

**Vinnytsia National Pirogov Memorial Medical University**

**Department of General Biology and Chemistry**

**Medical chemistry course**

**PROBLEMS AND EXERCISES IN MEDICAL CHEMISTRY**

**Part 2**

**"Equilibrium in Biological Systems at the interface "**

**For medical and dental faculty**



**Vinnytsia 2017**

A work sheet and methodical developments (Methodical of recommendation for practical classes from Medical chemistry for 1-st year foreign students) are made by the employees of department of biological and general chemistry of VNMMU Pirogov in accordance with a curriculum, worked out on principles of the European credit-transfer system (ECTS) for higher medical establishments of Ukraine III - IV levels of accreditation for specialities of “Medical Affairs” direction of the preparation “Medicine” is in accordance with education qualification descriptions (EQD) and scientific profesional programs (SPP) of the preparation of specialists, approved by an order MES Ukraine from 16.04.03 № 239.

It is considered and accepted on a meeting of the methodical soviet of medical-theoretical disciplines, protocol № 1 from 30.08.2017y.

It is discussed and approved on a meeting of the department of biological and general chemistry, protocol № 1 from 28.08.2017y.

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## THERMAL EFFECTS OF CHEMICAL REACTIONS AND THE ORIENTATION PROCESSES

Thermal effect of chemical reaction - is the amount of heat that is released or absorbed during the reaction.

**Hess's Law:** the thermal effect of chemical reaction does not depend on the path of its passage, but depends on its initial and final states.

The heat of formation (the first consequence of Hess's Law) - is the thermal effect of formation of 1 mol of substance from simple substances at 250C (298 K) and 101.3 kPa, is equal to the difference between the sum of the heats of formation of reaction products and the sum of heats of formation of the initial substances, taken in view of the stoichiometric coefficients reaction equation:

$$\Delta H_{\text{formation}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{source}}$$

Heat of combustion (second consequence of Hess's Law) - is the thermal effect of combustion of 1 mol of substance to CO<sub>2</sub>(g) and H<sub>2</sub>O(l) and T is the difference between the sum of the heats of combustion of the starting materials and the amount of combustion heat of the reaction products, taken in view of the stoichiometric coefficients of reactions:

$$\Delta H_{\text{burn}} = \sum \Delta H_{\text{source}} - \sum \Delta H_{\text{prod}}$$

Orientation process, or the possibility of chemical reaction is determined by the Gibbs energy.

Gibbs energy or the isobaric - isothermal potential –is a manifestation of the cumulative effect of the enthalpy H and entropy S factors.

$$\Delta G = \sum \Delta G_{\text{prod}} - \sum \Delta G_{\text{source}}$$

If  $\Delta G < 0$ , then the reaction is possible.

If  $\Delta G > 0$ , then the reaction is impossible (is the reverse reaction).

If  $\Delta G = 0$ , then the system is in equilibrium.

### Examples

**1). Calculate the heat of reaction of glucose oxidation, if  $\Delta H_{\text{formation}}$  glucose -1272.45 kJ / mol of carbon dioxide -393.6 kJ / mol, water -285.9 kJ / mol.**

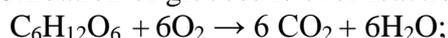
$$\Delta H_{\text{form}} (\text{C}_6\text{H}_{12}\text{O}_6) = -1272,4 \text{ kJ mol}$$

$$\Delta H_{\text{form}} (\text{CO}_2) = -393,6 \text{ kJ / mol}$$

$$\Delta H_{\text{form}} (\text{H}_2\text{O}) = -285,9 \text{ kJ / mol}$$

$$\Delta H_{\text{reaction}} = ?$$

1) Oxidation of glucose is over reaction:



2) Using the equation of the first consequences of the law of Hess:

$$\Delta H_{\text{formation}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{source}}$$

3) Substitute these  $\Delta H_{\text{formation}}$  reaction products and initial substances, taking into account the stoichiometric coefficients:

$$\Delta H_{\text{reaction}} = [ 6 \cdot (-393,6) + 6 \cdot (-285,9) ] - (-1272) = -2804,55 \text{ kJ / mol.}$$

Answer:  $\Delta H_{\text{reaction}} = -2804,55 \text{ kJ / mol.}$  exothermic reaction.

2. Calculate the reaction  $\text{Hg}_2\text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Hg}$ , if the Gibbs energy  $\text{Hg}_2\text{Cl}_2$  - 210,66 kJ/mol, and  $\text{HgCl}_2$  -185,77 kJ/ mol?

$$\begin{array}{l} \Delta G (\text{Hg}_2\text{Cl}_2) = - 210,66 \text{ kJ/mol} \\ \Delta G (\text{HgCl}_2) = - 185,77 \text{ kJ/mol} \\ \hline \Delta G \text{ reaction} =? \end{array}$$

1) Write the energy equation of Gibbs reaction

$$\Delta G = \sum \Delta G_{\text{prod}} - \sum \Delta G_{\text{source}};$$

2) Substitute the data from the equation anode:

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

Answer:  $\Delta G = 24,89 \text{ kJ / mol}$ . Reaction is impossible.

3) Calculate the heat of the reaction of acetylene from Benzene, if the values of the heats of combustion:

**Benzene - 2364.5 kJ / mol, acetylene - 1299.6 kJ / mol.**

$$\begin{array}{l} \Delta H_{\text{burn}} (\text{C}_6\text{H}_6) = - 3264.5 \text{ kJ mol} \\ \Delta H_{\text{burn}} (\text{C}_2\text{H}_2) = - 1299.6 \text{ kJ / mol} \\ \hline \Delta H_{\text{reaction}} =? \end{array}$$

1) Based on the second consequence of the Hess's Law:

$$\Delta H_{\text{reaction}} = \Delta H_{\text{burn}}(\text{C}_6\text{H}_6) - 3\Delta H_{\text{burn}}(\text{C}_2\text{H}_2);$$

2) Substitute the data from the equation anode:

$$\Delta H_{\text{reaction}} = - 3264.5 - 3 (- 1299.6) = 634.3 \text{ kJ / mol.}$$

Answer:  $\Delta H_{\text{reaction}} = 634.3 \text{ kJ / mol}$ .

4) The evaporation of 1 mol of water is 40.7 kJ. How much heat is spent in a day in the allocation of the skin 800.0 g of water?

$$\begin{array}{l} n (\text{H}_2\text{O}) = 1 \text{ mol} \\ \Delta H_{\text{evaporation}} = 40.7 \text{ kJ/mol} \\ m (\text{H}_2\text{O}) = 800.0 \text{ g} \\ \hline \Delta H =? \end{array}$$

1) Find the amount of substance in 800.0 grams of water:

$$v = 44,44 \text{ mol};$$

2) To determine the use of heat proportion:

$$1 \text{ mol } (\text{H}_2\text{O}) \quad - 40,7 \text{ kJ}$$

$$44.44 \text{ mol } (\text{H}_2\text{O}) \quad - X$$

$$X = 1808.9 \text{ kJ.}$$

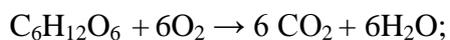
Answer: 1808.9 kJ.

5) Calculate the Gibbs energy change in the process of assimilation body of sucrose, which is reduced to its oxidation, if

$$\begin{array}{l} \Delta G_{\text{formation}}(\text{CO}_2) = - 394,4 \text{ kJ/mol} \\ \Delta G_{\text{formation}}(\text{H}_2\text{O}) = - 237 \text{ kJ/mol} \\ \Delta G_{\text{formation}}(\text{C}_6\text{H}_{12}\text{O}_6) = - 1545 \text{ kJ / mol} \\ \Delta G_{\text{formation}}(\text{C}_6\text{H}_{12}\text{O}_6) = - 1545 \text{ kJ mol} \\ \Delta G_{\text{formation}}(\text{H}_2\text{O}) = - 237 \text{ kJ / mol} \\ \hline \Delta G \text{ reaction} =? \end{array}$$

1) write the equation of oxidation saccharine:

$$\Delta G_{\text{formation}}(\text{CO}_2) = - 394,4 \text{ kJ / mol,}$$



2) We write the energy equation Gibbs' reaction:

$$\Delta G = \sum \Delta G_{\text{prod}} - \sum \Delta G_{\text{source}};$$

3) Substitute the data from the equation of the problem, taking into account stereo metric factors:

$$\Delta G_{\text{reaction}} = [12 \cdot (- 394,4) + 11 \cdot (- 237)] - (- 1,545) = - 5794 \text{ kJ / mol.}$$

Answer:  $\Delta G_{\text{reaction}} = - 5794 \text{ kJ/mol}$ .

6) The heat of formation of carbohydrates in the human body is 4.1 kcal / g. Daily demand for carbohydrates for students women's 383g. Calculate the daily needs of carbohydrate the student needs for energy.

$$\begin{array}{l} \Delta H_{\text{formation}}(\text{carb}) = 4.1 \text{ kcal/g} \\ m(\text{carb}) = 383\text{g} \\ \hline \Delta H(\text{day}) = ? \end{array}$$

1) To resolve this problem, we use direct proportion:

4.1 kcal per 1 g carbohydrate —

X — to 383g of carbohydrates

$$X = \frac{4,1 \cdot 383}{1} = 1570,3 \text{ kcal.}$$

Answer: 1570.3 kcal.

### Problems

1. Is the reaction:  $\text{Al}_2\text{O}_3 + 3\text{SO}_3 = \text{Al}_2(\text{SO}_4)_3$ , if the Gibbs energy  $\text{Al}_2\text{O}_3$  (to) = - 1576,4 kJ/mol,  $\text{SO}_3 = - 370,37$  kJ/mol,  $\text{Al}_2(\text{SO}_4)_3 = - 3091,9$  kJ/mol? (Answer: - 404,39 kJ/mol reaction is impossible)

2. Calculate the Gibbs energy for the reaction of glycolysis:  $\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_3\text{H}_6\text{O}_3$  (LACTIC ACID) if  $\Delta G^0$  lactic acid = - 539kJ/mol, and  $\Delta G^0$  glucose = - 917 kJ/mol. (Answer: - 161kJ/mol)

3. Heat of formation of proteins in the human body is 4.1 kcal / g. The average daily protein requirement for female students is 96g. Calculate the daily protein the student need for energy. (Answer: 393.6 kcal)

4. Check for threats that Nitrogen (I) oxide, used in medicine as a drug to be oxidized by atmospheric oxygen to toxic nitrogen (II) oxide, if  $\Delta G_{\text{formation}}(\text{N}_2\text{O}) = 104$  kDj/mol and  $\Delta G_{\text{formation}}(\text{NO}) = =87$ kDj/mol. (Answer:  $\Delta G = 140$ kJ/mol means oxidation is not possible)

5. In the Krebs cycle isocitrate is converted to  $\alpha$ -ketoglutarate:

isocitrate  $1/2\text{O}_2(\text{g}) \text{H} \leftrightarrow \alpha\text{-ketoglutarate} \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$ . Calculate  $\Delta G$  for this reaction, if  $\Delta G_{\text{formation}}(\text{isocitrate}) = - 1166,6$  kJ/mol,  $\Delta G_{\text{formation}}(\alpha\text{-ketoglutarate}) = - 796,8$  kJ / mol,  $\Delta G_{\text{formation}}(\text{CO}_2) = - 394,4$  kJ / mol;  $\Delta G_{\text{formation}}(\text{H}_2\text{O}) = - 237$  kJ/mol. (Answer: - 267,2 kJ / mol)

6. Determine the heat of reaction needed for the synthesis of diethyl ether, used in medicine for anesthesia, at 298 K:  $2\text{C}_2\text{H}_5\text{OH}_{(l)} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5_{(l)} + \text{H}_2\text{O}_{(l)}$ ;  
What is the standard heat of combustion of substances involved in the reaction:

$\Delta H_{\text{burn}}(2\text{C}_2\text{H}_5\text{OH}) = - 2727$ kJ/mol;

$\Delta H_{\text{burn}}(\text{C}_2\text{H}_5\text{OH})_{(l)} = - 1371$ kJ/mol. (Answer: - 15kJ/mol)

7. One of the ways of glucose metabolism is the process:

$\text{C}_6\text{H}_{12}\text{O}_6_{(\text{sol-n})} \rightarrow \text{C}_3\text{H}_7\text{COOH}_{(l)} + \text{CO}_2_{(g)} + \text{H}_2_{(g)}$ . Calculate  $\Delta G$  reaction if  $\Delta G(\text{C}_6\text{H}_{12}\text{O}_6_{(\text{sol-n})}) = - 917,0$  kJ/mol,  $\Delta G(\text{C}_3\text{H}_7\text{COOH}_{(l)}) = - 376$ kJ/mol,  $\Delta G(\text{CO}_2(\text{g})) = - 394,4$  kJ/mol.

(Answer: - 247,8 kJ/ mol)

## KINETICS OF BIOCHEMICAL PROCESSES

**Chemical kinetics** – is the doctrine of the rate and mechanism of chemical reactions.

**The chemical reaction rate** is - the change of substance concentration per unit time and per unit volume (for homogeneous reactions) or per unit area (for heterogeneous reactions).

$$V = -\frac{\Delta \nu}{\Delta \tau}$$

For homogeneous reactions:  $V = -\frac{\Delta \nu}{\nu \cdot \Delta \tau}$ ;

for heterogeneous reactions:  $V = -\frac{\Delta \nu}{S \cdot \Delta \tau}$ .

The chemical reaction rate depends on the nature of reactants, concentration, and temperature.

The law of mass action - **the chemical reaction rate** is directly proportional to the product of the concentrations of the reactants raised to a power equal to the stoichiometric coefficients.

For example, for the reaction  $aA + bB \rightarrow cC$

where  $k$  – rate constant for chemical reaction, is equal to the rate of chemical reactions at the concentrations of substances 1 mol/l, depending on the nature of matter and temperature.

**Rule Vant - Hoff** - with increasing temperature at  $10^0\text{C}$  the chemical reaction rate increases in 2 - 4 times.

$$\frac{V_{t_2}}{V_{t_1}} = \gamma^{\frac{t(2)-t(1)}{10}} \quad \text{or} \quad \frac{k_2}{k_1} = \gamma^{\frac{t(2)-t(1)}{10}}$$

Where  $\gamma$  - the temperature coefficient which shows how many times the speed of the chemical reaction changes when the temperature rises to  $100\text{C}$ .

**The activation energy  $E_a$**  - is the smallest excess energy of the active molecule, by which chemical reactions are possible.

**Arrhenius equation:**

$$V = A \cdot e^{-E_a/RT} [A]^a \cdot [B]^b \quad \text{or} \quad k = A \cdot e^{-E_a/RT}$$

### Examples

**1. How many times will the chemical reaction rate change  $\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{NOCl}_{(g)}$ , if the concentration of  $\text{NO}$  increased in 2 times?**

$[\text{NO}]_2 = 2 [\text{NO}]_1$	1) We write the reaction equation: $\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{NOCl}_{(g)}$
$\frac{V_2}{V_1} = ?$	2) The dependence of reaction rate on concentration expresses the law of mass

action:  $V_1 = k [\text{NO}]^2 \cdot [\text{Cl}_2]$ ;

3) After an increase of  $\text{NO}$  concentration equation is:

$$V_2 = k [2 \text{NO}]^2 \cdot [\text{Cl}_2];$$

4) Find the change in velocity:

$$\frac{V_2}{V_1} = \frac{k [2\text{NO}]^2 \cdot [\text{Cl}_2]}{k [\text{NO}]^2 \cdot [\text{Cl}_2]} = \frac{2^2}{1} = 4.$$

Answer: The rate will increase 4 times.

**2. How will the rate of reaction change  $A + B_2 \rightarrow AB$ , which flows in a closed vessel, if the system pressure is to increase by 5 times?**

$$P_2 = 5 P_1$$

1) The equation of the reaction:  $2A + B_2 \rightarrow 2AB$ ;

$$\frac{V_2}{V_1} = ?$$

2) In a closed vessel, the pressure may increase by increasing the concentration. If

pressure increases a factor of 5, then the concentration will increase a factor of 5.

3) Dependence of reaction rate on concentration is expressed in the law mass action. To increasing pressure:

$$V_1 = k[A]^2 \cdot [B];$$

4) When the pressure increases and, consequently, increasing the concentration

$$\text{equation is: } V_2 = k [5 A]^2 \cdot [5B];$$

5) Find the change in velocity:  $\frac{V_2}{V_1} = \frac{k[5A]^2 \cdot [5B]}{k[A]^2 \cdot [B]} = \frac{5^2 \cdot 5}{1} = 125.$

Answer: The rate of increase in 125 times.

**3. How many times will the rate of the reaction  $NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{(g)}$  change, if the system pressure is reduced to 4 times?**

$$P_1 = 4P_2$$

1) The equation of the reaction:  $NO_{(g)} + Cl_{2(g)} \rightarrow NOCl_{(g)}$

$$\frac{V_2}{V_1} = ?$$

2) If the pressure reduces 4 times, then the concentration is also decreased by 4

times. 3) Dependence of reaction rate on concentration is expressed in the law of mass action. Before the increase in pressure:  $V_1 = k[A]^2 \cdot [B];$

4) When the pressure increases and, consequently, increasing the concentration

$$\text{equation is: } V_2 = k [1/4 A]^2 \cdot [1/4 B];$$

5) Find the change in velocity:

$$\frac{V_2}{V_1} = \frac{k[1/4 \cdot A]^2 \cdot [1/4 \cdot B]}{k[A]^2 \cdot [B]} = \frac{0,25^3}{1} = 0,0156.$$

Answer: the rate of decline in  $1/0.0156$  time, 64 times

**4. The reaction rate constant with  $C + 2D \rightarrow K$  is  $0,4 \text{ l/mol} \cdot \text{sec}$ . The concentration of  $C = 3 \text{ mol/L}$ , and the substance  $D = 4 \text{ mol / litre}$ . Calculate the rate of direct reaction.**

$$[C] = 3 \text{ mol/L}$$

1) Write the reaction equation:  $C + 2D \rightarrow K$ ;

$$[D] = 4 \text{ mol/l}$$

2) Dependence of reaction rate on concentration

$$k = 0,4 \text{ l/mol sec}$$

expressed by the law of mass action:

$$V = ?$$

$$V = k [C] \cdot [D]^2;$$

3) Substitute the data from the problem and calculate

$$V = 0,4 \cdot 3 \cdot 4 = 4.8 \text{ mol / sec.}$$

Answer: The reaction rate is  $4.8 \text{ mol/sec}$ .

**5. Constant decay rate of penicillin at  $36^\circ \text{C}$  is  $6 \cdot 10^{-6} \text{ sec}^{-1}$ , and at  $41^\circ \text{C}$  –  $1,2 \cdot 10^{-5} \text{ sec}^{-1}$ . Calculate the temperature coefficient reaction.**

$$k(36^\circ \text{C}) = 6 \cdot 10^{-6} \text{ sec}^{-1}$$

1) Using the rule of Vant - Hoff:

$$k(41^\circ\text{C}) = 1,2 \cdot 10^{-5} \text{ sec}^{-1}$$

$$\gamma = ?$$

Answer:  $\gamma = 4$ .

$$\frac{k_2}{k_1} = \gamma^{\frac{t(2)-t(1)}{10}}; \text{ hence } \gamma^{\frac{41-36}{10}} = \frac{1,2 \cdot 10^{-5}}{0,6 \cdot 10^{-5}} = 2;$$

$$\gamma^{0,5} = 2; \quad \gamma = 4.$$

**6. How many times will rate of reaction increase, if the temperature increases to  $30^\circ\text{C}$  ( $\gamma = 3$ )?**

$$\Delta t = 30^\circ\text{C}$$

$$\gamma = 3$$

$$\frac{V_2}{V_1} = ?$$

1) Dependence of reaction rate on temperature expressed by the Vaunt-Hoff rule:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}};$$

2) Substitute the data from the equation anode:  $\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{30}{10}} = 3^3 = 27$ .

Answer: 27 times

**7. By increasing the temperature at  $20^\circ\text{C}$  the reaction rate increases by 16. Calculate the temperature coefficient of reaction.**

$$\Delta t = 20^\circ\text{C}$$

$$V_2 = 16V_1$$

$$\gamma = ?$$

1) Dependence of reaction rate on temperature expressed by the Vaunt-Hoff rule:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}};$$

2) Substitute the data from the equation anode:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{20}{10}}; \quad 16 = \gamma^2, \quad \gamma = 4.$$

Answer:  $\gamma = 4$

**8. How many times will the rate of reaction change, if the temperature of the reaction changes from  $18^\circ\text{C}$  to  $38^\circ\text{C}$ , and the temperature coefficient is equal to 3?**

$$t_1 = 18^\circ\text{C}$$

$$t_2 = 38^\circ\text{C}$$

$$\gamma = 3$$

$$\frac{V_2}{V_1} = ?$$

1) Dependence of reaction rate on temperature expressed by the vant Hoff rule:

$$\frac{V(t_2)}{V(t_1)} = \gamma^{\frac{t(2)-t(1)}{10}};$$

2) Substitute the data from the equation anode:

$$\frac{V(t_2)}{V(t_1)} = 3^{\frac{38-18}{10}} = 3^2 = 9.$$

Answer: 9 times

### Problems

- 1) What will be the change in chemical reaction rate  $\text{N}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightarrow \text{NH}_{3(\text{g})}$ , if the concentration of  $\text{H}_2$  increases by 2?  
(Answer: 8 times)
- 2) What will be change in the reaction rate of  $\text{C}_2 + \text{D} \rightarrow \text{CD}$ , which flows into closed vessel, if the system pressure is increased by 4?  
(Answer: to increase in 64 times)
- 3) What will be the rate of chemical reaction  $\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$ , if oxygen concentration decreases by 2 times?  
(Answer: reduce by 2 times)
- 4) What will be will the change in the reaction rate of  $\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$  if pressure in the system reduced in 3 times?  
(Answer: the rate of decline in 27 times)
- 5) The rate constant for acylation to sulfur dioxide ethyl oxalic acid at  $30^\circ\text{C}$  is equal to

- 2.34 mol·l<sup>-1</sup> min<sup>-1</sup>. Calculate the initial rate of this reaction, if the initial concentration of the reagents is the same and 0.05 moles per liter. (Answer: 0.00585 mol·l<sup>-1</sup> min<sup>-1</sup>)
- 6) What will be the increase in the rate of reaction if the temperature increase at 40 °C (γ = 3)? (Answer: in 265 times)
- 7) When the temperature increases to 30 °C the reaction rate increased 27 times. Calculate the temperature coefficient of reaction. (Answer: γ = 3).
- 8) What will be the change in the rate of reaction if the temperature during reaction changes from 25 °C to 55 °C and the temperature coefficient is equal to 2? (Answer: 8 times)

## CHEMICAL EQUILIBRIUM

State the **irreversible reactions** in which the starting materials are fully converted into reaction products, i.e. reaction goes to completion.

**Signs of the irreversibility:**

- a) precipitation:  $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow 2\text{NaCl} + \text{BaSO}_4\downarrow$ ;  
 b) the allocation of gas:  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$ ;  
 c) formation of a weak electrolyte:  $2 \text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ .

State the **reversible reactions** in which the final products interact to form the starting materials. Such reactions are not going to end, to a state of equilibrium.

**Chemical equilibrium - a state of the system in which speed forward and reverse reactions are equal.**

**Equilibrium is called concentration, which are installed on the equilibrium state** (for the initial equilibrium concentration of the substance is the amount of material which remained at the time of equilibrium for the reaction products - is the amount of matter, which was formed at the time of equilibrium).

Chemical equilibrium is characterized by the equilibrium constant  $K_e$ , which is the ratio of product concentrations of the reaction products to the product of the concentrations of substances in the initial degrees are stoichiometric coefficients.

In accordance with the law of mass action for the reversible reaction:

$aA + bB \rightarrow cC + dD$  expression of the  $K_e$  can be written as follows:

$$K_p = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

Thermodynamic equilibrium condition:

$$\Delta G = 0, \Delta F = 0.$$

$K_p$  shows how many times the rate of direct reaction greater than the rate of reverse reaction.

If the  $K_e > 1$ , the faster the direct reaction;  $\Delta G < 0$ .

If the  $K_e < 1$ , then quickly goes back reaction;  $\Delta G > 0$ .

If  $K_e = 1$ , then  $\Delta G = 0$  (equilibrium state).

$K_p$  depends on the nature of the reactants and temperature, and does not depend on the concentration of the catalyst.

**Displacement of chemical equilibrium** - is the transition system from one equilibrium state to another.

**Le Chatelier's principle:** if the system is in equilibrium, to produce effects (change the concentration, pressure, temperature), the equilibrium is shifted in the direction of the reaction, which weakens this effect.

Chemical equilibrium is established in a saturated solution of salt between the solid salt and

converts to a solution of ions. For example, in a saturated solution of sulphide cuprum equilibrium is established:



The equilibrium constant of this process is expressed by the equation:

$$K_e = \frac{[\text{Cu}^{2+}] \cdot [\text{S}^{2-}]}{[\text{CuS}]}$$

Concentration of CuS as a sparingly soluble substance constant, so

$$K_e \cdot [\text{CuS}] = \text{SP}$$

where SP - is the solubility product. Therefore:

$$\text{SP} = [\text{Cu}^{2+}] \cdot [\text{S}^{2-}]$$

Thus, ***in a saturated solution of electrolyte product concentration of its ions is constant and is called the solubility product SP.*** This value quantifies the ability of the electrolyte to dissolve.

The numerical value of SP can be found, knowing its solubility. Example, the solubility of CuSO<sub>4</sub> at 20°C is equal to  $1.5 \cdot 10^{-2}$ . This means that in the saturated solution concentration of each of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> equal to  $1.5 \cdot 10^{-2}$ .

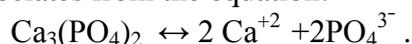
Consequently, the solubility product of this salt:

$$\text{SP} = [\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}] = 1.5 \cdot 10^{-2} \cdot 1.5 \cdot 10^{-2} = 2.25 \cdot 10^{-2}$$

If the electrolyte contains two or more identical ions, the concentrations of these ions in the calculation of the SP should be elevated to the appropriate extent.

For example, the solubility of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is equal to  $7.14 \cdot 10^{-7}$ .

Calcium phosphate dissociates from the equation:



$$\text{Then } [\text{Ca}^{2+}] = 3 \cdot 7.14 \cdot 10^{-7} = 21.42 \cdot 10^{-7};$$

$$[\text{PO}_4^{3-}] = 2 \cdot 7.14 \cdot 10^{-7} = 14.28 \cdot 10^{-7};$$

$$\text{SP} = (21.42 \cdot 10^{-7})^3 \cdot (14.28 \cdot 10^{-7})^2 = 2.0 \cdot 10^{-29}$$

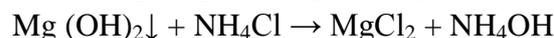
*If the product of ion concentration is less than SP, the residue does not fall out.*

*If the product of concentration is more than SP, then it's precipitated.*

*If the product of ion concentration equals SP, then there is equilibrium between saturated solution and precipitate.*

Condition that dissolves the precipitate: add a strong electrolyte, which has no common ion with the precipitate (and one of the ions precipitate yields a soluble compound).

For example, to dissolve the precipitate Mg(OH)<sub>2</sub> you need to add electrolyte NH<sub>4</sub>Cl:



### Examples

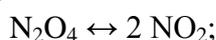
***1. The equilibrium constant for the reaction  $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$  is 0.26. Equilibrium concentration NO<sub>2</sub> is 0.28 moles per litre. Calculate the equilibrium and initial concentration of N<sub>2</sub>O<sub>4</sub> ..***

$$S_p = 0.26$$

$$[\text{NO}_2]_{\text{equally}} = 0.28 \text{ mol/l}$$

$$[\text{N}_2\text{O}_4]_{\text{equally}} = ?$$

1) We write the reaction:



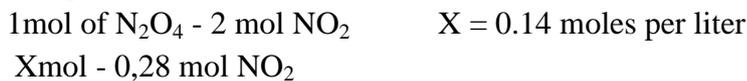
2) Write the equation of the S<sub>p</sub> for this reaction:

[N <sub>2</sub> O <sub>4</sub> ]source =?	$S_p = \frac{[NO_2]^2}{[N_2O_4]}$ ;
---	-------------------------------------

it follows: [N<sub>2</sub>O<sub>4</sub>] equally =  $\frac{[NO_2]^2}{\hat{E}_D} = \frac{0,28^2}{0,26} = 0,3 \text{ mol/l}$ ;

it is mean [N<sub>2</sub>O<sub>4</sub>], 3mol N<sub>2</sub>O<sub>4</sub> remains at the moment of equilibrium.

3) From the reaction equation follows:



0.14 mol N<sub>2</sub>O<sub>4</sub> reacts;

4) Total N<sub>2</sub>O<sub>4</sub>, its initial concentration is equal to:

$$[N_2O_4]_{ex.} = 0.14 + 0.3 = 0.44 \text{ moles per liter.}$$

Answer: [N<sub>2</sub>O<sub>4</sub>]ex. = 0.44 mol/liter.

**2. The system NO + O<sub>2</sub> ↔ NO<sub>2</sub> equilibrium concentrations of substances:**

**[NO] = 0,2 mol/l, [O<sub>2</sub>] = 0,3 mol/l, [NO<sub>2</sub>] = 0,4 mol/liter. Calculate the equilibrium constant.**

[NO] = 0,2 mol/l	1) Write the reaction:
[O <sub>2</sub> ] = 0,3 mol/l	2NO + O <sub>2</sub> ↔ 2NO <sub>2</sub> ;
[NO <sub>2</sub> ] = 0,4 mol/l	2) Expression of the S <sub>p</sub> for this reaction can be written as follows:
Ke =?	$K_e = \frac{[NO_2]^2}{[NO]^2 \cdot [O_2]} = \frac{0,4^2}{0,2^2 \cdot 0,3} = 13,3$

Answer: Ke = 13,3

**3. In what direction does the chemical equilibrium reaction N<sub>2</sub> + H<sub>2</sub> ↔ NH<sub>3</sub>, shifts if the system pressure to increase by 3 times?**

P <sub>2</sub> = 3P <sub>1</sub>	1) Write the reaction:
$\frac{\hat{E}_{D1}}{\hat{E}_{D2}} = ?$	N <sub>2</sub> + 3H <sub>2</sub> ↔ 2NH <sub>3</sub> ;
	2) Expression of the Ke for this reaction to improve
	Pressure: $K_{P1} = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3}$ ;

3) When the pressure is 3 times, the concentration increases too, by 3 times. Expression of the Ke to the reaction after increasing pressure:

$$K_{P1} = \frac{[3NH_3]^2}{[3N_2] \cdot [3H_2]^3} = \frac{1}{9};$$

4) Find the ratio of equilibrium constants:

$$\frac{K_{P1}}{K_{P2}} = \frac{1 \cdot 9}{1} = 9.$$

Ke<sub>1</sub> increases 9 times, then the balance shifts toward the direct reaction.

Answer: in the direction of the direct reaction.

4. In what direction will shift equilibrium of the reaction  $CO + H_2 \leftrightarrow CH_4 + CO_2$ , if the concentrations of all substances is reduce to a factor of 2?

$$\frac{C_1 = 2C_2}{\frac{\hat{E}_{D1}}{\hat{E}_{D2}} = ?}$$

1) Write the reaction:



2) Expression of the  $K_e$  for this reaction to reduce the concentration:

$$K_{P1} = \frac{[CH_4] \cdot [CO_2]}{[CO]^2 \cdot [H_2]^2}$$

3) The expression of the  $K_e$  to the reaction after reduction concentration:

$$K_{P2} = \frac{[0,5CH_4] \cdot [0,5CO_2]}{[0,5CO]^2 \cdot [0,5H_2]^2} = \frac{1}{0,25} = 4;$$

4) Find the ratio of equilibrium constants:

$$\frac{\hat{E}_{D1}}{\hat{E}_{D2}} = \frac{1}{4} = 0,25, \text{ or } \frac{\hat{E}_{D2}}{\hat{E}_{D1}} = 4.$$

or what is the balance shifted in the direction of the reverse reaction.

Answer: in the direction of the reverse reaction.

5. Calculate the solubility product of  $S_P$  plumbum phosphate  $Pb_3(PO_4)_2$ , if the solubility of this salt  $1,5 \cdot 10^{-9}$  moles/litre.

$$\frac{[Pb_3(PO_4)_2] = 1,5 \cdot 10^{-9} \text{ mol/L}}{S_P = ?}$$

1) Write the equation of the dissociation of salt



2)  $S_P$  is calculated as:  $S_P = [Pb^{+2}]^3 \cdot [PO_4^{-2}]^2$

3) Find the concentration of each ion in solution:

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

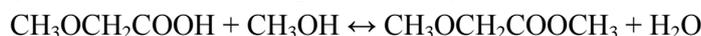
$$[PO_4^{-2}] = 2 \cdot 1,5 \cdot 10^{-9} = 3 \cdot 10^{-9}$$

4) Compute the  $S_P$ :  $S_P = (4,5 \cdot 10^{-9})^3 \cdot (3 \cdot 10^{-9})^2 = 8,2 \cdot 10^{-43}$

Answer:  $S_P = 8,2 \cdot 10^{-43}$ .

### Examples

1. Acetic methyl ester (intermediate product of synthesis of vitamin B<sub>6</sub>) get by the reaction:



Calculate the equilibrium constant of the  $S_P$  reaction, if at the time of equilibrium 1 mol of acid and 1 mol of alcohol was formed 0.562 mol complex ether. (Answer: 1.646)

2. The liver takes enzymatic reversible process:

glucose - 1 - phosphate  $\leftrightarrow$  glucose - 6 - phosphate. When the concentration of 37°C

glucose - 1 - phosphate is equal to 0.001 mol/l and glucose - 6 - phosphate - 0,019 moles per litre.

Calculate the  $S_P$ . (Answer: 19)

3. Calculate the equilibrium constant for the reversible reaction  $NO + O_2 \leftrightarrow NO_2$ , if at equilibrium  $[NO] = 0,056$  mol/L,  $[O_2] = 0,02$  mol/l  $[NO_2] = 0,044$  mol/litre. (Answer: 30.87)

4. Equilibrium in the  $2A + B \leftrightarrow 3C + D$  established under such equilibrium concentrations of A, B, C

- and D, respectively: 2,5, 1, 1,7; 0.8 mol/litre. Calculate the equilibrium constant. (Answer: 1.59)
5. Calculate the solubility product of barium hydroxide  $\text{Ba(OH)}_2$ , if the solubility of this salt is  $9.6 \cdot 10^{-2}$  mol/litre. (Answer:  $3.5 \cdot 10^{-3}$ )
6. Calculate product of solubility of argents arsenate  $\text{Ag}_3\text{AsO}_4$ , if solubility of this salt is  $1.4 \cdot 10^{-6}$  mol/litre.
7. In what direction will shift equilibrium of the reaction of  $\text{NO} + \text{NO}_2 \leftrightarrow \text{O}_2$  if concentrations of all substances decreased by 4 times. (Answer: in the direction of the reverse reaction)
8. For the reaction: L-glutamic acid pyruvate  $\leftrightarrow$   $\alpha$  – ketoglutaric acid L-alanine, the equilibrium constant for  $300^\circ\text{C}$  is 1,11. In what direction will the reaction go at the following concentrations: L-glutamic acid and pyruvate to 0.00003 mol/L,  $\alpha$  – ketoglutaric acid and L-alanine to 0,005 mol/l? (Answer in the opposite direction).
9. In aqueous solution, methylamine is the reason:  $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{NH}_3^+ + \text{OH}^-$ . Calculate the equilibrium constant, if the initial concentration of methylamine is 0.1 mol/l, and the concentration hydroxide ion after the equilibrium is equal to  $6.6 \cdot 10^{-3}$  mol/liter. (Answer:  $4.7 \cdot 10^{-4}$ )

### POTENTIOMETRIC METHOD OF ANALYSIS

**Galvanic cell** – is a system in which chemical energy is converted into electrical energy.

**Electrode** is the potential arising at the metal electrode immersed in a salt solution of this metal.

The scheme of this half-cell:  $\text{Me} | \text{Me}^{n+}$ .

The magnitude of the electrode potential can be calculated by the **Nernst equation**:

$$e = e_0 + \frac{RT}{nF} \ln a_{\text{Me}^{n+}}$$

Where  $e_0$  - normal electrode potential, this potential occurring at the electrode immersed in a salt solution of this metal with a concentration of 1 mol/l;

R – universal gas constant = 8.313 Dj/mol · K;

T – temperature in Kelvin;

n – ion is charge;

F – Faradays constant 96500 Cl/mol;

$a$  – activity of metal ions (or concentration).

At  $18^\circ\text{C}$  equation is:

$$e = e_0 + \frac{0,058}{n} \ln a_{\text{Me}^{n+}}$$

At  $25^\circ\text{C}$  equation is:

$$e = e_0 + \frac{0,059}{n} \ln a_{\text{Me}^{n+}} .$$

For example, the scheme and the equation for half-cell of silver electrodes at  $18^\circ\text{C}$ :

$$\text{Ag} | \text{AgNO}_3; \quad e = e_{\text{Ag}^+}^0 + \frac{0,058}{n} \lg C_{\text{Ag}^+}$$

Determine the concentration of H using a hydrogen electrode, the circuit has the form:

$\text{Pt} (\text{H}_2) | \text{H}^+$  (normal hydrogen electrode potential taken as 0) and the glass electrode: glass |  $\text{H}^+$ .

For intra gastric pH-metre using antimony electrode:



Potentials of these electrodes depend on the concentration of  $\text{H}^+$

Reference electrodes:

silver chloride  $\text{Ag} | \text{AgCl}, \text{KCl}$ , whose potential is 0.238 V and calomel  $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{KCl}$ , whose potential is 0.25 V.

*Scheme galvanic element Jacobi:*



Equation emf of a galvanic cell Jacobi:

$$\text{EMF} = e^\circ_{\text{Cu}} - e^\circ_{\text{Zn}} + \frac{RT}{nF} \ln \left[ \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \right]$$

Equation emf of a galvanic cell of the general type (the electrodes of different metals):

$$\text{EMF} = e^\circ_1 - e^\circ_2 + \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

$$\text{at } 18^\circ\text{C}: = e^\circ_1 - e^\circ_2 + \frac{0,058}{n} \lg \frac{C_1}{C_2}$$

$$\text{at } 25^\circ\text{C}: \text{EMF} = e^\circ_1 - e^\circ_2 + \frac{0,059}{n} \lg \frac{C_1}{C_2}$$

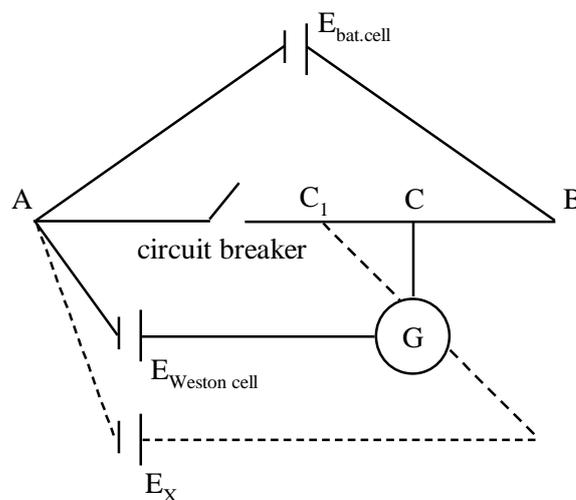
**Concentration** is called a galvanic cell consisting of one- metal electrodes immersed in solutions of different concentrations of salts. Scheme of the concentration of the element:



EMF equation of the concentration of the element:

$$\text{EMF} = \frac{0,058}{n} \lg \frac{C_1}{C_2};$$

Almost EMF element determine the compensation method.



Find the length of division reorder:

$$U_{\min} \text{ S.M.} = \frac{E_{\text{Westoncell}}}{AC}$$

where  $E_{\text{Weston cell}} = 1.018 \text{ V}$ ;

AC - a segment that is offset by an element of Weston cell.

Find the e.m.f of a galvanic cell

$$EMF = TS.D. \cdot AC_1$$

where  $AC_1$  – is a segment that is offset by a galvanic cell.

To determine the pH of the solutions of such cells and chains:

a) hydrogen - hydrogen element:



$$C_X < C_{\text{standart}}$$

$$\text{pH}_X = \text{pH}_{\text{standart}} + \frac{EMF}{0,058};$$



$$C_{\text{standard}} < C_X$$

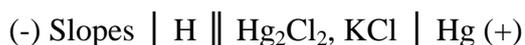
$$\text{pH}_X = \text{pH}_{\text{standard}} - \frac{EMF}{0,058}.$$

b) The hydrogen-calomel cell:



$$\text{pH} = \frac{EMF - 0,25}{0,058}$$

c) calomel-glass element:



$$\text{pH} = \frac{EMF - 0,25}{0,058}$$

d) hydrogen - an element of silver chloride:



$$\text{pH} = \frac{EMF - 0,238}{0,058}$$

### Examples

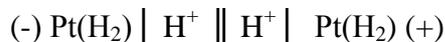
**1) An element consists of hydrogen electrodes immersed in the test solution and the normal hydrogen electrodes. Length division reorder 3.4 mV/mm, and analyzed element is compensated on a segment 40mm. Write down the scheme of this circuit and calculate the pH of test solution at 18°C.**

$$K_e = 3.4 \text{ mV/mm}$$

$$AC_1 = 40\text{mm}$$

$$t = 18^\circ\text{C}$$

1) This element concentration, as is of identical electrodes:



$$C_{\text{standard}} < C_X$$

$e^{\circ}N = 0$	2) At 18°C:
pH - ?	$pH_X = pH_{\text{standard}} + \frac{EMF}{0,058}$ ; pH standard = 0, then $pH_X = \frac{EMF}{0,058}$ ;

3) Find the emf:  $EMF = K_e = U_{\text{min}} \cdot AC_1 = 3.4 \cdot 40 = 136\text{mV} = 0.136 \text{ V}$ ;

4) Find the pHx:  $pH_X = \frac{0,136}{0,058} = 2,34$ .

Answer: pH = 2,34

**2) An element is composed of hydrogen electrodes immersed in a test solution and calomel electrode. Element Weston compensated on a segment reohord  $AC = 350\text{mm}$  and analysed element is compensated for a distance of  $200\text{mm}$ . Write down the scheme of this circuit and calculates the pH of test solution at 25°C.**

$AC = 350\text{mm}$
$AC_1 = 400\text{mm}$
$t = 25^{\circ}\text{C}$
pH = ?

1) Scheme of calomel - hydrogen elements:



2) calculation formula for pH calomel-hydrogen element:

$$\partial I = \frac{\overset{\circ}{A} - 0,25}{0,059}$$

3) Find the EMF:  $EMF = \frac{\overset{\circ}{A}_{\text{Westoncell}}}{\overset{\circ}{A}\tilde{N}} \cdot \overset{\circ}{A}\tilde{N}_1 = \frac{1,018}{350} \cdot 200 = 0,58\text{V}$

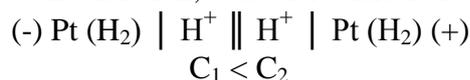
4) Find the pH:  $pH = \frac{E - 0,25}{0,058} = \frac{0,58 - 0,25}{0,059} = 5,59$ .

Answer: pH = 5.59.

**3) The element consists of two hydrogen electrodes. One of the electrodes immersed in a solution with a pH of 4, and the other in a solution with a pH of 1. Write down the scheme of this element and to calculate the EMF at 18°C.**

$pH_1=4$
$pH_2=1$
$t = 18^{\circ}\text{C}$
EMF = ?

1) It is an element concentration, as is of identical electrodes:



2) If the pH = 4, then  $[\text{H}^+] = 10^{-4}$ . If the pH = 1, then  $[\text{H}^+] = 10^{-1}$ .

3) The equation of the EMF of the concentration of the element at 18°C:

$$EMF = 0,058 \cdot \lg \frac{C_2}{C_1} = 0,058 \cdot \lg \frac{10^{-1}}{10^{-4}} = 0,058 \cdot \lg 10^3 = 0,174\text{V}$$

Answer: EMF = 0.174 V

**4) The element is composed of hydrogen electrodes immersed in the test solution and silver chloride electrodes. Length division reorder  $5.6 \text{ mV} / \text{mm}$  and analyzed element is compensated on a segment  $60\text{mm}$ . Write down the scheme of this circuit and calculate the pH of test solution at 18°C.**

$K_e = 3.4 \text{ mV/mm}$
$AC_1 = 60\text{mm}$
$t = 18^{\circ}\text{C}$

1) Scheme of hydrogen - silver chloride elements:



2) calculating the pH of the equation for this circuit:

$$e_{\text{AgCl}} = 0,238 \text{ B}$$

$$pH = \frac{EMF - 0,238}{0,058};$$

$$EMF = ?$$

3) Find the EMF:  $EMF = K_e = U_{\text{min}} \cdot AC_1 = 5,6 \cdot 60 = 336 \text{ mV} = 0.336 \text{ V};$

4) Find the pH:

$$pH = \frac{0,336 - 0,238}{0,058} = 1,69$$

Answer: pH = 1.69

**5) The element is composed of hydrogen electrodes immersed in the blood and calomel electrodes. EMF of the element 698mV. Write down the scheme of the chain and calculate the pH of blood at 37°C.**

$$EMF = 698 \text{ mV}$$

1) Scheme of the hydrogen-calomel element:

$$t = 37^\circ\text{C}$$



$$pH = ?$$

2) The equation for calculating the pH of this circuit at 37°C:

$$pH = \frac{EMF - 0,25}{0,061};$$

3) Find the pH of the blood:  $\delta I = \frac{0,698 - 0,25}{0,061} = 7,36.$

Answer: pH = 7.36.

**6) Calculate the EMF and the write scheme of copper - zinc element at 25°C, if the concentration of electrolytes in the half-cell: 1 M CuSO<sub>4</sub> and 0.01 M ZnSO<sub>4</sub>. ( $e^\circ_{\text{Zn}} = -0,76 \text{ V}; e^\circ_{\text{Cu}} = 0.34 \text{ V}$ ).**

$$C(\text{CuSO}_4) = 1 \text{ mol/l}$$

1) Scheme of copper-zinc cell or element Jacobi:

$$C(\text{ZnSO}_4) = 0,01 \text{ mol/l}$$



$$e^\circ_{\text{Zn}} = -0,76 \text{ V}$$

2) The equation of the EMF of this item:

$$e^\circ_{\text{Cu}} = +0,34 \text{ V}$$

$$EMF = e^\circ_{\text{Cu}} - e^\circ_{\text{Zn}} + \frac{RT}{nF} \ln \left[ \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \right]$$

$$EMF = ?$$

3) Substituting the data from the conditions of the problem, find the EMF at 25°C:

$$EMF = 0,34 - (-0,76) + \frac{0,059}{2} \lg \frac{1}{0,01} = 1,159 \text{ V}$$

Answer: EMF = 1.159 V

**7) EMF of hydrogen - the hydrogen element in the 25°C is 0.177 V. Proton concentration in a single half-cell is 10<sup>-4</sup>. Write down the scheme of this element and calculate the concentration of proton in the other half-cell, which is smaller than the known.**

$$EMF = 0.177 \text{ V}$$

1) This element concentration, as a member of the identical electrodes:

$$[\text{H}^+]_1 = 10^{-4}$$



$$t = 25^\circ\text{C}$$

2) The equation of the EMF at 25°C is as follows:

$$[\text{H}]_2 = ?$$

$$EMF = 0,059 \cdot \lg \frac{10^{-4}}{[\text{H}^+]_2};$$

3) We transform this equation:  $\frac{EMF}{0,059} = \lg 10^{-4} - \lg [H^+]_2$ ,

$$\text{Hence: } -\lg [H^+]_2 = \frac{EMF}{0,059} - \lg 10^{-4} = \frac{0,177}{0,059} + 4 = 7 \quad [H^+]_2 = \text{ant } \lg 7 = 10^{-7}$$

Answer:  $[H^+]_2 = 10^{-7}$

**8) Urine pH is measured by glass electrode. Electrode comparison — silver chloride. EMF of this element is compensated at 30cm interval and the scale multiplier of division 0.02 V/cm. Write down the scheme of this element and calculate the pH at 37°C.**

AC <sub>1</sub> = 30cm
Umin = 0.02 cm
t = 37°C
pH = ?

1) Scheme of glass - silver chloride elements:



2) the calculation formula for pH glass - silver chloride elements:

$$pH = \frac{EMF - 0,238}{0,058};$$

3) Find the EMF:

$$EMF = K_e = U_{min} \cdot AC_1 = 0,02 \cdot 30 = 0.6 \text{ V};$$

4) Find the pH:

$$pH = \frac{0,6 - 0,238}{0,059} = 6,14.$$

Answer: pH = 6.14.

### Problems

1) The element consists of two hydrogen electrodes. One electrode is immersed in a solution with a pH of 7, and the other in a solution with a pH of 3. Write down the scheme of this element and calculate the EMF at 18°C. (Answer: 0.232V)

2) Galvanic cell consists of hydrogen electrodes and calomel, immersed in the gastric juice, the EMF of the element in 25°C 0.327. Write down the scheme of this element and calculate pH of gastric juice. (Answer: pH = 1,3)

3) Calculate the pH of the blood by using hydrogen - silver chloride element. If the EMF of the element is compensated on a segment 30 cm, the scale multiplier of division 0.023 V/cm and the measurement is conducted at a temperature 37°C. Write down the scheme this circuit. (Corresponding to: m: pH = 7.36)

4) EMF of hydrogen - the hydrogen chain at 18°C is 0.232V. Proton concentration in a single half-cell is  $10^{-5}$ . Write down the scheme circuit and calculate the concentration of protons in the other half-cell, which is smaller than the first. (Answer:  $10^{-9}$ )

5) Calculate the EMF and write down the scheme of chrome - aluminium element at 25°C, if the concentration of electrolytes in the half-cell: 0,01 M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 0.1 M Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. ( $e^\circ_{Cr} = -0,71 \text{ V}$ ;  $e^\circ_{Al} = -1,56 \text{ V}$ ). (Answer: 0.869)

## OXIDATION-REDUCTION OR REDOX – SYSTEM

**Oxidation - reduction or redox - a system** in which the indifferent electrodes does not exchange ions with a solution, but only provides a supply or removal of electrons for the oxidation - reduction reaction in a solution containing oxidized and reduced forms of the same substance.

Scheme of redox - system: Pt | FeCl<sub>2</sub>, FeCl<sub>3</sub>.

Redox - the potential is calculated by the equation of Peters:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{RT}{nF} \ln \frac{[\text{oxidized form}]}{[\text{reducing formt}]};$$

where  $e^{\circ}_{\text{red}}$  - normal redox potential and this potential occurring at the electrode immersed in a solution at ratio in it oxidized and reduced forms equal to 1;

**n** - number electrons, which gives or receives a reducing oxidant.

At 18 ° C:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{0,058}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducing formt}]}$$

at 25 ° C:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{0,059}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducing formt}]}$$

### Examples

**1. How many electrons are involved in oxidation - reduction reaction, if  $e_{\text{red}} = 0,121 \text{ V}$ ,  $e^{\circ}_{\text{red}} = 0,18 \text{ V}$ , the concentration of oxidized form of 1 mol/l, and reduced 10mol/l ( $t = 25^{\circ}\text{C}$ )?**

$$e^{\circ}_{\text{red}} = 0,121 \text{ V}$$

$$e^{\circ}_{\text{red}} = 0,18 \text{ V}$$

$$[\text{Oxid.}] = 1 \text{ mol/l}$$

$$[\text{Reduct.}] = 10 \text{ mol/l}$$

$$t = 25^{\circ}\text{C}$$

$$n - ?$$

1) Write the equation of Peters:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{RT}{nF} \ln \frac{[\text{oxidized form}]}{[\text{reducing formt}]}$$

2) At 25°C equation is:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{0,059}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducing formt}]}$$

3) Substitute the data from the equation anode:

$$0,121 = 0,18 + \frac{0,059}{n} \lg \frac{1}{10}$$

$$0,121 - 0,18 = \frac{0,059}{n} \lg 10^{-1}$$

$$-0,059 = \frac{0,059 \cdot (-1)}{n} \quad n = 1$$

Answer: 1 electron

**2) Calculate the normal redox potential at 18 °C, if  $e_{\text{red}} = - 0,15 \text{ V}$ , and in the 60% oxidized form and 30% reduced form. In oxidation - reduction reaction two electrons are involved.**

$$e_{\text{red}} = - 0,15 \text{ V}$$

$$[\text{Oxide.}] = 60\%$$

$$[\text{Redact.}] = 30\%$$

1) Write the equation of Peters:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{RT}{nF} \ln \frac{[\text{oxidized form}]}{[\text{reducing formt}]}$$

2) For 18°C equation is:

$$t = 18^{\circ}\text{C}$$


---


$$e^{\circ}_{\text{red}} = ?$$

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{0,058}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducing form}]}$$

3) Substitute the data from the conditions of the problem:

$$-0,15 = e^{\circ}_{\text{red}} + \frac{0,058}{2} \lg \frac{60}{30};$$

$$-0,15 = e^{\circ}_{\text{red}} + 0,029 \lg 2; \quad -0,15 = e^{\circ}_{\text{red}} + 0,029 \cdot 0,3;$$

$$e^{\circ}_{\text{red}} = -0,15 - 0,0087 = 0,1587\text{V}$$

Answer: 0.1578 V

**3) For the oxidation - reduction of pyruvate - lactate  $e_{\text{red}} = 0,22\text{ V}$ ,  $e^{\circ}_{\text{red}} = 0,180$ . In the reaction involves two electrons. Calculate the ratio of oxidized and reduced forms of matter at  $18^{\circ}\text{C}$ .**

$$e_{\text{red}} = 0,22\text{ V}$$

$$e^{\circ}_{\text{red}} = 0,180\text{ V}$$

$$n = 2$$

$$t = 18^{\circ}\text{C}$$

$$\frac{[\text{oxidized form}]}{[\text{reducing form}]} = ?$$

1) Write the equation of Nernst:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{RT}{nF} \ln \frac{[\text{oxidized form}]}{[\text{reducing form}]}$$

2) At  $18^{\circ}\text{C}$  equation is:

$$e_{\text{red}} = e^{\circ}_{\text{red}} + \frac{0,058}{n} \lg \frac{[\text{oxidized form}]}{[\text{reducing form}]}$$

3) Substitute the  $0,22 = 0,18 + \frac{0,058}{2} \lg \frac{[\text{oxidized form}]}{[\text{reducing form}]}$ ;

$$\lg \frac{[\text{oxidized form}]}{[\text{reducing form}]} = \frac{0,22 - 0,18}{0,029} = 1,4;$$

$$\frac{[\text{oxidized form}]}{[\text{reducing form}]} = 25.$$

Answer: 25

**4) The EMF of a galvanic cell  $(-) \text{Pt} (\text{H}_2) / [\text{H}^+] = 1 \parallel \text{Mn}^{+2}, \text{MnO}_4^- | \text{Pt} (+)$  is  $1.52\text{ V}$ . Calculate the redox - potential at  $25^{\circ}\text{C}$ .**

$$\text{EMF} = 1.52\text{ V}$$

$$t = 25^{\circ}\text{C}$$

$$e_{\text{red}} = ?$$

1) e.m.f of a galvanic cell is equal to the difference

$$\text{electrode potentials: } \text{EMF} = e_{\text{Mn}^{+2} / \text{MnO}_4^-} - e_{\text{H}}$$

2) The potential of hydrogen electrode is equal to 0, since electrode immersed in a solution with  $[\text{H}^+] = 1$ , it normal hydrogen electrode;

3) Solve the equation for  $e_{\text{red}}$ :  $e_{\text{Mn}^{+2} / \text{MnO}_4^-} = \text{EMF} - e_{\text{H}} = 1,52 - 0 = 1,52$ .

Answer: 1,52 V.

**5) The element consists of a calomel electrode and redox - a system  $\text{Fe}^{2+} - \text{Fe}^{3+}$ . EDS of this element is compensated on a segment 20 cm, and element of Weston - at 60cm interval. Write the scheme of this element and to calculate  $e_{\text{red}}$  at  $18^{\circ}\text{C}$ .**

$$\text{AC}_1 = 60\text{cm}$$

$$\text{AC}_2 = 20\text{cm}$$

$$t = 18^{\circ}\text{C}$$

$$e_{\text{red}} = ?$$

1) Write the schema element, suggesting that redox potential negative with respect to calomel:  $(-) \text{Pt} | \text{Fe}^{+2}, \text{Fe}^{+3} \parallel \text{Hg}_2\text{Cl}_2, \text{KCl} | \text{Hg} (+)$

2) The equation of the EMF as the difference of electrode potentials:

$$\text{EMF} = e_{\text{cal.}} - e_{\text{red}}; \text{ hence } e_{\text{red}} = e_{\text{cal.}} - \text{EMF};$$

3) Find the e.m.f data:

$$\text{EMF} = \frac{1,018}{60} \cdot 20 = 0,339\text{V};$$

4) We find  $e_{\text{red}}$ :  $e_{\text{red}} = 0,25 - 0,339 = -0,089 \text{ V}$ .

Answer:  $-0,089 \text{ V}$

**6) Are oxidized cytochromes restored in the redox - a system, if  $e_{\text{red}}$  flavin enzyme - 0,06 V and 0,5 V cytochromes?**

Solution: as redox - potential flavin enzyme (negative), the enzyme will be the restorer of respect to the cytochrome. Consequently, the cytochromes are recovered.

**7) What properties - of oxidizer and a reducing agent – does have cytochrome C ( $e_{\text{red}} = 0,26 \text{ V}$ ) relative to a system of pyruvate/lactate ( $e_{\text{red}} = 0,18 \text{ V}$ )?**

Solution: as redox - potential cytochrome with more positive, than redox - potential pyruvate / lactate, the cytochrome C is oxidizer.

### Problems

1) Calculate the normal oxidation - reduction potential at  $25^\circ \text{C}$ , if  $e$  is red =  $-0,3 \text{ V}$  and the system is 80% oxidized and 20% reduced forms of matter. In oxidation - reduction reactions involving 2 electrons. (Answer:  $-0,3174 \text{ B}$ )

2) The potential of oxidation - reduction of the electrode system  $\text{FeCl}_3 - \text{FeCl}_2$  is  $0,880 \text{ V}$ ,  $E^\circ_{\text{red}} \text{Fe}^{+3} - \text{Fe}^{+2} = 0,77 \text{ V}$ . Calculate the ratio of the concentration of oxidized and reduced forms in the system ( $t = 18^\circ \text{C}$ ). (Answer: 78/1)

3) The element consists of a calomel electrode and redox - a system  $\text{Cr}^{+2} - \text{Cr}^{+3}$ . EMF of this element is compensated at 35cm interval, and graduation reorder  $0,02 \text{ V/cm}$ . Write the scheme of this element and to calculate  $e_{\text{red}}$  at  $25^\circ \text{C}$ . (Answer:  $-0,45 \text{ V}$ )

4) What properties - an oxidizer and a reducing agent - has ascorbic acid ( $e_{\text{red}} = 0,14 \text{ V}$ ) with respect to system pyruvate / lactate ( $e_{\text{red}} = 0,18 \text{ V}$ )? (Answer: reductant)

5) To determine the ascorbic acid ( $e_{\text{red}} = 0,14 \text{ V}$ ) applied dye 2,6-dichlorophenolindophenol ( $e_{\text{red}} = 0,217 \text{ V}$ ). Oxidized or reduced ascorbic acid under the influence of the dye? (Answer: oxidized)

6) To determine the system succinate - fumes ( $e_{\text{red}} = -0,03 \text{ V}$ ) use a dye ( $e_{\text{red}} = 0,217 \text{ V}$ ). .)

Oxidized or reduced system succinate-fumes under the influence of the dye? (Answer: oxidized)

### STRUCTURE OF COLLOIDAL PARTICLES (MICELLES)

**Colloidal solutions (or sols) - is micro heterogeneous system with particle size of  $10^{-7} - 10^{-9} \text{ m}$ .**

Methods of preparation of colloidal systems:

a) variance:                      a method of colloid mill  
   ultrasonic  
   peptization.

b) condensing:                    physical condensation  
   method of replacing the solvent  
   chemical condensation (oxidation, recovery, share, hydrolysis).

Conditions for obtaining colloidal systems by the chemical condensation:

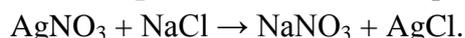
- low concentration of precursors;
- the excess of one of the starting materials;
- low solubility of one of the reaction products.

Colloidal particles are called **micelles**.

The most common method of obtaining colloidal particles is the method of chemical condensation, which uses different chemical reactions.

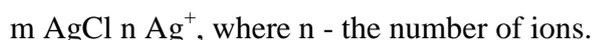
**A) Preparation of sols of the double-exchange reaction.**

**a) Structure of colloidal particles**, we the example of formation of micelle sol AgCl.

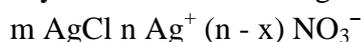


Components of the micelles: core, an adsorption layer, diffuse layer.

**Micelle core** is a collection of many water-insoluble molecules AgCl. You can write this next way is as follows:  $m \text{ AgCl}$ . The kernel is a solid particle. And any solid surface has adsorption properties. Kernel can adsorb ions from solution. In the formation of sol solution formed ions  $\text{Na}^+$ ,  $\text{NO}_3^-$ , as well as ions Ag, which appear in the solution, if taken in excess of  $\text{AgNO}_3$ . Adsorption of ions is selectively according to the rule Paneth - faience. Thus, the three ions,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{Ag}^+$  selectively adsorb ions are Ag, since they show chemical affinity to the core (or part of the nucleus). Written as follows:

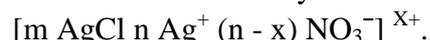


Now the particle is positively charged and attracts negatively charged ions from solution, ie, ions  $\text{NO}_3^-$  in quantity less than the ions Ag. Written as follows:

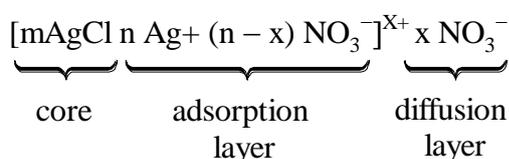


$\text{Ag}^+$  ions and  $\text{NO}_3^-$  constitute an **adsorption layer**. Ions of  $\text{Ag}^+$ , which are adsorbed to the first **potential-called ions**, and the ions  $\text{NO}_3^-$  — **counterions**.

Kernel, along with an adsorption layer is called are **granules**. Granule has a charge, since the positively charged ions in the adsorbed layer more active:



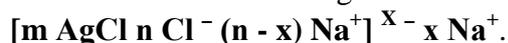
Granule is a particle, which moves in an electric field. Micelle as a whole is electrically neutral, ie the charge of pellets is neutralized by negative ions in the amount of  $\text{NO}_3^- x$ :



Thus, the micelle is formed by the stabilizing action of the ions Ag.

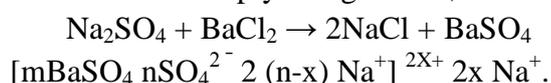
b) If an excess of NaCl:  $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{NaNO}_3 + \text{AgCl}$ ,

then the structure of micelles is the following:



Ion - the stabilizer  $\text{Cl}^-$  ions

c) If a solution contains multiply charged ions, it is necessary to take into account the factors:



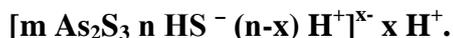
d) Formation of sol Arsenic sulfide.



Since hydrogen sulphide is passed through a solution of arsenic acid it is abundant and is a stabilizer:

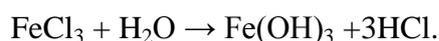


The structure of the micelles can be written as follows:

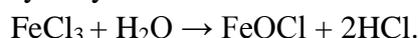


B) *The formation of sol hydrolysis reaction.*

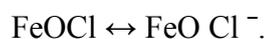
Hydrolysis is usually obtained from sol of metal hydroxides  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ , etc. For example, the sol  $\text{Fe}(\text{OH})_3$  is prepared by adding boiling water solution  $\text{FeCl}_3$ :



In water, salt  $\text{FeCl}_3$  is hydrolyzed:



The resulting basic salt  $\text{FeOCl}$  dissociates:



Ion  $\text{FeO}$  is the stabilizer.

The structure of the micelles can be written as follows:



C) *The formation of sols in the dissociation of surface ionogenic groups.*

For example, obtaining salt  $\text{H}_2\text{SiO}_3$ , whose molecules dissociate:

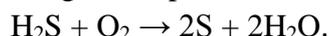


The structure of the micelles can be written as follows:



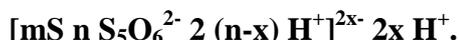
D) *Preparation of sols by oxidation reactions.*

For example: obtaining sol sulphur S.



Sol stabilizers are polyphonic acids, which are formed during the oxidation of sulphur, for example, pentationic acid  $\text{H}_2\text{S}_5\text{O}_6$ .

The structure of the micelles can be written as follows:



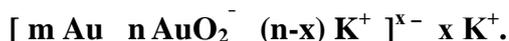
D) *Preparation of sols by the reduction reaction.*

For example, obtaining sol sulphur Au.



Stabilizer is potassium aurate  $\text{KAuO}_2$ .

The structure of the micelles can be written as follows:



*Examples:*

1) Write the structure of micelles of these salts:

$\text{AgBr}$  subject to an excess of  $\text{KBr}$ ;

$\text{AgI}$  subject to an excess of  $\text{AgNO}_3$ ;

$\text{AgBr}$  provided excess  $\text{CaBr}_2$ ;

PbCrO<sub>4</sub> provided excess K<sub>2</sub>CrO<sub>4</sub>;

SrSO<sub>4</sub> provided excess SrCl<sub>2</sub>;

BaSO<sub>4</sub> subject to an excess of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>;

Prussian blue, subject to an excess of yellow blood salt K<sub>4</sub>[Fe(CN)<sub>6</sub>];

Cuprum (II) hexacyanoferrate Cu<sub>2</sub>[Fe(CN)<sub>6</sub>] provided an excess of CuCl<sub>2</sub>;

BaCrO<sub>4</sub> subject to an excess of BaCl<sub>2</sub>.

Co(OH)<sub>2</sub> under the condition of excess CoCl<sub>2</sub>;