# A buffer system as a conjugated protolytic pair

Practicum. Theme № 4

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# What will we study?



KEEP CALM AND STUDY ON

- Buffer's mechanism
- Calculation of the buffer solutions pH
- Blood's buffer systems
- Acid-base balance in the body and types of its disorders

# What does mean "buffer"?

• <u>A buffer solution</u> is a system of conjugated acid-base pairs, whose components are in a ratio of 1:1 or one component can predominate over the other by a factor of 10.



#### What does mean "buffer"?

 <u>The power characteristic</u> of a conjugated acidbase pair is the acidity index of the pKa. Therefore, the buffer has the same power characteristic. And given the definition, we get the buffer equation in General form (the Henderson-Hasselbach equation)

#### **The Henderson-Hasselbach equation**

#### Vocabulary:

 $[\kappa]$  – molar concentration of acid

K – acid

[o] – molar concentration of base

$$pH = pK_a(\kappa/o) + \lg \frac{[0]}{[K]}$$
(1)

 $pH = pK_{\alpha}(\kappa/o) + p\frac{[\kappa]}{[o]}$  или

где [к] и [о] равновесные молярные концентрации соответствующих компонентов буфера (кислоты и сопряженного основания).

В самом деле, если [o] :  $[\kappa]=1:1$ , то  $pH_6 = pK_a(\kappa/o)$ .

Если отношение  $\frac{[0]}{[K]} = 10$ , ([0] преобладает в 10 раз) то  $pH_{\delta} = pK_a(\kappa/o) + 1$ .

Наконец, если  $\frac{[0]}{[K]} = 10^{-1}$ , ([к] преобладает в 10 раз) то  $pH_6 = pK_a(\kappa/o) - 1$ . Таким образом, каждый буфер, по своему определению, обладает зоной буферного действия:  $pK_a \pm 1$ .





# **Types of buffers**

- <u>acid buffer</u> (CH<sub>3</sub>COOH/CH<sub>3</sub>COO<sup>-</sup> acetate buffer; H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> hydrocarbonate buffer)
- <u>base buffer</u> (**NH**<sub>4</sub><sup>+</sup>/**NH**<sub>3</sub> ammonia buffer)
- <u>salt buffer</u> (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> phosphate buffer)

#### How to calculate the buffer components?

To calculate the buffer components, equation 1 (slide 4) is converted so that the equilibrium molar concentrations are expressed in terms of analytical and volume values:

$$pH_6 = pK_a(\kappa/o) + \lg \frac{C \cdot V(oc - \pi)}{C \cdot V(\kappa - \tau b)}$$

И, если С(основания) = С(кислоты), то все упрощается:

$$pH_{6} = pK_{a}(\kappa/o) + \lg \frac{V(oc-\pi)}{V(\kappa-\pi b)}$$
(2)

Число под логарифмом (соотношение объемов компонентов) находим путем антилогарифмирования, обозначив  $pH_6 - pK_a(\kappa/o) = \Delta pH$ :

 $\Delta pH = lg \frac{V(o)}{V(\kappa)},$ откуда  $\frac{V(o)}{V(\kappa)} = a lg \Delta pH = 10^{\Delta pH}$  (научиться антилогарифмировать!) *Vocabulary: C* – concentration (molar or equivalent) *K* – acid



# How to prepare it for a given pH?

If the buffer volume is set, you can calculate the volume of each component separately by solving a system of two equations with two unknowns:

$$\begin{cases} \frac{V(o)}{V(\kappa)} = a \lg \Delta p H & \# \Delta p H \text{ берется с учетом знака + или -.} \\ V(o) + V(\kappa) = V(буфера) \end{cases}$$
Откуда  $V(\kappa) = \frac{V(6y \varphi epa)}{1 + a \lg \Delta p H}$  (3)  
Затем  $V(o) = V(6y \varphi epa) - V(\kappa)$ 

Thus, we have a general formula (3) for calculating the volume of components of any buffer

# About log (lg) and antilog (alg)

- In this topic, all logarithms and exponents are to base 10, and decimal answers are rounded appropriately.
- The *logarithm* of a number is the power to which 10 must be raised to equal that number.
   Some simple examples:
- 10<sup>2</sup>=100, therefore log100=2
- 10<sup>3</sup>=1000, therefore log1000=3
- log200=2.301

# About *log* (lg) and *antilog* (alg) <u>How to calculate it?</u>

1/ You can use a calculator with logarithm and anti-logarithm function

2/ If you don't have this so you can use a **«Bradis decimal logarithm table»** 

#### Bradis decimal logarithm small table

number	logarithm	number	logarithm	number	logarithm	number	logarithm
1,0	0,0000	3,4	0,5315	5,8	0,7634	8,0	0,9031
1,1	0.0414	3,5	0,5441	5,9	0.7709	8,1	0,9085
1,2	0,0792	3,6	0,5563	6,0	0,7782	8,2	0,9138
1,3	0,1139	3,7	0,5682	6.1	0,7853	8,3	0,9191
1.4	0.1461	3,8	0,5798	6.2	0,7924	8.4	0,9243
1,5	0,1761	3,9	0,5911	6,3	0,7993	8,5	0,9294
1,6	0,2041	4,0	0,6021	6,4	0,8062	8,6	0,9345
1,7	0,2304	4,1	0,6128	6,5	0,8129	8,7	0,9395
1,8	0,2553	4,2	0,6232	6,6	0,8195	8,8	0,9445
1,9	0,2788	4,3	0,6335	6,7	0.8261	8,9	0,9494
2,0	0,3010	4.4	0,6435	6.8	0,8325	9,0	0,9542
2,1	0,3222	4,5	0,6532	6,9	0,8388	9,1	0,9590
2,2	0.3424	4,6	0,6628	7.0	0,8451	9,2	0,9638
2,3	0,3617	4.7	0,6721	7.1	0.8513	9.3	0,9685
2,4	0,3802	4.8	0,6812	7,2	0,8573	9,4	0,9731
2,5	0,3979	4,9	0,6902	7,3	0,8633	9,5	0.9777
2,6	0,4150	5,0	0,6990	7.4	0,8692	9,6	0,9823
2,7	0,4314	5,1	0,7076	7.5	0.8751	9.7	0,9868
2,8	0,4472	5,2	0,7160	7.6	0.8808	9,8	0,9912
2,9	0,4624	5,3	0,7243	7.7	0.8865	9,9	0,9956
3,0	0,4771	5,4	0,7324	7.8	0,8921	10,0	1,0000
3,1	0,4914	5,5	0,7404	7.9	0,8976	0.000000000	1.110755.53552532
3,2	0,5051	5,6	0.7482	202010/2021	1000110001		
3,3	0,5185	5,7	0,7559				

### Calculate it

- lg (3.3) =
- lg (9.0) =
- lg (1.8) =
- lg (6.5) =
- alg (0.51) =
- alg (0.95) =
- alg (0.25) =
- alg (0.812) =

#### Case

A buffer solution obtained by draining 50 ml of a 0.1e solution of CH<sub>3</sub>COOH and 100 ml of 0.2e CH<sub>3</sub>COONa. pKa (CH<sub>3</sub>COO/CH<sub>3</sub>COO<sup>-</sup>)=4.8. Calculate the pH of the buffer solution.

#### Answer

• Write down a summary of the case and its solution.

Краткое изложение задачи:  $pH_{\delta} - ?$   $V(CH_{3}COOH)=50 \text{ MЛ}$   $C_{3}(CH_{3}COOH)=0,1 \text{ МОЛЬ/Л}$   $V(CH_{3}COONa)=100 \text{ MЛ}$   $C_{3}(CH_{3}COONa)=0,2 \text{ МОЛЬ/Л}$   $pK_{a}(CH_{3}COOH/CH_{3}COO<sup>-</sup>)=4,8.$  Pewenue: $pH_{\delta} = pK_{a} + \lg \frac{C \cdot V(CH_{3}COO<sup>-</sup>)}{C \cdot V(CH_{3}COOH)} = 4,8 + \lg \frac{0,2 \cdot 100}{0,1 \cdot 50} = 4,8 + \lg 4 = 4,8 + 0,6 = 5,4$ 

#### Case

- You need to prepare 100 ml of a bicarbonate buffer solution with pH 7.1. pKa (H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup>) = 6.4 at 25°C. What volumes of bicarbonate buffer components with the same initial concentration should be taken for this?
  Answer
  - Write down a summary of the case and its solution.
    Краткое изложение

 $V(H_2CO_3) -?$   $V(NaHCO_3) -?)$   $C_3(H_2CO_3) = C_3(NaHCO_3)$   $V(6y\phi epa) = 100 мл$ pH 7.1  $pK_a(H_2CO_3/HCO_3^-) 6,4$  Используем формулу для нахождення объема кислотного компонента, а затем и основного:

 $\underline{V}(H_2CO_3) = \frac{V(6y\phi epa)}{1+\alpha lg(pH-pK_a)} = := \frac{100}{1+\alpha lg(0.7)} = = \frac{100}{1+\alpha lg(0.7)} = \frac{100}{16.4} = \frac{100}{16.4$ 

 $\underline{V}(\text{NaHCO}_3) = V(6y\phi) - V(H_2\text{CO}_3) =$ = 100 - 16.4 = 83.6 мл

#### The buffer action mechanism

The buffer action mechanism can be shown schematically in a general way:



# The buffer action mechanism

<u>Acid protection</u>: when a strong acid (H<sup>+</sup>) is added, the main component of the buffer comes into reaction, binding hydrogen protons to the weak acid component of the buffer. Therefore, the pH of the medium practically does not change. Acid protection will continue as long as the main component is present in the buffer. In other words, the buffer has a certain capacity for acid.

<u>Alkali protection</u>: when adding alkali (OH<sup>-</sup>), the acid component of the buffer comes into operation, and, giving its H<sup>+</sup> to OH<sup>-</sup>, binds them to water, which can not affect the pH of the medium. At the same time, the acid component of the buffer turns into a conjugate base – the buffer component. Therefore, the pH of the medium practically does not change. The alkali protection will continue as long as there is an acidic component in the buffer. In other words, the buffer has a certain capacity at the base.

#### For example, for an acetate buffer:

Защита от кислоты:



 $CH_3COO^- + H^+ \rightarrow CH_3COOH$  (в ионном виде)  $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ 

Защита от щелочи:

 $CH_3COOH + HO^- \rightarrow HOH + CH_3COO^-(в ионном виде)$  $CH_3COOH + NaOH \rightarrow HOH + CH_3COONa$ 

# **Buffer capacity**

• **Buffer capacity (B)** is the amount of strong electrolyte equivalents (*cun.эл*) that must be added to 1 liter of buffer to change its pH by one.

$$B = \frac{C_3 \cdot V(сил.эл)}{V(буф) \cdot \Delta pH}$$
, моль/л

# **Buffer capacity**

• In the blood, the main components of the buffer  $(HCO_3^-, HPO_4^{2-})$  predominate over the acidic ones  $(H_2CO_3, H_2PO_4^-)$ .

Does this make biological sense?



 Definitely. The blood receives more acid-type catabolism products (pyruvic acid, lactic acid). There are fewer products of the main type (ammonia, urea, creatine and creatinine), and they are weaker bases. Therefore, it is necessary to protect the body from acids.

# ABB – acid/base balance

- Blood plasma buffer systems: bicarbonate H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> (pKa 6,1 at 37°C), phosphate H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> (pKa 6.8-7.2), protein (HPt/Pt<sup>-</sup>), amino acid. In whole blood, the main buffer capacity (75%) is accounted for by the hemoglobin HHb/Hb<sup>-</sup> (pKa 8.2) and the oxyhemoglobin system HHb\*O<sub>2</sub>/Hb\*O<sub>2</sub><sup>-</sup> (pKa 6.95) of red blood cells. All biochemical buffer systems work in conjunction with physiological ones: the pulmonary and renal.
- The joint functioning of these systems allows maintaining the main parameters of acid-base balance (ABB) in a healthy person: blood pH 7.36±0.04 and the equilibrium partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) 40 mm Hg.

# **Disorders of acid/base balance**

- A decrease in blood pH at a constant P(CO<sub>2</sub>) is defined <u>as metabolic acidosis</u>, and at a change in P(CO<sub>2</sub>) – <u>as respiratory acidosis</u>.
- An increase in blood pH at a constant P(CO<sub>2</sub>) is defined <u>as metabolic alkalosis</u>, and at a change in P(CO<sub>2</sub>) – <u>as respiratory alkalosis</u>.
- The joint functioning of these systems allows maintaining the main parameters of acid-base balance (ABB) in a healthy person: blood pH 7.36±0.04 and the equilibrium partial pressure of CO<sub>2</sub> (P<sub>CO2</sub>) 40 mm Hg.

## **Disorders of acid/base balance**

Disorder	pH	[H*]	Primary disturbance	Secondary response
Metabolic acidosis	↓	1	↓ [HCO3-]	↓ pCO <sub>2</sub> or normal
Metabolic alkalosis	1	¥	<b>↑ [HCO</b> <sub>3</sub> ·]	1 pCO <sub>2</sub> or normal
Respiratory acidosis	t	1	↑ pCO₂	<b>↑ [HCO</b> <sub>3</sub> -]
Respiratory alkalosis	1	¥	↓ pCO <sub>2</sub>	↓ [HCO <sub>3</sub> -]

#### Case

Acid-base balance (ABB) of the patient: pH blood 7.1;

P ( $CO_2$ )=60 mm Hg. Which ABB disorder does the patient have and what are the biochemical causes of this disorder?

#### Answer

Compare: normal pH 7.4, and  $P(CO_2)=40$  mm Hg. Lowering of blood pH to 7.1 and violated P indicates respiratory acidosis. Further actions of the doctor - to differentiate the pathology of the respiratory organs and the oppression of the respiratory center