4±0.05
Pancreatic juice	7.5-8.0
Bile in bladder	5.4-6.9
Milk	6.6-6.9
Lacrimal fluid	7.4±0.1
Skin	6.2-7.5

The concept of buffer solutions

Buffer solutions are solutions that resist change in hydrogen ion and the hydroxide ion concentration (and consequently pH) upon addition of small amounts of acid or base, or upon dilution.

Buffer solutions

Weak acid + salt: HA + NaA

$$\mathrm{HA} \rightleftarrows \mathrm{H^+} + \mathrm{A^-}$$

$$\overset{C}{\mathrm{NaA}} \rightarrow \mathrm{Na^+} + \overset{C}{\mathrm{A^-}}$$

$$K_a = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{[\mathrm{H^+}]\left(C_{\mathbf{salt}} + [\mathrm{H^+}]\right)}{C_{\mathbf{acid}} - [\mathrm{H^+}]} \approx \frac{[\mathrm{H^+}]\,C_{\mathbf{salt}}}{C_{\mathbf{acid}}}$$

$$[\mathrm{H^+}] = \frac{K_a C_{\mathbf{acid}}}{C_{\mathbf{salt}}} \qquad \mathrm{pH} = \mathrm{p}K_a + \lg\frac{C_{\mathbf{salt}}}{C_{\mathbf{acid}}}$$

Name of the buffer	Composition	pH Range
Phosphatic	$HPO_4^{2-} + H_2PO_4^-$	5.4 – 8.0
Acetated	$AcOH + AcO^-$	4.0 – 5.0

The resistive action is the result of the equilibrium between the weak acid (HA) and its conjugate base (A^-):

$H^+(aq) + A^-(aq) \rightarrow HA(aq)$
$OH^-(aq) + HA(aq) \rightarrow A^-(aq) + H_2O(l)$

Henderson-Hasselbah equation

$$pH = pK_a + \lg \frac{C_b}{C_a}$$

Buffer capacity

- **Buffer capacity (B) - the number of moles of equivalents of strong acid or alkali to be added to 1 liter of buffer solution to shift the pH unit**

- Bac.= $\dfrac{C_H(HA)\cdot V(HA)}{|pH - pH_0|\cdot V}$,

- Bbas.= $\dfrac{C_H(B)\cdot V(B)}{|pH - pH_0|\cdot V}$,

Buffer capacity

- Buffer capacity is maximal at a ratio of acid salt 1:1 => pH = pK.
- Good – at [pK+0.5, pK-0.5]
- Sufficient – at [pK+1, pK-1]
- The higher the concentration of the solution, the greater the buffer capacity. The concentration of acid and salt in the buffer solutions usually about 0.05-0.20 M.

- **The relative contribution% buffer systems in the blood to maintain homeostasis it protolytic**
- **Buffer systems plasma**
- Hydrogen carbonate 35%
- Protein 7%
- Hydrogen phosphate 1%
- TOTAL 43%
- **Buffer systems erythrocytes**
- Hemoglobin 35%
- Hydrogen carbonate 18%
- Hydrogen phosphate 4%

Hydrocarbonate buffer system

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

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

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

$$pH = pK_a + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

- pKa1(H_2CO_3)=6.1
- pH of a blood plasma = 7.4

$$7.4 = 6.1 + \lg\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\lg\frac{[HCO_3^-]}{[H_2CO_3]} = 7.4 - 6.1 = 1.3$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.3} = 19.95 \approx 20$$

Alkaline reserve

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

Phosphate buffer system

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

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

$$pH = pK_a + \lg \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

- *The mechanism of action of phosphate buffer:*

- *1. acid addition*
- $2\ Na^{+} + HPO_4^{2-} + H^{+} + Cl^{-} \rightarrow NaH_2PO_4 + Na^{+} + Cl^{-}$

- 2. adding alkali :
- $NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$

- *Excess hydrogen phosphate monobasic and removed through the kidneys. Full recovery of relations in the buffer occurs only 2-3 days.*

pKa($H_2PO_4^-$)=6.8

pH of a blood plasma = 7.4

$$7.4 = 6.8 + \lg \frac{[HPO_4^{\ 2-}]}{[H_2PO_4^{\ -}]}$$

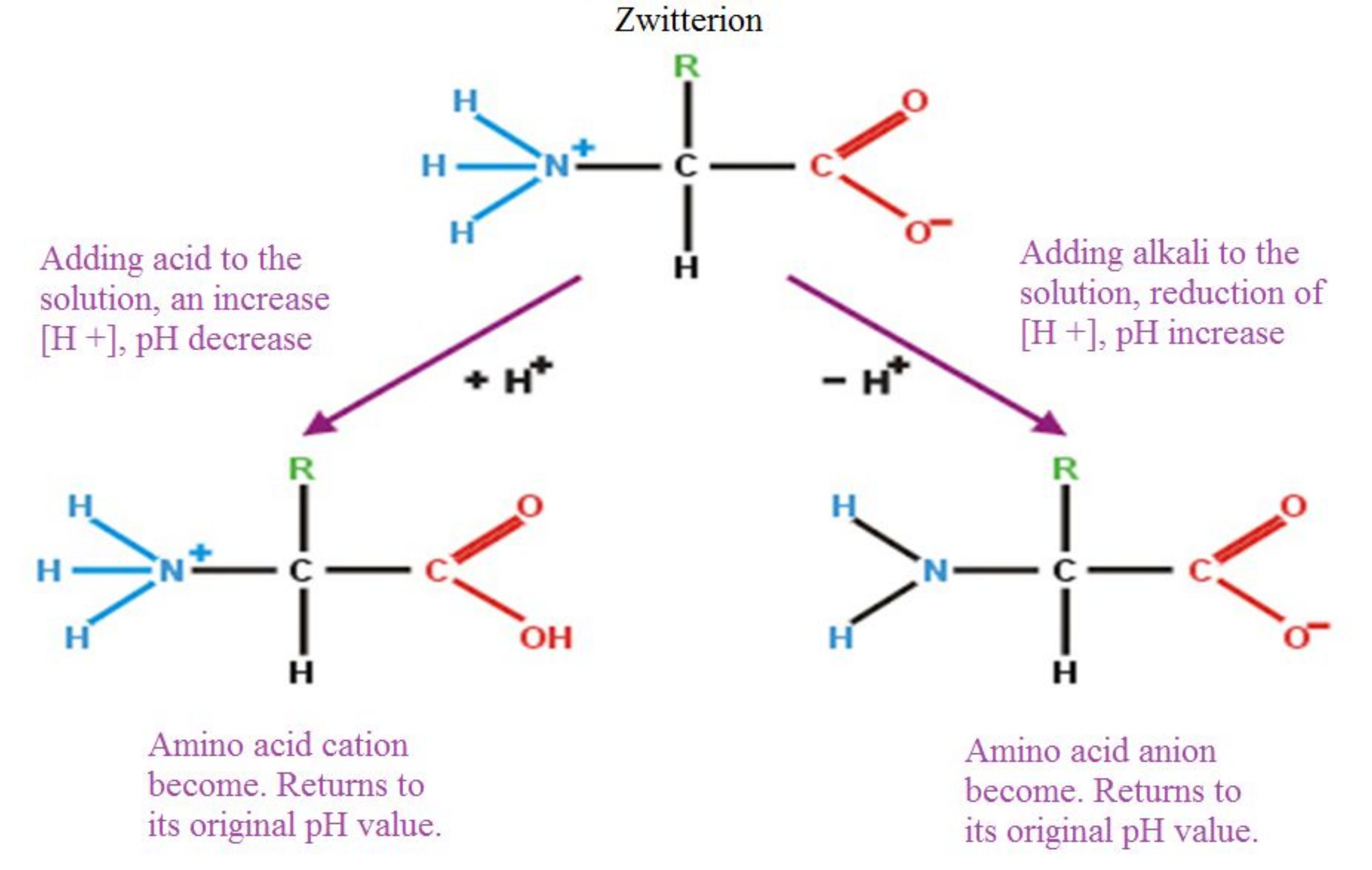
$$\lg \frac{[HPO_4^{\ 2-}]}{[H_2PO_4^{\ -}]} = 7.4 - 6.8 = 0.6$$

$$\frac{[HPO_4^{\ 2-}]}{[H_2PO_4^{\ -}]} = 10^{0.6} = 3.98 = 4$$

Protein buffer systems

The *plasma proteins (albumins, globulins)* are less important than the *hemoglobin* for maintenance of pH.

PROTEIN acid-base buffer system



Adding acid to the solution, an increase [H +], pH decrease

Adding alkali to the solution, reduction of [H +], pH increase

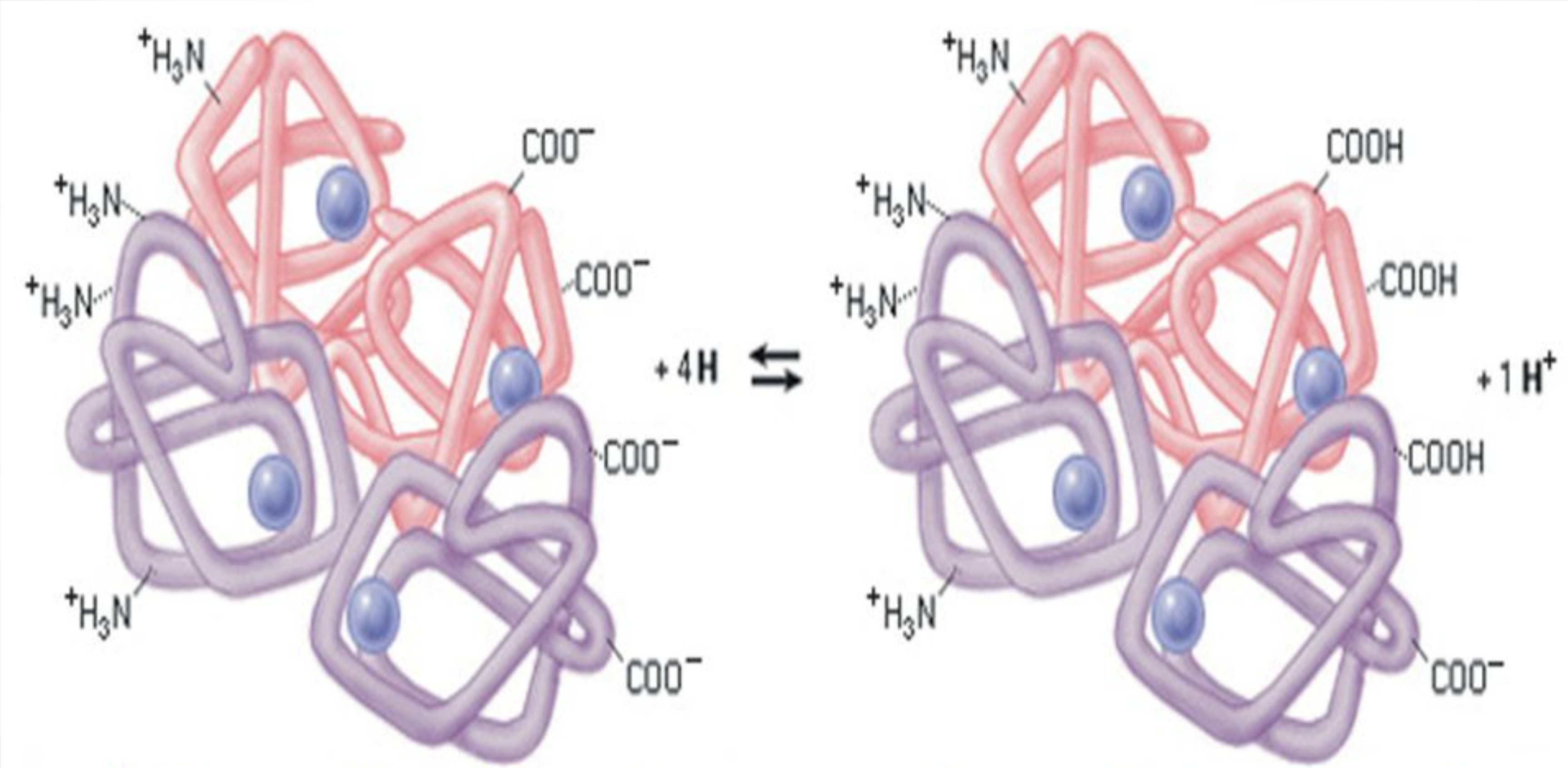
Amino acid cation become. Returns to its original pH value.

Amino acid anion become. Returns to its original pH value.

Hemoglobin buffer system


science.memebase.com

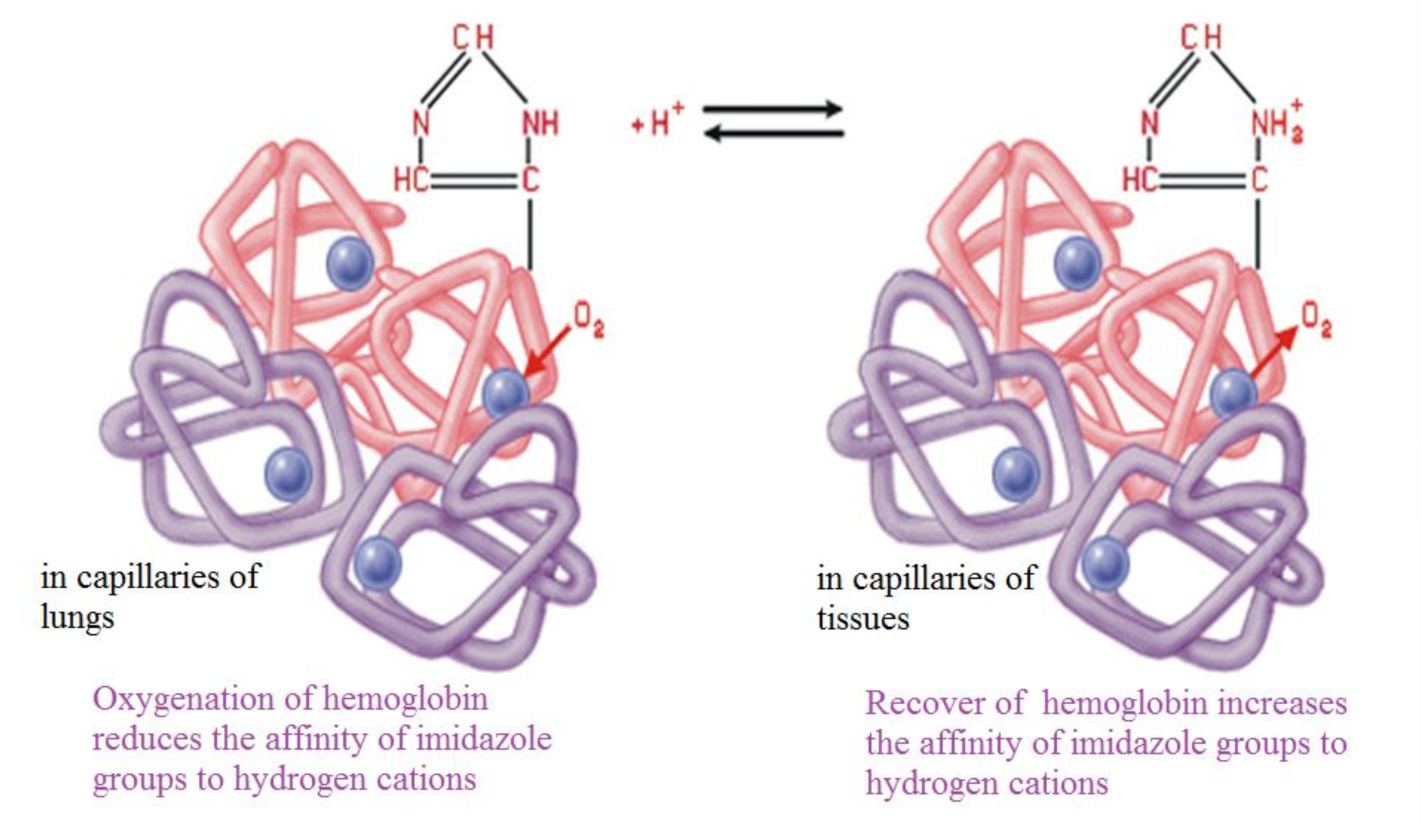
Hemoglobin acid-base buffer system BLOOD



Isoelectric protein. The total charge = 0

Titration acid. The total charge = 3 +

Binding of hydrogen cations imidazole groups of hemoglobin.



in capillaries of lungs

Oxygenation of hemoglobin reduces the affinity of imidazole groups to hydrogen cations

in capillaries of tissues

Recover of hemoglobin increases the affinity of imidazole groups to hydrogen cations

Hemoglobin buffer system

$HHb + O_2 \rightleftharpoons HHbO_2$

Hemoglobin is a **weaker** acid (pKa HHb = 8.2) than oxyhemoglobin (pKa $HHbO_2$ = 6.95). Therefore Hb^- ions being anions of weaker acid are capable stronger to bind H^+ ions than HbO_2^- ions.

Undissociated molecules $HHbO_2$ lose O_2 easier than the ions HbO_2^-

a) the hemoglobin buffer system:

$HHb \rightleftharpoons H^+ + Hb^-$;

b) the buffer system formed by oxyhemoglobin:

$HHbO_2 \rightleftharpoons H^+ + HbO_2^-$.

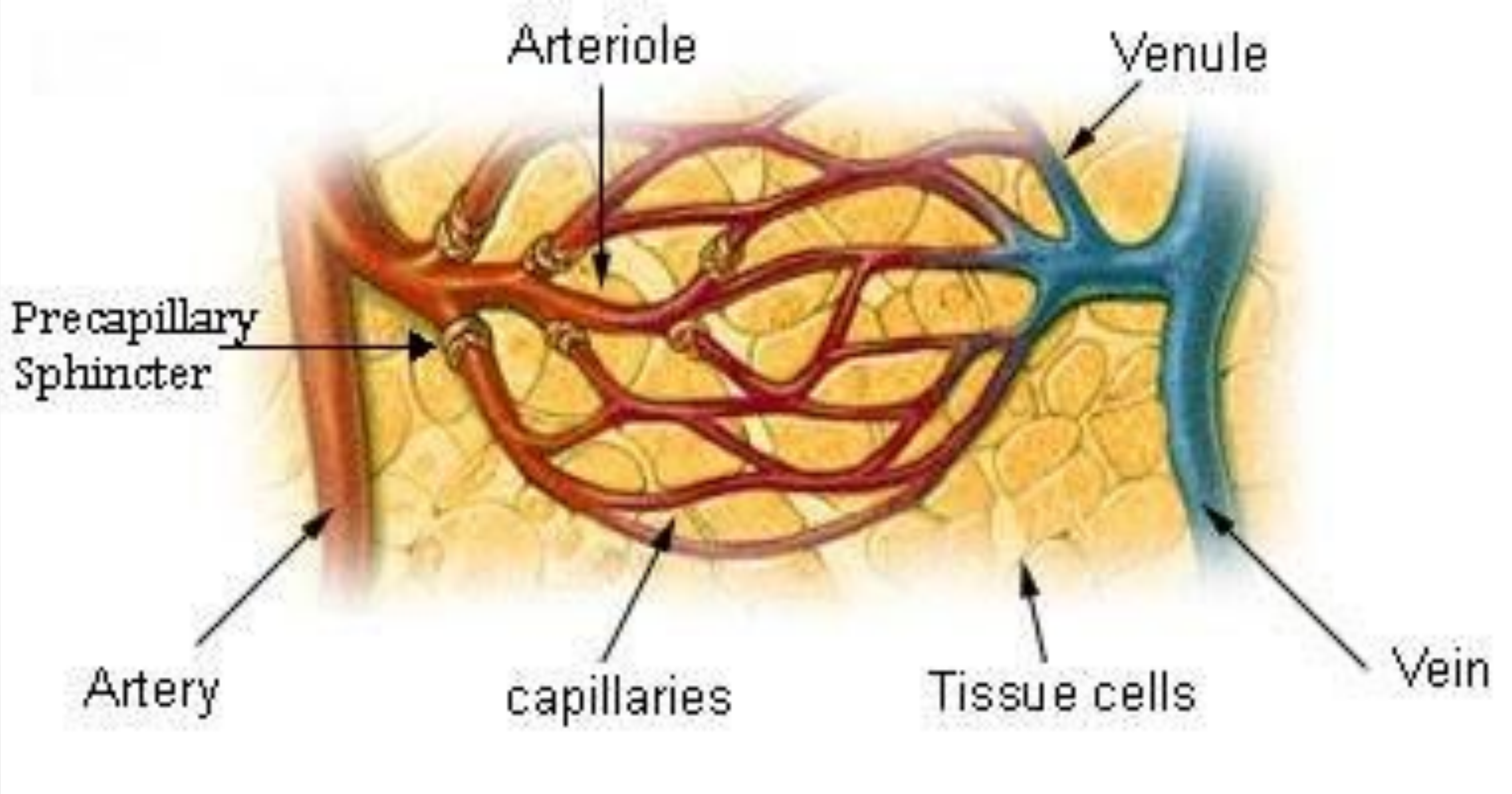
In erythrocytes:

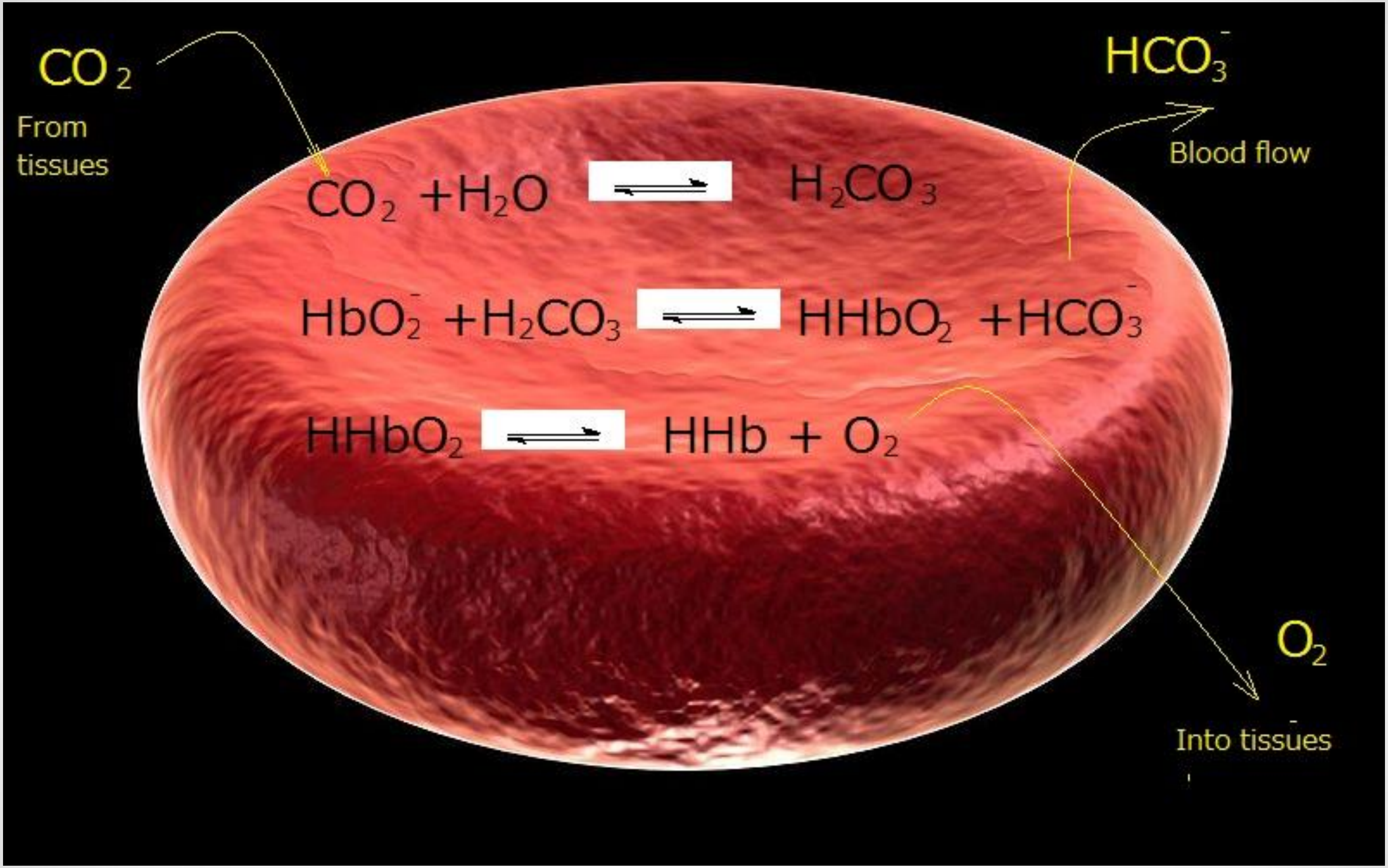
$HHbO_2 \rightleftharpoons HHb + O_2$ (1)

$HHbO_2 \rightleftharpoons H^+ + HbO_2^-$ (2)

$HbO_2^- \rightleftharpoons Hb^- + O_2$ (3)

In vessels of tissues





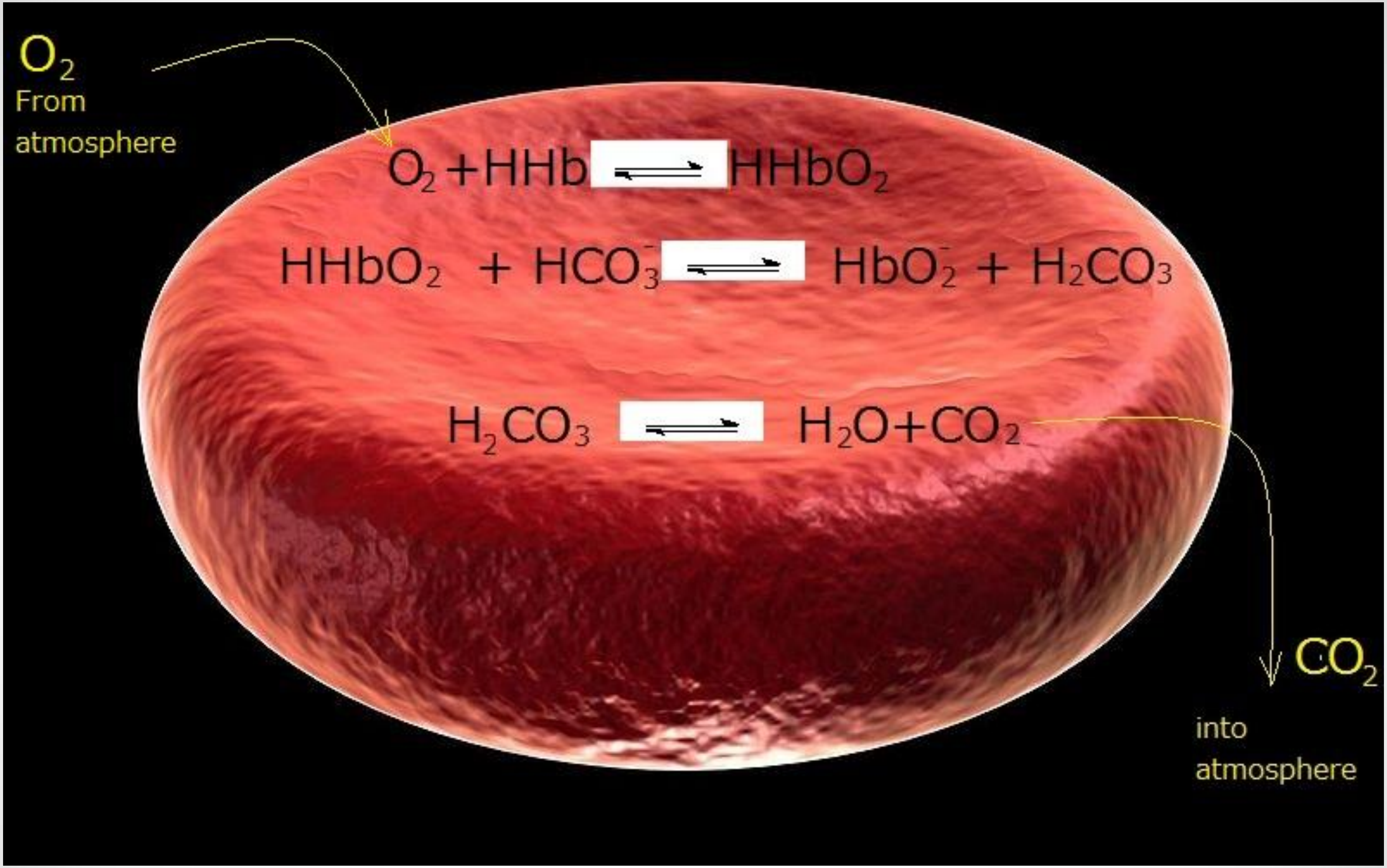
In vessels of tissues

$$CO_2 + H_2C \rightleftharpoons H_2CO_3$$

$$HbO_2^- + H_2CO_3 \rightleftharpoons IHbO_2 + HCO_3^-$$

$$HHbO_2 \rightleftharpoons HHb + O_2$$

In lungs



O_2 From atmosphere

$$O_2 + HHb \rightleftharpoons HHbO_2$$

$$HHbO_2 + HCO_3^- \rightleftharpoons HbO_2^- + H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

CO_2 into atmosphere

In lungs

$HHb + O_2 \rightleftharpoons HHbO_2$

$HHbO_2 + HCO_3^- \rightleftharpoons HbO_2^- + H_2CO_3$

$H_2CO_3 \rightleftharpoons CO_2 + H_2O$

Acidosis and alkalosis

Acidosis	Alkalosis
Gaseous (respiratory)	Gaseous (respiratory)
Non gaseous -metabolic; -excretory; - exogenous.	Non gaseous -metabolic; -excretory; - exogenous.

Literature

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2. http://www.chemeurope.com/en/encyclopedia/Buffer_solution.html