MINISTRY OF HEALTH OF UKRAINE Zaporizhzhya State Medical University Analytical Chemistry Department

## **MEDICAL CHEMISTRY**

Manual for independent work of students of the 1-st course of the International Faculty specialty "General Medicine"

> Zaporizhzhya 2017

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The Manual is considered and approved at the meeting of The Committee of Physical and Chemical Subjects of Zaporizhzhya State Medical University (« » \_\_\_\_, Proceedings № \_), at the meeting of The Central Methodical Council of Zaporizhzhya State Medical University («\_\_\_\_\_» \_\_\_, Proceedings № \_)

#### PREFACE

Medical chemistry is studied according to the approved standard of academic curriculum of 2013 year for students of the Universities of the III-IV levels of accreditation of Ukraine for specialty 7.12010002 "Pediatrics" established accordsng to the training curriculm approved by the order of the Ministry of Education of Ukraine from 08.07.2010 № 539 on Amendments to the curriculum training educational qualification level "specialist" qualifications "doctor" in higher educational establishments of IV level of accreditation on specialities "Medicine", "Pediatrics", "Medical-preventive work", approved by the Ministry of Health (the order of 19.10. 2009 № 749).

Organization of studying process is proceed according to the requirements of European Credit Transfer System (ECTS).

Study of Medical Chemistry is carried out during 1 semester.

The curriculum consists of a discipline module, including 4 blocks of topic modules:

1. Chemistry of biogenic elements. Complex formation in biological fluids.

2. Acid – base equilibriums in biological fluids.

3. Thermodynamic and kinetic processes regularities and electrokinetic phenomena in biological systems.

4. Physics and chemistry of surface effects. Lyophobic and lyophilic disperse systems.

This manual was developed by the Department of Analytical Chemistry for independent work of English-speaking students in the absence of such materials that allow students to consolidate and apply their knowledge of medical chemistry for specific problems and numerical tasks solving.

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**TOPIC MODULE 1** 

# CHEMISTRY OF BIOGENIC ELEMENTS.

# **COMPLEXING IN BIOLOGICAL FLUIDS**

#### Tutorial № 1-2

Topic: Biogenic s- and p-elements, biological role, applications in medicine. Biogenic d-elements, the biological role, use in medicine Objective: To study the properties of the compounds of s-, p-, and d- elements and their medical and biological effects on the human body

#### Assignments for self-study:

1. Write the electronic formula of atoms and ions:

Sodium Potassium Calcium Magnesium Barium, Zinc, Chromium (III) Phosphorus (V), Iron (II and III).

2. Write the electronic configuration of the atoms of sulfur, manganese, copper, molybdenum in the steady and excited states.

3. Write the products and external effects off reactions:

 $2K^{+} + Na^{+} + [Co(NO_{2})_{6}]^{3-} \rightarrow$   $Na^{+} + [Sb(OH)_{6}]^{-} \leftrightarrow$   $2Ba^{2+} + Cr_{2}O_{7}^{2-} + H_{2}O \rightarrow$ 

$$Ca^{2+} + C_2O_4^{2-} \rightarrow$$
$$Mg^{2+} + HPO_4^{2-} + NH_3 \rightarrow$$

4. Determine which of these formulas is a formula for bleach? Quicklime? Hydrated lime? Gypsum?

- 1)  $CaCl_2$
- 2) Ca(ClO)<sub>2</sub>
- 3) CaCO<sub>3</sub>
- 4)  $Ca(ClO_2)_2$
- 5) Ca(OH)<sub>2</sub>
- 6) CaO
- 7) CaSO<sub>4</sub>

5. Write the qualitative equations reactions for Cl-, Br-, I- ions with silver nitrate. What medium do these reactions occur in? What is the difference of external effects?

6. Using the appropriate reaction equations describe the chemical properties of the following substances:

 $H_2SO_4$ , HCl,  $HNO_3$ ,  $H_3PO_4$ ,  $NH_3 \cdot H_2O$ , NaOH,  $H_2O_2$ .

7. Write the products and external effects of the reactions:

$$3Zn^{2+} + 2K^{+} + 2[Fe(CN)_{6}]^{4-} \rightarrow$$

$$Zn^{2+} + S^{2-} \rightarrow$$

$$3Fe^{2+} + 2[Fe(CN)_{6}]^{3-} \rightarrow$$

$$4Fe^{3+} + 3[Fe(CN)_{6}]^{4-} \rightarrow$$

$$Fe^{3+} + nSCN^{-} \rightarrow$$

$$CuCl_{2} + NH_{4}OH_{eq.} \rightarrow$$

# **Examples of assignments:**

Task 1. Write the electronic configuration of atoms and ions of copper and sodium.

Solution. 
$$Cu^0 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$
  
 $Cu^0 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^0$ 

$$Na^{0} 1s^{2}2s^{2}2p^{6}3s^{1}$$
  
 $Na^{+} 1s^{2}2s^{2}2p^{6}3s^{0}$ 

Task 2. Indicate the product and the external effect of the reaction:

 $Fe^{3+} + nSCN^{-} \rightarrow$ 

Solution.

$$\operatorname{Fe}^{3+} + \operatorname{nSCN}^{-} \rightarrow [\operatorname{Fe}(\operatorname{SCN})_n]^{3-n}$$

External effect: The stained solution is red.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 225-255, 292-301.

2. Medical chemistry: textbook. / V. A. Kalibabchuk, V. I. Hryshchenko, V. I. Halinska; editing by V. A. Kalibabchuk. – K.: Medicine, 2008. – P. 379-389.

Общая химия. Биофизическая химия. Химия биогенных элементов:
 Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред.
 Ю. А. Ершова. – М. Высш. шк., 2000. – С. 254-299.

4. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 626-649.

#### Tutorial № 3

1. THEME: Complexing in biological systems

# 2. PURPOSE: To study the theory of complexing, the properties of coordination compounds, their properties and their use in medicine

#### Assignments for self-study:

**1.** Write the names of the coordination compounds, determine the charge of inner sphere ions:

- $1) \qquad [Cr(NH_3)_6]Cl_3$
- $2) \qquad K[Ag(CN)_2]$
- 3)  $Na_3[FeF_6]$
- $4) \qquad [Cu(SCN)_2(NH_3)]$
- 5)  $K_2[PtCl_6]$
- $6) \qquad [Co(NH_3)_6]Cl$
- 7)  $Cu[PtCl(OH)_5]$
- 8)  $[Ag(NH_3)_2]OH$
- 9)  $[Cr(H_2O)_6]Cl_3$
- 10) Na[Al(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]
- 11) [Cu (NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)Cl]NO<sub>3</sub>
- 12)  $[Cr(NH_3)_5Br]SO_4$
- 13)  $[Ag(NH_3)_2][Ag(CN)_2]$
- 14)  $[Pt_4(OH)_4](ClO_4)_4$
- 15)  $[Co(NH_3)_5SO_4]Cl$

- **2.** Write the formula of the coordination compounds:
- 1) potassium pentacyanoaquaferrate (II).
- 2) diamminedichloroplatinum (II).
- 3) sodium hexahydroxoaluminate (III).
- 4) tiocyanopentaammincobalt nitrate (III).
- 5) potassium dihydroxotetrachloroplatinate (IV)
- 6) tetraamminecopper sulfate (II).
- 7) hexaaquaalyuminium chloride (III).
- 8) ammonia dihydroxotetrachloroplatinate (IV).
- 9) dibromodiamminplatinum (II).
- 10) sodium hexahydroxochromium (III).
- 11) dihydroxoaquatriamminechromium bromide (III).
- 12) cesium (I) tetracyanodifluoroplatinate (IV).
- 3. Write the equations of constant instability and stability for the complex ion:
- 1)  $[Cu(CN)_4]^{2-}$
- 2)  $[Pt(CN)_4Br_2]^{2-1}$
- 3)  $[Ag(S_2O_3)_2]^{3-1}$
- 4)  $[HgI_4]^{2-}$
- 5)  $[Fe(P_2O_7)_4]^{5-}$
- 6)  $[Co(NH_3)_5SO_4]^+$
- 7)  $[Cr(NH_3)_5Br]^{2+}$

8)  $[Pt_4(OH)_4]^{4+}$ 

9) 
$$[PtCl(OH)_5]^{2-}$$

10)  $[\text{FeF}_6]^{3-}$ 

### **Examples of assignments:**

**Task 1.** Name the complex compounds and determine the charge of the complexing agent:  $K[Pt(NH_3)_2Cl_5]$ .

#### Solution.

Potassium pentachlorodiammineplatinate (IV).

Charge of the complexing agent: +1+X+(-5)=0, then X=+4

**Task 2.** Write the equations of instability and stability constant for the inner sphere ion  $[Cu(CN)_4]^{2^-}$ .

Solution. Inner sphere ion dissociates according to the scheme:

$$[Cu(SCN)_4]^{2-} \leftrightarrow Cu^{2+} + 4SCN^{-}$$

$$\mathbf{K}_{\text{inst.}} = \frac{[Cu^{2+}] \cdot [SCN^{-}]^{4}}{[[Cu(SCN)_{4}]^{2-}]}; \quad \beta = \frac{[[Cu(SCN)_{4}]^{2-}]}{[Cu^{2+}] \cdot [SCN^{-}]^{4}}$$

#### Literature

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 231-233.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 379-382. 2008.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – С. 254-299.

4. Ленский А. С. Введение в бионеорганическую и биофизическую химию : Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 219-227.

5. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 71-83, 658-665.

**TOPIC MODULE 2** 

ACID-BASE EQUILIBRIA IN BIOLOGICAL FLUIDS

#### Tutorial № 4

**1. THEME:** Characteristics of the quantitative composition of solutions. Solution preparation.

2. PURPOSE: To consolidate knowledge on methods expressing solution concentration.

#### Assignments for self-study:

- Calculate the weight for preparing of 3 l of 0,1 M HCl solution. (answer: 10,96 g)
- 2. Calculate the molar concentration of a solution which contains 30 g of NaOH in2 liters (answer: 0,375 mol / 1)
- 3. How much water is necessary to dissolve 1,5 mole of NaOH to obtain a 5% solution? (Answer: 1140 mL)
- 4. In what ratio should 37% HCl solution and water be taken to make 8,2% solution. (Answer: 1 ml 37% HCl solution and 3,5 ml of water)
- 5. What volume of water must be added to 50 g of 2% NaCl solution to prepare a solution of 0,9%? (Answer: 48,9 ml of water)
- 6. In arsenic compounds poisoning unitiol is injected at the rate of 56 mg of the substance per 10 kg of body weight. Calculate the amount of 5% unitiol solution, which must be injected to a patient of 60 kg. (the density of the solution  $\rho = 1,12$ ). (Answer: 6 mL)

- 7. The patient of 76 kg must be injected of 0,66 mmol / kg NaHCO<sub>3</sub>. How many ml of 4,2% solution must be taken of the solution? (Answer: 100 ml)
- 8. What volume of water must be taken to dissolve the 2 mol of NaOH to obtain a 10% solution? (Answer: 320 g)
- 9. Aminophylline solution is produced as 2.4% solution in 10 ml ampules. How many mg of pure substance is in an ampoule? (Answer: 240 mg)
- 10. Calculate the weight to prepare 0.5 1 of ascorbic acid solution with a mass fraction of 5% ( $\rho = 1,08$ ).(Answer: 27 g)
- 11. Calculate the molar concentration of  $H_2SO_4$  solution with mass fraction of 30% ( $\rho = 1,22$ , fe = 1/2). (Answer: 7.47 mol / 1.)
- 12. What volume of 10%  $H_2SO_4$  solution ( $\rho = 1,065$ ) is required for the preparation of 5 l of its solution with molar concentration of equivalent  $C_{eq} = 0,1$  mol / l (fe = 0,5). (Answer: 230 ml)
- 13. Calculate the weight of NaCl to prepare 4 liters of hypertonic solution with  $\omega = 10\%$  (Answer: 42,8 g)
- 14. How many ml of 30%  $H_2O_2$  solution ( $\rho = 1,11$ ) should be taken for preparation of 2 L of pharmaceutical preparation with  $\omega$  ( $H_2O_2$ ) = 3% ( $\rho = 1,007$ )? (Answer: 181 ml)
- 15. Children are injected No-spa at the rate of 2 mg / kg of body weight ( $\rho = 1,04$ ). How many of 2% solution of the drug is necessary to inject a child weighing 25 kg? (Answer: 0,2 mL)

- 16. It is known that 1 ED of insulin helps to absorb 5 g of glucose in the body. How many units of insulin should be added to 500 ml of 5% glucose solution? (Answer: 5 ED)
- 17. What amount of 30%  $H_3PO_4$  solution ( $\rho = 1,18$ ) is necessary for the preparation of 5 L solution with the molar concentration of equivalent ( $C_{eq}$ ) 2 mol / 1, if the acid reacts completely? (Answer: 922 ml.)
- 18. 250 ml solution containes 26,5 g Na<sub>2</sub>CO<sub>3</sub>. Calculate Ceq. (Answer: 2 mol / l).
- 19. How many grams of oxalic acid must be dissolved in 200 ml of water to obtain a 10% solution? (Answer: 22,2 g)

#### **Examples of assignments:**

**Task 1**. Calculate the weigh of NaOH for preparing of 2 liters of 0,3 M solution.

*Solution*. Write the formula of the molar concentration:

$$C = \frac{a_x}{M_x \cdot V}$$

From this formula we find  $a_x$ :  $a_x = C \cdot M_x \cdot V$  $a_x = 0,3 \cdot 40 \cdot 2 = 24 \text{ g}$ 

Answer: 24 g NaOH.

**Task 2.** What is the molar concentration corresponding to the solution of hydrochloric acid in gastric juice, if HCl mass fraction is 0,52% in it?

#### Solution.

1) Suppose there are 100 grams of gastric juice. It contains 0,52 g HCl. The molar concentration is calculated per 1000 ml of solution. Taking gastric density as 1, we can find the weight hydrochloric acid in 1000 ml solution:

100 g of a solution – 0,52 g HCl 1000 g (ml) - X

$$\mathbf{X} = \frac{1000 \cdot 0,52}{100} = 5,2g$$

2) Find the molar concentration of HCl:

$$C = \frac{a_x}{M_x \cdot V}$$
$$C = \frac{5.2_x}{36.5 \cdot 1} = 0.142 \text{ mol} / 1$$

Answer: 0.142 mol / 1

**Task 3**. How many grams of KMnO<sub>4</sub> are necessary to prepare 2 liters of a solution with the Ceq = 0,1 mol / 1, if  $f_e \text{ KMnO}_4 = 1/5$ ?

*Solution.* Write the formula of molar concentration of equivalent:

$$C_{e.} = \frac{a_x}{M_{e.x} \cdot V}, \text{ then } M_{e.x} = f_e \cdot M.$$
  
Hence:  
$$a_x = C \cdot f_e \cdot M_x \cdot V$$
$$a_x = 0,1 \cdot 1/5 \cdot 158 \cdot 2 = 31,6 \Gamma$$
  
Answer: 31,6 g

**Task 4.** Children are injected etimizol: 1 mg of etimizol per 1 kg of body weight. How many ml of 1,5% drug solution is necessary for a child weighing 2,8 kg.

#### Solution.

Find the mass of etimizol, which should be injected to the child:
 1mg of etimizol - per 1 kg of body weight
 X mg - per 2,8 kg of body weight
 X = 2,8 mg = 0,0028 g;

2) Find the mass of etimizol solution:

 $m = \frac{a \cdot 100}{\omega} = \frac{0,0028 \cdot 100}{1,5} = 0,187 \text{ g}$ 

3) The density of the solution is not given, then it is accepted

as 1. Then, the solution volume is equal to its mass -0.19 ml.

Answer: 0,19 ml.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 87-110.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 106-126.

3. Мороз А. С, Яворська Л. П., Луцевич Д. Д. та ін. Біофізична та колоїдна хімія. – Вінниця: Нова книга, 2007. – С. 110-122.

4. Ленский А. С. Введение в бионеорганическую и биофизическую химию : Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 93-102.

#### Tutorial № 5

**1. THEME:** Acid-base equilibrium in a body. Hydrogen ion exponent (pH) of biological fluids. Buffer systems.

2. PURPOSE: To learn to assess and predict the processes, depending on the change of the medium reaction. To learn to assess the actious of the buffer systems to maintain a certain pH level.

#### Assignments for self-study:

- **1.** Calculate the pH of 0,0001 M HCl solution. (Answer: pH = 4)
- 2. Calculate the pH of the solution with hydrogen ions concentration of  $3,7 \cdot 10-5$  mol/l. (Answer: pH = 4,43)
- 3. Calculate the pH of formic acid solution Ceq = 0.1 mol/l. (Answer: pH = 2,37)
- 4. Calculate the pH of 0.2 M acetic acid solution. (Answer: pH = 2,88)
- 5. In a biological fluid the hydrogen ion concentration is  $4.46 \cdot 10^{-8}$  mol/l. Calculate the pH, pOH and [OH<sup>-</sup>]. What the biological fluid is this?
- Calculate the pH of sodium hydroxide solution, 1 liter of which contains 4 g of NaOH. (Answer: pH = 13)
- 7. Calculate the pH of0,01 M potassium acetate solution.(Answer: pH = 8,38)

- 8. Calculate the pH of NH<sub>4</sub>OH solution with a molar concentration of 0,15 mol /
  1. (Answer: pH = 11,21)
- 9. How will pH change after mixing equal volumes of HCl solution with Ceq = 0,8 mol / 1 and NaOH with Ceq = 0,2 mol / 1? (Answer: the pH will increase 5 times)
- 10. Calculate the pH of 4% KOH solution. (Answer: 13.75)
- 11. How will pH change if 20 ml of 0,1 M NaOH solution is added to 50 ml of water change (Answer: 5,45)
- 12. Calculate [H  $^+$ ], if pOH of a solution is 3,58. (Answer: 3,80 $\cdot$ 10 $^{-11}$ )
- 13. Calculate the pH of HCl solution with mass fraction of 2%. (Answer: 0,26)
- 14. Calculate the pH of phosphate buffer consisting of 60 ml of 0,1 M  $NaH_2PO_4$  solution and 40 ml of 0,1 M  $Na_2HPO_4$  solution. pKa  $(H_2PO_4) = 7,2.$  (Answer: 6,62)
- 15. Calculate the pH of ammonia buffer solution which consists of 70 ml of 0,15 M  $NH_4NO_3$  solution and 50 ml of 0,1 M  $NH_4OH$  solution. pKb ( $NH_4OH$ ) = 4,75. (Answer: 8,93)
- 16. Acetate buffer solution is used in laboratory studies. Calculate pH of the buffer solution prepared by mixing 100 ml of 0,1 M CH<sub>3</sub>COOH and 200 ml

CH<sub>3</sub>COONa.

pKa (CH<sub>3</sub>COOH) = 4,75. (Answer: 5,35)

of

17. Calculate the pH of the acetate buffer, consisting of 50 ml 0,1 M CH<sub>3</sub>COOH solution and 40 ml of 0,15 M CH<sub>3</sub>COONa solution. pKa (CH3COOH) = 4,75. (Answer: 4,95)

0.2M

- 18. Calculate the buffer capacity of the acetate buffer, which consists of 90 ml  $0,15 \text{ M CH}_3\text{COOH}$  solution and 70 ml of 0,12 M solution CH<sub>3</sub>COONa if its 5 ml titration consumed 3,5 ml of 0,1 M NaOH solution. pKa (CH<sub>3</sub>COOH) = 4,75. (Answer: 0,018)
- 19. Calculate the buffer capacity of the blood serum on acid if its 20ml titration takes 3,6 ml of 0,1 M HCl solution; pH serum thus changed to 7,0. (Answer: 0,05)
- 20. Calculate pH of the phosphate buffer solution, prepared from 100 ml of sodium phosphate, C (Na<sub>2</sub>HPO<sub>4</sub>) = 0,05 mol / L and 50 ml of sodium dihydrogen phosphate, C (NaH<sub>2</sub>PO<sub>4</sub>) = 0,1 M, pKa (H<sub>2</sub>PO<sub>4</sub>-) = 7.2. (Answer: 7,20)
- 21. 36 ml of 0,05 M HCl solution was added to 100 ml of buffer solution and the pH changed from 7,3 to 7,0. Calculate the buffer capacity on acid. (Answer: 0,06)
- 22. 25 ml of HCl ( $C_{(HCl)} = 0,05 \text{ mol/l}$ ) is necessary to add to 100 ml of buffer solution to change its pH from 7,6 to 7,0 Calculate a buffer capacity on acid. (Answer: 0,02)

- 23. 12 ml of 0,1 M NaOH solution was added to 100 ml of buffer solution and the pH changed from 7,4 to 9,34. Calculate the buffer capacity on alkali. (Answer: 0,006)
- 24. 14 ml of NaOH solution ( $C_{(NaOH)} = 0,1 \text{ mol/l}$ ) were added to 100 ml of blood and the pH changed from 7,36 to 9,36. Calculate the buffer capacity of the blood on alcali. (Answer: 0,07)
- 25. 36 ml of HCl solution ( $C_{(HCl)} = 0,1 \text{ mol/l}$ ) were added to 100 ml of blood, and the pH changed from 7,36 to 6,64. Calculate the buffer capacity of the blood on acid. (Answer: 0,05)

#### **Examples of assignments:**

Task 1. Calculate the pH 0,001M NaOH solution.

Solution.

$$pOH = -lg [OH^{-}] = -lg 10^{-3} = 3.$$
  
 $pH = 14 - pOH = 14 - 3 = 11.$ 

**Answer:** 11.

Task 2. Calculate the pH of 0,05M solution of sodium benzoate.

*Solution*. Sodium benzoate - an anionic base, so we use a formula for weak bases:

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}lgC_b$$

From the "Handbook of Analytical Chemistry":  $pK_a (C_6H_5OOH) = 4,2.$  $pH = 7 + \frac{1}{2} \cdot 4,2 + \frac{1}{2} \log 0,05 = 7 + 2,1 + \frac{1}{2} \cdot (-1,3) = 8,45.$  **Task 3.** Determine the pH of the solution obtained after mixing equal volumes of 0,3 M and 0,1 M NaOH.

#### Solution.

1) The mixed solutions of the acid and alkali react according to the equation:

 $HCl + NaOH \rightarrow NaCl + H_2O.$ 

From the equation it is seen that the alkali and acid are react in a ratio of 1:1. Since the acid was taken 0,3 mole and alkali – 0,1 mole, so after the reaction remained acid is: 0,3 - 0,1 = 0,2 mole. Since the volume of the mixture has increased by 2 times, then the acid concentration is: 0,2/2 = 0,1 mol/1.

2) Find the pH:

 $[H^+] = 0,1 = 10^{-1}.$ pH = - lg  $[H^+] = - lg 10^{-1} = 1.$ 

**Task 4**. Calculate the pH of acetate buffer consisting of 70 ml of 0,1 M  $CH_3COOH$  and 40 ml of 0,15M  $CH_3COONa$  solutions. pKa ( $CH_3COOH$ ) = 4,76.

Solution. pH of a buffer system can be calculated according to the formula:

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

$$pH = pK_a + lg \frac{C_b}{C_a} = 4,76 + lg \frac{0,15 \cdot 40}{0,1 \cdot 70} = 4,76 + lg 0,857 = 4,69$$

Answer: 4,69.

**Task 5**. Calculate the buffer capacity of blood serum on acid if its 5 ml titration takes 7,5 ml of 0,1 M HCl solution.

#### Solution.

 $pH_0$  is serum pH = 7.36;

 $pH_1$  is pH after titration = 4,4 (since in serum methyl orange has yellow colour, and changes color to pink at pH=4,4 when is titrated by acid).

The buffer capacity of acid is calculated by the formula:

$$\mathbf{B} = \frac{\mathbf{C}_{Me} \cdot \mathbf{V}}{\mathbf{V}_{buff.sol} \cdot (\mathbf{pH}_1 - \mathbf{pH}_0)}$$

$$B_{(HCI)} = \frac{0,1 \cdot 7,5}{5 \cdot (7,36 - 4,4)} = 0,05 \text{ mol}/1$$

Answer: 0,05 mol / 1.

**Task 6.** Calculate bicarbonate buffer capacity (pH = 6,34), if the titration of 5 mL of this buffer took 4,8 ml of 0,1 M NaOH solution.

#### Solution.

Buffer capacity on alkali is calculated using the formula:

$$\mathbf{B}_{(\text{NaOH})} = \frac{\mathbf{C}_{\text{M} \ni (\text{NaOH})} \cdot \mathbf{V}_{(\text{NaOH})}}{\mathbf{V}_{\text{buff.sol}} \cdot (\mathbf{pH}_1 - \mathbf{pH}_0)}.$$

 $pH_0 = 6,34$ 

 $pH_1$  – This is pH after titration, that contributes to the lower point of the coloring interval of phenolphthalein indicator (8,2).

$$B_{(NaOH)} = \frac{0,1 \cdot 4,8}{5 \cdot (8,2-6,34)} = 0,05 \text{ mol/l}.$$

Answer: 0.05 mol/l.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 129-176.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 141-179.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – С. 80-129.

4. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – С. 59-90.

5. Ленский А. С. Введение в бионеорганическую и биофизическую химию : Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 126-160.

6. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 152-178.

7. Мороз А. С, Яворська Л. П., Луцевич Д. Д. та ін. Біофізична та колоїдна хімія. – Вінниця: Нова книга, 2007. – С. 174-190.

#### Tutorial № 6

1. THEME: Fundamentals of titrimetric analysis. Acid-base titration. Acidimetry, alkalimetry

2. PURPOSE: To learn the basics of quantitative analysis, to study the general principles of titrimetric methods and techniques of acid-base titration. To understand the essence of acidimetry and learn how to use this method in clinical analysis, in sanitary and hygienic studies

#### Assignments for self-study:

- 1.Calculate the factor of equivalence and the molar mass of equivalent for the following substances in complete acid-base interaction:
  - 1) 2) HNO<sub>3</sub> NaOH: 3)  $NH_3$ ; 4)  $H_2SO_4;$ 5) KHSO<sub>4</sub>; 6)  $Na_{2}B_{4}O_{7} \cdot 10H_{2}O;$ 7)  $Na_2CO_3$ ; 8) NaHCO<sub>3</sub>; 9)  $H_2C_2O_4;$ 10)  $Ba(OH)_2$ ; 11)  $H_3PO_4$ ; 12)  $H_2CO_3$ .
- 2. Calculate the sample of sodium tetraborate for the preparation of 0,5 l of titrant with Ceq =  $0,1 \mod / l$ . (Answer: 4,55 g)
- 3. How many milliliters of 2,00 M HNO<sub>3</sub> solution you need to take to prepare 3 liters of 0,1000 M solution? (Answer: 150 ml.)
- 4. Calculate Ceq of phosphate acid solution which contains 7,5 g of the acid in 1,5 l of the solution. (Answer: 0,15 mol / L)
- 5. Calculate the molar concentration of hydrochloric acid, if 700 ml of the solution contains 3,5 g of HCl (answer: 0,13 mol / l)

- 6. Calculate the molar equivalent concentration of sulfuric acid if the content of the solution is 5,5 g in 600 ml (Answer: 0,18 mol / 1)
- 7. Calculate Ceq of hydrochloric acid solution, if 200 ml of the solution contains 15 g of the acid. (Answer: 0,2 mol / l).
- 8. How many grams of H<sub>2</sub>SO<sub>4</sub> is contained in 5 L of solution, if the titration of this solution takes 25,00 ml, 22,50 ml of 0,0950 N. KOH solution? (Answer: 20,97 g)
- 9. How many gram-equivalents are: a) in 1.8909 g of oxalic acid H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O; b) in 20 ml of 0,12 M NaOH solution? (Answer: a) 0,030; b) 0,0024)
- 10. How many milligram-equivalents are: a) in 0,4240 g Na<sub>2</sub>CO<sub>3</sub> b) in 50 ml of 0,20 N solution of H<sub>2</sub>SO<sub>4</sub>? (Answer: a) 8,00; b) 10)
- 11. The titration of 10,00 mL of 0,09518 N. sodium tetraborate solution consumed 9,23 mL of hydrochloric acid. Calculate the titer and the molar equivalent concentration of HCl solution. (Answer: 0,1031 mol / 1)
- 12. Calculate the molar equivalent concentration of sodium hydroxide solution, if the titration of 20,00 mL of 0,1025 M sulfuric acid consumed 20,50 ml of this solution. (Answer: 0,2 mol / l)
- 13. The titration of 25,00 ml of 0,1082 N of sodium hydroxide solution consumed 23,10 ml of hydrochloric acid solution. Calculate the molar equivalent concentration of HCl solution. (Answer: 0,1171 mol / l)

- 14. The titration of 10,00 mL of 0,05125 N potassium hydroxide solution consumed 5,63 mL of hydrochloric acid. Calculate the titer and the molar equivalent concentration of HCl solution. (Answer: 0,09103 mol / L)
- 15. Calculate the molar equivalent concentration and titer of sodium hydroxide solution, if the titration of 20,00 ml 0,05036 N of sulfuric acid consumed 18,30 mL of this solution. (Answer: 0,05504 mol / L; 0,002202 g / ml)

#### **Examples of assignments:**

**Task 1.** The titration of 5,00 ml of 0,1099 N. sodium tetraborate consumed 9,53 ml of hydrochloric acid. Calculate the titer and the molar equivalent concentration of HCl solution.

Solution.

According to the law of equivalents:

 $C_{M_{\mathfrak{I}}}(Na_{2}B_{4}O_{7}) \cdot V(Na_{2}B_{4}O_{7}) = C_{M_{\mathfrak{I}}}(HCl) \cdot V(HCl),$ 

where the molar concentration of equivalent of HCl solution is:

 $C_{M_{\Im}(HCl)} = \frac{C_{M_{\Im}(Na_{2}B_{4}O_{7})} \cdot V_{(Na_{2}B_{4}O_{7})}}{V_{(HCl)}} = \frac{0,1099 \cdot 5,00}{9,53} = 0,05746 \text{ mol/l}$ 

Calculate the titer of HCl solution according to the formula:

$$T = C_{M9}(HCl) \cdot M9'(HCl);$$

M(HCl) = 36,46 g/mol;f<sub>9</sub>(HCl) = 1;

$$M\mathfrak{I}'(HCl) = M(HCl) \cdot \mathfrak{f}\mathfrak{I}(HCl) : 1000 = 0,03646.$$
  
T = 0,05746 \cdot 0,03646 = 0,002102.  
Answer: 0,002102 g/ml; 0,05746 mol/l.

**Task 2.** Calculate  $Na_2CO_3$  sample weight to prepare 3 L of standard solution with Ceq = 0.5 mol/l.

*Solution:* We calculate Na<sub>2</sub>CO<sub>3</sub> molar mass of equivalent:

$$\begin{split} M(Na_2CO_3) &= 106 \text{ g/mol}; \\ f_9(Na_2CO_3) &= 1/2; \\ M_9(Na_2CO_3) &= M(Na_2CO_3) \cdot f_9(Na_2CO_3) = 106 \cdot 1/2 = 53 \text{ g/mol}. \end{split}$$

Find a sample of sodium carbonate, using the formula:

$$\mathbf{C}_{_{\mathsf{ЭKB.}}} = \frac{\mathbf{a}_{_{X}}}{\mathbf{M}_{_{\mathsf{ЭKB.X}}} \cdot \mathbf{V}} \,,$$

Hence:

a  $(Na_2CO_3) = C_{eqw}(Na_2CO_3) \cdot M_{eqw}(Na_2CO_3) \cdot V$ a  $(Na_2CO_3) = 0.5 \cdot 53 \cdot 3 = 79.5$  g.

Answer: 79,5 г.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 313-336.

2. Харитонов Ю. Я. Аналитическая химия (аналитика). В 2 кн. Кн. 2. Количественный анализ. Физико-химические (инструментальные) методы анализа. – М.: Высшая школа, 2001. – С. 5-7, 68-77, 81-117.

#### Tutorial № 7

# THEME: Colligative properties of solutions PURPOSE: To learn how to use data on the osmotic pressure in medical practice

#### Assignments for self-study:

- 1. Calculate the osmotic pressure of 0,2 M glucose solution.
- 2. Calculate the osmotic pressure of 0,3 M NaCl solution.
- 3. Calculate the osmotic pressure of 10% CaCl<sub>2</sub> solution.
- 4. Are 2% solutions of acetic acid and glucose isotonic?
- 5. Are 1% solutions of urea and sodium chloride isotonic?
- 6. Calculate the molar concentration of hemoglobin if its 1% solution has an osmotic pressure equal to 0,004 bar.
- 7. Calculate the osmotic pressure of 0,2 M solution of potassium chloride.
- 8. Calculate the osmotic pressure of 4% glucose solution.

- 9. Calculate the temperature of the freezing point for 2 M NaCl solution if kr. =  $1,86 \ {}^{0}C/m$
- 10. 1% potassium permanganate solution is used in medicine for external use. Calculate the osmotic pressure of the solution at 25  $^{0}$ C ( $\rho = 1,02$  g / ml).
- 11. Calculate the osmotic pressure of 2% calcium bromide solution ( $\rho = 1,01$  g / ml) at 37 <sup>o</sup>C. Is the solution isotonic to blood (the answer to be explained).
- 12. Calculate the boiling point of sucrose aqueous solution containing 50 g  $C_{12}H_{22}O_{11}$  in 350 g of water. K= 0.52  $^{0}C$  / m.
- 13. Calculate the freezing point of zinc chloride aqueous solution containing 5,7 g of the substance in100 g of water.  $k = 1,86 \ ^{0}C / m$ .
- 14. 10% aqueous solution of calcium chloride is used as hemostatic. Calculate the boiling point of the solution. k 0,52 <sup>0</sup> C / m.
- 15. Calculate the freezing temperature of sucrose solution  $(S_{12}H_{22}O_{11})$  containing 18,39 g of sucrose in 100 g of wate.  $k = 1,86 \ ^{0}C / m.$
- 16. Calculate the freezing point of 30% sodium chloride aqueous solution.  $k_{kr}$ . = 1,86  $^{0}C$  / m.

17. Iodine solution in ethanol is used as antiseptic. Calculate the boiling temperature of the solution which contains 27 g of crystalline iodine and 200 ml of ethanol. (t<sub>b.</sub> of ethanol = 78,4  $^{0}$ C;. K<sub>eb</sub> = 1,16;  $\rho$  = 0,8 g / mL

#### **Examples of assignments:**

**Task 1.** Calculate the osmotic pressure (in kPa and in atm.) for 0,1 M urea solution at 25  $^{\circ}$ C.

*Solution.* Urea is non-electrolyte, therefore the osmotic pressure is calculated by the following formula:

T= 25+273=298 K  $\pi$  = CRT = 0,1<sup>•</sup> 8,314<sup>•</sup> 298 = 247,7 kPa.

If 1 atm. = 101,325 kPa, then:

 $\pi = 247,7: 101,325 = 2,44$  atm.

Answer: 247,7 kPa or 2,44 atm.

**Task 2.** Calculate the osmotic pressure of 20% solution of sodium chloride at 273 K. The degree of dissociation of the sodium chloride is 1, and the solution density is 1,04 g/ml.

*Solution.* Osmotic pressure of the electrolyte solution is calculated as follows:

$$\pi = i \cdot C_{M} \cdot R \cdot T$$

First calculate the molar concentration of sodium chloride solution and the isotonic coefficient:

$$C_{M} = \frac{\omega \cdot \rho \cdot 10}{M} = \frac{10 \cdot 1,04 \cdot 10}{58,5} = 1,78 \text{ mol/l.}$$

NaCl - is a strong electrolyte and dissociates onto two ions, it means n = 2, then:

 $i = 1 + \alpha (n - 1) = 1 + 1 (2 - 1) = 2;$ 

 $\pi = 2 \cdot 1,78 \cdot 8,314 \cdot 273 = 8080 \text{ kPa}$ 

Answer: 8080 kPa.

**Task 3.** Calculate the depression of the freezing point of 3,6% glucose solution ( $\rho = 1,014$ ,. Kkr. = 1,86  $^{0}$ C / m).

*Solution.* As glucose is non-electrolyte, so we use the fallowing formula for depression calculating:

$$\Delta T = k \cdot C,$$

Calculate the molar concentration (it is also molal concentration in this case) of glucose solution:

$$C_{\rm M} = \frac{\omega \cdot \rho \cdot 10}{M} = \frac{3.6 \cdot 1.014 \cdot 10}{180} = 0.2028 \text{ mol/l}$$

Then:

 $\Delta T = k \cdot C = 1,86 \cdot 0,2028 = 0,38 \ ^{0}C$ 

*Answer:* 0,38 <sup>0</sup>C

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 111-128.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 126-141.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000, – С. 61-76.

4. Мороз А. С, Яворська Л. П., Луцевич Д. Д. та ін. Біофізична та колоїдна хімія. – Вінниця: Нова книга, 2007. – С. 130-150.

#### Tutorial № 8

1. THEME: Seminar «Chemistry of biogenic elements. Complexing in biological fluids. Acid-base equilibriua in biological fluids»

2. PURPOSE: To summarize the material, check the students' knowledge on the topic and the ability to apply this knowledge in biomedical research.

**Control test questions** 

# 1. Chemistry of biogenic elements. Complexing in biological fluids.

1. General characteristics of s-, p-, d-elements and their compounds according to their position in the periodic table of Mendeleev. Their chemical properties. Electronic configuration of atoms and ions.

2. Biological and medical significance of s-, p-, d-elements and their important compounds.

3. Coordination compounds. Modern concept of the coordination compounds structure and their classification.

4. Instability and stability constants of coordination compounds. Chelate compounds.

# 2. Acid – base equilibria in biological fluids

1. Modern ideas of solutions. The role of fluids in vital activity.

2. The solubility of gases in liquids. The solubility of liquids and solids in liquids.

3. Equilibria in electrolytes solutions. Dissociation of strong and weak electrolytes.

4. Dissociation of water. Ionic product of water. pH of body fluids.

5. Calculation of pH of solutions of strong and weak electrolytes.

6. Protolytic acid-base theory. The main types of protolytic reactions.

7. Hydrolysis of salts. The degree and the constant of hydrolysis. The role of hydrolysis in biochemical processes.

8. Buffer systems, protolytic equilibrium in them. Buffer capacity. Examples of the buffer systems: phosphate, hydrocarbonate. Calculation of buffer system pH.

9. Buffer systems of the human body: protein, hemoglobin. The mechanism of action. Significance of buffer systems for living organisms.

10. Fundamentals of titrimetric methods of analysis.

11. Acid-base titration. Titrants. Acid-base indicators, and the principles of their selection.

12. Application of acid-base titration methods in clinical analysis, in sanitary and hygienic studies.

13. Colligative properties of diluted solutions. Rault's Law and its corollaries. Cryometry (depression), ebulliometry.

14. Diffusion and osmosis. Osmotic pressure. Van't Hoff's Law.

15. Plasmolysis and hemolysis.

16. Colligative properties of diluted solutions. Isotonic coefficient.

17. Isotonic, hypertonic and hypotonic solutions in medicinal practice.

18. The role of osmosis and osmotic pressure in biological systems.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – 776 с.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 400.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – 560 с.

4. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – 688 с.

5. Мороз А. С, Яворська Л. П., Луцевич Д. Д. та ін. Біофізична та колоїдна хімія. – Вінниця: Нова книга, 2007. – 600 с.

6. Левітін Є. Я., Бризицька А. М., Клюєва Р. Г. Загальна та неорганічна хімія. – Вінниця: Нова книга, 2003. – 464 с.

7. Глинка Н. Л. Общая химия. – Ленинград: Химия, 1984. – 702 с.

 Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. – М.: Высш. шк., 1975. – 256 с.

9. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – 272 с.

Евстратова К. И., Купина Н. А., Малахова Е. Е. Физическая и коллоидная химия : Учеб. для фарм. вузов и факультетов / под ред. К. И. Евстратовой. – М.: Высш. шк., 1990. – 487 с.

 Ленский А. С. Введение в бионеорганическую и биофизическую химию : Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – 256 с.

## **TOPIC MODULE 3**

# THERMODYNAMIC AND KINETIC REGULERITY OF REACTION BEHAVIOR AND ELECTROKINETIC PHENOMENA IN BIOLOGICAL SYSTEMS

1. THEME: The thermal effects of chemical reactions. Process directions

2. PURPOSE: To study the laws of chemical thermodynamics, as the theoretical base of bioenergy. Be able to interpret the basic laws of thermodynamics for describing biological processes

#### **Assignments for self-study:**

- In Krebs' cycle isocitrate is converted into α-ketoglutarate: isocitrate + 1/2O<sub>2</sub> (g) + H +↔α-ketoglutarate+H<sub>2</sub>O (g) + CO<sub>2</sub> (g). Calculate the ΔG of the reaction, if ΔG° prod. (isocitrate) = -1166,6 kJ / mol ΔG° prod. (α-ketoglutarate) = -796,8 k / mol ΔG° prod. (CO<sub>2</sub>) = -394,4 kJ / mol.; ΔG° prod.. (H<sub>2</sub>O) = -237 kJ / mol. (Answer: - 267,2 kJ / mol)
- 2. Determine the thermal effect of synthesis reaction of diaethyl aether used in medicine for anesthesia, at 298 K:
  2S<sub>2</sub>N<sub>5</sub>ON (g) → S<sub>2</sub>N<sub>5</sub>OS<sub>2</sub>N<sub>5</sub> (g) + H<sub>2</sub>O (g);
  if combustion enthalpies are: ΔH° <sub>comb.</sub> (S<sub>2</sub>N<sub>5</sub>OS<sub>2</sub>N<sub>5</sub>) = -2727 kJ / mol; ΔH° <sub>comb.</sub> ((C<sub>2</sub>H<sub>5</sub>OH) =
  = -1371kJ / mol. (Answer: 15 kJ / mol)
- 3. One of the way of glucose metabolism is the process:  $C_6H_{12}O_6 (liq) \rightarrow C_3H_7COOH (liq) + CO_2 (g) + H_2 (g).$ Calculate  $\Delta G$  of the reaction if  $\Delta G^\circ (C_6H_{12}O_6) = -917,0 \text{ kJ / mol}, \Delta G^\circ (C_3H_7COOH) - 376k = J / mol, \Delta G^\circ (CO_2) =$ = -394,4 kJ / mol. (Answer: -247,8 kJ / mol)

- 4. Carboxyhemoglobin (Hb-CO) is formed from the hemoglobin (Hb). Write the equation of reaction of destruction of carboxyhemoglobin and determine whether the spontaneous flow of the reaction is possible.  $\Delta G^{o}_{f.}$  (Hb) = -1821.3 kJ / mol,  $\Delta G^{o}_{f.}$  (Hb-CO) = -2901kDzh / mol. (Answer: probably)
- 5. Is the reaction possible:  $Al_2O_3 + 3SO_3 = Al_2(SO_4)_3$ , if the Gibbs energy of  $Al_2O_3(s) -1576,4$  kJ / mol,  $SO_3 -370,37$  kJ /mol,  $Al_2(SO_4)_3$ -3091,9 kJ/mol? (Answer: -404,39kJ / mol, reaction is possible)
- 6. Calculate the Gibbs energy for the reaction of glycolysis:  $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$ , If  $\Delta G(C_3H_6O_3) = -539$ kJ / mol and  $\Delta G \Delta G(C_6H_{12}O_6) =$ = -917 kJ / mol. (Answer: -161 kJ / mol)
- 7. If there is a threat, that nitrogen (I) oxide, used in medicine for anesthesia, will be oxidized by atmosphere oxygen to toxic nitrogen (II) oxide, if  $\Delta G^{o}_{f}$ . (N<sub>2</sub>O) = 104 kJ / mol and  $\Delta G^{o}_{f}$  (NO) = 87kJ / mol. (Answer:  $\Delta G = 140$  kJ / mol, the reaction is impossible)
- 8. Calculate the value of the enthalpy of ethanol oxidation in the human body:  $C_2H_5OH+3O_2 = 2CO_2 + 3H_2O_3$

The standard heat of formation of carbon dioxide, ethanol and water are: -393.5 kJ / mol and -277.6 kJ / mol and -285,84 kJ / mol respectively. (Answer: -1366,92 kJ / mol)

9. Calculate the enthalpy value for urea hydrolysis reaction:  $CO(NH_2)_2 + H_2O \rightarrow CO_{2\uparrow} + 2NH_3$  if the standard heat of formation of the urea, carbon dioxide and water are respectively: -333,3 kJ / mol,

-393.5 KJ / mol and -285,84 kJ / mol (answer: 225,64 kJ / mol).

10. Calculate the value of the enthalpy of glucose oxidation in the human body:  $C_6H_{12}O_6 + 6O_{2\uparrow} \rightarrow 6CO_{2\uparrow} + 6H_2O$ if  $\Delta H^o$  formation. pf glucose is -1272.45 kJ / mol. of carbon dioxide is

-393.6 KJ / mol, of water is -285.84 kJ / mol. (Answer: -2804,55 kJ / mol)

- Calculate the thermal effect of methane (CH<sub>4</sub>) formation reaction the enthalpies of combustion of methane, hydrogen and carbon are: -890 kJ / mol, 286 kJ / mol, and -394 kJ / mol. (Answer:-76 kJ / mol)
- 12. Calculate the thermal effect of acetylene  $(C_2H_2)$  from benzene  $(C_6H_6)$  formation reaction if the values of the heats of combustion of benzene and acetylene are -2364,5 kJ / mol and -1299,6 kJ / mol (Answer: 634,3 kJ / mol).
- 13. Calculate the Gibbs' energy change in the process of sucrose digestion in the human body, which leads to its oxidation: C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> (s) + 11O<sub>2</sub> (g) → 12CO<sub>2</sub> (g) + 11H<sub>2</sub>O (liq);
  ΔG° (CO<sub>2</sub>) = -394.4 kJ / mol,
  ΔG° (H<sub>2</sub>O) = -237 kJ / mol. (Answer: -5794 kJ / mol)
- 14. Calculate the thermal effect of the reaction

2KNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → K<sub>2</sub>SO<sub>4</sub> + 2HNO<sub>3</sub>, if the standard enthalpies of substances are:  $\Delta$ H<sup>o</sup> (KNO<sub>3</sub>) = -492,5,  $\Delta$ H<sup>o</sup> (HNO<sub>3</sub>) = -133.9,  $\Delta$ H<sup>o</sup> (K<sub>2</sub>SO<sub>4</sub>) = -1433,7,  $\Delta$ H<sup>o</sup> (H<sub>2</sub>SO<sub>4</sub>) = -814,0 kJ / mol. (Answer: 97,5 kJ / mol) 15. The process of formaldehyde reduction the following reaction occurs:

 $CH_2O + H_2 \rightarrow CH_3OH$ . Calculate the enthalpy of the reaction, if the heat of formation of formaldehyde, hydrogen and methanol are equal to -115,9 kJ / mol, -286 kJ / mol, - 227,6 kJ / mol.

#### **Examples of assignments:**

**Task 1.** Is the fallowing reaction possible if Gibbs energy of  $Hg_2Cl_2$  and  $HgCl_2$  are -210,66 and -185,77 kJ / mol respectively&

$$Hg_2Cl_2 \rightarrow HgCl_2 + Hg.$$

Solution.

Write Gibbs energy equation for the reaction

$$\Delta G = \Sigma \Delta G^{o}_{prod} - \Sigma \Delta G^{o}_{react.}$$

Hence:

$$\Delta G = -185,77 - (-210,66) = 24,89 \text{ kJ} / \text{mol.}$$

*Answer:* The reaction is not possible, since the change in Gibbs free energy is higher than zero ( $\Delta G > 0$ ).

Task 2. Calculate the enthalpy of the reaction:

 $CaC_2$  (s) + 2H<sub>2</sub>O (liq) = Ca(OH)<sub>2</sub>(s) + C<sub>2</sub>H<sub>2</sub>(g) if the heat of formation of calcium carbide, calcium hydroxide, water, and acetylene are equal to -62.8 kJ / mol, -986.6 KJ / mol and -285.84 kJ / mol and 52.25 kJ / mol respectively.

#### Solution.

Use the equation of the first consequences of the law of Hess:

 $\Delta H = \sum \Delta H_{prod.}^{\circ} - \sum \Delta H_{react.}^{\circ}$ Hence:  $\Delta H = (-986,6 + 52,25) - (-62,8 + 2(-285,84)) = -934,35 - (-634,48) = -299,87 \text{ kJ / mol}$ Answer: -299,87 kJ / mol

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 366-418.

2. Medical Chemistry : textbook / V. A. Kalibabchuk [and ol.] ; ed. by V. A. Kalibabchuk. - K. : Medicine, 2008. – P. 59-80.

3. Ленский А. С. Введение в бионеорганическую и биофизическую химию: Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 151-160.

4. Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. – М.: Высш. шк., 1975. – С. 10-21.

5. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – С. 8-29, 35-37.

**1. THEME: Kinetics of biochemical reactions** 

2. PUROSE: To study the laws and rules of the kinetics and be able to interpret them for the characterization of biological processes

## Assignments for self-study:

- How many times will the chemical reaction rate change if the concentration of H<sub>2</sub> is 2 times increased?
   N<sub>2</sub>(g) + 3H<sub>2</sub>(g) → 2NH<sub>3</sub>(g).
   (Answer: 8 times)
- 2. How will the rate of the reaction change, if the pressure in the system is 4 times increased?

 $\mathrm{C_2} + \mathrm{2D} \rightarrow \mathrm{2CD}$ 

(Answer: increases to 64 times)

3. How will the rate of the reaction change, if the oxygen concentration is 2-fold decreased?

 $SO_2 + O_2 \rightarrow SO_3$ 

(Answer: reduces 2-fold)

4. How many times will the reaction rate change if the system pressure is reduced by 3 times?
CO(g) + O<sub>2</sub>(g) → CO<sub>2</sub>(g)
(A many number of a constraint of a const

(Answer: reduces by 27 times)

- 5. How many times will the reaction rate increase when the temperature increase to  $400 \text{ C} (\gamma = 3)$ ? (Answer: 81 times)
- 6. When the temperature increased to 30°C the reaction rate increased by 27 times. Calculate the temperature coefficient. (Answer:  $\gamma = 3$ ).
- 7. How many times will the reaction rate change, if the temperature increases from 25 °C to 55 °C and the temperature coefficient is equal to 2? (Answer: 8 times)
- 8. How many times will the reaction rate change, if the temperature increases from 0 to 50 ° C and the temperature coefficient is equal to 3? (Answer: 243 times)
- 9. How many times will the rate of chemical reaction increase when the temperature rises from 20 °C to 80 °C? Temperature rate coefficient (gamma) is equal to 2. (Answer: 64 times)
- 10. How many times will the rate of a chemical reaction change
   NO(g) + Cl<sub>2</sub>(g) → NOCl (g), if the concentration of NO is 2-fold increased?
   (Answer: increase by 4 times)
- 11. How will the rate of the reaction change  $2A + B2 \rightarrow 2AV$  if the pressure in the system increases by 5 times? (Answer: increase by 125 times)
- 12. How many times will the reaction rate change
  2NO (g) + Cl<sub>2</sub> (g) → 2NOCl (g) if the system pressure is reduced by 4 times? (Answer: decreases 64 times)

- 13. The reaction rate constant C + 2D → K is 0,4 l<sup>2</sup>/mol·s. Concentration of the substance C is 2 mol/l, and of substance D 3 mol/l. Calculate the rate of direct reaction. (Answer: 7,2 mol/s)
- 14. How many times will the reaction rate increase when the temperature increase by 40°C ( $\gamma = 4$ )? (Answer: 246 times).
- 15. When the temperature increases 20°C the reaction rate is increased by 16 times. Calculate the temperature coefficient. (Answer:  $\gamma = 4$ )?

## **Examples of assignments:**

**Task 1.** How will the rate of the reaction change 2NO (g) + Cl<sub>2</sub> (g)  $\rightarrow$  2NOCl (g), if the concentration of the reactants increases by 2 times?

*Solution*. From the law of mass action reaction rate is equal to:

$$v = k[NO]^2 \cdot [Cl_2].$$

Hence:

$$v = k[2NO]^2 \cdot [2Cl_2] = 8k[NO]^2 \cdot [Cl_2].$$

$$\frac{\upsilon_2}{\upsilon_1} = \frac{8k[NO]^2 \cdot [O_2]}{k[NO]^2 \cdot [O_2]} = 8.$$

Answer: increase by 8 times.

**Task 2.** How many times will the reaction rate change, if the reaction temperature is changed from 18°C to 38 °C, and the temperature coefficient is equal to 3?

Solution.

$$\frac{\upsilon_2}{\upsilon_1} = \gamma^{\frac{t_2 - t_1}{10}} = 3^{\frac{38 \cdot 18}{10}} = 3^2 = 9.$$

Answer: 9 times.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 420-487.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – P. 82-98.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000, – С. 391-422.

4. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 92-106.

5. Ленский А. С. Введение в бионеорганическую и биофизическую химию : Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 55-79.

6. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – С. 140-165.

1. THEME: Chemical equilibrium. Solubility product

**2. PUROSE:** To learn to determine the direction of chemical reactions and to evaluate the effect of different factors on the behavior of chemical processes

#### Assignments for self-study:

- 1. Calculate the equilibrium constant for the reversible reaction  $2NO+O_2 \leftrightarrow 2NO_2$ , when at equilibrium [NO] = 0,056 mol/L, [O<sub>2</sub>] = 0,02 mol/l, [NO<sub>2</sub>] = 0,044 mol/L. (Answer: 30.87)
- 2. The equilibrium of the system 2A + B ↔ 3C + D established under such equilibrium concentrations of A, B, C and D, respectively: 2,5; 1; 1,7; 0,8 mol/l. Calculate the equilibrium constant. (Answer: 1,59)
- 3. Methoxyacetic acid methyl ester (intermediate product of the synthesis of vitamin B6) is prepared by reaction:

 $CH_3OCH_2COOH+CH_3OH\leftrightarrow CH_3OCH_2COOCH_3+H_2O.$ 

Calculate the equilibrium constant for the reaction, if 1 mole of acid and 1 mole of alcohol formed 0.562 mole of ester at equilibrium. (Answer: 1.646)

4. Reversible enzymatic process takes place in the liver: glucose - 1 - phosphate  $\leftrightarrow$  glucose - 6 - phosphate. At 37<sup>0</sup>C the concentration of glucose-1-phosphate is 0,001 mol/1, and of glucose- 6- phosphate is 0,019 mol/1. Calculate the K<sub>r</sub>. (Answer: 19) 5. In what direction will the reaction equilibrium shift

 $2NO + O_2 \leftrightarrow 2NO_2$  if the concentrations of all substances is reduced by 4 times. (Answer: in the direction of the reverse reaction).

6. For the reaction: L-glutamic acid + Pyruvate  $\leftrightarrow$ 

 $\alpha$ -ketoglutaric acid + L-alanine, the equilibrium constant is equal to 1,11 at 30 °C. In which direction will go the reaction at the following concentrations: L-glutamic acid and pyruvate – 0,00003 mol/L,  $\alpha$ -ketoglutaric acid and L-alanine – 0,005 mol/l? (Answer: in the reverse direction).

7. Methylamine is the base in aqueous solution:

CH<sub>3</sub>NH<sub>2</sub> + H<sub>2</sub>O ↔ CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> + OH<sup>-</sup>. Calculate the equilibrium constant, if the initial concentration of methylamine is 0,1 mol/l, and the concentration of hydroxide ion in equilibrium is 6,6 10<sup>-3</sup> mol/l. (Answer:  $4.7 \times 10^{-4}$ )

- 8. In which direction will the reaction equilibrium shift
  CO + H<sub>2</sub> ↔ CH<sub>4</sub> + CO<sub>2</sub> if concentrations of all compounds reduced in 2 times? (Answer: in the opposite direction).
- 9. The equilibrium constant of the reaction N<sub>2</sub>O<sub>4</sub> ↔ NO<sub>2</sub> is 0,26. Equilibrium concentration of NO<sub>2</sub> is 0,28 mol/l. Calculate the equilibrium and original concentration of N<sub>2</sub>O<sub>4</sub>. (Answer: 0,44 mol/L)
- 10. Calculate the solubility product of calcium oxalate  $CaC_2O_4$  if the solubility of this salt is 4,47 10<sup>-4</sup> mol/l.
- 11. Calculate the solubility product of silver phosphate  $-Ag_3PO_4$ , if the solubility of this salt is 1,6 x 10<sup>-5</sup> mol/l.

- 12. Calculate the solubility of  $BaSO_4$  and ion concentration of  $[Ba^{2+}]$  and  $[SO_4^{2-}]$  if solubility product of the substance is 1,1 10<sup>-10</sup>.
- 13. The solubility product of  $PbCl_2$  is  $1.6 \times 10^{-5}$  at 25 °C. Determine the concentration of  $PbCl_2$  in saturated solution at this temperature.
- 14. Calculate the solubility product of calcium carbonate and magnesium carbonate, if the solubility of these salts in g / 100 ml, are  $6.5 \times 10^{-3}$  and  $1.2 \times 10^{-3}$  respectively.
- 15. Calculate the solubility product of  $CaSO_3$  and  $PbSO_4$ , if the solubility of these substances are  $4.3 \times 10^{-3}$  and  $4.1 \ge 10^{-3} \text{ g}/100 \text{ ml}$ .
- 16. What is solubility of PbI in water in mol/l and in g/l at 25  $^{\circ}$  C, if the solubility product of the salt is 8,1 10<sup>-9</sup>?
- 17. Calculate the solubility of calcium sulfate (CaSO<sub>4</sub>), calcium fluoride (CaF<sub>2</sub>) and calcium hydrogen phosphate (CaHPO<sub>4</sub>), in mol/L if the solubility product of these salts are equal to 6,3  $10^{-5}$ ; 4,0  $10^{-11}$ ; 2,7 ×  $10^{-7}$ . Which of the salts is the most soluble? The least soluble?
- 18. Calculate the solubility product of zinc sulfide ZnS, if the solubility of this salt is  $1,26 \ 10^{-12} \ \text{mol} \ / \ 1$ .
- 19. Using the reference data of solubility products arrange the hydroxides of iron (III), iron (II), magnesium, zinc and copper in order of their water solubility increasing. Explaine your answer.

20. Calculate the solubility of silver chloride, bromide and iodide in mol/l and g/100 ml, when the solubility product of these salts are, respectively,  $1.8 \cdot 10^{-10}$ ;  $5.3 \cdot 10^{-13}$  and  $1.1 \cdot 10^{-16}$ .

#### **Examples of assignments:**

**Task 1.** In which direction will the chemical equilibrium of the reaction  $N_2 + 3H_2 \leftrightarrow 2NH_3$  shift, if the pressure in the system increases three-fold?

Solution. The equilibrium constant before the change of pressure:

$$\operatorname{Ke}_{1} = \frac{[\operatorname{NH}_{3}]^{2}}{[\operatorname{N}_{2}] \cdot [\operatorname{H}_{2}]^{3}}$$

With increasing pressure in three times the concentration of all substances also increased by 3 times. The equilibrium constant pressure after the change:

$$\mathrm{Kc}_{2} = \frac{[3\mathrm{NH}_{3}]^{2}}{[3\mathrm{N}_{2}] \cdot [3\mathrm{H}_{2}]^{3}} = \frac{3^{2}}{3 \cdot 3^{3}} = \frac{1}{9}$$

The ratio of equilibrium constants:

$$\frac{\mathrm{Kc}_{1}}{\mathrm{Kc}_{2}} = \frac{1 \cdot 9}{1} = 9$$

**Answer:** The equilibrium constant increases in 9 times, because the chemical equilibrium will shift to the direct reaction.

**Task 2.** In the system  $2NO + O_2 \leftrightarrow 2NO_2$  equilibrium concentration of the substances are [NO] = 0,2 mol/ 1, [O<sub>2</sub>] = 0,3 mol/1, [NO<sub>2</sub>] = 0,4 mol/ 1. Calculate the equilibrium constant.

*Solution.* The equilibrium constant is:

Kc = 
$$\frac{[NO_2]^2}{[NO]^2 \cdot [O_2]} = \frac{0.4^2}{0.2^2 \cdot 0.3} = \frac{0.16}{0.012} = 13.3$$

Answer: 13,3.

**Task 3.** Calculate the solubility product of  $Pb_3(PO4)_2$  if the solubility of the salt is 1,5 10<sup>-9</sup> mol/l.

*Solution.*  $Pb_3(PO_4)_2$  dissociates by the equation:

$$Pb_3(PO_4)_2 \leftrightarrow 3Pb^{2+} + 2PO_4^{3-}$$

The concentrations of ions in the solution are:

 $[Pb^{2+}] = 3 \cdot 1,5 \cdot 10^{-9} = 4,5 \cdot 10^{-9} \text{ mol } / 1$  $[PO_4^{3-}] = 2 \cdot 1,5 \cdot 10^{-9} = 3 \cdot 10^{-9} \text{ mol } / 1;$ 

SP is calculated from the formula: SP =  $[Pb^{+2}]^3 \cdot [PO_4^{3-}]^2$ ; SP Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> =  $(4,5 \cdot 10^{-9})^3 \cdot (3 \cdot 10^{-9})^2 = 8,2 \cdot 10^{-43}$ .

Answer: 8,2·10<sup>-43</sup>.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 176-184, 414-419.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – P. 98-105, 179-189.

3. Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – С. 32-40,129-131.

4. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 121-126, 226-234.

5. Ленский А. С. Введение в бионеорганическую и биофизическую химию: Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 80-92.

1. THEME: Evaluation of oxidation-reduction potential

2. PURPOSE: To learn to use the redox potentials for the explanation of biological oxidation in living organisms

#### Assignments for self-study:

- 1. The potential of a hydrogen electrode immersed in the test solution in standard conditions is equal to -0,267 V. Calculate the pH of the solution. (Answer: 4,5)
- 2. Calculate the potential of a hydrogen electrode immersed in the solution, which pH is 5,2. (Answer: -0,307 V.)
- 3. The potential of a hydrogen electrode immersed in the test solution is -0,188 V. Compute the pH of the solution and the real potential of the reference electrode, if the system EMF is equal zero. (Answer: 3,2, -0,188 V.)
- 4. Calculate the glass electrode potential (K = -0,56), immersed in a solution with concentration of hydrogen ions  $10^{-3}$ . (Answer: -0,383 V.)
- 5. Calculate the value of the standard redox potential if  $E_{p_{Ox/Red}} = -0,33$  V, and the system has 80% of oxidized and 20% a reduced form of a substance. In reaction 2 electrons are redistributed. (Answer: -0,348 V.)
- 6. Calculate EMF of a system if the indicator and the standard potentials of the electrodes are -0.15 V and 0,228 V respectively. (Answer: 0,378 V.)

- 7. The electrochemical cell of silver chloride and hydrogen electrodes was used to determine the pH and EMF was measured as 0,465 V. Calculate the real potential of a silver chloride electrode if the concentration of hydrogen ions in the solution is 0,001 mol / 1. (Answer: 0.288 V.)
- Calculate the real potential of the indicator electrode, if the real potential of the reference electrode is 0,201 V and EMF is 0,325 V. (Answer: -0.124 V.)
- 9. EMF of electrochemical cell consisting of hydrogen and silver chloride electrodes is 0,232 V. Hydrogen ion concentration in the solution is 10<sup>-5</sup> mol / 1. Determine the real potential of the silver chloride electrode. (Answer: -0,063 V.)
- 10. Calculate  $E_p$  of the redox system  $I_2 / 2I^-$  if  $I_2$  concentration is 0,1 mol / 1, the concentration of  $I^-$  is- 0,02 mol/L and the standard redox potential of the redox couple is equal to 0,535 V. (Answer: 0,555 V)
- 11. Calculate  $E^0$  for the redox couple  $BrO^{3-} / Br^-$  in the half reaction:  $BrO_3^- + 6H^+$   $\Rightarrow Br^+ 3H_2O$ , if it Ep = 1,463 The concentrations of oxidized and reduced forms – 0,01 and 0,001 mol / 1, and the concentration of hydrogen ions is 1 mol / 1. (Answer: 1,45)
- 12. Calculate the ratio of the oxidized and reduced forms of the redox system  $I_2 / \Gamma$ , if its  $E^0 = 0,54$  V, Ep = 0,599 V. (Answer: 100)
- 13. Calculate the real redox potential of the redox couple in the following reaction:  $2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-}$ , if the standard potential RP is 0,09 V, and the concentration ratio of oxidized and reduced forms is 1:50. (Answer: 0,140 V.)

- 14. Calculate the real redox potential of the system  $Ce^{4+} / Ce^{3+}$ , if the standard redox potential of this redox couple is 1,44 V and the concentrations of oxidized and reduced forms are 0,1 and 0,001 respectively. (Answer: 1,56 V.)
- 15. Determine pH of blood if a system of glass and silver chloride (K = -0,87) electrodes was used. EMF was measured, which was 0,634. Silver chloride electrode potential is 0,201 V. Calculate the pH of the blood. (Answer: 7,4)

#### **Examples of assignments:**

**Tusk 1.** Calculate real redox potential of the redox couple  $MnO_4^-/Mn^{2+}$  involved in the half-reaction:

 $MnO_4^- + 8H^+ \leftrightarrow Mn^{2+} + 4H_2O$ ,

if the concentration of the oxidized and reduced forms are 0,2 and 0,002 mol / L,  $E^0 = 1,51$  V and pH = 0.

#### Solution.

Ep can be calculated from Nernst's equation:

$$E_{p \text{ Ox/Red}} = E_{\text{Ox/Red}}^0 + \frac{0.059}{n} \cdot \lg \frac{[\text{Ox}]}{[\text{Red}]}$$

From the reaction equation is determined that 5 electrons take part in the reaction and the oxidized form is  $MnO4^{-}$ , which is reduced to  $Mn^{2+}$ :

$$MnO_4^- + 8H^+ + 5\bar{e} \leftrightarrow Mn^{2+} + 4H_2O$$

Since in this half reaction, hydrogen ions are involved, it is necessary to take into account their concentration, which is calculated by the formula:

$$[H^+] = 10^{-pH} = 10^0 = 1 \text{ mol/l}$$

Then:

$$E_{MnO_{4}^{-}/Mn^{2+}} = E_{MnO_{4}^{-},/Mn^{2+}}^{0} + \frac{0,059}{5} lg \frac{[MnO_{4}^{-}] \cdot [H^{+}]^{8}}{[Mn^{2+}]}$$

$$E_{MnO_{4}^{-}/Mn^{2+}} = 1,51 + \frac{0,059}{5} \lg \frac{[0,2] \cdot [1]^{8}}{[0,002]} = 1,534$$

Answer: 1,534 V.

**Task 2**. Using the cell of silver chloride and hydrogen electrodes the pH of the solution was measured, which was 6,52. EMF of the system is equal to 0,635 V at a temperature 298°K. Calculate the silver chloride electrode potential.

Solution. First, calculate the real potential of the hydrogen electrode:

 $E_{_{2H^+|_{H_2}\uparrow}} = -0,059 pH = -0,059 \cdot 6,52 = -0,385 V.$ 

Then the value of silver chloride electrode potential is easy to calculate from the formula for EMF calculating:

$$EMF = E_{st.el.} - E_{ind.el.,}$$
$$EMF = E_{Ag|AgCl,KCl} - E_{2H^{+}|H_{2}\uparrow}$$

Substitute the available data into the formula:

 $0,635 = E_{Ag|AgCl,KCl} + 0,385$ ,

 $E_{Ag|AgCl,KCl} = 0,635 - 0,385 = 0,250$  V.

Answer: 0,250 V.

**Task 3.** Calculate the potential of the glass electrode (K = -0.85), immersed in a solution which pH is 2.8.

*Solution.* Glass electrode potential is calculated by the formula:

 $E_{p} = K + 0.059 pH$ 

Hence:

$$E_p = -0.85 + 0.059 \cdot 2.8 = -0.685 V.$$

Answer: -0,685 V.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 506-551.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – P. 195-215.

3. Ленский А. С. Введение в бионеорганическую и биофизическую химию: Учеб. пособие для студ. мед. вузов. – М.: Высш. шк., 1989. – С. 231-238.

## **TOPIC MODULE 4**

# PHYSICAL CHEMISTRY OF SURFACE PHENOMENA LYOPHOBIC AND LYOPHILIC DISPERSE SYSTEMS

**1. THEME:** Sorption of biologically active substances at the inteface

2. PURPOSE: To get knowledge of the sorption processes and regularities occurring in the interfacial layer

#### **Assignments for self-study:**

- 1. Calculate the area occupied by the surfactant, if the limiting adsorption is  $8,3 \times 10^{-6}$  mol/m<sup>2</sup>. (Answer:  $2,0 \times 10^{-19}$ )
- 2. Calculate the length of butyric acid molecule, if the area occupied by a molecule in the surface layer is  $S_0 = 3.2 \cdot 10^{-10} \text{ m}^2$ ,  $\rho = 978 \text{ kg/m}^3$ , M = 0.088 kg/mol. (Answer:  $4.7 \cdot 10^{-10}$ )
- 3. Calculate the length of the surfactant molecule, if the limiting adsorption is equal to  $8.5 \times 10^{-6} \text{ mol/m}^2$ , the molar mass of a substance is 0.074 kg/mol, density is 800 kg/m3. (Answer:  $7.9 \cdot 10^{-10}$ )
- 4. Determine the value of adsorption of a solution containing 0,1 mol/m<sup>3</sup> caproic acid C<sub>6</sub>H<sub>13</sub>COOH at 25°C. The surface tension of water at this temperature is  $72,75 \cdot 10^{-3}$  N/m, and of the test solution is  $51,2\cdot10^{-3}$  N/m. (Answer: 8,6  $\cdot 10^{-6}$ )
- 5. Determine the value of surfactant limiting adsorption, if the area per a molecule in the adsorption layer is equal to  $3,37 \cdot 10^{-17}$  m<sup>2</sup>. (Answer: 4,910<sup>-7</sup>)

- 6. Determine the area occupied by a surfactant molecule, if the length of the molecule is  $7.9 \cdot 10^{-10}$  m, density is 787 kg/m<sup>3</sup>, the molar mass of a substance is 0,095 kg/mol. (Answer:  $2.55 \cdot 10^{-19}$ )
- 7. Determine the adsorption value of a solution containing 2 mol/m<sup>3</sup> of heptanoic acid at 20 °C. The surface tension of the water at this temperature is  $72,75 \times 10^{-3}$  N/m, and of the test solution  $67,0 \times 10^{-3}$  N/m. (Answer: 2,36 x  $10^{-6}$ )
- Using the Duclos-Traube rule determine how many times the surface activity of heptanol CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OH is higher than the surface activity of ethanol CH<sub>3</sub>CH<sub>2</sub>OH. (Answer: 335 times)
- 9. Check the Duclos-Traube rule for diluted solutions of saturated organic acids, if the surface activity of stearic acid ( $C_{17}H_{35}COOH$ ) is 23,49  $\cdot 10^{-3}$  N/m, and capric acid activity ( $C_9H_{19}COOH$ ) is 21,37  $\cdot 10^{-3}$  N/m.
- 10. Using the Duclos-Traube rule determine how many times the surface activity of valeric acid ( $C_4H_9COOH$ ) is less than the surface activity of palmitic acid ( $C_{15}H_{31}COOH$ ). (Answer: in 360000 times)
- 11. Check the Duclos-Traube rule for diluted solutions of saturated organic acids, if the surface activity of caproic acid ( $C_6H_{13}COOH$ ) is 4,85 $\cdot$ 10<sup>-3</sup> N/m, and caprylic is ( $C_7H_{15}COOH$ ) 17,01  $\cdot$ 10<sup>-3</sup> N/m.
- 12. Using the Duclos-Traube rule determine how many times the surface activity of butyric acid ( $C_3H_7COOH$ ) is less than surface activity of caproic acid ( $C_6H_{13}COOH$ ). (Answer: in 32,77 times)

#### **Examples of assignments:**

**Task 1.** Using the Duclos-Traube rule determine how many times the surface activity of palmitic acid ( $C_{15}H_{31}COOH$ ) is higher than the surface activity of caprylic acid ( $C_7H_{15}COOH$ ).

#### Solution.

According to the Duclos-Traube rule by increasing hydrocarbon radical per one methylene group -CH<sub>2</sub>- surface activity increases an average in 3,2 times.

 $\frac{g_{C_{15}H_{31}COOH}}{g_{C_{7}H_{15}COOH}} = 3,2^{8} = 10995$ 

Answer: in 10995 times.

**Tusk 2.** Calculate the length of the surfactant molecule if the area occupied by a molecule in the surface layer is  $S_0 = 2.8 \cdot 10^{-17} \text{ m}^2$ ,  $\rho = 888 \text{ kg/m}^3$ , M = 0.073 kg/mol

*Solution.* First, we calculate the value of the limiting adsorption by the formula:

$$\Gamma_{\infty} = \frac{1}{\mathbf{S}_0 \cdot \mathbf{N}_A};$$

$$\Gamma_{\infty} = \frac{1}{2.8 \cdot 10^{-17} \cdot 6.02 \cdot 10^{23}} = 5.93 \cdot 10^{-8} \, \text{mol/m}^2$$

The length of the molecule is:

 $1 = \frac{\Gamma_{\infty} \cdot \mathbf{M}}{\rho};$ 

$$1 = \frac{5,93 \cdot 10^{-8} \cdot 0,073}{888} = 4,87 \cdot 10^{-12} \,\mathrm{m}.$$

Answer:  $4,87 \times 10^{-12}$  m.

**Tusk 3.** Determine the adsorption value of a solution containing 0,05 mol/l of valeric acid at 15 °C d. The surface tension of the water at this temperature 74.2 ×  $10^{-3}$  N/ m, and the test solution  $63 \times 10^{-3}$  N/m.

*Solution.* The quantity of adsorption at the limit liquid - gas is calculated by Gibbs' equation:

$$\Gamma = -\frac{C_{\rm M}}{\mathbf{R} \cdot \mathbf{T}} \cdot \frac{\Delta \sigma}{\Delta C}$$

 $\Gamma = -\frac{0.05}{8.31 \cdot 288} \cdot \frac{(63 \cdot 10^{-3} - 74.2 \cdot 10^{-3})}{(0.05 - 0)} = 4.68 \cdot 10^{-6} \text{ mol/m}^2$ 

Answer:  $4,68 \times 10^{-6} \text{ mol/m}^2$ .

#### Literature:

- 1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. Вінниця: Нова книга, 2011. С. 562-594.
- Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. K.: Medicine, 2008. P. 217-244.
- Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – С. 423-449.

1. THEME: Ion exchange. Chromatography.

2. PUROSE: To learn the theoretical basis of adsorption and ion exchange, the possibility of their use in medical practice

#### Assignments for self-study:

- 1. Calculate the retention factor if the solvent covered the distance of 22 cm, a glucose solution 12,8 cm fructose solution 15,4 cm, and sucrose 17,3 cm.
- 2. Using paper chromatography the fallowing results were obtained: the distance from the start line to the finish line is 15 cm, the distance from the start line to the center of spots 5,5 cm and 3,6 cm. Find out what these cations are, if  $R_f$  for magnesium, strontium, barium cations are: 0,37; 0,43, 0,24 respectively.
- 3. Using thin layer chromatography separation of a mixture of benzoic (1) and para-aminobenzoic acid (2), the values of  $R_f$  were obtained: 0,44 and 0,32. Calculate the relative retention factors ( $R_s$ ) for both acids, if the standard ortohlorbenzoic acid has  $R_f = 0,58$ .
- 4. Calculate the value of the retention factor and the relative retention factor for glycine, if the distance from the start line to the finish line of solvent is 7 cm, the distance from the start line to the center of the spot of alanine is 5,5 cm, the distance from the start line to the center of the spot of a standard substance is 5,6 cm.

- 5. For which of the amino acids cysteine or tyrosine will the rate of the movement on the paper in a water-phenol mixture be higher if it is known that the  $R_f$  for these substances are 0,19 and 0,52 respectively?
- 6. Which substance does Rf = 0,47 correspond, if the distance from the start line to the finish line of solvent is 16 cm and the distances from the start line to the centers of stains are as follows: for streptocid 6,4 cm; etazole 7,5 cm; sulfadimezine 6,7 cm; for sodium sulfacyle 8,1 cm.
- 7. Calculate  $R_f$  of substance X, if the distance from the start line to the finish line of solvent is 10 cm, the distance from the starting line to the center of the stain of substance X – 8,1 cm, the distance from the start line to the center of the standard substance stain – 7,8 cm.
- 8. When separating a mixture of methionine (1) and alanine (2) by thin layer chromatography the following results were obtained: the distance from the starting to the finish line of solvent is 13 cm, the distance from the starting line to the center of the stains are 4,4 cm and 5,2 cm respectively. Calculate the value of Rf and Rs for both amino acids, if the standard (glycine)  $R_f = 0,38$ .
- 9. On the chromatographic paper the distance from the solvent starting line to the finish line is 12 cm, and the distance from the starting line to the center of amino acid stain is 8,2 cm. Identify the amino acid if R<sub>f</sub> for leucine 0,74.; alanine 0,63; glycine 0,81, methionine 0,68.
- 10. Calculate  $R_f$  for monosaccharides if the distance from the start line to the finish line of a solvent is 15 cm, the distance from the starting line to the center of the standard substance stain 11,3 cm, glucose 10,8 cm, sucrose 11,7 cm.

#### **Examples of assignments:**

**Task 1.** Calculate the value of  $R_f$  and  $R_s$  for the amino acid tyrosine, if during thin layer chromatographic analysis the fallowing data were revealed. The solvent front moved to 10 cm and the distance from the start line to the center of the amino acid stain was 5,3 cm, the distance from the start line to the center of the standard substance stain– 5,8 cm.

**Solution.** Calculate the value of  $R_f$  for tyrosine and a standard substance using the formula:

$$R_f = \frac{x}{L}$$
, where

x - distance from the starting line to the center of a stain;L - distance traversed during the same time by the solvent.

$$R_{f \text{ subst.}} = \frac{5,3}{10} = 0,53.$$
  
 $R_{f \text{ st.}} = \frac{5,8}{10} = 0,58.$ 

Value for Rs tyrosine is calculated as follows:

$$R_{s} = \frac{R_{f \text{ subst}}}{R_{f \text{ st}}}$$
$$R_{s} = \frac{0.53}{0.58} = 0.91$$

Answer: 0,53; 0,91.

## Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 594-601.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – P. 244-249.

3. Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. – М.: Высш. шк., 1975. – С. 168-174.

**1. THEME: Preparation, purification and properties of colloidal solutions. Coagulation of colloidal solutions. Colloidal protection.** 

2. PURPOSE: To form the idea of the structure and properties of biologically important colloids. Basing on the systemic learning process of coagulation sols learn to predict the effects of various factors on the stability of biologically important colloidal systems

#### Assignments for self-study:

- 1. Write the structure of these micelles sols:
  - 1) AgBr in excess of KBr;
  - 2) AgI in excess of AgNO<sub>3</sub>;
  - 3) AgBr in excess of SaBr<sub>2</sub>;
  - 4) PbCrO<sub>4</sub> in excess of K2CrO<sub>4</sub>;
  - 5) BaSO<sub>4</sub> in excess of  $Al_2(SO4)_3$ ;
  - 6)  $Fe_4[Fe(CN)_6]$  in if excess of  $K_4[Fe(CN)_6]$ ;
  - 7) Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] in excess of CuCl<sub>2</sub>;
  - 8) BaCrO<sub>4</sub> if excess of BaCl<sub>2</sub>.
- 2. Write the scheme structure of strontium sulfate SrSO<sub>4</sub> micelles, forming in excess of a) strontium chloride SrCl<sub>2</sub>, b) sodium sulfate Na<sub>2</sub>SO<sub>4</sub>.
- 3. Write the scheme structure of cobalt hydroxide  $Co(OH)_2$  micelles forming with an excess of a) cobalt chloride  $CoCl_2$ , b) sodium hydroxide NaOH.
- 4. Write the scheme structure of barium sulfate BaSO<sub>4</sub> micelles, forming in excess of a) barium chloride BaCl<sub>2</sub>, b) potassium sulfate K<sub>2</sub>SO<sub>4</sub>.

- 5. Copper hexacyanoferrate (II) sol is prepared by the action of  $K_4[Fe(CN)_6]$  excess on CuSO<sub>4</sub>. Write the micelle formula and specify the granule charge. Which electrode will sol particles move in electric field to?
- 6. Silver bromide sol is prepared by mixing 12 ml of 0,02 M KBr solution and 75 ml of 0,005 M AgNO<sub>3</sub> solution. Which of the substances is taken in excess? Write the micelle formula and specify the granule charge.
- 7. The silver iodide sol is obtained by mixing 15 ml 0,01 M KI solution and 20 ml of 0,005 M AgNO<sub>3</sub> solution. Write the micelle formula and specify the granule charge.
- 8. Fe<sub>4</sub>[Fe(CN)<sub>6</sub>] sol is obtained by mixing equal volumes of 0,01 n. FeCl<sub>3</sub> solution and 0,005 n. solution of  $K_4$ [Fe(CN)<sub>6</sub>]. Write the micelle formula and specify the granule charge.
- 9. Write a micelle of a sol obtained by reaction of  $Pb(NO_3)_2$  and  $K_2CrO_4$ . Which of the electrolytes is taken in excess, if the particles are moved by electrophoresis towards the cathode?
- 10. Write a micelle of a sol, obtained by the reaction of  $Na_2S$  and  $ZnSO_4$ . Which of the electrolytes is taken in excess, if the electrophoretic particles move toward the anode?
- 11. Write a micelle of a sol obtained by the reaction of  $BaCl_2$  and  $Na_2SO_4$ . Which of the electrolytes is taken in excess, if the particles are moved by electrophoresis towards the cathode?

- 12. Write a micelle of a sol obtained by the reaction of AgNO<sub>3</sub> and NaCl. Which of the electrolytes is taken in excess, if the electrophoretic particles move toward the anode?
- 13. Which of the following substances:  $Zn(NO_3)_2$ ,  $Na_3PO_4$ ,  $K_2SO_4$  is the most economical coagulator for:
  - Sol of BaSO<sub>4</sub>, formed with an excess of Na<sub>2</sub>SO<sub>4</sub>,
  - Sol of ZnS, formed with an excess of ZnSO<sub>4</sub>,
  - Sol SrSO<sub>4</sub>, formed with an excess of SrCl<sub>2</sub>
  - Sol Co(OH)<sub>2</sub> formed with an excess of CoCl<sub>2</sub>
  - Sol PbCrO<sub>4</sub>, formed with an excess of K<sub>2</sub>CrO<sub>4</sub>
  - Sol AgBr, formed with an excess of AgNO<sub>3</sub>.
- 14. The sol of iron hydroxide (III) which particles are positively charged is coagulated by electrolytes. Which of the electrolytes has the highest coagulating ability and why: calcium chloride, sodium phosphate, sulfate, iron (II), aluminum nitrate or sodium carbonate?
- 15. Which cation has the smallest coagulating ability towards AgI sol with negatively charged particles: Rb<sup>+</sup>, Cs<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>.
- 16. The silver iodide sol is obtained in potassium iodide excess. Which of the coagulating electrolytes will have the lowest coagulation threshold: zinc nitrate, potassium sulfate, aluminum nitrate, iron (III) chloride, potassium hexacyanoferrate (III)?
- 17. The coagulation thresholds of NaCl and  $CaCl_2$  for an electrolyte sol are the same. What conclusion can be drawn with respect to the charge of the colloidal particles?

- 18. Determine the sign of sol particles charge, if its coagulation by electrolytes has the following values of the coagulation thresholds (mmol/L):  $C_{c(NaCl)} = 300$ ,  $C_{c}(1/2MgCl_{2}) = 320$ ,  $C_{c}(1/3Na_{3}PO_{4}) = 0.6$ ,  $C_{c}(Na_{2}SO_{4}) = 20$ .
- 19. Coagulation of iron hydroxide (III) hydrosol occurred after adding 2 ml of sodium sulfate solution with the equivalent molar concentration of 0,0025 mol/L. Calculate the coagulation threshold.
- 20. The coagulating ability of aluminum ion to arsenic (III) sulfide sol is 10,1 mmol/l. Calculate the minimum equivalent molar concentration of the electrolyte causing the sol complete coagulation.
- 21. 100 ml of AgI sol was poured into three flasks. It was required to add 9,5 ml of 1 n. NaCl, 24,0 ml of 0,001 n. Na<sub>3</sub>PO<sub>4</sub> and 35,5 ml of 0,02 n.  $K_2SO_4$  to cause coagulation of the sol. Calculate the coagulation threshold for each electrolyte and determine the sign of the sol particles charge.
- 22. 15,5 ml of 0,002 n. Al(NO<sub>3</sub>)<sub>3</sub> and 18,0 ml of 0,02 n. Na<sub>2</sub>SO<sub>4</sub> were taken for coagulation of 200 ml AgBr sol. Calculate the coagulation threshold for each electrolyte and determine the sign of sol particles charge.
- 23. Coagulation thresholds of  $Na_3PO_4$  and  $Al(NO_3)_3$  to AgI sol are 0,295 and 7,3 mmol/l respectively. Determine the granules charge and how many times the coagulating power of aluminum nitrate is higher than coagulating power of sodium phosphate.

24. Coagulation thresholds of  $CaCl_2$  and  $K_2Cr_2O_7$  to  $Fe(OH)_3$  sol are 0,38 and 19,25 mmol/l respectively. How many times coagulating power of calcium chloride is higher than coagulating power of potassium dichromate?

### **Examples of assignments:**

**Task 1.** Silver iodide sol was obtained by mixing 0,05 M KI solution and 0,1 M AgNO<sub>3</sub> solution. Which electrode will particles of the sol move to?

*Solution.* We write the reaction of precipitation

 $AgNO_3 + KI \leftrightarrow AgI \downarrow + KNO_3$ 

Based on the concentration of the interacting the solutions silver nitrate was taken in an excess, then the resultant micelle formula is:

$$\{[(mAgCl)nAg^+](n-x)NO_3^-\}^+ x NO_3^-$$

Potential-determining ions are silver cations, the granule charge is positive. Thus, in electric field the particles will move toward the electrode with negative charge, i.e. to the cathode.

Answer: to the cathode.

**Task 2.** 40 ml of 0,02 N. NaCl solution was mixed with 75 ml of 0,01 N. silver nitrate solution to obtain silver chloride sol. Write the micelle formula, indicate the sign of the granule charge.

### Solution.

Find the number of mmol of NaCl:  $40 \cdot 0.02 = 0.80$  mmol. Determine the number of mmol of silver nitrate:

 $75 \cdot 0,01 = 0,75$  mmol.

Therefore, the solution contains an excess of sodium chloride.

$$AgNO_3 + NaCl \leftrightarrow AgCl \downarrow + NaNO_3$$

Micelle: {[(mAgCl)nCl<sup>-</sup>](n -x) Na<sup>+</sup>} x Na<sup>+</sup>

The sign of the granule charge is negative.

**Tusk 3.** 100 ml of  $BaSO_4$  sol was poured into three flasks. It was required to add 7,5 ml of 1 n.  $Na_2SO_4$ , 75 ml of 0,02 n.  $CaCl_2$  and 27,0 ml of 0,001 n.  $Al(NO_3)_3$  to cause coagulation of the sol. Calculate the coagulation threshold for each electrolyte.

*Solution.* Coagulation threshold is the minimum number of mmol of electrolyte causing coagulation of 1 liter of the sol.

Determine the coagulation threshold for Na<sub>2</sub>SO<sub>4</sub>:

$$C_{c} = \frac{C_{(el.)} \cdot V_{(el.)} \cdot 1000}{V_{(sol)} + V_{(el.)}} = \frac{1 \cdot 7,5 \cdot 1000}{100 + 7,5} = 69,8 \text{ mol/l}.$$

Determine the coagulation threshold for CaCl<sub>2</sub>:

$$C_{c} = \frac{C_{(el.)} \cdot V_{(el.)} \cdot 1000}{V_{(sol)} + V_{(el.)}} = \frac{0.02 \cdot 75 \cdot 1000}{100 + 75} = 8.6 \text{ mol/l}.$$

To determine the coagulation threshold for  $Al(NO_3)_3$ :

$$C_{c} = \frac{C_{(el.)} \cdot V_{(el.)} \cdot 1000}{V_{(sol)} + V_{(el.)}} = \frac{0,001 \cdot 27 \cdot 1000}{100 + 27} = 0,21 \text{ mol/l}$$

The granules charge of  $BaSO_4$  sol obtained in excess of  $K_2SO_4$  is negative as potential-determining ions are sulfate ions -  $SO_4^{2^-}$ . Thus, the coagulating ions are the cations. Electrolytes  $CaCl_2$ ,  $Na_2SO_4$ ,  $Al(NO_3)_3$  contain cations of different charge. When the charge of the ion is higher, the coagulation threshold is lower.  $Al^{3+}$  ions have the least coagulation threshold (but the highest coagulating power).

**Tusk 4.** Coagulation thresholds of  $Na_2SO_4$  and  $Al(NO_3)_3$  for the negatively charged Prussian blue sol are 22,5 and 0,325 mmol/l respectively. How many times coagulating power of aluminum nitrate is higher than coagulating power of sodium sulfate?

**Solution.** Coagulating power of electrolytes  $(V_c)$  is inverse value to their coagulation threshold:

$$V_{c} = \frac{1}{C_{c}}$$

$$V_{c N_{s}2SO4} = \frac{1}{22,5} = 0,044$$

$$V_{c AI(NO3)3} = \frac{1}{0,325} = 3,07$$

$$VNa_{2}SO_{4} : VAI(NO_{3})_{3} = 3,07 : 0,044 = 7$$

Answer: coagulating power of aluminum nitrate is 70 times higher than coagulating power of sodium sulfate for a given sol.

#### Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – С. 568-657, 730-758.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – P. 252-315.

 Общая химия. Биофизическая химия. Химия биогенных элементов: Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред. Ю. А. Ершова. – М. Высш. шк., 2000. – С. 491-525.

4. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – С. 265-291.

5. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – С. 187-237.

 Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. – М.: Высш. шк., 1975. – С.175-195.

## Tutorial № 16

 THEME: Properties of biopolymers solutions. Isoelectric point of proteins
 PURPOSE: To learn to estimate the properties of polymer materials based on the chemical nature and the characteristics of the molecules

## **Assignments for self-study:**

- 1. Which electrode will the protein particles move to if pI = 4,9, and the pH of the solution is 6,5.
- 2. The isoelectric point of muscles' myosin is 5,0. At which values of pH 3,0; 5,0;6,0 or 7,0 will electrophoretic mobility be the highest? Motivate the answer.
- 3. Myoglobin (pI = 7,0) was placed in a solution with pH = 8,8. What charge do the particles of myoglobin have in this solution? Which electrode will particles of the protein move to in electrophoresis? Motivate the answer.
- 4. Which electrode will protein move to if pH is 7,0 and the isoelectric point is 5,2? Motivate the answer.
- 5. Casein has pI=4,5. What charge do casein particles have in solutions with pH=2,0 and pH=8,0? Which electrode will the protein particles move to under these conditions? Motivate the answer.
- 6. The protein solution contains a mixture of myoglobin (pI = 7), casein (pI = 4,5) and myosin (pI = 5,0). At what pH can these proteins be separated by electrophoresis?

- 7. The solution contains a mixture of proteins: zein (pI = 6,2), casein (pI = 4,8), and lysozyme (pI = 11,0). At what pH can they be separated by electrophoresis? Motivate the answer.
- 8. At what pH can proteins be separated by electrophoresis if their isoelectric points are 6,0 and 11,0? Motivate the answer.
- 9. Egg protein albumin (pI = 4,6) and corn protein zein (pI = 6,2) are placed in a buffer solution with pH = 5,2. What is the charge of the proteins particles? Which of the electrodes will their particle move to in electrophoresis? Motivate the answer.
- 10. At what pH can two enzymes A and B be separated by electrophoresis if their isoelectric points are 4,0 and 7,0? What are the charges of enzymes A and B at pH 4,0; 5,0; 6,0; 7,0; 8,0; 9,0?
- 11. What are the particles charges of hemoglobin (pI = 6,8) in buffer solutions with pH = 5 and pH = 11? Which electrode will the particles of protein move to? Motivate the answer.
- 12. 100 g of swelling rubber absorbed 455 ml of chloroform (density 1,9 g/ml).Calculate rubber swelling degree, and the mass fraction of the substance in the resulting gel.
- 13. Calculate the specific viscosity of a polymer solution when its concentration is 0,1 mol/l, the molar mass is 65,000 g / mol, and k = 1,2. (Answer 7,8 x  $10^3$ )

- 14. 5 g of a polymer were placed in a flask with water. After 30 minutes, the polymer was removed from the flask and weighed. The weight became 5,75 g. Calculate the polymer swelling degree (in %). (Answer: 15%)
- 15. Calculate the mass of a polymer taken in dry form if its swelling degree was 30% and mass became 12,5 g after 20 min. in a flask with benzine (Answer: 9,6 g)

## **Examples of assignments:**

**Task 1**. Which electrode will hemoglobin (pI = 6,8) move to in buffer solutions with pH = 8,5 and pH = 2,7? What are the charges of the protein in each solution?

### Solution.

The pH, at which the protein molecule is neutral and remains at the start in electrophoresis, is called the isoelectric point (pI).

At pH> pI protein is negatively charged and at pH <pI is positively charged.

Thus, at pH = 8,5, which is higher than pI (6,8), the protein is negatively charged and move toward the anode which has a positive charge. A pH = 2,7, which is lower than pI, the protein is positively charged and move toward the cathode (negatively charged electrode).

**Task 2**. 15 g of gelatin was placed in a flask with water for swelling. After 60 minutes it was removed from the flask and weighed, the mass became 21,75 g Calculate the swelling degree of the polymer (in%).

#### Solution.

The swelling degree of a polymer is determined by the formula:

$$\alpha = \frac{\mathbf{m} - \mathbf{m}_0}{\mathbf{m}_0} \cdot 100\%, \text{ where}$$

- m<sub>0</sub> polymer mass before swelling;
- m polymer mass after swelling.

$$\alpha = \frac{\mathbf{m} - \mathbf{m}_0}{\mathbf{m}_0} \cdot 100\% = \frac{21,75 - 15}{15} \cdot 100 = 45\%.$$

Answer: the swelling degree of gelatin in water is 45%.

### Literature:

- 1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. Вінниця: Нова книга, 2011. С. 676-728.
- Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. K.: Medicine, 2008. P. 318-341.
- Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. М.: Высш. шк., 1975. – С. 196-199, 208-212, 214-217.
- 4. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. К.: Вища школа, 1986. С. 238-258.

#### Tutorial № 17

1. THEME: Final control of learning module 1 "Medical Chemistry"

2. PURPOSE: To assess the knowledge and skills of students in the subject "Medical Chemistry".

Assignments for self-study:

Revise the theoretical material and the numerical problems on the topics № 1-16.

## Literature:

1. Мороз А. С, Луцевич Д. Д. Яворська Л. П. Медична хімія: підручник для студ. вищ. навч. мед. закл. – Вінниця: Нова книга, 2011. – 776 с.

2. Medical Chemistry: textbook / V. A. Kalibabchuk [and ol.]; ed. by V. A. Kalibabchuk. - K.: Medicine, 2008. – 400 p.

 Равич-Щербо М. И., Новиков В. В. Физическая и коллоидная химия. – М.: Высш. шк., 1975. – 255 с.

4. Садовничая Л. П., Хухрянский В. Г., Цыганенко А. Я. Биофизическая химия. – К.: Вища школа, 1986. – 271 с.

Общая химия. Биофизическая химия. Химия биогенных элементов:
 Учеб. для вузов / Ю. А. Ершов, В. А. Попков, А. С. Берлянд и др.: Под ред.
 Ю. А. Ершова. – М. Высш. шк., 2000. – 560 с.

6. Зеленин К. Н. Химия: Учеб. для мед. вузов. – СПб: «Специальная литература», 1997. – 677 с.

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