

BOGOMOLETS NATIONAL MEDICAL UNIVERSITY

Department of Analytical, physical and colloid chemistry

**METHODICAL INSTRUCTIONS
TO INDIVIDUAL WORK ON STUDYING THE COURSE
"PHYSICAL AND COLLOID CHEMISTRY"**

For pharmacy students

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CONTENT

1. Thermal effects of chemical reactions in solutions. Direction of processes.....	4
2. Kinetics of biochemical reactions.....	18
3. Chemical equilibrium. The solubility product.....	29
4. Determination of redox potential.....	44
5. Sorption of biologically active substances at the interface. Ion xchange. Chromatography.....	59
6. Preparation, purification and properties of colloidal solutions.....	71
7. Coagulation of colloidal solutions. Properties of biopolymer solutions.....	79
Additions.....	86

1. Thermal effects of chemical reactions in solutions. Orientation of processes.

Basic thermodynamic quantities

Parameter	Designation, unit of measurement	Semantic meaning
Internal energy	$U,$ $J, \kappa J$	The total energy of the system, which includes all types of energy of motion and interaction of constituent structural units (molecules, atoms, nuclei, electrons), except for the kinetic energy of the system as a whole and its potential energy in the field of external forces. Internal energy is a function of state. The absolute value of U cannot be determined even for the simplest systems, but this is not necessary, because both in theory and in practice use the change of this value $\Delta U = U_2 - U_1$ in the transition of the system from state 1 to state 2.
Heat	$Q,$ $J, \kappa J, cal, \kappa cal$	Microscopic form of energy transfer through chaotic collisions between particles, as a result of which there is a change in the kinetic energy of particles and the temperature is equalized. Energy passes from the hotter parts of the system to the less heated (or from the hotter system to the less heated). If the system gives off heat (exothermic process), then Q is considered a negative value ($Q < 0$), and if it receives (endothermic process), then Q is a positive value ($Q > 0$).
Work	$A,$ $J, \kappa J$	Macroscopic form of energy transfer from an ordered translational flow of a large number of particles of the system to particles of the environment with the creation of a similar flow. If the system is working on the external environment, then A is considered a positive value, and if the external environment is working on the system, then A is considered a negative value. As one of the types of work in thermodynamics is considered the mechanical work of expansion

		<p>(compression) of the system, equal to $A = p(V_2 - V_1) = p\Delta V$</p> <p>The system performs expansion work ($A > 0$), the external environment performs compression work on the system ($A < 0$).</p>
Enthalpy	<p>$H,$ $J, \kappa J;$</p> <p>$H = U + pV$ $\Delta H = \Delta U + p\Delta V$</p>	<p>State function that characterizes the energy state of the system in isobaric conditions. The physical content of enthalpy can be defined as the energy of an extended system, or as the internal energy, taking into account the work that must be expended for the system to occupy a certain volume under a certain pressure.</p>
Thermal effect of a chemical reaction	<p>$Q,$ $\kappa J \text{ or } \kappa J/mol,$ $cal \text{ or } \kappa cal/mol$</p> <p>thermal effect of isochoric process ($V = const$): $Q_V = \Delta U$</p> <p>thermal effect of the isobaric process ($p = const$): $Q_P = \Delta H$</p>	<p>The amount of heat released or absorbed as a result of a chemical process in a thermomechanical system at constant pressure or volume ($p = const$ or $V = const$) and the equality of temperatures of starting materials and products. The thermal effect can be attributed to the whole reaction (measured in κJ) or to 1 mol of any i-th participant of the reaction (measured in $\kappa J / mol$ of the i-th substance).</p>
Standard enthalpy of reaction	<p>$\Delta H_{298}^0,$ $\kappa J \text{ or } \kappa J/mol$</p>	<p>Thermal effect of isobaric-isothermal process, attributed to standard thermodynamic conditions: $p = 101325 \text{ Pa} = 1 \text{ atm} = 760 \text{ mm Hg}$,, which means the index "0" on the top right; $T = 298.15 \text{ K}$, indicating the index "298" at the bottom right.</p> <p>The sign Δ indicates that it is a change in enthalpy as a result of the reaction, but for the sake of brevity, the word "change" is omitted.</p>
Standard enthalpy of substance formation	<p>ΔH_{f298}^0 (sub., state of m.) $\kappa J/mol$</p>	<p>Thermal effect (standard enthalpy ΔH_{f298}^0) of the reaction of formation of 1 mol of a given complex substance from the corresponding amount of simple substances in standard conditions.</p> <p>The standard enthalpy of formation of any simple substance in its most thermodynamically stable aggregate and allotropic state is 0.</p>

Standard enthalpy of combustion of matter	$\Delta H_{c,298}^0$ (sub., st. of m.), kJ/mol	Thermal effect (standard enthalpy $\Delta H_{c,298}^0$) of the oxidation reaction of 1 mol of a substance with oxygen with the formation of higher oxides under standard conditions. By definition, the standard enthalpy of combustion of oxygen, water, carbon monoxide (IV) and other higher oxides is 0, because they are not oxidized by oxygen.
Entropy	S , $\frac{J}{K}$ or $\frac{J}{mol \cdot K}$; $\Delta S = S_2 - S_1$ for isothermal processes $\Delta S = \frac{Q}{T}$	Thermodynamic function, the physical content of which can be defined as a measure of molecular chaos, disorder of the system. Entropy is a function of state, its change (ΔS) depends only on the initial and final state of the system. The concept of entropy is introduced into thermo-dynamics to determine the degree of irreversible energy dissipation, the degree of deviation of the real process from the ideal. The value of entropy cannot be measured, it can only be calculated.
Standard entropy of matter	S_{298}^0 , J/(K · mol)	Entropy of 1 mol of substance under standard conditions.
Connected energy	TS $T\Delta S$	The value of TS indicates what part of the internal energy of the system can be converted exclusively into heat. The value of $T\Delta S$ shows what part of the energy during the change of internal energy is converted exclusively into heat (given or received by the system depending on the sign of ΔS).
Gibbs free energy	G , J, kJ, $G = H - TS$ $\Delta G = \Delta H - T\Delta S$	Generalized thermodynamic function of the system state, which takes into account the energy and disorder of the system in isobaric-isothermal conditions (p, T = const). Another name is isobaric-isothermal potential. The free Gibbs energy shows what part of ΔH is converted to work.
Standard free Gibbs energy of matter	$\Delta G_{f,298}^0$ (sub., st. of m.) kJ/mol	The standard Gibbs energy is the formation of 1 mol of this compound from simple substances under standard thermodynamic conditions.

Free Helmholtz energy	$F,$ $J, \kappa J,$ $F = U - TS$ $\Delta F = \Delta U - T\Delta S$	Generalized thermodynamic function of the system state, which takes into account the energy and disorder of the system in isochoric-isothermal conditions ($V, T = \text{const}$). Another name is isochoric-isothermal potential. The free Helmholtz energy shows what part of ΔU is converted to work.
Caloric content of food	$\kappa J/g$ or $\kappa \text{cal/g}$	The amount of heat of combustion of the product, taken with the opposite sign and reduced to a unit mass.

Laws of thermodynamics

The first law of thermodynamics.

Energy does not arise and does not disappear, but can only pass from one form to another (including heat and work), without changing quantitatively.

The heat supplied to the closed system is used to increase the internal energy of the system and to carry out the system's work against external environmental forces.

$$Q = \Delta U + A$$

The second law of thermodynamics.

In isolated systems, such processes occur spontaneously, in which the entropy increases.

$$\Delta S > 0$$

The third law of thermodynamics.

The entropy of a pure ideal crystal at absolute zero is zero.

Criteria for the direction of the spontaneous process in a closed system

Real processes are carried out, as a rule, in closed systems in isobaric-isothermal ($p, T = \text{const}$) or isochoric-isothermal ($V, T = \text{const}$) conditions. The criterion for the direction of the spontaneous process in these cases is the sign of the change in the Gibbs energy ΔG (in the case of isobaric-isothermal processes) or the Helmholtz energy ΔF (in the case of isochoric-isothermal processes)

$\Delta G = 0$ ($G = G_{min}$) at $p, T = \text{const}$ або $\Delta F = 0$ ($F = F_{min}$) at $V, T = \text{const}$	the system is in a state of thermodynamic equilibrium.
$\Delta G < 0$ ($G \rightarrow G_{min}$) at $p, T = \text{const}$ або $\Delta F < 0$ ($F \rightarrow F_{min}$) at $V, T = \text{const}$	the process spontaneously occurs in the forward direction, ie thermodynamically possible
$\Delta G > 0$ ($G \rightarrow G_{max}$) at $p, T = \text{const}$ або $\Delta F > 0$ ($F \rightarrow F_{max}$) at $V, T = \text{const}$	only the reverse process occurs spontaneously, the direct process is thermodynamically impossible.

Analysis of the equation $\Delta G = \Delta H - T\Delta S$ shows that the sign and value of ΔG , and hence the thermodynamic possibility of spontaneous flow of the reaction depend on two factors: enthalpy (energy) ΔH and entropy $T\Delta S$. On the one hand, the system seeks to reach a minimum level of energy, releasing part of it into the environment in the form of heat or work ($\Delta H < 0$). On the other hand, the system tends to occupy the most probable state, which is characterized by a maximum of molecular chaos, ie, a maximum of entropy ($\Delta S > 0$). Possible options:

$\begin{cases} \Delta H < 0 \\ \Delta S > 0 \end{cases}$	In this case $\Delta G < 0$ at any temperature values, the process is thermodynamically possible at any temperature;
$\begin{cases} \Delta H < 0 \\ \Delta S < 0 \end{cases}$	In this case $\Delta G < 0$ if $ \Delta H > T\Delta S $, the reaction is thermodynamically possible at a relatively low temperature.
$\begin{cases} \Delta H > 0 \\ \Delta S > 0 \end{cases}$	In this case $\Delta G < 0$ if $ \Delta H < T\Delta S $, the reaction is thermodynamically possible at a relatively high temperature.
$\begin{cases} \Delta H > 0 \\ \Delta S < 0 \end{cases}$	Both factors act in an unfavorable direction, the reaction is thermodynamically impossible at any temperature.

Hess's law and its consequences

Hess's law: The thermal effect of the reaction does not depend on the course of the reaction, but is determined only by the type and condition of the starting materials and products

Consequences of Hess's law.

According to Hess's law, it is possible to calculate the thermal effect of a reaction using the heat (enthalpy) of the formation or combustion of substances without performing an experiment.

1. The thermal effect of the direct reaction is equal to the thermal effect of the reverse reaction with the opposite sign.

$$\Delta H_d. = -\Delta H_r.$$

2. The thermal effect of the reaction is equal to the sum of the heats (enthalpies) of the formation of products minus the sum of the heats (enthalpies) of the formation of reagents taking into account the stoichiometric coefficients, ie:

$$\Delta H = \sum_i n_i (\Delta H_i)_f^{prod.} - \sum_j n_j (\Delta H_j)_f^{reag.}$$

3. The thermal effect of the reaction is equal to the sum of heat (enthalpy) of combustion of reagents minus the sum of heat (enthalpy) of combustion of products taking into account stoichiometric coefficients, ie:

$$\Delta H = \sum_i n_i (\Delta H_i)_c^{reag.} - \sum_j n_j (\Delta H_j)_c^{prod.}$$

Examples of exercises

Example 1

Calculate the caloric content of 250 g of sour cream, the composition of which is: 25% fat, 2.7% carbohydrates and 2.6% protein, if their heat (enthalpy) of combustion is equal to -39.9 kJ / g, -17 kJ / g, -17 kJ / g.

Given:

$$\begin{aligned}\Delta H_c(c.) &= -17 \text{ kJ/g} \\ \Delta H_c(p.) &= -17 \text{ kJ/g} \\ \Delta H_c(f.) &= -39,9 \text{ kJ/g} \\ \omega(c.) &= 2,7\% = 0,027 \\ \omega(p.) &= 2,6\% = 0,026 \\ \omega(f.) &= 25\% = 0,25 \\ m(\text{sour cream}) &= 250\text{g}\end{aligned}$$

Find:

caloric content of 250 g of sour cream

Solution:

Calculate the heat of combustion of sour cream in terms of 1 g of product, taking into account the heat (enthalpy) of combustion and mass fractions of proteins, fats and carbohydrates:

$$\Delta H_c(s. c.) = \sum \omega(x) \cdot \Delta H_c(x)$$

$$\begin{aligned}\Delta H_c(s.c.) &= 0,027 \cdot (-17 \text{ kJ/g}) + 0,026 \cdot (-17 \text{ kJ/g}) + 0,25 \cdot (-39,9 \text{ kJ/g}) = \\ &= -10,876 \text{ kJ/g}\end{aligned}$$

The caloric content of food is the amount of heat of combustion, taken with the opposite sign and reduced to a unit of mass.

Therefore, the caloric content of sour cream per 1 g of product is equal to $10,876 \text{ kJ/g}$, and the caloric content of 250 g of sour cream:

$$250 \text{ g} \cdot 10,876 \text{ kJ/g} = 2719 \text{ kJ} = 650 \text{ kcal}$$

Answer: The caloric content of 250 g of sour cream is 2719 kJ (or 650 kcal).

Example 2

Oatmeal contains 5.8% fat, 65.4% carbohydrates and 11.8% protein. Calculate the mass of oatmeal, which is equivalent to energy loss due to sweating 720 g of water, if the enthalpy of water evaporation is 41 kJ/mol, and heat (enthalpy) of combustion of proteins, fats and carbohydrates is equal to -39.9 kJ/g, -17 kJ/g, -17 kJ/g, respectively.

Given:

$$\begin{aligned}\Delta H_c(c.) &= -17 \text{ kJ/g} \\ \Delta H_c(p.) &= -17 \text{ kJ/g} \\ \Delta H_c(f.) &= -39,9 \text{ kJ/g} \\ \omega(\text{B.}) &= 65,4\% = 0,654 \\ \omega(\text{б.}) &= 11,8\% = 0,118 \\ \omega(\text{ж.}) &= 5,8\% = 0,058 \\ m(\text{H}_2\text{O}) &= 720 \text{ g} \\ \Delta H_{ev.}^0(\text{H}_2\text{O}) &= 41 \text{ kJ/mol}\end{aligned}$$

Find:

$$m(\text{oatm.}) - ?$$

Solution:

- 1) Sweating cools the body because water is needed to evaporate water. Water evaporation occurs at constant pressure, so you can equate the enthalpy of water evaporation to the amount of heat that must be allocated:

$$Q = n(\text{H}_2\text{O}) \cdot \Delta H_{ev.}^0(\text{H}_2\text{O}) = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} \cdot \Delta H_{ev.}^0(\text{H}_2\text{O})$$

$$Q = \frac{720 \text{ g}}{18 \text{ g/mol}} \cdot 41 \text{ kJ/mol} = 1640 \text{ kJ}$$

- 2) Calculate the heat (enthalpy) of combustion of oatmeal, taking into account the heat (enthalpy) of combustion and mass fractions of proteins, fats and carbohydrates per 1 g of product:

$$\Delta H_c(\text{oatm.}) = \sum \omega(x) \cdot \Delta H_c(x)$$

$$\begin{aligned}\Delta H_c(\text{oatm.}) &= 0,654 \cdot (-17 \text{ kJ/g}) + 0,118 \cdot (-17 \text{ kJ/g}) + 0,058 \cdot (-39,9 \text{ kJ/g}) = \\ &= -13,182 \text{ kJ/g}\end{aligned}$$

Therefore, the caloric content of oatmeal per 1 g of product is equal to $13,182 \text{ kJ/g}$, and the mass of cereals, which is equivalent to the loss of 1640 kJ of heat:

$$m(\text{oatm.}) = \frac{1640 \text{ kJ}}{13,182 \text{ kJ/g}} = 124,4 \text{ g}$$

Answer:

$$m(\text{oatm.}) = 124,4 \text{ g}$$

Example 3

Determine the possibility of oxidation of nitrogen oxide (I), used in medicine for inhalation anesthesia, oxygen to toxic nitrogen oxide (II) under standard conditions. Calculate the enthalpy and entropy of the reaction under standard conditions, estimate the contributions of enthalpy and entropic factors. Use the values of standard thermodynamic values for calculations.

Given:

standard conditions.

Find:

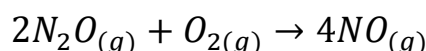
$$\Delta S_{298}^0 - ?$$

$$\Delta G_{298}^0 - ?$$

$$\Delta H_{298}^0 - ?$$

Solution:

Write the reaction equation:



Write reference data:

$$S_{298}^0(\text{N}_2\text{O}_{(g)}) = 220,0 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S_{298}^0(\text{O}_{2(g)}) = 205,2 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$S_{298}^0(\text{NO}_{(g)}) = 210,8 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta H_{f,298}^0(\text{N}_2\text{O}_{(g)}) = 81,6 \text{ kJ/mol}$$

$$\Delta H_{f,298}^0(\text{NO}_{(g)}) = 91,3 \text{ kJ/mol}$$

$$\Delta G_{f,298}^0(\text{N}_2\text{O}_{(g)}) = 103,7 \text{ kJ/mol}$$

$$\Delta G_{f,298}^0(\text{NO}_{(g)}) = 87,6 \text{ kJ/mol}$$

- 1) *The standard entropy (change in the entropy of the process occurring under standard thermodynamic conditions) of a chemical reaction is determined by the difference between the sums of the standard entropies of the stoichiometric amount of reaction products and starting materials:*

$$\Delta S_{298}^0 = \sum_i n_i (S_{298}^0)_{\text{prod.}} - \sum_j n_j (S_{298}^0)_{\text{reag.}}$$

$$\Delta S_{298}^0 = 4 \cdot S_{298}^0(\text{NO}_{(g)}) - [2 \cdot S_{298}^0(\text{N}_2\text{O}_{(g)}) + S_{298}^0(\text{O}_{2(g)})]$$

$$\Delta S_{298}^0 = 4 \text{ mol} \cdot 210,8 \frac{\text{J}}{\text{mol} \cdot \text{K}} - \left[2 \text{ mol} \cdot 220,0 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 1 \text{ mol} \cdot 205,2 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right] = 198 \text{ J/K}$$

- 2) *The standard enthalpy (change in the enthalpy of a process occurring under standard thermodynamic conditions) of a reaction according to the first consequence of Hess's law can be defined as the algebraic difference of the sums of enthalpies of formation of stoichiometric quantities of reaction products and starting materials:*

$$\Delta H_{298}^0 = 4 \cdot \Delta H_{f,298}^0(\text{NO}_{(g)}) - [2 \cdot \Delta H_{f,298}^0(\text{N}_2\text{O}_{(g)}) + \Delta H_{f,298}^0(\text{O}_{2(g)})]$$

$$\Delta H_{298}^0 = 4 \text{ mol} \cdot 91,3 \text{ kJ/mol} - [2 \text{ mol} \cdot 81,6 \text{ kJ/mol} + 0] = 202 \text{ kJ}$$

3) The standard free Gibbs energy (the change in the Gibbs energy of the process that occurs under standard thermodynamic conditions) of the reaction, which is a criterion for the spontaneous flow of processes, at this stage can be calculated in two ways:

I Using pre-calculated values ΔH_{298}^0 and ΔS_{298}^0

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0$$

$$\Delta G_{298}^0 = 202 \cdot 10^3 \text{ J} - 298 \text{ K} \cdot 198 \frac{\text{ J}}{\text{ mol} \cdot \text{ K}} = 142996 \text{ J/mol} \cong 143 \text{ kJ/mol}$$

II Using reference values of standard Gibbs energies of substance formation. The Gibbs energy of the reaction is equal to the algebraic sum of the Gibbs energies of formation of stoichiometric quantities of products minus the algebraic sum of Gibbs energies of formation of stoichiometric quantities of reagents:

$$\Delta G_{298}^0 = \sum_i n_i (G_{298}^0(i))_f^{prod.} - \sum_j n_j (G_{298}^0(j))_f^{reag.}$$

$$\Delta G_{298}^0 = 4 \cdot \Delta G_{f,298}^0(\text{NO}_{(g)}) - [2 \cdot \Delta G_{f,298}^0(\text{N}_2\text{O}_{(g)}) + \Delta G_{f,298}^0(\text{O}_{2(g)})]$$

$$\Delta G_{298}^0 = 4 \text{ mol} \cdot 87,6 \text{ kJ/mol} - [2 \text{ mol} \cdot 103,7 \text{ kJ/mol} + 0] = 143 \text{ kJ}$$

Answer:

$$\Delta S_{298}^0 = 198 \text{ J/K}$$

$$\Delta H_{298}^0 = 202 \text{ kJ}$$

$$\Delta G_{298}^0 = 143 \text{ kJ}$$

$\Delta S > 0$, entropy factor contributes to the spontaneous course of the reaction;
 $\Delta H > 0$, enthalpy factor prohibits the spontaneous course of the reaction;
because $\Delta G > 0$, the oxidation of N_2O to NO under standard conditions is impossible.

Example 4

The interaction of acetic acid with ammonia occurs through the stage of formation of the ammonium salt; when heated, the salt undergoes dehydration to form acetamide. Calculate the thermal effect of the acetamide synthesis reaction under standard conditions, using the values of the standard enthalpies of combustion of the reaction participants.

Given:

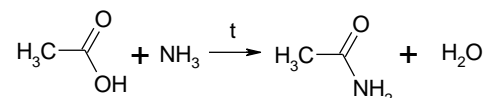
standard conditions

Find:

ΔH_{298}^0 - ?

Solution:

Write the reaction equation:



Write reference data:

$$\Delta H_{c,298}^0(\text{CH}_3\text{COOH}_{(l)}) = -874,2 \text{ kJ/mol}$$

$$\Delta H_{c,298}^0(\text{NH}_{3(g)}) = -382,8 \text{ kJ/mol}$$

$$\Delta H_{c,298}^0(\text{CH}_3\text{CONH}_{2(l)}) = -1184,6 \text{ kJ/mol}$$

$$\Delta H_{c,298}^0(\text{H}_2\text{O}) = 0$$

The thermal effect (change in the enthalpy of the process) of the reaction according to the second consequence of Hess's law can be defined as the algebraic difference of the sums of standard heats (enthalpies) of combustion of stoichiometric quantities of starting materials and reaction products:

$$\Delta H_{298}^0 = [\Delta H_{c,298}^0(\text{CH}_3\text{COOH}) + \Delta H_{c,298}^0(\text{NH}_3)] - [\Delta H_{c,298}^0(\text{CH}_3\text{CONH}_2) + \Delta H_{c,298}^0(\text{H}_2\text{O})]$$

$$\Delta H_{298}^0 = [-874,2\text{kJ} + (-382,8\text{kJ})] - [-1184,6\text{kJ} + 0] = -72,4\text{kJ}$$

Answer: $\Delta H_{298}^0 = -72,4\text{kJ}$

Example 5

Diethyl ether is a classic remedy for inhalation anesthesia. One of the disadvantages of using diethyl ether as an anesthetic is its high explosiveness. Calculate the amount of heat that will be released during the complete combustion of 100 g of diethyl ether at s.u., using reference values of standard heat (enthalpy) of combustion of substances.

Given:

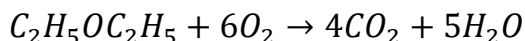
$$m(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) = 100\text{g}$$

Find:

$$Q - ?$$

Solution:

Write the equation of the combustion reaction of diethyl ether:



Write reference data:

$$\Delta H_{c,298}^0(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) = -2723,9 \text{ kJ/mol}$$

Calculate the amount of heat released during the combustion of 100 g of diethyl ether:

$$Q = -\Delta H_{c,298}^0(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) \cdot n(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) = -\Delta H_{c,298}^0(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) \frac{m(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)}{M(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)}$$

$$Q = -(-2723,9 \text{ kJ/mol}) \cdot \frac{100 \text{ g}}{74 \text{ g/mol}} = 3680,9 \text{ kJ}$$

Answer: $Q = 3680,9 \text{ kJ}$

Example 6

200 g of cheese contains 47 g of protein and 59 g of fat. Calculate a) the caloric content of 200 g of cheese (in kJ); b) caloric content of cheese per 1 g of product (in kJ / g), if the caloric content of proteins and fats is 17 kJ / g and 39.9 kJ / g, respectively.

Given:

$$m(p.) = 47 \text{ g}$$

$$m(f.) = 59 \text{ g}$$

$$m(\text{cheese}) = 200 \text{ g}$$

$$\text{caloric content of proteins} = 17 \text{ kJ/g}$$

$$\text{caloric content of fats} = 39,9 \text{ kJ/g}$$

Find:

a) caloric content of 200 g of cheese

b) caloric content of cheese per 1 g of product

Solution:

a) Caloric content of 200 g of cheese is calculated taking into account the masses of proteins and fats contained in it, and their caloric content:

$$47 \text{ g} \cdot 17 \text{ kJ/g} + 59 \text{ g} \cdot 39,9 \text{ kJ/g} = 3153,1 \text{ kJ}$$

b) Caloric content of cheese per 1 g of product:

$$\frac{3153,1 \text{ kJ}}{200 \text{ g}} = 15,76 \text{ kJ/g}$$

Caloric content can be expressed in kcal, knowing that 1 kcal = 4,184 kJ:

$$\frac{3153,1}{4,184} = 844,4 \text{ kcal} \quad \frac{15,76}{4,184} = 3,77 \text{ kcal/g}$$

Answer: a) caloric content of 200 g of cheese is 3153,1 kJ (або 844,4 kcal);

b) caloric content of cheese in terms of g of product is equal to 15,76 kJ/g (or 3,77 kcal/g)

Self-test questions

1.1 Without performing calculations, evaluate the sign of the change in entropy in the following reactions:

- 1) $2HBr_{(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + Br_{2(l)}$
- 2) $2Pb(NO_3)_{2(s)} \rightleftharpoons 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$
- 3) $Cl_{2(g)} + H_{2(g)} \rightleftharpoons 2HCl_{(g)}$
- 4) $NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4Cl_{(s)}$
- 5) $CO_{(g)} + O_{3(g)} \rightleftharpoons CO_{2(g)} + O_{2(g)}$

1.2 Calculate the change in entropy of the reactions given in problem 1.1, and determine the direction of the spontaneous process in an isolated system (T = 298 K). Use the values of standard entropies of substances for calculations (Appendix 1).

Answer:

reaction №	1)	2)	3)	4)	5)
$\Delta S_{298}^0, J/K$	-94,5	878,4	20	-283,1	-17,6

1.3 Calculate the change in the standard enthalpy of reactions given in Problem 1.1. For calculations use the values of standard enthalpies of formation of substances (Appendix 1).

Answer:

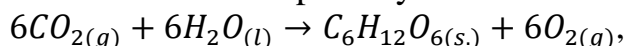
reaction №	1)	2)	3)	4)	5)
$\Delta H_{298}^0, kJ$	-112	1177	-184,6	-176,2	-415,7

1.4 Calculate the standard Gibbs energy of the reactions given in Problem 1.1 and determine the direction of the spontaneous process in a closed system (T = 298 K). Calculations should be performed using the values ΔS_{298}^0 та ΔH_{298}^0 , calculated in Problems 1.2 and 1.3.

Answer:

reaction №	1)	2)	3)	4)	5)
$\Delta G_{298}^0, kJ$	-83,8	915,2	-190	-91,8	-410,45

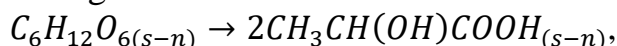
1.5 Calculate the thermal effect of the photosynthesis reaction



using the values of heat (enthalpy) of the formation of starting materials and reaction products (Appendix 1). Where does the energy needed to carry out the reaction come from?

Answer: $\Delta G = 2818,6 kJ$

1.6 Calculate the enthalpy, entropy and Gibbs energy of the lactic acid fermentation reaction of glucose

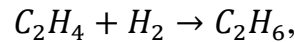


using the values of standard thermodynamic values of the reaction participants (Appendix 1). Determine the possibility of spontaneous course of this reaction

under standard conditions. Assess the contributions of enthalpy and entropy factors.

$$\begin{aligned}\text{Answer: } \Delta S_{298}^0 &= 174,5 \text{ J/K} \\ \Delta H_{298}^0 &= -108,2 \text{ kJ} \\ \Delta G_{298}^0 &= -160,2 \text{ kJ}\end{aligned}$$

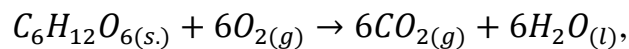
1.7 Calculate the standard enthalpy of the ethylene hydrogenation reaction



using the values of standard enthalpies of combustion of the reaction participants (Appendix 2).

$$\text{Answer: } \Delta H_{298}^0 = -136,3 \text{ kJ}$$

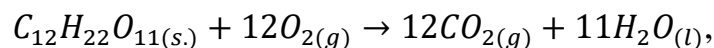
1.8 Calculate the amount of heat released during the complete oxidation of 50 g of glucose under standard conditions:



using reference values of standard heats (enthalpies) of combustion of substances (Appendix 2).

$$\text{Answer: } Q = 778,5 \text{ kJ}$$

1.9 Calculate the mass of sucrose, with complete oxidation of which under standard conditions released 824.5 kJ of heat:



using reference values of standard heats (enthalpies) of combustion of substances (Appendix 2).

$$\text{Answer: } m(C_{12}H_{22}O_{11}) = 50 \text{ g}$$

1.10 100 g of chips contains 6 g of protein, 53 g of carbohydrates, 30 g of fat. Calculate a) the energy that will be released during the assimilation of 250 g of chips (in J); b) caloric content of chips per 1 g of product (in kJ / g), if the heat (enthalpy) of combustion of proteins, fats and carbohydrates is equal to -39.9 kJ / g, -17 kJ / g and -17 kJ / g, respectively.

$$\begin{aligned}\text{Answer: } \text{a) } &5500 \text{ kJ} \\ \text{b) } &22 \text{ kJ/g}\end{aligned}$$

1.11 Calculate the energy (in kJ or kcal) that will be released during the assimilation of a portion of red caviar weighing 30 g. Red caviar contains an average of 32% protein, 12% fat; the caloric content of proteins and fats is 17 kJ / g and 39.9 kJ / g, respectively.

$$\text{Answer: } 306,84 \text{ kJ (73,34 kcal)}$$

1.12 How many Nuts bars weighing 50g are equivalent to losing 785 kcal of energy? Product composition: 7.1% protein, 25.1% fat, 62.8% carbohydrates. The caloric content of proteins, fats and carbohydrates is 17 kJ / g, 39.9 kJ / g and 17 kJ / g, respectively.

$$\text{Answer: } 3$$

1.13 Calculate the mass of kefir, which is equivalent to the loss of energy due to sweating 360 g of water, if the enthalpy of evaporation of water is 41 kJ / mol. Kefir contains 2.5% fat, 3.5% carbohydrates and 3.0% protein; the heat (enthalpy) of combustion of proteins, fats and carbohydrates is equal to -39.9 kJ / g, -17 kJ / g and -17 kJ / g, respectively.

Answer: $m = 408 \text{ g}$

1.14 What is the number of eggs weighing 60 g equivalent to the loss of energy due to sweating 900 g of water, if the enthalpy of evaporation of water is 41 kJ / mol. Egg contains 12% fat, 69% protein, 3% carbohydrates; the heat (enthalpy) of combustion of proteins, fats and carbohydrates is equal to -39.9 kJ / g, -17 kJ / g and -17 kJ / g, respectively.

Answer: 2

1.15* *To perform all the functions of the body, a person spends a total of 2200-2400 kcal for women and 2550-2800 kcal for men. When performing heavy physical activity (sports, work of miners, builders, etc.), a person's energy expenditure increases to 3500 - 4000 kcal. The smallness of food should be 3-4 times a day. With three meals a day, breakfast should be 30% of the diet, lunch 45-50%, and dinner 20-25%. Dinner should not exceed a third of the daily diet.*

Of the products (at least 5) listed in the table, offer a version of the daily menu, based on the fact that the daily requirement is 2500 kcal, and breakfast is 30%, lunch 50%, dinner 20%.

Table of caloric content of products **

Product	Percentage, %				kcal**
	water	proteins	Fat	carbohydrates	
Yogurt nat., 1,5% fat content	88	5	1,5	3,5	
Low-fat kefir	91,4	3	0,1	3,8	
Milk	88,5	2,8	3,2	10,8	
Sour cream 10%	82,7	3	10	2,9	
Dutch cheese	38,8	26,8	27,3	0	
Cottage cheese	64,7	14	18	1,3	
Vegetable oil	0,1	0	99,9	0	
Butter	15,8	0,6	82,5	0,9	
Rye bread	42,4	4,7	0,7	4,9	
Wheat bread	34,3	7,7	2,4	53,4	
Buckwheat	14	12,6	2,6	68	
Fig	14	7	0,6	73,7	
White cabbage	90	1,8	-	5,4	
Potato	76	2	0,1	19,7	
Soil cucumbers	95	0,8	-	3	
Soil tomatoes	93,5	1,5	-	4,2	
Apples	86,5	0,4	-	11,3	
Orange	87,5	0,9	-	8,4	
Grapefruit	89	0,9	-	7,3	

Beef	67,6	16,3	15,3	0	
Lean pork	54,8	16,4	27,8	0	
Chicken egg	74	12,7	11,5	0,7	
Crucian	78,9	17,7	1,8	0	
Pollock	80,1	15,9	0,7	0	
Carp	79,1	16	3,6	0	

*The data in the table are all very approximate. The content of proteins, fats, carbohydrates, respectively, the caloric content of the product depends on many factors: the type of product and the method of preparation, the peculiarities of the recipe and technological process of different manufacturers. Even, for example, from the fact that some plant grew in the hot or rainy summer.

** Calculate the caloric content yourself.

2. Kinetics of biochemical reactions

Basic kinetic quantities

Parameter	Marking, Unit	Semantic meaning
Average reaction rate	$v, \text{mol}/(\text{l} \cdot \text{s})$ for reaction $A + B \rightarrow AB$: $v = -\frac{\Delta c_A}{\Delta \tau}$ or $v = \frac{\Delta c_{AB}}{\Delta \tau}$	Change in concentration of reagent or product per unit time. The reaction rate can be monitored by the consumption of one of the reagents (A or B), or the accumulation of product (AB). During the reaction, the concentrations of the reagents are constantly decreasing, and the rate of chemical conversion changes accordingly.
True reaction rate	$v = -\frac{dc_A}{d\tau}$ or $v = \frac{dc_{AB}}{d\tau}$	True reaction rate ($\Delta \tau \rightarrow 0$).
Kinetic equation	for a homogeneous reaction $aA + bB \rightarrow cC + dD:$ $v = k \cdot c_A^n \cdot c_B^m$	Expresses the dependence of the reaction rate on the concentration of reactants. The kinetic equation is a mathematical expression of the law of active masses for kinetics: <i>at a constant temperature, the rate of the chemical reaction is directly proportional to the product of the molar concentrations of the reagents.</i>
The order of reaction by substance	in the kinetic equation $v = k \cdot c_A^n \cdot c_B^m$ n – the order of reaction for substance A, m – the order of reaction for substance B	An indicator of the degree to which the reagent concentration is included in the kinetic equation. For simple reactions, the order of the reaction is an integer value that coincides with the molecularity of the reaction. For complex reactions, the orders can be determined only experimentally. And they can have both integer and fractional, as well as zero value.

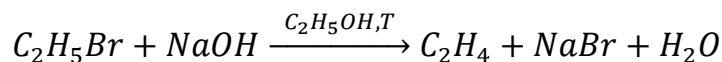
General order of reaction	$n+m$	The sum of the reaction orders for all reagents.
Half-life	$\tau_{1/2}$, s, min, h, day	The time during which the concentration of the reactant will be halved ($c = c_0/2$)
Reaction rate constant	<p>k, reaction order</p> <p>0 $\frac{mol}{l \cdot s}$</p> <p>1-st s^{-1}</p> <p>2-nd $\frac{l}{mol \cdot s}$</p> <p>3-d $\frac{mol^2 \cdot s}{l^2}$</p>	The individual characteristic of the reaction, numerically equal to the reaction rate at reagent concentrations equal to 1 mol / l. Units of measurement depend on the order of the reaction.
Kinetic equation of the first order	<p>differential form: $-\frac{dc}{dt} = kc$</p> <p>integral form: $lnc = lnc_0 - kt$,</p> <p>where: $c = c_0 \cdot e^{-kt}$,</p> $k = \frac{1}{t} \ln \frac{c_0}{c}$ <p>or</p> $k = \frac{\ln 2}{\tau_{1/2}}$ <p>the transition from natural to decimal logarithm gives:</p> $k = \frac{2,3}{t} \lg \frac{c_0}{c}$ <p>and</p> $k = \frac{2,3 \cdot \lg 2}{\tau_{1/2}}$	<p>The integral form of the equation expresses the linear dependence of the variables lnc and t.</p> <p>k – 1st order reaction rate constant;</p> <p>c_0 - the concentration of the starting material at the initial time;</p> <p>c – the concentration of the substance at time t;</p> <p>t - the time elapsed since the beginning of the reaction.</p>
Vant-Goff Rule	$v_2 = v_1 \cdot \gamma^{\frac{T_2-T_1}{10}}$ $k_2 = k_1 \cdot \gamma^{\frac{T_2-T_1}{10}}$ <p>where v_2 and v_1 - are the reaction rates at temperature T_2 and T_1 respectively; k_2 and k_1 – reaction rate constants at temperatures T_2 and T_1.</p>	With increasing temperature for every 10 degrees, the rate of chemical reaction increases by 2-4 times.

Activation energy	$E_a, kJ/mol$	The minimum excess energy of the interacting particles is sufficient for these particles to enter into a chemical reaction.
Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{RT}},$ $\ln k = \ln A - \frac{E_a}{RT}$ $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ <p>or</p> $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$	Establishes a relationship between the reaction rate constant, activation energy and temperature. The quantity A included in the equation "Arrhenius constant" or "preexponent" is determined for each specific reaction and has the same dimension as the rate constant k.

Examples of exercises.

Example 1

Calculate the average reaction rate (in mol / (l · s)) of dehydrogen halogenation of bromomethane in an alkaline alcohol solution, if after 1 minute of boiling the solution the concentration of bromomethane was 0.1 mol / l, and after 20 minutes - 0.075 mol / l.



Given:

$$c_1(C_2H_5Br) = 0,1 \text{ mol/l}$$

$$c_2(C_2H_5Br) = 0,075 \text{ mol/l}$$

$$t_1 = 1 \text{ min} = 60 \text{ s}$$

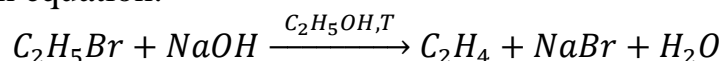
$$t_2 = 20 \text{ min} = 1200 \text{ s}$$

Find:

$$v - ?$$

Solution:

Write the reaction equation:



The reaction rate is defined as the change in the concentration of the substance involved in the time period during which the change occurred:

$$v = -\frac{c_2(C_2H_5Br) - c_1(C_2H_5Br)}{t_2 - t_1} = -\frac{0,075 \frac{\text{mol}}{\text{l}} - 0,1 \text{ mol/l}}{1200\text{s} - 60\text{s}} = 2,2 \cdot 10^{-5} \frac{\text{mol}}{\text{l} \cdot \text{s}}$$

Answer:

$$v = 2,2 \cdot 10^{-5} \frac{\text{mol}}{\text{l} \cdot \text{s}}$$

Example 2

The reaction $2NO + O_2 \rightarrow 2NO_2$ has the third order. How will the rate of NO_2 formation change if a) the pressure in the system is increased threefold; b) reduce the NO_2 concentration by 4 times; c) reduce the NO concentration by 4 times.

Solution:

According to the law of active masses, the rate of this reaction is proportional to the product of the molar concentration of NO raised to the second degree and the molar concentration of O_2 :

$$v = k \cdot c^2(NO) \cdot c(O_2)$$

a) You can change the concentration of reactants due to the pressure in the vessel. From the Clapeyron-Mendeleev equation it follows that the molar concentration of each gas is directly proportional to the pressure:

$$pV = nRT \implies c = \frac{n}{V} = \frac{p}{RT}.$$

When the pressure increases three times, the concentration of each gas - both NO and O_2 - will increase three times:

$$c_2(NO) = 3c_1(NO), \quad c_2(O_2) = 3c_1(O_2),$$

and the reaction rate is determined by their product, so it will increase 27 times:

$$v_1 = k \cdot c_1^2(NO) \cdot c_1(O_2),$$

$$v_2 = k \cdot c_2^2(NO) \cdot c_2(O_2) = k \cdot (3c_1(NO))^2 \cdot 3c_1(O_2) = 27v_1$$

b) The reaction rate does not depend on the concentration of products, in this case NO_2 (the rate of direct reaction is determined only by the left side of the equation), so it will not change when the concentration of NO_2 is reduced by 4 times.

c) The reaction rate will decrease 16 times:

$$c_2(NO) = \frac{c_1(NO)}{4}$$

$$v_2 = k \cdot c_2^2(NO) \cdot c(O_2) = k \cdot \left(\frac{c_1(NO)}{4}\right)^2 \cdot c(O_2) = \frac{v_1}{16}$$

Answer: a) will increase 27 times;
b) will not change;
c) will decrease 16 times.

Example 3

The reaction $A + B \rightarrow AB$ is bimolecular. Initial concentrations of substances are as follows:

$c_0(A) = 2.5 \text{ mol}$, $c_0(B) = 1.5 \text{ mol}$. The reaction rate constant $k = 0.8 \text{ l}/(\text{mol} \cdot \text{s})$. Calculate a) the initial reaction rate; b) the concentration of substance A and the reaction rate until the concentration of substance B is equal to 0.5 mol/l .

Given:

$$c_0(A) = 2,5 \text{ mol/l}$$

Find:

$$c(A) - ?$$

$$\begin{array}{l|l} c_0(B) = 1,5 \text{ mol/l} & v-? \\ c(B) = 1,5 \text{ mol/l} & \\ k = 0,8 \text{ л/(mol} \cdot \text{s)} & \end{array}$$

Solution:

a) The rate of bimolecular reaction $A + B \rightarrow AB$ is directly proportional to the concentrations of substances A and B, the kinetic equation is:

$$v = k \cdot c(A) \cdot c(B),$$

therefore, the initial reaction rate is equal to

$$v_0 = k \cdot c_0(A) \cdot c_0(B) = 0,8 \frac{\text{l}}{\text{mol} \cdot \text{s}} \cdot 2,5 \text{ mol/l} \cdot 1,5 \text{ mol/l} = 3 \frac{\text{mol}}{\text{l} \cdot \text{s}}$$

b) At the time when the concentration of substance B was 0.5 mol / l, the change in the concentration of substance B was:

$$\Delta c(B) = c_0(B) - c(B) = 1,5 \text{ mol/l} - 0,5 \text{ mol/l} = 1 \text{ mol/l}.$$

According to the reaction equation, 1 mol of substance B reacts with 1 mol of substance A, so the change in the concentration of substance A at the moment of the reaction is 1 mol, and the concentration of substance A is equal to:

$$c(A) = c_0(A) - \Delta c(A) = 2,5 \text{ mol/l} - 1 \text{ mol/l} = 1,5 \text{ mol/l},$$

and the reaction rate at this time is equal to:

$$v = 0,8 \frac{\text{l}}{\text{mol} \cdot \text{s}} \cdot 1,5 \text{ mol/l} \cdot 0,5 \text{ mol/l} = 0,6 \frac{\text{mol}}{\text{l} \cdot \text{s}}$$

Answer:

$$\begin{array}{l} \text{a) } v_0 = 3 \frac{\text{mol}}{\text{l} \cdot \text{s}}; \\ \text{b) } c(A) = 1,5 \text{ mol/l}, v = 0,6 \frac{\text{mol}}{\text{l} \cdot \text{s}} \end{array}$$

Example 4

How many times to increase the rate constant of a chemical reaction at elevated temperature by 50°C, if $\gamma = 4$?

$$\begin{array}{l|l} \text{Given:} & \text{Find:} \\ \gamma = 4 & \frac{k_2}{k_1} -? \\ \Delta t = 50^\circ\text{C} & \end{array}$$

Solution:

The change in the reaction rate constant with increasing temperature is determined by the Vant-Goff rule:

$$\frac{k_2}{k_1} = \gamma^{\frac{\Delta t}{10}} = 4^{\frac{50}{10}} = 4^5 = 1024$$

Answer: the rate constant will increase by 1024 times.

Example 5

How many degrees should the temperature be increased so that the reaction rate increases 32 times ($\gamma = 2$)?

Given:

$$\gamma = 2$$

$$\frac{v_2}{v_1} = 32$$

Find:

$$\Delta t - ?$$

Solution:

$$\frac{v_2}{v_1} = \gamma^{\frac{\Delta t}{10}}$$

$$32 = 2^{\frac{\Delta t}{10}}$$

$$\lg 32 = \frac{\Delta t}{10} \lg 2$$

$$\frac{\Delta t}{10} = \frac{\lg 32}{\lg 2}$$

$$\Delta t = 10 \frac{\lg 32}{\lg 2} = 50$$

Answer: The temperature should be raised by 50 °C.

Example 6

When the temperature rises from 20°C to 50°C, the reaction rate increases 20 times. Calculate the temperature coefficient of the reaction.

Given:

$$\frac{v_2}{v_1} = 20$$

$$t_1 = 20^\circ\text{C}$$

$$t_2 = 50^\circ\text{C}$$

Find:

$$\gamma - ?$$

Solution:

$$\frac{v_2}{v_1} = \gamma^{\frac{\Delta t}{10}}$$

$$\gamma^{\frac{60-20}{10}} = 20$$

$$\gamma^3 = 20$$

$$\gamma = \sqrt[3]{20} = 2,7$$

Answer $\gamma = 2,7$

Example 7

The mass concentration of sucrose in the initial solution is 100 g / l. Hydrolysis of sucrose in 1 liter of solution (pH = 1) at a temperature of 20°C for 5 hours formed 3.96 g of glucose. Determine a) the rate constant of sucrose hydrolysis at 20°C; b) the half-life.

Given:

$$\rho_0(C_{12}H_{22}O_{11}) = 100 \text{ g/l}$$

$$m(C_6H_{12}O_6) = 3,96 \text{ g}$$

$$V(s - n) = 1 \text{ l}$$

$$t = 5 \text{ h.}$$

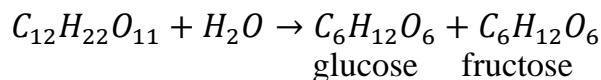
Find:

$$\text{a) } k - ?$$

$$\text{b) } \tau_{1/2} - ?$$

Solution:

Write the reaction equation:



Sucrose inversion is a first-order reaction, the kinetic equation is:

$$v = k \cdot c(C_{12}H_{22}O_{11})$$

1) Initial molar concentration of sucrose:

$$c_0(C_{12}H_{22}O_{11}) = \frac{\rho_0(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11})} = \frac{100 \text{ g/l}}{342 \text{ g/mol}} = 0,292 \text{ mol/l}$$

2) According to the reaction equation, 1 mol of glucose is formed from 1 mol of sucrose, and 0.022 mol of glucose is formed under the condition of the problem:

$$n(C_6H_{12}O_6) = \frac{m(C_6H_{12}O_6)}{M(C_6H_{12}O_6)} = \frac{3,96 \text{ g}}{180 \text{ g/mol}} = 0,022 \text{ mol}$$

therefore, 0.022 mol of sucrose reacted.

3) At the time when the solution formed 3.96 g of glucose, the concentration of sucrose decreased by 0,022 mol / l (under the condition of the problem $V(s - n) = 1 \text{ l}$):

$$c(C_{12}H_{22}O_{11}) = 0,292 \text{ mol/l} - 0,022 \text{ mol/l} = 0,27 \text{ mol/l}$$

4) The rate constant is calculated using the integral form of the kinetic equation of the reaction of the first order:

$$k = \frac{2,3}{t} \lg \frac{c_0(C_{12}H_{22}O_{11})}{c(C_{12}H_{22}O_{11})}$$

$$k = \frac{2,3}{5 \text{ h}} \lg \frac{0,292 \text{ mol/l}}{0,27 \text{ mol/l}} = 0,0156 \text{ h}^{-1} \quad (4,35 \cdot 10^{-6} \text{ s}^{-1})$$

5) The half-life is inversely proportional to the rate constant:

$$\tau_{1/2} = \frac{2,3 \cdot \lg 2}{k} = \frac{2,3 \cdot \lg 2}{0,0156 \text{ h}^{-1}} = 44,4 \text{ h}$$

Answer:

$$\text{a) } k = 0,0156 \text{ h}^{-1} \quad (\text{or } 4,35 \cdot 10^{-6} \text{ s}^{-1});$$

$$\text{b) } \tau_{1/2} = 44,4 \text{ h}$$

Example 8

The rate of excretion of phenobarbital from the body is described by a first-order kinetic equation. Withdrawal time of 50% of the drug is 80 hours. Determine the time during which 99% of phenobarbital will be excreted from the body after taking a tablet containing 0.1 g of the drug.

Given:**Find:**

$$\left. \begin{array}{l} m_0 = 0,1g \\ m_{\text{ВИБ.}} = 0,99m_0 = 0,099g \\ \tau_{1/2} = 80h \end{array} \right| t-?$$

Solution:

1. After excretion of 0.099 g (99% of the administered 0.1 g) in the body left 0.001 g of the drug:

$$m = m_0 - m_{\text{exc.}} = 0,1g - 0,099g = 0,001g$$

2. Calculate the rate constant using the values of the half-life:

$$k = \frac{2,3 \cdot \lg 2}{\tau_{1/2}} = \frac{2,3 \cdot \lg 2}{80h} = 8,65 \cdot 10^{-3} h^{-1}$$

3. Write the kinetic equation of the reaction of the first order:

$$k = \frac{2,3}{t} \lg \frac{c_0}{c} \implies t = \frac{2,3}{k} \lg \frac{c_0}{c}$$

replace the ratio of molar concentrations with the ratio of masses:

$$c(x) = \frac{m(x)}{M(x) \cdot V(s-n)} \implies \frac{c_0}{c} = \frac{m_0}{m} \implies t = \frac{1}{k} \ln \frac{m_0}{m},$$

therefore, the excretion time of 99% of the drug is equal to

$$t = \frac{2,3}{k} \lg \frac{m_0}{m} = \frac{2,3}{8,65 \cdot 10^{-3}} \lg \frac{0,1}{0,001} = 532h \approx 22day$$

Answer: $\approx 22 \text{ days}$

Self-test questions

2.1 Calculate the average reaction rate (in mol / (l · s)) of dehydrogen halogenation of bromethane in alkaline alcohol solution, if the initial concentration of bromethane was 0.1 mol / l, and after 33 hours of stirring at room temperature - 0.75 mol / l. The obtained answer is compared with example 1.

Answer: $v = 2,1 \cdot 10^{-7} \frac{\text{mol}}{\text{l} \cdot \text{s}}$

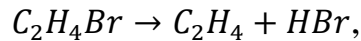
2.2 2 l of solution of substance A (concentration 0.6 mol / l) was mixed with 3 l of solution of substance B (0.4 mol / l). After 30 minutes, the concentration of substance A in the reaction mixture was 0.1 mol / L. Calculate the concentration of substance B in the reaction mixture at the moment and the average reaction rate $A + B \rightarrow AB$.

Answer: $v = 7,8 \cdot 10^{-5} \frac{\text{mol}}{\text{l} \cdot \text{s}}$
 $c(B) = 0,1 \text{ mol/l}$

2.3 Hydrolysis of sucrose in 1 l of aqueous solution at 50 ° C in the presence of acid (pH = 1) for 30 minutes formed 17.8 g of glucose. Determine the average rate of hydrolysis of sucrose.

Answer: $v = 5,5 \cdot 10^{-5} \frac{\text{mol}}{\text{l} \cdot \text{s}}$

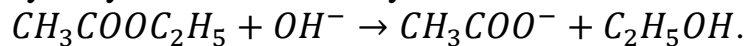
2.4 How will the rate of homogeneous gas-phase reaction change?



if a) the pressure in the system is halved; b) reduce the HBr concentration by 2 times; c) reduce the concentration of $\text{C}_2\text{H}_4\text{Br}$ by 3 times.

Answer: a) will increase 2 times;
b) will not change;
c) will decrease 3 times.

2.5 The alkaline hydrolysis reaction of ethyl acetate is of the second order



How will the rate of hydrolysis of ethyl acetate change, if a) the concentration of ions OH^- increase 2 times, and the concentration of ethyl acetate decrease 4 times. b) reduce the concentration of $\text{C}_2\text{H}_5\text{OH}$ times.

Answer: a) will decrease by 2 times;
b) will not change.

2.6 Homogeneous gas-phase reaction $\text{A} + 2\text{B} \rightarrow \text{AB}_2$ has the third order. How will the reaction rate change if a) the pressure in the system is reduced by 4 times; b) increase the concentration of AB_2 4 times; c) increase the concentration of B 4 times.

Answer: a) will increase 64 times;
b) will not change;
c) will increase 16 times.

2.7 Alkaline hydrolysis of ethyl acetate is a 2nd order reaction with a rate constant $k = 0,084 \text{ l}/(\text{mol} \cdot \text{s})$ at 25°C . The initial concentrations are as follows: $c_0(\text{CH}_3\text{COOC}_2\text{H}_5) = 0,05 \text{ mol/l}$; $c_0(\text{OH}^-) = 0,1 \text{ mol/l}$. Calculate a) the initial reaction rate; b) the concentration of ethyl acetate and the reaction rate at the moment when the concentration of ions OH^- will be equal to $0,07 \text{ mol/l}$.

Answer: $v_0 = 4,2 \cdot 10^{-4} \text{ mol}/(\text{l} \cdot \text{s})$;
 $v = 1,2 \cdot 10^{-4} \text{ mol}/(\text{l} \cdot \text{s})$;
 $c(\text{CH}_3\text{COOC}_2\text{H}_5) = 0,02 \text{ mol/l}$.

2.8 In the gas reaction of the 2nd order $\text{A} + \text{B} \rightarrow \text{AB}$, the initial concentrations of substances are equal to $0,5 \text{ mol/l}$ and $1,2 \text{ mol/l}$, respectively. The initial reaction rate is $1,2 \cdot 10^{-3} \text{ mol}/(\text{l} \cdot \text{s})$. Calculate the rate constant and the reaction rate at the moment when the concentration of substance B is 1 mol/l

Answer: $k = 2 \cdot 10^{-3} \text{ l}/(\text{mol} \cdot \text{s})$;
 $v = 6 \cdot 10^{-4} \text{ mol}/(\text{l} \cdot \text{s})$.

2.9 The reaction $2\text{A} + \text{B} \rightarrow \text{AB}$ is trimolecular. The initial concentrations of substances are as follows: $c_0(\text{A}) = 2,5 \text{ mol/l}$, $c_0(\text{B}) = 1,5 \text{ mol/l}$. The reaction rate constant $k = 0,8 \text{ l}^2/(\text{mol}^2 \cdot \text{s})$. Calculate the concentration of substance A and the

reaction rate at a time when the concentration of substance B will be equal to 0.5 mol / l.

Answer: $c(A) = 0,5 \text{ mol/l};$
 $v = 0,2 \text{ mol/(l} \cdot \text{s)}.$

2.10 How many times will the rate constant of a chemical reaction increase with increasing temperature from 0 ° C to 70 ° C if $\gamma = 2$?

Answer: 128

2.11 Calculate the rate of the chemical reaction at a temperature of 100°C, if at 50°C, the rate of this reaction was equal to $1,2 \cdot 10^{-3} \text{ mol/(l} \cdot \text{s)}$ ($\gamma = 3$).

Answer: $v = 0,292 \text{ mol/(l} \cdot \text{s)}.$

2.12 How many degrees should the temperature be increased so that the reaction rate increases 256 times ($\gamma = 4$)?

Answer: $\Delta t = 40^\circ\text{C}$

2.13 To what temperature should the reaction mixture be heated so that the reaction rate increases to 0.1134 mol/ (1 s), if at 20 ° C it is equal to $1,4 \cdot 10^{-3} \text{ mol/(l} \cdot \text{s)}$ ($\gamma = 3$)?

Answer: $t = 60^\circ\text{C}$

2.14 When the temperature rises from 20°C to 50°C, the reaction rate increases 27 times. Calculate the temperature coefficient of the reaction.

Answer: $\gamma = 3$

2.15 Calculate the temperature coefficient of the reaction if the rate constant of this reaction at 0 ° C and at 60 ° C is equal to $1,8 \cdot 10^{-5} \text{ mol/(l} \cdot \text{s)}$ and $1,152 \cdot 10^{-3} \text{ mol/(l} \cdot \text{s)}$ respectively.

Answer: $\gamma = 2$

2.16 The temperature coefficient of the gas reaction $2A + B \rightarrow AB$ is equal to 3. How will the reaction rate change when the temperature increases from 40°C to 80°C and simultaneously increases the pressure by 2 times?

Answer: will increase 648 times

2.17* The mass concentration of sucrose in the initial solution is equal to 200 g / l. During the hydrolysis of sucrose in 1 liter of solution (pH = 1) at a temperature of 50°C for 1 hour formed 63.2 g of glucose. Determine a) the constant of the rate of hydrolysis of sucrose at 50°C; b) the half-life. The obtained answer compare with example 7.

Answer: a) $k = 2,54 \cdot 10^{-4} \text{ s}^{-1}$;
b) $\tau_{1/2} = 45,4 \text{ min}.$

2.18* The rate of excretion of acetylsalicylic acid (aspirin) from the body is described by a first-order kinetic equation. Withdrawal time of 50% of the drug is 15 minutes. Determine the time during which 99% of aspirin will be excreted from the body after taking a tablet containing 0.5 g of the drug.

Answer: 100min

2.19* The rate of excretion of chlorpromazine from the body is described by a first-order kinetic equation. Withdrawal time of 50% of the drug is 40 hours. Determine the time during which 90% of chlorpromazine will be excreted from the body after taking a tablet containing 0.025 g of the drug.

Answer: 133h

2.20* The rate of excretion of the drug arbidol-lens from the body is described by the kinetic equation of the 1st order. Withdrawal time of 50% of the drug is 19 hours. How often do you need to take the drug (tablet contains 0.1 anhydrous substance) to maintain its amount in the body at a level not lower than 0.075 g?

Answer: every 8 hours

2.21* Decomposition of novocaine in aqueous solution is a first-order reaction, the rate constant at 20 ° C is equal to $1,4 \cdot 10^{-6} h^{-1}$. Determine the time during which the mass fraction of novocaine in the solution stored at 20°C will decrease from 2% to 1.94%.

Answer: 906days

2.22* The rate constant of ascorbic acid decomposition at 25 ° C is equal to $5,25 \cdot 10^{-6} h^{-1}$. Calculate the time for which 10% of the drug disintegrates.

Answer: 835 days

2.23* What proportion (%) of novocaine will decompose in 100 days of its storage at 25°C, if the rate constant of decomposition of novocaine at 25°C is equal to $2 \cdot 10^{-6} h^{-1}$.

Answer: 0.48% of the original amount

3. Chemical equilibrium. The product of solubility

The main values used to describe the equilibrium states

Parameter	Marking, Unit	Content value
Equilibrium constant (expressed by concentration)	<p>For the reaction</p> $aA + bB \rightleftharpoons cC + dD$ $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$ $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^{b'}}$ <p>where the square brackets denote the equilibrium concentrations of the participants in the reaction (in mol / l).</p>	<p>Equals the ratio of the product of the equilibrium concentrations of the reaction products to the product of the equilibrium concentrations of the reagents in degrees equal to the stoichiometric coefficients. Knowing the equilibrium constant of the reaction, it is possible to calculate the equilibrium composition of the reaction mixture, the yield of products, to determine the direction of the reaction. The greater the K value, the stronger the equilibrium is shifted toward the formation of direct reaction products. Very large value of K (corresponds to almost complete conversion of starting materials into products, and very small value (indicates that the direct reaction is practically impossible.</p>
Dissociation constant	<p>For acid: $HAn \rightleftharpoons H^+ + An^-$</p> $K_a = \frac{[H^+] \cdot [An^-]}{[HAn]}$ <p>For the basics:</p> $KtOH \rightleftharpoons Kt^+ + OH^-$	<p>Dissociation constant</p> <p>For acid: For the basics: An equilibrium constant describing the dissociation of a weak</p>

	$K_b = \frac{[OH^-] \cdot [Kt^+]}{[KtOH]}$	electrolyte is used to quantify the electrolyte force.
Instability constant	$MeL_n \rightleftharpoons Me + nL$ $K_{inst.} = \frac{[Me] \cdot [L]^n}{[MeL_n]}$	An equilibrium constant describing the dissociation of a complex ion is used to quantify the stability of the inner sphere of the coordination compound.
Solubility product	$Kt_n An_m \rightleftharpoons nKt^{m+} + mAn^{n-}$ $SP = [Kt^{m+}]^n \cdot [An^{n-}]^m$	Equilibrium constant describing equilibrium between ions in saturated solution and solid phase; used to quantify the solubility of a low soluble electrolyte. Equilibrium constant describing equilibrium between ions in saturated solution and solid phase; used to quantify the solubility of a low soluble electrolyte.

Shift of chemical equilibrium.

Le Chatelier principle: If an equilibrium system exerts an external influence, the equilibrium will shift to reduce the effect of the external influence.

Chemical equilibrium can be offset by changes in temperature, pressure or concentrations of substances by their removal or introduction into the system.

1. Increasing temperature shifts the equilibrium toward cooling, that is, promotes the reaction in which heat is absorbed. If the direct reaction is exothermic, the equilibrium when heated shifts to the left, and if the direct reaction is endothermic, then to the right. Lowering the temperature shifts the equilibrium towards heating, that is, promotes an exothermic reaction.

2. Pressure affects only reversible gas reactions, and only those in which the total number of gas molecules changes. Increasing the pressure shifts the equilibrium towards the reaction, which goes with the decrease in the total number of gas molecules, and the decrease in pressure - towards the reaction, which goes with the increase in the number of molecules.

3. Adding to the equilibrium mixture of any of the components of the reaction shifts the equilibrium toward reducing the amount of substance of this component.

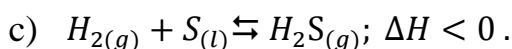
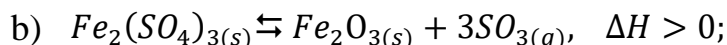
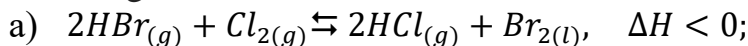
Increasing the concentration of starting materials and removing the reaction products shift the equilibrium toward a direct reaction.

4. Catalysts do not affect the equilibrium position, but only accelerate the equilibrium state.

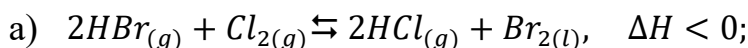
Examples of exercises.

Example 1

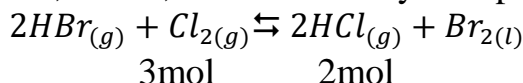
How will the increase in pressure and temperature affect the equilibrium of the following reactions:



Solution:

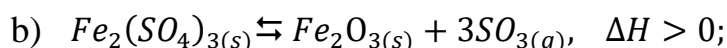


The reaction in the forward direction leads to a decrease in the total number of gas molecules, that is, a decrease in system pressure:

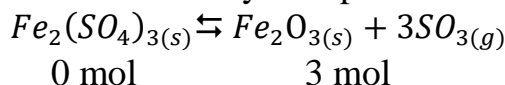


Therefore, according to the Le Chatelier principle, an increase in pressure causes a shift of equilibrium towards a direct reaction (right).

As can be seen from the reaction equation, the direct reaction is exothermic ($\Delta H < 0$), that is, with heat release. Therefore, an increase in temperature causes a shift in equilibrium toward the endothermic feedback (left).

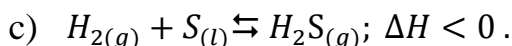


The reaction in the forward direction leads to an increase in the total number of gas molecules, that is, an increase in system pressure:

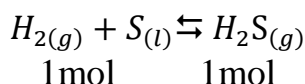


Therefore, according to the Le Chatelier principle, an *increase in pressure* causes a shift of equilibrium toward a backward reaction (left).

As can be seen from the reaction equation, the direct reaction is endothermic ($\Delta H > 0$), that is, it goes with heat absorption. Therefore, an *increase in temperature* causes a shift of equilibrium toward a direct reaction (right).



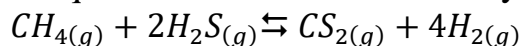
The *pressure* does not affect the position of chemical equilibrium, since in the forward and reverse reactions the total number of gas molecules does not change:



As can be seen from the reaction equation, the direct reaction is exothermic ($\Delta H < 0$), that is, with heat release. Therefore, *an increase in temperature* causes a shift in equilibrium toward the endothermic feedback (left).

Example 2

How it will affect the equilibrium concentration of hydrogen in the system



increasing the concentration of methane CH_4 ?

Solution:

According to the Le Chatelier principle, as the concentration of the starting materials increases, the equilibrium shifts towards product formation, ie to the right. Therefore, increasing the concentration of methane starting material will lead to an increase in the rate of direct reaction and, accordingly, an increase in the equilibrium concentration of hydrogen.

Example 3

What conditions (temperature, pressure) help to increase the yield of reaction products in the following cases:

- a) $NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4Cl_{(s)}, \quad \Delta H < 0;$
b) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}, \quad \Delta H > 0.$

Solution:

To increase the yield of products it is necessary to cause a shift of chemical equilibrium towards a direct reaction.

- a) $NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4Cl_{(s)}, \quad \Delta H < 0;$

The direct reaction is exothermic, its flow will be facilitated by a decrease in temperature. Direct reaction leads to a decrease in the total number of gas molecules, its leakage will contribute to the increase in pressure.

Therefore, the optimal conditions for increasing the yield of the reaction products are low temperature, high pressure.

- b) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}, \quad \Delta H > 0.$

The direct reaction is endothermic, its flow will be facilitated by an increase in temperature. Direct reaction leads to an increase in the total number of gas molecules, its leakage will contribute to a decrease in pressure.

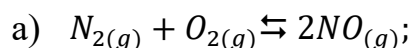
Therefore, the optimal conditions for increasing the yield of the reaction products are high temperature, low pressure.

Example 4

Write an expression for the equilibrium constants of the following reactions:

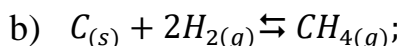
- a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)};$
b) $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)};$
c) $HF_{(so-n)} \rightleftharpoons H^+_{(so-n)} + F^-_{(so-n)}.$

Solution:



The coefficient at NO is 2, so the concentration of nitrogen oxide in expression for the equilibrium constant is squared; other concentrations are the expression for the equilibrium constant in the first degree. The concentration of the product - NO - in the numerator, the concentration of starting materials - N₂ and O₂ - in the denominator:

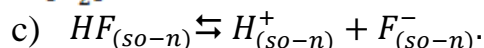
$$K = \frac{[NO]^2}{[N_2] \cdot [O_2]} .$$



Carbon in this reaction is a pure solid; it is not included in the expression for the equilibrium constant, since the concentration of a pure solid or liquid is always constant. Only gases are included in the equilibrium constant, since their concentration depends on the conditions, and (or) liquid and solids in solution, where their concentration may change

For this reaction, the expression for the equilibrium constant includes only the concentrations of hydrogen and methane. The coefficient at H₂ is 2, so the concentration of hydrogen in the expression for the equilibrium constant is squared; the concentration of methane is an expression for the equilibrium constant in the first degree. The concentration of the product - CH₄ - in the numerator, the concentration of the starting material - H₂ - in the denominator:

$$K = \frac{[CH_4]}{[H_2]^2} .$$

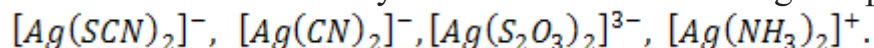


The reaction occurs in solution, so the expression for the equilibrium constant includes the concentrations of all three particles involved in the reaction, with all concentrations in the first degree. The concentration of the starting material - undissociated HF - in the denominator, the concentration of the products - H⁺ and F⁻ - in the numerator:

$$K = \frac{[H^+] \cdot [F^-]}{[HF]} .$$

Example 5

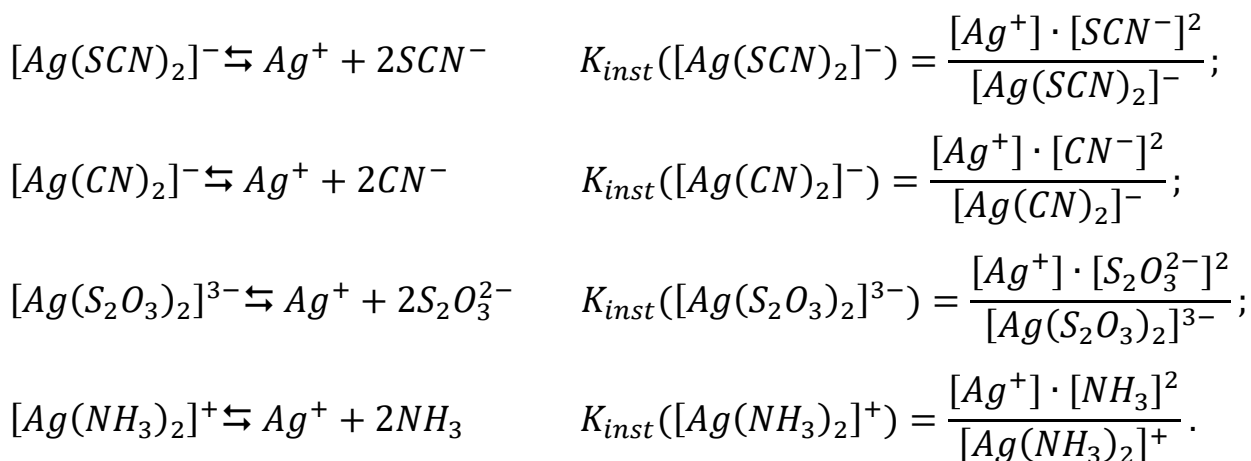
Write the instability constants of the following complex ions:



Which of the following complex ions is the most stable and which is the least stable?

Solution:

The dissociation of the complex ion in solution is quantitatively characterized by the instability constant (the equilibrium constant of the dissociation process of the complex ion):



The stability of homogeneous complex ions can be compared by comparing the values of the instability constants (see Annex 3):

$$K_{inst}([Ag(SCN)_2]^-) = 5,89 \cdot 10^{-9} \text{ mol}^2 / \text{l}^2;$$

$$K_{inst}([Ag(CN)_2]^-) = 1 \cdot 10^{-21} \text{ mol}^2 / \text{l}^2;$$

$$K_{inst}([Ag(S_2O_3)_2]^{3-}) = 3,47 \cdot 10^{-14} \text{ mol}^2 / \text{l}^2;$$

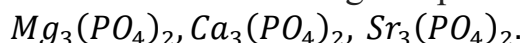
$$K_{inst}([Ag(NH_3)_2]^+) = 1,0 \cdot 10^{-7} \text{ mol}^2 / \text{l}^2.$$

The smaller the instability constant, the more stable the complex ion is.

Answer : the most stable is the complex ion $[Ag(CN)_2]^-$
least stable - $[Ag(NH_3)_2]^+$.

Example 6

Write the solubility expressions of the following compounds:



Which of the following compounds is most soluble in water?

Solution:

Solubility Product Expressions:

$$SP(Mg_3(PO_4)_2) = [Mg^{2+}]^3 \cdot [PO_4^{3-}]^2;$$

$$SP(Ca_3(PO_4)_2) = [Ca^{2+}]^3 \cdot [PO_4^{3-}]^2;$$

$$SP(Sr_3(PO_4)_2) = [Sr^{2+}]^3 \cdot [PO_4^{3-}]^2$$

The solubility of the same low-soluble electrolytes can be compared by comparing the values of the solubility products (see Annex 4):

$$\therefore SP(Mg_3(PO_4)_2) = 1,04 \cdot 10^{-24} \text{ mol}^5 / \text{l}^5;$$

$$SP(Ca_3(PO_4)_2) = 2,07 \cdot 10^{-33} \text{ mol}^5 / \text{l}^5;$$

$$SP(Sr_3(PO_4)_2) = 1,0 \cdot 10^{-31} \text{ mol}^5 / \text{l}^5.$$

The greater the solubility product, the more soluble the compound is.

Answer: the most water-soluble compound $Mg_3(PO_4)_2$.

Example 7

What processes will occur in a solution containing equal amounts of ions Cl^- , Br^- , I^- , when cation is added to it Ag^+ ?

Solution:

The solution will consistently precipitate. The competition for the common ion is won by the poorly soluble electrolyte that binds strongly (the lowest value of SP) to the precipitant ion.

The solubilities of the compounds are given in Annex 4:

$$SP(AgI) = 8,52 \cdot 10^{-17} \text{ mol}^2/\text{l}^2;$$

$$SP(AgBr) = 5,35 \cdot 10^{-13} \text{ mol}^2/\text{l}^2;$$

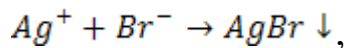
$$SP(AgCl) = 1,77 \cdot 10^{-10} \text{ mol}^2/\text{l}^2.$$

Because

$$SP(AgI) < SP(AgBr) < SP(AgCl)$$

then the first precipitates $Ag^+ + I^- \rightarrow AgI \downarrow$,

then



and last $Ag^+ + Cl^- \rightarrow AgCl \downarrow$.

Example 8

What changes will occur if the solution is in equilibrium with the precipitate $CaSO_4$, add H_2SO_4 ?

Solution:

Solubility product - the value of steel at a certain temperature

$$SP(CaSO_4) = [Ca^{2+}] \cdot [SO_4^{2-}] = \text{const}$$

When H_2SO_4 is added to a saturated solution of $CaSO_4$, the concentration of ions SO_4^{2-} increases, causing the concentration of ions Ca^{2+} decreases in such a way that their output remains constant.

Answer : $SP(CaSO_4)$ will not change, the molar concentration of Ca^{2+} ions will decrease, because the molar concentration of SO_4^{2-} ions will increase

Example 9

Bone tissue begins to form in the blood plasma. Is it enough the concentration of calcium cation in the free state $c(\text{Ca}^{2+}) = 1,0 \cdot 10^{-3} \text{ mol/l}$ to precipitate CaHPO_4 ? With respect to the concentration of hydrophosphate ions, it is in the blood plasma $c(\text{HPO}_4^{2-}) = 2,9 \cdot 10^{-4} \text{ mol/l}$.

Given:

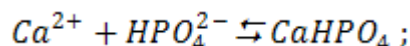
$$c(\text{Ca}^{2+}) = 1,0 \cdot 10^{-3} \text{ mol/l}$$
$$c(\text{HPO}_4^{2-}) = 2,9 \cdot 10^{-4} \text{ mol/l}$$

Find:

$$Q - ?$$

Solution:

Record the reaction equation:



The precipitate is a ratio $Q > SP$, where Q - the product of concentrations of ions of the insoluble electrolyte; SP - solubility product (reference value, see Annex 4):

$$SP(\text{CaHPO}_4) = 2,7 \cdot 10^{-7} \frac{\text{mol}^2}{\text{l}^2}$$

Calculate the product of concentrations

$$\begin{aligned} \Delta K &= c(\text{Ca}^{2+}) \cdot c(\text{HPO}_4^{2-}) = 1,0 \cdot 10^{-3} \text{ mol/l} \cdot 2,9 \cdot 10^{-4} \text{ mol/l} \\ &= 2,9 \cdot 10^{-7} \text{ mol}^2/\text{l}^2; \end{aligned}$$

Compare the calculated value of the product of concentrations with the table value of the product of solubility:

$$2,9 \cdot 10^{-7} > 2,7 \cdot 10^{-7} \implies \text{a precipitate is formed}$$

Answer: a precipitate is formed because $Q > SP$

Example 10

Will precipitation precipitate when mixing equal volumes of AgNO_3 and H_2SO_4 solutions with a molar concentration of 0.02 mol/l ?

Given:

$$c_0(\text{AgNO}_3) = 0,02 \text{ mol/l}$$

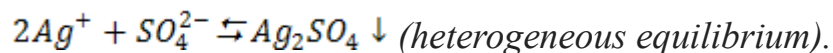
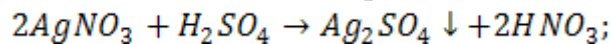
Find:

$$Q - ?$$

$$\begin{array}{l} c_0(H_2SO_4) = 0,02 \text{ mol/l} \\ V(AgNO_3) = V(H_2SO_4) \end{array} \quad \left| \right.$$

Solution:

1. Record the reaction equation:



The precipitate is a ratio $Q > SP$, where Q - the product of concentrations of ions of the insoluble electrolyte; SP - solubility product (reference value, see Annex 4):

$$SP(Ag_2SO_4) = 1,2 \cdot 10^{-5} \text{ mol}^3/\text{l}^3$$

2. Under the condition of the problem, the solution volumes are merged, so the salt concentration is halved:

$$c(AgNO_3) = \frac{c_0(AgNO_3)}{2} = \frac{0,02 \text{ mol/l}}{2} = 0,01 \text{ mol/l};$$

$$c(Na_2SO_4) = \frac{c_0(Na_2SO_4)}{2} = \frac{0,02 \text{ mol/l}}{2} = 0,01 \text{ mol/l}.$$

3. Because salts $AgNO_3$ and Na_2SO_4 are strong electrolytes, molar concentrations Ag^+ and SO_4^{2-} equal to the total concentrations $AgNO_3$ and Na_2SO_4 :

$$c(Ag^+) = c(AgNO_3) = 0,01 \text{ mol/l};$$

$$c(SO_4^{2-}) = c(Na_2SO_4) = 0,01 \text{ mol/l}.$$

4. Calculate the product of concentrations Ag^+ and SO_4^{2-} in resulting solution

$$Q(Ag_2SO_4) = c^2(Ag^+) \cdot c(SO_4^{2-})$$

$$Q(Ag_2SO_4) = (0,01 \text{ mol/l})^2 \cdot 0,01 \text{ mol/l} = 1 \cdot 10^{-6} \text{ mol}^3/\text{l}^3$$

Compare the calculated value of the product of concentrations with the table value of the product of solubility:

$$1 \cdot 10^{-6} < 1,2 \cdot 10^{-5} \implies$$

no precipitate is formed.

Answer: a precipitate is not formed because
 $Q < SP$

Example 11

Calculate the mass concentration of argentum bromide ρ (AgBr) in saturated solution if the product of AgBr solubility is $5,35 \cdot 10^{-13} \text{ mol}^2/\text{l}^2$. $M(\text{AgBr}) = 188 \text{ g/mol}$.

Given:

$$SP(\text{AgBr}) = 5,35 \cdot 10^{-13} \text{ mol}^2/\text{l}^2$$

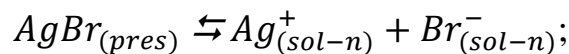
$$M(\text{AgBr}) = 188 \text{ g/mol}$$

Find:

$$\rho(\text{AgBr}) - ?$$

Solution:

- Record the heterogeneous equilibrium equation and the expression for the solubility product *AgBr*:



$$SP(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-].$$

- Calculate the molar concentration of AgBr in saturated solution:

$$[\text{Ag}^+] = [\text{Br}^-] = c(\text{AgBr})$$

$$SP(\text{AgBr}) = [\text{Ag}^+][\text{Br}^-] = c^2(\text{AgBr})$$

$$c(\text{AgBr}) = \sqrt{SP} = \sqrt{5,35 \cdot 10^{-13} \text{ mol}^2/\text{l}^2} = 7,31 \cdot 10^{-7} \text{ mol/l}$$

- Calculate mass concentration *AgBr*:

$$\rho(\text{AgBr}) = M(\text{AgBr}) \cdot c(\text{AgBr})$$

$$\rho(\text{AgBr}) = 188 \text{ g/mol} \cdot 7,31 \cdot 10^{-7} \text{ mol/l} = 1,37 \cdot 10^{-4} \text{ g/l}$$

Answer: $\rho(\text{AgBr}) = 1,37 \cdot 10^{-4} \text{ g/l}$

Example 12

Will the precipitate Ag_2SO_4 fall as the mass concentration of Ag_2SO_4 in solution to $3,12 \text{ g/l}$.

Given:

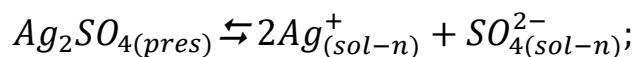
$$\rho(\text{Ag}_2\text{SO}_4) = 3,12 \text{ g/l}$$

Find:

$$Q(\text{Ag}_2\text{SO}_4) - ?$$

Solution:

1. Record the heterogeneous equilibrium equation and the expression for the solubility product Ag_2SO_4 :



$$SP = [Ag^+]^2[SO_4^{2-}];$$

Tabular value $SP(Ag_2SO_4) = 1,2 \cdot 10^{-5} mol^3/l^3$.

2. Calculate the molar concentration Ag_2SO_4 in solution:

$$c(Ag_2SO_4) = \frac{\rho(Ag_2SO_4)}{M(Ag_2SO_4)} = \frac{3,12 g/l}{312 g/mol} = 0,01 mol/l.$$

3. Calculate the product of concentrations Ag^+ and SO_4^{2-} in solution :

$$c(Ag^+) = 2 \cdot c(Ag_2SO_4);$$

$$c(SO_4^{2-}) = c(Ag_2SO_4);$$

$$\begin{aligned} Q(Ag_2SO_4) &= c^2(Ag^+) \cdot c(SO_4^{2-}) = (2 \cdot c(Ag_2SO_4))^2 \cdot c(Ag_2SO_4) \\ &= 4 \cdot c^3(Ag_2SO_4) \end{aligned}$$

$$Q(Ag_2SO_4) = 4 \cdot (0,01 mol/l)^3 = 4 \cdot 10^{-6} mol^3/l^3.$$

Compare the calculated value of the product of concentrations with the table value of the product of solubility:

$$4 \cdot 10^{-6} < 1,2 \cdot 10^{-5} \implies$$

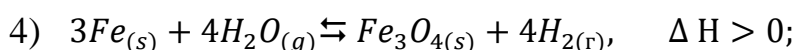
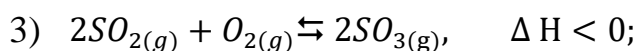
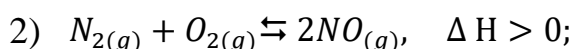
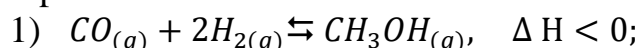
no precipitate is formed.

Answer: the precipitate will not fall out because $Q < SP$.

Self-test questions.

3.1 For subsequent reversible homogeneous and heterogeneous reactions

- ✓ write expressions of equilibrium constants;
- ✓ determine how the increase in a) pressure and b) temperature will affect the equilibrium state;
- ✓ indicate the action of which factors can increase the yield of direct reaction products.



- 5) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, $\Delta H > 0$;
- 6) $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$, $\Delta H < 0$;
- 7) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, $\Delta H < 0$;
- 8) $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$, $\Delta H > 0$;
- 9) $MnO_{2(s)} + 2H_{2(g)} \rightleftharpoons MnO_{(s)} + 2H_2O_{(g)}$, $\Delta H > 0$;
- 10) $NH_{3(g)} + CO_{2(g)} + H_2O_{(g)} \rightleftharpoons NH_4HCO_{3(s)}$, $\Delta H < 0$.

3.2 Compare the stability of complex ions:

- 1) $[CaCit]^-$, $[CaEdta]^{2-}$, $[Ca(P_2O_7)]^{2-}$, $[Ca(P_3O_9)]^-$, $[Ca(P_4O_{12})]^{2-}$;
- 2) $[Fe(C_2O_4)_3]^{3-}$, $[FeF_6]^{3-}$, $[Fe(SCN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$;
- 3) $[CaEdta]^{2-}$, $[HgEdta]^{2-}$, $[PbEdta]^{2-}$, $[CdEdta]^{2-}$.

3.3 Write expressions of solubility products for the given compounds. Determine which compound is a) the most soluble; b) the least soluble in water.

- 1) $AgBr$, FeS , $AlPO_4$, $PbSO_4$;
- 2) $PbCl_2$, PbI_2 , CaF_2 , BaF_2 ;
- 3) CaC_2O_4 , $PbCO_3$, CdC_2O_4 , NiS , $BaSO_4$.

3.4 What processes will take place in a solution containing equal amounts of ions Cl^- , Br^- , I^- , when the cation Pb^{2+} is added to it?

3.5 What processes will take place in a solution containing equal amounts of ions Ba^{2+} , Mg^{2+} , Ca^{2+} , Pb^{2+} when anion $C_2O_4^{2-}$ is added to it?

3.6 What changes will occur if a) Na_2CO_3 solution is added to a solution that is in equilibrium with $SrCO_3$ precipitate; b) a solution of $Sr(NO_3)_2$?

3.7 What changes will occur if a) Na_2S solution is added to a solution that is in equilibrium with the MnS precipitate; b) a solution of $MnSO_4$?

3.8 Kidney stone disease is the deposition of sparingly soluble Ca (II) salts of various compositions (urates, phosphates and oxalates). Does the formation of a precipitate of CaC_2O_4 increase the concentration of oxalate ions in blood plasma to $c(C_2O_4^{2-}) = 2 \cdot 10^{-4}$ mol/l; relative to the concentration of calcium cation in the free state, it is in the blood plasma with $c(Ca^{2+}) = 1,0 \cdot 10^{-3}$ mol/l.

Answer: $Q = 2 \cdot 10^{-7} \text{ mol}^2 / \text{l}^2$
precipitate is formed

3.9 Liver stone disease is associated with the formation of insoluble salt of calcium carbonate. Does an increase in the mass concentration to $\rho(\text{CaCO}_3) = 2,0 \cdot 10^{-3} \text{ g/l}$ lead to the formation of CaCO_3 precipitate? $M(\text{CaCO}_3) = 100 \text{ g/mol}$.

Answer: $Q = 4 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$
no precipitate is formed

3.10 Will CdC_2O_4 precipitate when the mass concentration of CdC_2O_4 in the solution increases to 0.06 g/l . $M(\text{CdC}_2\text{O}_4) = 200 \text{ g/mol}$.

Answer: $Q = 9 \cdot 10^{-8} \text{ mol}^2/\text{l}^2$
precipitate is formed

3.11 Will BaF_2 precipitate when the mass concentration of BaF_2 in the solution increases to 0.06 g . $M(\text{BaF}_2) = 175 \text{ g/mol}$.

Answer: $Q = 4,03 \cdot 10^{-11} \text{ mol}^3/\text{l}^3$
no precipitate is formed

3.12 Will precipitate $\text{Ag}_2\text{C}_2\text{O}_4$ with increasing mass concentration of $\text{Ag}_2\text{C}_2\text{O}_4$ in solution to 0.06 g/l . $M(\text{Ag}_2\text{C}_2\text{O}_4) = 304 \text{ g/mol}$.

Answer: $Q = 7,69 \cdot 10^{-12} \text{ mol}^3/\text{l}^3$
precipitate is formed

3.13 Will a precipitate be formed when mixing equal volumes of $\text{Pb}(\text{NO}_3)_2$ and CaCl_2 solutions with a molar concentration of 0.03 mol/l ?

Answer: $Q = 3,375 \cdot 10^{-6} \text{ mol}^3/\text{l}^3$
no precipitate is formed

3.14 Will precipitate be formed when mixing equal volumes of BaCl_2 and Na_2SO_4 solutions with a molar concentration of 0.01 mol/l ?

Answer: $Q = 2,5 \cdot 10^{-5} \text{ mol}^2/\text{l}^2$
precipitate is formed

3.15 Will a precipitate of equal volumes of $\text{Ca}(\text{NO}_3)_2$ and Na_2SO_4 solutions with a molar concentration of 0.01 mol/l be precipitated?

Answer: $Q = 2,5 \cdot 10^{-5} \text{ mol}^2/\text{l}^2$
no precipitate is formed

3.16 Calculate the mass concentration of Nickel sulfide $\rho(\text{NiS})$ in saturated solution. $M(\text{NiS}) = 91 \text{ g/mol}$.

Answer: $\rho(\text{NiS}) = 2,78 \cdot 10^{-9} \text{ g/l}$

3.17 Calculate the mass concentration of PbI_2 in saturated solution. $M(\text{PbI}_2) = 461 \text{ g/mol}$.

Answer: $\rho(\text{PbI}_2) = 0,986 \text{ g/l}$

3.18 Calculate the mass concentration of SrSO_4 in saturated solution. $M(\text{SrSO}_4) = 184 \text{ g/mol}$.

Answer: $\rho(\text{SrSO}_4) = 0,108 \text{ g/l}$

3.19 Calculate the mass concentration of Ag_2CO_3 in saturated solution. $M(\text{Ag}_2\text{CO}_3) = 276 \text{ g / mol}$.

Answer: $\rho(\text{Ag}_2\text{CO}_3) = 0,056 \text{ g/l}$

4. Determination of redox potential

List of basic terms, parameters, characteristics for the topic "Determination of redox potential"

Term	Definition
<i>Conductor</i>	A substance that conducts electrical current.
<i>Type I Conductor</i>	Conductors in which the charge carriers are electrons (metals and some non-metals, such as graphite).
<i>Type II Conductor</i>	Conductors in which the charge carriers are ions (electrolyte solutions and melts).
<i>Electrode</i>	A system consisting of a type I conductor (metal or semiconductor) and a type II conductor (electrolyte solution or melt).
<i>Electrode processes</i>	Physicochemical processes occurring at the interface between the conductors of the I and II conductor's types and are accompanied by the transition through this boundary of electrons and (or) ions.
<i>Electrode potential</i>	The difference between the electrostatic potentials at the boundary between the electrode and the solution, the main reason for its existence is the movement of ions between the metal surface and the solution, the spatial separation of charges of the opposite sign at the phase separation boundary, and the appearance of a double electric layer.
<i>Electroplating element</i>	A device in which the chemical energy of a redox reaction is converted into electrical energy by the spatial separation of oxidation and reduction processes. Structurally, the galvanic element consists of two electrodes forming the inner circuit: $(-)\text{Анод} \text{Анодний розчин} \text{Катодний розчин} \text{Катод}(+)$ Anode is the electrode on which the oxidation process takes place; it charges negatively in the electroplating element. A cathode is an electrode on which the recovery process takes place; in the galvanic element is charged positively. The cathode in the galvanic element becomes an electrode with a higher value of potential, the anode - an electrode with a lower value of potential.
<i>Potentiometry</i>	Physicochemical method of analysis, which is based on the dependence of the equilibrium potential of the electrode on the activity (concentration) of the test ion. To record the potential, a galvanic element (GE) must be drawn from a suitable indicator electrode and a reference electrode.
<i>Comparison electrode</i>	The electrode, whose potential is practically constant, is easily reproducible and does not depend on the occurrence of adverse reactions.

<i>Detection electrode (indicated)</i>	An electrode whose potential depends on the activity (concentration) of the detectable ions and practically does not depend on the content of other ions in solution.
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Classification of electrodes

Electrodes with electrochemical reaction

Electrodes without electrochemical reaction

Ion-exchange (ion-selective) electrodes are electrochemical circuits whose potential is determined by the processes of ion distribution between the inner (standard) solution, the membrane separating the standard and test solutions, and the external (test) solution.

Reversible relative to the cation and anion of the insoluble salt (Type II Electrodes)

The electrodes of the second kind are a metal covered with a layer of its insoluble salt. When immersed in a solution containing the anions of the same name, the electrode potential is determined by the activity (concentration) of the anions in solution

Reversible relative to ions in solution

Type I Electrodes

consist of an elemental substance in contact with a solution containing its own ions.

A *plate* made of a simple substance (*metal or non-metal*) and immersed in a solution containing ions of the metal or non-metal.

A *gas electrode* as a component of the electrode vapor contains gas (H₂, Cl₂, etc.) adsorbed on a chemically inert conductor of the first kind (usually a platinum plate covered with a layer of fine-dispersed platinum).

Redox electrodes

consist of an electrochemically inert conductor (platinum, graphite, etc.) immersed in a solution containing substances comprising the same element to varying degrees of oxidation. This solution is called the redox system.

The potential of these electrodes does not involve the electrode material. The inert electrode plays the role of a mediator in the transfer of electrons from the reduced form to the oxidized one.

Basic parameters used in potentiometry

Parameter	Designation, unit of measure	Content value
Potential of type I electrodes	$E_{M^{n+}/M}, \text{ B}$ <p>Nernst's type I electrode equation: $E_{M^{n+}/M} = E_{M^{n+}/M}^0 + \frac{2,3RT}{nF} \lg a(M^{n+})$ where: R – gas constant, $8,31 \frac{\text{V} \cdot \text{C}}{\text{mol} \cdot \text{K}}$; T – temperature, K; F – Faraday's constant, $96500 \frac{\text{C}}{\text{mol}}$; n – the number of electrons involved in the electrode process $M^{n+} + ne^- \rightleftharpoons M$; $a(M^{n+})$ – the activity of metal ions in solution, mol/l; in diluted electrolyte solutions, the activity coefficients are not very different from one, so in the Nernst equation, instead of the activity of metal cations, their molar concentration can be used; $E_{M^{n+}/M}^0$ - standard electrode potential. $T = 298\text{K}$: $E_{M^{n+}/M} = E_{M^{n+}/M}^0 + \frac{0,059}{n} \lg a(M^{n+})$</p>	<p>A leap in potential arising at the boundary between a metal and a solution containing ions of that metal.</p> <p>The absolute value of the electrode potential cannot be measured. Therefore, in practice, a so-called reference electrode is selected, the potential of which is taken to be 0 at any temperature and the potentials of all other electrodes are measured relative to it. The standard electrode is taken as the reference electrode.</p> <p><i>The electrode potential is equal to the EMF of the galvanic element composed of a standard hydrogen electrode and a test electrode.</i></p>
Standard potential for hydrogen electrode	$E_{H^+/H_2}^0 = 0$	<p>The potential of a hydrogen electrode in which the activity of H^+ ions in the solution is 1 mol / l and the pressure of hydrogen gas over the solution is 101.3 kPa (1 atm).</p>
Potential for hydrogen electrode	$E_{H^+/H_2}, \text{ V}$ <p>Nernst's equation for hydrogen electrode (when $T = 298\text{K}, p_{H_2} = 101,3\text{kPa}$): $E_{H^+/H_2} = 0,059 \cdot \lg a(H^+)$ or $E_{H^+/H_2} = -0,059 \cdot pH$</p>	<p>Depends on the activity of H^+ ions, temperature and pressure of hydrogen gas over the solution.</p>

Standard electrode potential	$E_{M^{n+}/M}^0, B$	<p>The value of the electrode potential, measured under standard conditions:</p> $T = 298K$ $a(M^{n+}) = 1 \text{ моль/л}$
Silver Chloride electrode potential (type II electrode)	<p>Nernst's equation for chlorine silver electrode (when $T = 298K$):</p> $E_{SC} = E_{x_{ce}}^0 - 0,059 \cdot \lg a(Cl^-)$ <p>де</p> $E_{SC}^0 = E_{Ag^+/Ag}^0 + 0,059 \cdot \lg SP(AgCl)$ $SP(AgCl) = a(Ag^+) \cdot a(Cl^-)$	<p>Chlorine silver electrode potential is determined by the activity (concentration) of ions Cl^- in solution.</p> <p><i>The potential of CSE in a saturated solution of KCl has a practically constant value (depends only on temperature), so it is often used as a reference electrode in potentiometric measurements.</i></p> <p><i>At 298K, the potential of saturated CSE is 0.201V</i></p>
The potential of glass pH-sensitive electrode	<p>Nernst's equation for glass electrode (при $T = 298K$):</p> $E_{ck} = const + 0,059 \cdot \lg a(H^+)$ <p>або</p> $E_{ck} = const - 0,059 \cdot pH$ <p>where <i>const</i> – the constant, which is an individual characteristic of each particular glass electrode, depends on the composition and thickness of the glass.</p>	<p>The potential of the glass electrode is determined by the activity of H^+ ions in the test solution.</p> <p><i>A glass electrode is usually used as an indicator electrode for potential metric pH determination.</i></p>
Redox potential	$E_{Ox/Red}, B$ <p>The Nernst-Peters equation (when $T = 298K$):</p> $E_{Ox/Red} = E_{Ox/Red}^0 + \frac{0,059}{n} \lg \frac{a(Ox)}{a(Red)}$ <p>n – the number of electrons involved in the redox process</p> $Ox + ne^- \rightleftharpoons Red;$ <p>a(Ox) and a(Red) – the activity (concentration) of the oxidized and reduced forms in solution, mol/l;</p> <p>$E_{Ox/Red}^0$ - standard redox potential.</p>	<p>A leap of potential arising on an inert platinum electrode immersed in a solution containing a conjugated redox pair.</p>
Standard redox potential	$E_{Ox/Red}^0, V$	<p>A leap of potential arising at the interface of platinum - a solution in which the activity of the oxidized and</p>

		reduced forms is 1 mol / l (or simply equal to each other with the equality of their stoichiometric coefficients)
Electromotive force of the galvanic element	EMF, V $E_{PC} = E_c - E_a$	The potential difference of the cathode and the anode.

Examples of exercises.

Example 1

Calculate the potential of the zinc electrode at $T = 298K$, in a solution of zinc chloride $ZnCl_2$, in which the activity of Zn^{2+} ions is equal to 0.07 mol / l.

Given:

$$T = 298K$$

$$a(Zn^{2+}) = 0,07 \text{ mol/l}$$

Find:

$$E_{Zn^{2+}/Zn} - ?$$

Solution:

Write the Nernst equation for the zinc electrode at 298K:

$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0 + \frac{0,059}{2} \lg a(Zn^{2+})$$

(2- the number of electrons in the electrode reaction $Zn^{2+} + 2e^- \rightleftharpoons Zn$)

Write the tabular value of the standard potential of the zinc electrode (Annex 5)):

$$E_{Zn^{2+}/Zn}^0 = -0,763V$$

Обчислити значення потенціалу цинкового електрода в заданому розчині:

$$E_{Zn^{2+}/Zn} = -0,763 + \frac{0,059}{2} \lg 0,07 = -0,797 \text{ B}$$

Answer: $E_{Zn^{2+}/Zn} = -0,797 \text{ V}$

Example 2

Calculate the value of the potential of the redox electrode $Pt|Sn^{4+}, Sn^{2+}$ at $T = 298K$, if the concentrations $SnCl_2$ and $SnCl_4$ are equal to 0.01 and 0.05 mol / l (assume that the activity of ions is equal to the concentration).

Given:

$$T = 298K$$

$$c(SnCl_2) = 0,01 \text{ mol/l}$$

$$c(SnCl_4) = 0,05 \text{ mol/l}$$

Find:

$$E_{Sn^{4+}/Sn^{2+}} - ?$$

Solution:

The dependence of the potential of the redox electrode on the ratio of concentrations (activities) of the oxidized and reduced forms is determined by the Nernst-Peters equation and at $T = 298K$ for this redox system has the form:

$$E_{Sn^{4+}/Sn^{2+}} = E_{Sn^{4+}/Sn^{2+}}^0 + \frac{0,059}{2} \lg \frac{c(Sn^{4+})}{c(Sn^{2+})}$$

(2- the number of electrons in the electrode reaction $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$
Tabular value of the standard redox potential for this system (see Annex 5): (2-
 $E_{Sn^{4+}/Sn^{2+}}^0 = 0,151 V$.

Calculate the value of the potential at given concentrations of oxidized and reduced forms ($c(Sn^{2+}) = c(SnCl_2)$, $c(Sn^{4+}) = c(SnCl_4)$):

$$E_{Sn^{4+}/Sn^{2+}} = 0,151 + \frac{0,059}{2} \lg \frac{0,05}{0,01} = 0,151 + 0,021 = 0,172 V$$

Answer: $E_{Sn^{4+}/Sn^{2+}} = 0,172 V$

Example 3

Calculate the activity of ions Ag^+ in solution at $T = 298K$, if the potential of the silver electrode is equal to 623mV.

Given: $T = 298K$ $E_{Ag^+/Ag} = 623mV = 0,623 V$		Find: $a(Ag^+) - ?$
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Solution:

Write the Nernst equation for a silver electrode at 298K:

$$E_{Ag^+/Ag} = E_{Ag^+/Ag}^0 + \frac{0,059}{1} \lg a(Ag^+)$$

(1- number of electrons in the electrode reaction $Ag^+ + e^- \rightleftharpoons Ag$) Write the tabular value of the standard potential of the zinc electrode (see Annex 5):

$$E_{Ag^+/Ag}^0 = 0,800V$$

Substitute the values $E_{Ag^+/Ag}$ and $E_{Ag^+/Ag}^0$ into the Nernst equation:

$$0,623 = 0,800 + 0,059 \cdot \lg a(Ag^+)$$

Обчислити значення активності іонів Ag^+ в даному розчині:

$$\lg a(Ag^+) = \frac{0,623 - 0,800}{0,059} = -3$$

$$a(Ag^+) = 10^{-3} \text{ molo/l}$$

Answer: $a(Ag^+) = 10^{-3} \text{ mol/l}$

Example 4

Calculate the concentration of ions Cu^{2+} in solution at $T = 298K$, if the potential of the copper electrode is 118 mV less than its standard value.

Given: $T = 298K$ $E_{Cu^{2+}/Cu}^0 - E_{Cu^{2+}/Cu} = 118mV = 0,118V$		Find: $c(Cu^{2+}) - ?$
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Solution:

Write the Nernst equation for a copper electrode at 298K:

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu}^0 + \frac{0,059}{2} \lg c(Cu^{2+})$$

(2- number of electrons in the electrode reaction $Cu^{2+} + 2e^- \rightleftharpoons Cu$
 Express the concentration of ions Cu^{2+}) from the Nernst equation:

$$-\frac{0,059}{2} \lg a(Cu^{2+}) = E_{Cu^{2+}/Cu}^0 - E_{Cu^{2+}/Cu}$$

$$\lg a(Cu^{2+}) = -\frac{2(E_{Cu^{2+}/Cu}^0 - E_{Cu^{2+}/Cu})}{0,059} = -\frac{2 \cdot 0,118}{0,059} = -4$$

$$a(Cu^{2+}) = 10^{-4}$$

Answer: $a(Cu^{2+}) = 10^{-4}$

Example 5

Calculate the EMF of the galvanic cell at 298K, composed of two copper electrodes with $c_1(Cu^{2+})=10^{-2} \text{ mol / l}$ and $c_2(Cu^{2+})=10^{-4} \text{ mol / l}$.

Given:

$T = 298K$

$c_1(Cu^{2+}) = 10^{-2} \text{ mol/l}$

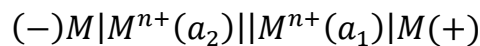
$c_2(Cu^{2+}) = 10^{-4} \text{ mol/l}$

Find:

$EMF - ?$

Solution:

Concentration galvanic cells consist of the same electrodes, which differ in different activities (concentrations) of the potential-determining ion M^{n+} in solution. From the Nernst equation it follows that for $a_1 > a_2$ EMF of the concentration element



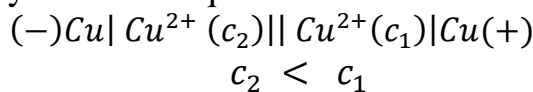
is equal to:

$$EPC = E_{1M^{n+}/M} - E_{2M^{n+}/M}$$

$$EMF = \left(E_{M^{n+}/M}^0 + \frac{0,059}{n} \lg a_1(M^{n+}) \right) - \left(E_{M^{n+}/M}^0 + \frac{0,059}{n} \lg a_2(M^{n+}) \right)$$

$$EMF = \frac{0,059}{n} \lg \frac{a_1(M^{n+})}{a_2(M^{n+})}$$

Therefore, for a concentration galvanic cell composed of copper electrodes (assume that the activity of ions is equal to the concentration):



$$EMF = \frac{0,059}{2} \lg \frac{c_1(Cu^{2+})}{c_2(Cu^{2+})}$$

$$EMF = \frac{0,059}{2} \lg \frac{10^{-2}}{10^{-4}} = \frac{0,059}{2} \lg 10^2 = 0,059 \text{ (V)}$$

Answer: EPC = 0,059 (V)

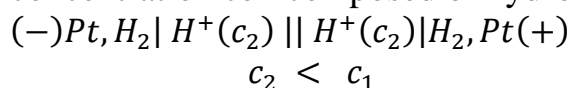
Example 6

Calculate the EMF of a galvanic cell at 298K, composed of two hydrogen electrodes with $pH_1 = 1$ i $pH_2 = 6$.

Given:	Find:
$T = 298K$	$EMF - ?$
$pH_1 = 1$	
$pH_2 = 6$	

Solution:

Scheme of a galvanic concentration cell composed of hydrogen electrodes:



$$EMF = E_{1_{H^+/H_2}} - E_{2_{H^+/H_2}} = 0,059 \cdot \lg c_1(H^+) - 0,059 \cdot \lg c_2(H^+)$$

taking into account that $pH_1 = -\lg c_1(H^+)$, $pH_2 = -\lg c_2(H^+)$:

$$\boxed{EMF = 0,059(pH_2 - pH_1)}$$

$$EMF = 0,059 \cdot (6 - 1) = 0,295 \text{ V}$$

Answer: $EMF = 0,295 \text{ V}$

Example 7

Calculate the EMF of a galvanic cell at 298K composed of a zinc electrode with $c(Zn^{2+}) = 10^{-2} \text{ mol/l}$ and a copper electrode with $c(Cu^{2+}) = 10^{-3} \text{ mol/l}$.

Given:	Find:
$T = 298K$	$EMF - ?$
$c(Zn^{2+}) = 10^{-2} \text{ mol/l}$	
$c(Cu^{2+}) = 10^{-3} \text{ mol/l}$	

Solution:

Tabular values of standard electrode potentials (see Annex 5):

$$E_{Zn^{2+}/Zn}^0 = -0,763V$$

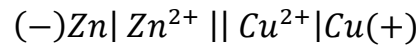
$$E_{Cu^{2+}/Cu}^0 = 0,340V$$

The potentials of the individual electrodes according to the Nernst equation are equal to:

$$E_{Cu^{2+}/Cu} = E_{Cu^{2+}/Cu}^0 + \frac{0,059}{2} \lg c(Cu^{2+}) = 0,340 + \frac{0,059}{2} \lg 10^{-3} = 0,252 \text{ (V)}$$

$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0 + \frac{0,059}{2} \lg c(Zn^{2+}) = -0,763 + \frac{0,059}{2} \lg 10^{-2} = -0,822 \text{ (V)}$$

Of the two electrodes, the cathode will be a copper electrode because it has a larger potential value. Scheme of galvanic cell:



$$EMF = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn} = 0,252V - (-0,822V) = 1,074V$$

Answer: $EMF = 1,074V$

Example 8

Calculate the EMF of a galvanic cell at 298 K composed of a silver electrode with $c(Ag^+) = 10^{-2} \text{ mol/l}$ and a silver chloride electrode immersed in a saturated KCl solution. $E_{SC} = 0,201V$.

Given:

$$c(Ag^+) = 10^{-2} \text{ mol/l}$$

$$E_{Ag^+/Ag}^0 = 0,800V$$

$$E_{SC} = 0,201V$$

Find:

$$EMF - ?$$

Solution:

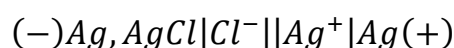
The potential of the silver electrode according to the Nernst equation is equal to:

$$E_{Ag^+/Ag} = E_{Ag^+/Ag}^0 + 0,059 \cdot \lg c(Ag^+) = 0,800 + 0,059 \cdot \lg 10^{-2} = 0,682 \text{ V};$$

the standard potential of the silver electrode is given in Annex 5,

$$E_{Ag^+/Ag}^0 = 0,800V.$$

Of the two electrodes, the cathode will be a silver electrode because it has a larger potential value. Scheme of galvanic cell:



$$EMF = E_{Ag^+/Ag} - E_{SC} = 0,682V - 0,201V = 0,481V$$

Answer: $EMF = 0,481V$

Example 9

The EMF of a galvanic cell in which the anode is a hydrogen electrode ($p(H_2) = 1 \text{ atm}$) immersed in an acetic acid solution and the cathode is a silver chloride electrode (saturated KCl solution) is 0.467 V. Calculate the pH of the solution and the total molar concentration of acetic acid degree of dissociation 0.5%).

$$E_{SC} = 0,201V.$$

Given:

$$T = 298K$$

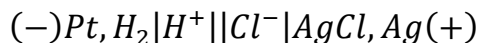
Find:

$$pH - ?$$

$$\begin{array}{l|l}
 EMF = 0,467V & c(CH_3COOH) - ? \\
 p(H_2) = 1atm & \\
 \alpha = 0,5\% = 0,005 & \\
 E_{SC} = 0,201V &
 \end{array}$$

Solution:

1. Scheme of galvanic cell:



To calculate the pH of the solution it is necessary to calculate the value of the potential of the hydrogen electrode in this solution:

$$EMF = E_{xce} - E_{H^+/H_2} \implies E_{H^+/H_2} = E_{SC} - EMF,$$

than

$$E_{H^+/H_2} = 0,201 - 0,467 = -0,266 V.$$

The dependence of the potential of the hydrogen electrode on the pH of the solution at ($T = 298K$, $p(H_2) = 1atm$) is expressed by the equation

$$E_{H^+/H_2} = -0,059pH,$$

where the pH is equal to:

$$pH = -\frac{E_{H^+/H_2}}{0,059} = -\frac{-0,266}{0,059} = 4,51.$$

2. The equation of dissociation of acetic acid:



To calculate the total molar concentration of acetic acid, it is necessary to calculate the equilibrium concentration of H^+ ions:

$$pH = -\lg[H^+] \implies [H^+] = 10^{-pH} = 10^{-4,51} = 3,1 \cdot 10^{-5} \text{ моль/л}.$$

Then

$$c(CH_3COOH) = \frac{[H^+]}{n \cdot \alpha} = \frac{3,1 \cdot 10^{-5} \text{ mol/l}}{1 \cdot 0,005} = 6,2 \cdot 10^{-3} \text{ mol/l}$$

(n – the number of acidic protons in the acid molecule)

Answer: $pH = 4,51$; $c(CH_3COOH) = 6,2 \cdot 10^{-3} \text{ mol/l}$

Example 10

The glass electrode connected to the galvanic cell with the silver chloride electrode at $T = 298K$ was first immersed in a solution with $pH = 3$ and then in the test sample of gastric juice. The potential of the glass electrode increased by $0.055 V$. Calculate the pH of gastric juice.

Given:

$$T = 298K$$

$$pH_1 = 3$$

$$E_{2gl} - E_{1gl} = 0,055V$$

Find:

$$pH_2 - ?$$

Solution:

The potential of the glass electrode at $T = 298\text{K}$ depends on the pH of the solution according to the equation

$$E_{gl} = \text{const} - 0,059\text{pH},$$

where *const* is an individual characteristic of each particular electrode, depending on the composition of the glass, the thickness of the pH-sensitive surface layer of the membrane.

The potential of the glass electrode immersed in a solution with $\text{pH} = 3$ is equal to

$$E_{1gl} = \text{const} - 0,059 \cdot 3,$$

The potential of the glass electrode immersed in the test sample of gastric juice is

$$\text{equal to } E_{2gl} = \text{const} - 0,059\text{pH}_2,$$

Then

$$E_{2gl} - E_{1gl} = (\text{const} - 0,059\text{pH}_2) - (\text{const} - 0,059 \cdot 3) = 0,059(3 - \text{pH}_2)$$

Under the condition of the problem

$$E_{2gl} - E_{1gl} = 0,055\text{V}, \text{ then}$$

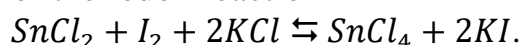
$$0,055 = 0,059(3 - \text{pH}_2)$$

$$\text{pH}_2 = 3 - \frac{0,055}{0,059} = 2,1$$

Answer: $\text{pH}_2 = 2,1$

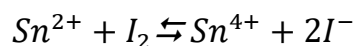
Example 11

Using reference data on the standard electrode potentials of the half-reactions, determine the direction of the redox reaction

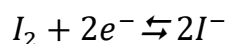
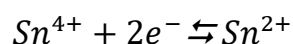


Solution:

The reaction equation in ionic form has the form



Two electrochemical systems take part in reaction:



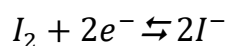
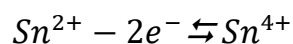
The values of the standard redox potentials are given in Annex 5,

$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0,151\text{V},$$

$$E_{\text{I}_2/2\text{I}^-}^0 = 0,621\text{V}.$$

In this case $E_{\text{I}_2/2\text{I}^-}^0 > E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0$.

The half-reaction with a higher value of the potential will proceed in the direction of reduction of the oxidized form of the oxidant, and the half-reaction with a lower value of the potential - in the direction of oxidation of the reduced form of the reducing agent corresponding to the processes:



Thus, a given reaction will spontaneously proceed in the forward direction (from left to right).

Self-test questions

4.1 Calculate the potential of this electrode $T = 298\text{K}$ in the electrolyte solution, given the concentration of the potential ion.

Nº	Electrode	Ion concentration, mol/l
1)	$\text{Fe}^{2+} \text{Fe}$	$c(\text{Fe}^{2+}) = 0,001$
2)	$\text{Cd}^{2+} \text{Cd}$	$c(\text{Cd}^{2+}) = 0,002$
3)	$\text{Ni}^{2+} \text{Ni}$	$c(\text{Ni}^{2+}) = 0,005$
4)	$\text{Ag}^+ \text{Ag}$	$c(\text{Ag}^+) = 0,01$
5)	$\text{H}^+ \text{H}_2(p_{\text{H}_2} = 1 \text{ atm})$	$c(\text{H}^+) = 0,001$

Answer:

Nº	1)	2)	3)	4)	5)
E, B	-0,5355	-0,483	-0,325	0,682	-0,177

4.2 Calculate the concentration of these ions in the electrolyte solution at $T = 298\text{K}$, if the value of the electrode potential is given.

Nº	Electrode	Electrode potential, V	Ion
1)	$\text{Mn}^{2+} \text{Mn}$	-1,244	Mn^{2+}
2)	$\text{Co}^{2+} \text{Co}$	-0,310	Co^{2+}
3)	$\text{Zn}^{2+} \text{Zn}$	-0,848	Zn^{2+}
4)	$\text{Ag}^+ \text{Ag}$	0,664	Ag^+
5)	$\text{H}^+ \text{H}_2(p_{\text{H}_2} = 1 \text{ atm})$	-0,236	H^+

Answer:

Nº	1)	2)	3)	4)	5)
$c, \text{mol/l}$	0,01	0,096	0,001	0,005	10^{-4}

4.3 Calculate the value of the potential of this redox electrode at $T = 298\text{K}$, given the concentrations of oxidized and reduced forms, as well as protons (in cases where they participate in the half-reaction).

N ^o	Electrode	Ion concentration, mol/l
1)	$Fe^{3+}, Fe^{2+} Pt$	$c(Fe^{2+}) = 0,01$ $c(Fe^{3+}) = 0,001$
2)	$Co^{3+}, Co^{2+} Pt$	$c(Co^{2+}) = 0,001$ $c(Co^{3+}) = 0,01$
3)	$MnO_4^-, Mn^{2+}, H^+ Pt$	$c(MnO_4^-) = 0,005$ $c(Mn^{2+}) = 0,01$ $c(H^+) = 0,01$
4)	$Cr_2O_7^{2-}, Cr^{3+}, H^+ Pt$	$c(Cr_2O_7^{2-}) = 0,01$ $c(Cr^{3+}) = 0,005$ $c(H^+) = 0,1$

Answer:

N ^o	1)	2)	3)	4)
E, B	0,712	1,979	1,315	1,120

4.4 Calculate the EMF of a galvanic cell at 298K, composed of two silver electrodes with $c_1(Ag^+) = 10^{-3} \text{ mol/l}$ and $c_2(Ag^+) = 10^{-1} \text{ mol/l}$.

Answer: $EMF = 0,118V$

4.5 Calculate the EMF of a galvanic cell at 298K, composed of two zinc electrodes with $c_1(Zn^{2+}) = 10^{-3} \text{ mol/l}$ and $c_2(Zn^{2+}) = 10^{-4} \text{ mol/l}$.

Answer: $EMF = 0,0295V$

4.6 Calculate the EMF of a galvanic cell at 298K, composed of two hydrogen electrodes with $pH_1 = 2$ and $pH_2 = 7$.

Answer: $EMF = 0,295V$

4.7 Calculate the EMF of a galvanic cell at 298K, consisting of a hydrogen electrode immersed in a solution with $pH_1 = 4$, and a silver chloride electrode (saturated KCl solution). $E_{SC} = 0,201V$.

Answer: $EPC = 0,437V$

4.8 Calculate the EMF of a galvanic cell at 298K composed of a silver electrode with $c(Ag^+) = 10^{-3} \text{ mol/l}$ and a copper electrode with $c(Cu^{2+}) = 10^{-2} \text{ mol/l}$.

Answer: $EPC = 0,342V$

4.9 Calculate the EMF of a galvanic cell at 298K composed of a zinc electrode with $c(Zn^{2+}) = 10^{-2} \text{ mol/l}$ and a hydrogen electrode with $pH = 7$.

Answer: $EMF = 0,406V$

4.10 Calculate the EMF of a galvanic cell at 298 K composed of a glass electrode pH-sensitive electrode ($E^0 = 0.35\text{V}$) immersed in a solution with $\text{pH} = 2$, and a silver chloride electrode (saturated KCl solution).

$E_{\text{SC}} = 0,201\text{V}$.

Answer: $EMF = 0,031\text{V}$

4.11 Calculate the EMF of a galvanic cell at 298 K composed of a hydrogen electrode immersed in a solution with $\text{pH} = 2$, and a silver chloride electrode (saturated KCl solution). $E_{\text{SC}} = 0,201\text{V}$.

Answer: $E_{\text{PC}} = 0,319\text{V}$

4.12* The EMF of a galvanic cell consisting of a glass pH-sensitive electrode ($\text{const} = 0.31\text{V}$) immersed in the test solution and a silver chloride electrode (saturated KCl solution) at 298 K is equal to 50 mV. Calculate the pH of the test solution, if the cathode in this element is a glass electrode. $E_{\text{SC}} = 0,201\text{V}$.

Answer: $\text{pH} = 1$

4.13* The EMF of a galvanic cell consisting of a hydrogen electrode immersed in the test solution and a silver chloride electrode (saturated KCl solution) at 298 K is equal to 0.366V. Calculate the pH of the test solution, taking into account that the hydrogen electrode is negatively charged relative to the silver chloride electrode. $E_{\text{SC}} = 0,201\text{V}$.

Answer: $\text{pH} = 2,8$

4.14* The EMF of a galvanic cell consisting of a glass pH-sensitive electrode ($\text{const} = 0.30\text{ V}$) immersed in a solution of sulfuric acid and a silver chloride electrode (saturated KCl solution) at 298 K is 78 mV. Calculate the mass concentration of sulfuric acid in the test solution (degree of dissociation 100%), if the cathode in this element is a reference electrode. $E_{\text{SC}} = 0,201\text{V}$.

Answer: $\rho(\text{H}_2\text{SO}_4)$
 $= 0,049\text{ g/l}$

4.15* The glass electrode connected in a galvanic circuit to the reference electrode at 298 K was first immersed in phosphate buffer solution with $\text{pH} = 7.2$ and then in the test milk sample. The potential of the glass electrode increases by 130 mV. The pH of milk is normally in the range of 6.6-6.9. Evaluate the result of the milk test.

Answer: $\text{pH} = 5$

4.16* The glass electrode connected in a galvanic circuit to the reference electrode at 298 K was first immersed in acetate buffer solution with $\text{pH} = 4.76$ and then in the test blood sample. The potential of the glass electrode decreases by 0.155 V. Evaluate the result of the blood test.

Answer: $\text{pH} = 7,39$

4.17* The EMF of a galvanic cell consisting of a platinum electrode immersed in a solution containing Fe^{3+} and Fe^{2+} , and a silver chloride electrode (saturated KCl solution) at 298 K is equal to 0.688V. Calculate the ratio of concentrations of oxidized and reduced forms $c(\text{Fe}^{3+})/c(\text{Fe}^{2+})$ in the test solution, taking into account that the platinum electrode is positively charged relative to the silver chloride electrode. $E_{\text{SC}} = 0,201\text{V}$.

$$\text{Answer: } \frac{c(\text{Fe}^{3+})}{c(\text{Fe}^{2+})} = \frac{100}{1}$$

4.18* The EMF of a galvanic cell consisting of a platinum electrode immersed in a solution containing Sn^{4+} and Sn^{2+} , and a silver chloride electrode (saturated KCl solution) at 298 K is equal to 0.109V. Calculate the ratio of the concentrations of oxidized and reduced forms $c(\text{Sn}^{4+})/c(\text{Sn}^{2+})$ in the test solution, taking into account that the platinum electrode is negatively charged relative to the silver chloride electrode. $E_{\text{SC}} = 0,201\text{V}$.

$$\text{Answer: } \frac{c(\text{Sn}^{4+})}{c(\text{Sn}^{2+})} = \frac{1}{100}$$

4.19* Using reference data on the standard electrode potentials of the half-reactions, determine the direction of the redox reaction.

- 1) $3\text{H}_2\text{O}_2 + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightleftharpoons 3\text{O}_2 + 6\text{H}^+ + 2\text{Cr}^{3+} + 7\text{H}_2\text{O};$
- 2) $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightleftharpoons \text{I}_2 + 2\text{H}_2\text{O};$
- 3) $2\text{Fe}^{2+} + \text{Sn}^{4+} \rightleftharpoons 2\text{Fe}^{3+} + \text{Sn}^{2+};$
- 4) $\text{MnO}_2^- + 5\text{Co}^{3+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Co}^{3+} + 4\text{H}_2\text{O};$
- 5) $5\text{Sn}^{4+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \rightleftharpoons 5\text{Sn}^{4+} + 2\text{MnO}_4^- + 16\text{H}^+.$

5. Sorption of biologically active substances at the interface. Ion exchange. Chromatography.

List of basic terms

Term	Content value
Adsorption	The spontaneous process of concentrating the solute at the interface.
Rule Duklo Traube	In the homologous series of carboxylic acids, alcohols, amines, when increasing the length of the hydrocarbon chain by one CH ₂ group, the surface activity of the substances increases by 3 - 3.5 times.
Adsorbent	The substance on which the adsorption occurs.
Adsorbate, and adsorbent	Substance that is adsorbed on the surface of the adsorbent.
Rebinder polarity alignment rule	Polar adsorbents are better adsorbed polar substances from non-polar or low-polar solvents, and non-polar adsorbed non-polar substances from polar solvents.
Adsorption equilibrium	This is the state of the system adsorbent - adsorbate, when the adsorption rate is equal to the rate of desorption.
Hemosorption	A method of direct purification of blood, in which the blood is stripped of toxins by passing it through a column with an adsorbent connected to the blood circulation system.
Plasma sorption	An effective method of detoxifying the body, the essence of which is to pass the plasma, before being separated from the blood cells, through a column with sorbent, after which the purified plasma connects with the blood cells and returns to the vascular bed.
Lymphosorption	Kind of sorption detoxification of the body, which is the transmission of lymph, excreted from the thoracic lymphatic flow on the neck, through the column with sorbent, and the subsequent introduction of toxic lymph-free substances to the patient's vascular system.
Liquid adsorption	Kind of detoxification of the body, in which the cerebrospinal fluid is passed through a layer of sorption material, and then returned purified to the spinal canal.
Application sorption	One type of sorption detoxification that helps to heal infected wounds and burns and restore the integrity of the skin, as well as mucous membranes by sorption absorption of toxins from the wound or burn area.
Enterosorption	A type of sorption detoxification of the body, in which the sorbent enters the oral cavity, after which, at different speeds through the digestive system, it adsorbs toxic substances and products of metabolism.

Paneth-Fajans Rule	Preferably, on the surface of the crystal adsorbed are those ions that can complete its crystal lattice, or are isomorphic to its ions, thus forming soluble compounds with crystal ions.
Ion exchange adsorption	The process by which the adsorbent and solution exchange in equal quantities with simultaneously charged ions.
Cationites	These are ionites capable of exchanging cations with solution.
Anionites	These are ion exchangers capable of exchanging anions with solution.
Chromatography	Physico-chemical method of separation and analysis of mixtures of substances based on their different distribution between two phases, one of which is fixed (solid or liquid) and the other is mobile (gas or liquid), which is filtered through stationary.

In **chromatography**, the partition coefficient is denoted as R_f . In paper chromatography, to determine R_f , the distance from the start line (place of application of the substance on paper) to the center of the spot on the chromatogram corresponding to that substance is primarily measured. Also measure the distance from the start line to the finish line (solvent front). The ratio of the path traveled by the substance to the path traveled by the solvent will be the coefficient of distribution R_f of the substance between the mobile and stationary phases (Fig. 1). Therefore, R_f is a qualitative characteristic of the substance. Comparison of the experimentally obtained partition coefficients with the reference ones (Table 1) makes it possible to identify the substances included in the mixture.

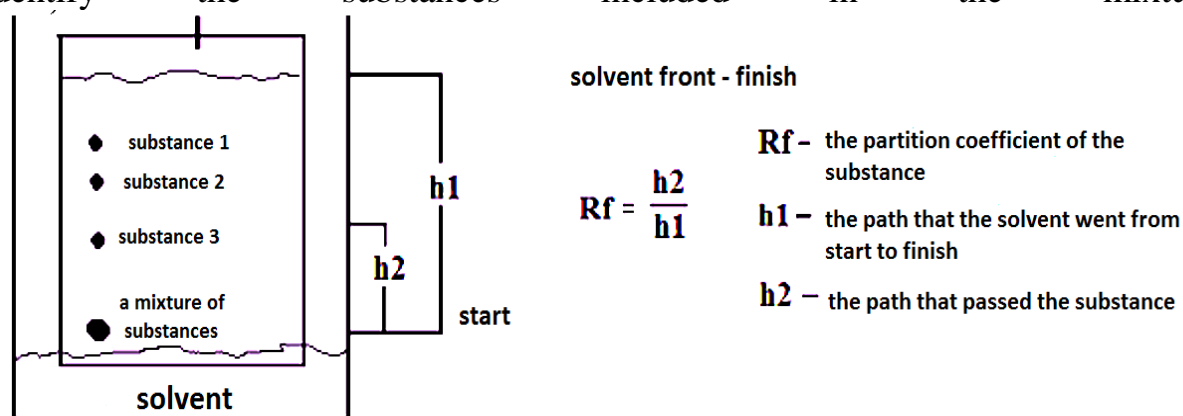
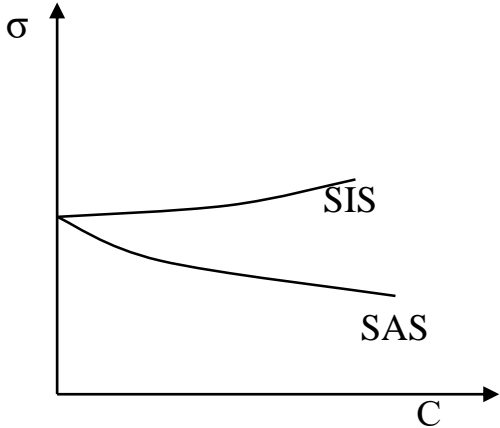


Figure 1. Schematic representation of distributive chromatography.

Table 8. Partition coefficients of some amino acids

Amino acid	R_f	Amino acid	R_f
Aspartic acid	0,07	Arginine	0,41
Glutamic acid	0,16	Tyrosine	0,52
Cysteine	0,19	Alanine	0,55
Glycol	0,30	Leucine	0,79
Methionine	0,39		

List of basic parameters, characteristics of surface phenomena

Parameter	Marking, Unit	Content value
Surface tension	$\sigma = \frac{G_s}{S},$ kJ / m ² or N / m.	The surface tension (σ) is numerically equal to the work that must be done to form a unit of surface.
Surface activity	$\left(-\frac{\Delta\sigma}{\Delta c} \right), J \cdot m / mol$	A measure of the ability of solutes to change the surface tension of a fluid is the surface activity, which quantitatively characterizes the change in surface tension as the concentration changes.
Surfactants	For surfactants, surface activity $-\frac{\Delta\sigma}{\Delta c} > 0$	Substances that reduce the surface tension of water
Surfactants are inactive	For surfactants are inactive? surface activity $-\frac{\Delta\sigma}{\Delta c} < 0$	Substances that increase the surface tension of water.
Surfactants inactive substances	For Surfactants inactive substances surface activity $-\frac{\Delta\sigma}{\Delta c} = 0$	Substances that do not affect the surface tension of water.
The surface tension isotherm		Graphical dependence of surface tension on solute concentration at constant temperature.
Gibbs equation	$\Gamma = -\frac{C_p}{RT} \cdot \frac{\Delta\sigma}{\Delta C},$ Γ – the amount of adsorption, mol / m ² ; C_p – equilibrium concentration of substance, mol / l;	An equation that allows us to determine the amount of adsorption in solutions based on experimental data on changes in surface

	$-\frac{\Delta\sigma}{\Delta C}$ – surface activity of the substance, J / m ² ; R – a universal gas constant equal to 8.31 J / mol · K; T – absolute temperature, K.	tension with changes in solute concentration.
The area occupied by one molecule	$S_0 = \frac{l}{\Gamma_{\max} \cdot N_A},$ де S ₀ – The area occupied by one molecule Γ _{max} – limit adsorption, N _A – Avogadro number	Based on the fact that per unit area of the surface when forming a monolayer of surfactant molecules is adsorbed Γ _{max} moles of matter, that is Γ _{max} ·N _A molecules, N _A – Avogadro number, the area occupied by one molecule, can be found by the corresponding formula.
The length of the molecule	$l = \frac{\Gamma_{\max} \cdot M(x)}{\rho},$ l – the length of the molecule, ρ – density of matter, M(x) the molar mass of the substance	Allows you to calculate the length of the molecule, if the value of the maximum adsorption is known.
The Langmuir adsorption isotherm equation	$\Gamma = \Gamma_{\max} \cdot \frac{C}{C + K},$ Γ – adsorption of the substance; Γ _{max} – limit adsorption; C – equilibrium concentration of the substance; K – a constant numerically equal to the concentration at which the adsorption is half the limit adsorption.	Studying adsorption at the interface of solid - gas and liquid - gas, and summarizing practical experience, Langmuir proposed the equation of an adsorption isotherm, where the adsorption boundary corresponds to the adsorption on the surface of the monolayer.
Freundlich's empirical equation	$\frac{x}{m} = k \cdot c^n,$ де x – the amount of adsorbed substance; m – the mass of the adsorbent;	Generalization of the results of solubility adsorption studies on a solid surface indicates that the most successful dependence of solubility adsorption on their concentration in solution is

	c – equilibrium concentration of the substance; $\frac{1}{k \tau a^n}$ – empirical constants.	described by the empirical Freundlich equation
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Examples of exercises.

Example 1

For which of the amino acids (cysteine or tyrosine) will the speed of movement on paper in a mixture of water and phenol be higher if it is known that R_f for these acids is equal to, respectively, 0.19 and 0.52? Motivate the answer

Solution:

If we take into account that R_f is equal to the ratio of the speed of movement of the analyzed component to the speed of movement of the solvent water-phenol on paper, the tyrosine having $R_f = 0.52$ will move faster than cysteine, which has $R_f = 0.19$. It is also known that paper is a hydrophilic substance, then the stationary liquid on the surface will be water, and the amino acid, which moves more slowly, is characterized by greater hydrophilicity (cysteine $R_f = 0.19$).

Example 2

Which of the amino acids - glutamic or aspartic - have greater hydrophilicity, if the paper chromatography shows that R_f for these acids when using phenol as a mobile phase, water as a stationary phase, and paper as an inert carrier is, respectively, 0.16 and 0, 07? Motivate the answer.

Solution:

Given that R_f is equal to the ratio of the speed of movement of the analyzed component to the speed of movement of the solvent on paper. Also, the fact that the stationary phase is water, the more hydrophilic the substance, the lower its speed of movement on the carrier and the lower the value of R_f . Therefore, because the R_f of aspartic acid is less, this amino acid is more hydrophilic.

Example 3

When using phenol as the mobile phase, water as the stationary phase, and paper as the inert carrier, R_f for amino acids - glutamic acid, glycol and leucine - was equal, respectively, 0.16, 0.30, 0.79. What conclusion can be drawn about the relative hydrophobicity of these amino acids (arrange them in a row in ascending order of hydrophobicity).

Solution:

The partition coefficient R_f is equal to the ratio of the speed of movement of the analyzed component to the speed of movement of the solvent on the paper. It is also known that paper is a hydrophilic substance, ie the stationary liquid on the surface will be water, and the amino acid, which moves more slowly (has a lower

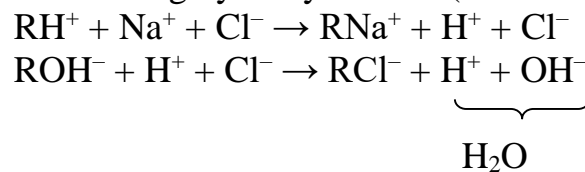
value of R_f), is characterized by greater hydrophilicity. Accordingly, it is possible to arrange the amino acids in a row in ascending order of hydrophobicity: glutamic acid, glycocol, leucine.

Example 4

How to purify water from sodium chloride with the help of ion exchangers?

Solution:

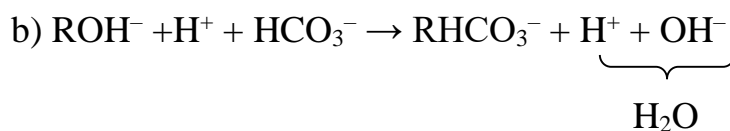
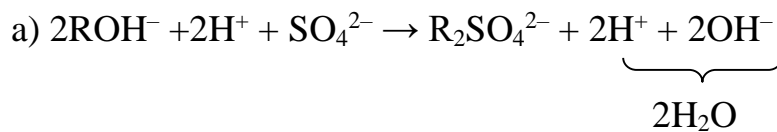
To purify water from sodium chloride with ion exchangers, it is necessary to pass water through a layer of cation exchange resin containing hydrogen cations (denote such cation exchange resin RH^+), and then through a layer of anion exchange resin containing hydroxyl anions (denote ROH^-).



Example 5

Give the scheme of water purification from SO_4^{2-} and HCO_3^- ions on the anion exchange resin in OH^- form.

Solution:



Example 6

Calculate the mass of Ca^{2+} ions in a solution of calcium chloride, if it is known that the titration of the filtrate obtained by passing it through the anion exchange resin in H^+ form took 6 ml of potassium hydroxide solution with a molar concentration of $c(KOH) = 0.1 \text{ mol/l}$.

Given:

$$\begin{aligned} V(KOH) &= 6 \text{ ml} = 0,006 \text{ l} \\ c(KOH) &= 0,1 \text{ mol/l} \end{aligned}$$

Find:

$$m(Ca^{2+}) - ?$$

Solution:

1) Write the equation for calculating the mass of ions by titration:

$$m(Ca^{2+}) = c(KOH) \cdot V(KOH) \cdot M\left(\frac{1}{2}Ca^{2+}\right)$$

2) Calculate the mass of ions Ca^{2+} :

$$m(Ca^{2+}) = 0,1 \text{ mol/l} \cdot 0,006 \text{ l} \cdot \frac{40}{2} \text{ g/mol} = 0,012 \text{ g}$$

Answer: $m(\text{Ca}^{2+}) = 0,012\text{r}$

Example 7

Compare the surface activity of propionic and butyric acids in aqueous solutions, if known:

Acid	c, mol/l	σ , J/m ²
Propionic	0,0312	0,0695
	0,0625	0,0677
Butyric acid	0,0312	0,0658
	0,0625	0,0604

Does the Duclos-Traube rule hold in a given concentration range?

Solution:

1) Calculate the value of surface activity for the corresponding substances

$$g = - \left(\frac{\Delta\sigma}{\Delta c} \right)$$

$$g(\text{C}_2\text{H}_5\text{COOH}) = - \frac{(0,0677 - 0,0695) \text{ J/m}^2}{(0,0625 - 0,0312) \cdot 10^{-3} \text{ mol/m}^3} = 57,5 \cdot 10^{-6} \frac{\text{J} \cdot \text{m}}{\text{mol}}$$

$$g(\text{C}_3\text{H}_7\text{COOH}) = - \frac{(0,0604 - 0,0658) \text{ J/m}^2}{(0,0625 - 0,0312) \cdot 10^{-3} \text{ mol/m}^3} = 172,5 \cdot 10^{-6} \frac{\text{J} \cdot \text{m}}{\text{mol}}$$

2) According to the Duclo-Traube rule in the homologous series of carboxylic acids, alcohols, amines with increasing length of the hydrocarbon chain by one CH₂ group, the surface activity of substances increases by 3 - 3.5 times:

$$\frac{g(\text{C}_3\text{H}_7\text{COOH})}{g(\text{C}_2\text{H}_5\text{COOH})} = \frac{172,5 \cdot 10^{-6}}{57,5 \cdot 10^{-6}} \approx 3$$

Answer: Therefore, in a given range of concentrations, the Duclo-Traube rule is fulfilled.

Example 8

Calculate the value of the adsorption of propionic acid on a solid adsorbent, if its equilibrium concentration is 0.22 mol / l, and the constants in the Freundlich equation are equal to K = 0.50 mol / g, n = 0.45.

Given:

$$C_p = 0,22 \text{ mol/l}$$

$$K = 0,50 \text{ l/g}$$

$$n = 0,45$$

Find:

$$\Gamma - ?$$

Solution:

Calculate the amount of adsorption using the Freundlich equation:

$$\Gamma = \frac{x}{m} = k \cdot c^n, \text{ if } n > 1; \frac{x}{m} = k \cdot c^n, \text{ if } n < 1, \text{ than:}$$

$$\Gamma = 0,50 \text{ l/g} \cdot 0,22^{0,45} \text{ mol/l} = 0,253 \text{ mol/g} = 253 \text{ mmol/g}$$

Answer: $\Gamma = 0,253 \text{ mol/g} = 253 \text{ mmol/g}$

Example 9

Calculate the adsorption of organic acid from an aqueous solution at 298 K, if its equilibrium molar concentration is 0.1 mol / l and the surface activity is $8,9 \cdot 10^{-4} \text{ J} \cdot \text{m} / \text{mol}$.

Given:

$$T = 298 \text{ K}$$

$$C_p = 0,1 \text{ mol/l} = 100 \text{ mol/m}^3$$

$$\frac{\Delta\sigma}{\Delta c(x)} = -8,9 \cdot 10^{-4} \frac{\text{J} \cdot \text{m}}{\text{mol}}$$

Find:

$$\Gamma - ?$$

Solution:

Calculate the amount of adsorption using the Gibbs equation:

$$\Gamma = -\frac{c_p}{RT} \cdot \frac{\Delta\sigma}{\Delta c(x)}$$

$$\Gamma = -\frac{100 \text{ mol/m}^3}{8,31 \text{ J}/(\text{mol} \cdot \text{K}) \cdot 298 \text{ K}} \cdot (-8,9 \cdot 10^{-4}) \frac{\text{J} \cdot \text{m}}{\text{mol}} = 3,6 \cdot 10^{-5} \text{ mol/m}^2$$

Answer: $\Gamma = 3,6 \cdot 10^{-5} \text{ mol/m}^2$

Example 10

When the concentration of novocaine in the solution decreased from 0.2 mol / l to 0.15 mol / l, the surface tension increased from $6,9 \cdot 10^{-2} \text{ J} / \text{m}^2$ to $7,1 \cdot 10^{-2} \text{ J} / \text{m}^2$. Calculate the amount of adsorption in this concentration range. $T = 293 \text{ K}$.

Given:

$$C_1 = 0,2 \text{ mol/l}$$

$$C_2 = 0,15 \text{ mol/l}$$

$$\sigma_1 = 6,9 \cdot 10^{-2} \text{ J/m}^2$$

$$\sigma_2 = 7,1 \cdot 10^{-2} \text{ J/m}^2$$

$$T = 293 \text{ K}$$

Find:

$$\Gamma - ?$$

Solution:

Calculate the amount of adsorption using the Gibbs equation:

$$\Gamma = -\frac{C_p}{RT} \cdot \frac{\Delta\sigma}{\Delta C},$$

where G is the amount of adsorption of solute; c_e - equilibrium molar concentration of solute, in narrow intervals of measurements is calculated as the average value $\frac{c_1 + c_2}{2}$; $-\frac{\Delta\sigma}{\Delta c}$ - surface activity; $\Delta\sigma = \sigma_2 - \sigma_1$, $\Delta C = C_2 - C_1$; R -

universal gas stable. Therefore, the amount of adsorption of novocaine is equal to:

$$\Gamma = - \frac{\frac{(0,2+0,15)}{2} \text{ mol/l}}{8,31 \text{ J}/(\text{mol} \cdot \text{K}) \cdot 298 \text{ K}} \cdot \frac{(7,1 - 6,9) \cdot 10^{-2} \text{ J/m}^2}{(0,15 - 0,2) \text{ mol/l}} = 2,87 \cdot 10^{-6} \text{ mol/m}^2$$

Answer: $\Gamma = 2,87 \cdot 10^{-6} \text{ mol/m}^2$

Example 11

Calculate the adsorption of isoamyl alcohol from solution by the Langmuir equation, if its equilibrium molar concentration is equal to 0.7 mol / l; $\Gamma_{\max} = 8,7 \cdot 10^{-12} \text{ mol/m}^2$; $K = 0.042$, $T = 293 \text{ K}$.

Given:

$$C_p = 0,7 \text{ mol/l} = 700 \text{ mol/m}^3$$

$$\Gamma_{\max} = 8,7 \cdot 10^{-12} \text{ mol/m}^2$$

$$K = 0,042 \text{ mol/l} = 42 \text{ mol/m}^3$$

$$T = 293 \text{ K}$$

Find:

$$\Gamma - ?$$

Solution:

Calculate the amount of adsorption using the Langmuir equation:

$$\Gamma = \Gamma_{\max} \cdot \frac{c_p}{c_p + K}$$

$$\Gamma = 8,7 \cdot 10^{-12} \text{ mol/m}^2 \cdot \frac{700 \text{ mol/m}^3}{700 \text{ mol/m}^3 + 42 \text{ mol/m}^3} = 8,2 \cdot 10^{-12} \text{ mol/m}^2$$

Answer: $\Gamma = 8,2 \cdot 10^{-12} \text{ mol/m}^2$

Example 12

25 ml of acetic acid solution with a molar concentration of 0.05 mol / l was shaken with 1 g of activated carbon. After reaching equilibrium, 2 ml of the solution was followed by 2 ml of sodium hydroxide solution with a molar concentration of 0.1 mol / l. Find the value of adsorption of acetic acid in mol / g.

Given:

$$V(\text{CH}_3\text{COOH}) = 25 \text{ ml} = 0,025 \text{ l}$$

$$C_0(\text{CH}_3\text{COOH}) = 0,05 \text{ mol/l}$$

$$m_{\text{coal}} = 1 \text{ g}$$

$$V'(\text{CH}_3\text{COOH}) = 5 \text{ ml} = 0,005 \text{ l}$$

$$V(\text{NaOH}) = 2 \text{ ml} = 0,002 \text{ l}$$

$$c(\text{NaOH}) = 0,1 \text{ mol/l}$$

Find:

$$a - ?$$

Solution:

1) Write the equation for calculating the amount of adsorption from the solution on a solid surface:

$$a = \frac{[C_0(\text{CH}_3\text{COOH}) - C_p(\text{CH}_3\text{COOH})] \cdot V(\text{CH}_3\text{COOH})}{m}$$

2) Calculate the equilibrium molar concentration C_e :

$$C_p = \frac{c(\text{NaOH}) \cdot V(\text{NaOH})}{V'(\text{CH}_3\text{COOH})} = \frac{0,1 \cdot 2 \cdot 10^{-3}}{5 \cdot 10^{-3}} = 0,04 \text{ mol/l}$$

3) Calculate the amount of adsorption of acetic acid on coal:

$$a = \frac{[0,05 - 0,04] \cdot 25 \cdot 10^{-3}}{1} = 2,5 \cdot 10^{-4} \text{ mol/g}$$

Answer: $a = 2,5 \cdot 10^{-4} \text{ mol/g}$

Example 13

Calculate the length (l_0) and area (S_0) of the isopentanol molecule in the saturated adsorption layer, if the limiting adsorption $\Gamma_{\max} = 7,6 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$, the density of isopentanol $\rho = 0,81 \text{ g} \cdot \text{cm}^{-3}$, relative molecular mass $M_r = 88$.

Given:

$$\begin{aligned} \Gamma_{\max} &= 7,6 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \\ \rho &= 0,81 \text{ g} \cdot \text{cm}^{-3} = 810 \cdot 10^3 \cdot \text{g} \cdot \text{m}^{-3} \\ M_r &= 88 \text{ g} \cdot \text{mol}^{-1} \end{aligned}$$

Find:

l_0 ; S_0 -?

Solution:

1) Write down the formulas for calculating the area occupied by the surfactant molecule and the length of the surfactant molecule::

$$\boxed{S_0 = \frac{1}{\Gamma_{\max} \cdot N_A}} \quad \boxed{l_0 = \frac{\Gamma_{\max} \cdot M(x)}{\rho}}$$

2) Calculate the area of the molecule of isopentanol:

$$3) S_0 = \frac{1}{7,6 \cdot 10^{-6} \text{ mol/m}^2 \cdot 6,02 \cdot 10^{23} \text{ mol}^{-1}} = 2,19 \cdot 10^{-19} \text{ m}^2$$

3) Calculate the length of the isopentanol molecule:

$$l_0 = \frac{7,6 \cdot 10^{-6} \text{ mol/m}^2 \cdot 88 \text{ g/mol}}{810 \cdot 10^3 \text{ g/m}^3} = 8,25 \cdot 10^{-10} \text{ m}$$

Answer: $S_0 = 2,19 \cdot 10^{-19} \text{ m}^2$; $l_0 = 8,25 \cdot 10^{-10} \text{ m}$

Example 14

Determine the limiting adsorption of isopentanol Γ_{\max} , if the area per molecule in the saturated adsorption layer is $25 \cdot 10^{-20} \text{ m}^2$.

Given:

$$S_0 = 25 \cdot 10^{-20} \text{ m}^2$$

Find:

Γ_{\max} -?

Solution:

1) Write the formula for calculating the area, where we express the value of the limiting adsorption:

$$S_0 = \frac{1}{\Gamma_{\max} \cdot N_A} \implies \Gamma_{\max} = \frac{1}{S_0 \cdot N_A}$$

2) Calculate the limiting adsorption of isopentanol:

$$\Gamma_{max} = \frac{1}{25 \cdot 10^{-20} m^2 \cdot 6,02 \cdot 10^{23} mol^{-1}} = 6,64 \cdot 10^{-6} mol/m^2$$

Answer: $\Gamma_{max} = 6,64 \cdot 10^{-6} mol/m^2$

Self-test questions

5.1 The hydrophilicity of glutamic acid molecules is greater than that of tyrosine. As this property is reflected in the value of R_f when using phenol as a stationary phase, and paper as an inert carrier.

5.2 Establish the dependence of R_f (in paper partition chromatography) on the hydrophilicity of the amino acid molecule.

5.3 Indicate for which of the amino acids (cysteine and tyrosine) the speed of movement on paper in a mixture of phenol - water will be higher (see Table 1).

5.4 The partition coefficient for aspartic acid and arginine in between phenol and water is 0.07 and 0.41, respectively. How this property is reflected in the speed of their movement on paper in a mixture of phenol - water.

5.5 To make the scheme of water purification from $Ca(NO_3)_2$ by means of ion exchangers.

5.6 To make the scheme of water purification from KCl by means of ion exchangers.

5.7 To make the scheme of water purification from Li_2SO_4 by means of ion exchangers.

5.8 Calculate the mass of Br^- ions in $NaBr$ solution, if it is known that the titration of the filtrate obtained by passing it through the ion exchanger in OH^- form took 5 ml of HCl solution with a molar concentration of $c(HCl) = 0.1 mol/l$.

Answer: $m(Br^-) = 0,04g$

5.9 Calculate the mass of the drug sodium salicylate contained in the aqueous solution, if it is known that the titration of the filtrate obtained by passing it through the resin in H^+ -form, took 17 ml of sodium hydroxide solution with a molar concentration of $c(NaOH) = 0.05 mol/l$. $M(C_7H_5O_2Na) = 160 g/mol$.

Answer: $m(C_7H_5O_2Na) = 0,136 g$

5.10* Determine the surface activity of valeric acid, if it is known that at an average molar concentration of $0.1 mol/l$ and a temperature of $298 K$ its adsorption is equal to $3,6 \cdot 10^{-5} mol/m^2$.

Answer: $-\left(\frac{\Delta\sigma}{\Delta c}\right) = 8,9 \cdot 10^{-4} \frac{J \cdot m}{mol}$

5.11* Calculate the surface activity of an organic acid if the surface tension of its solutions with a molar concentration of 0.02 and 0.2 mol / l at 298 K is, respectively, $70,15 \cdot 10^{-3}$ and $64,3 \cdot 10^{-3}$ J / m².

Answer: $-\left(\frac{\Delta\sigma}{\Delta c}\right) = -3,2 \cdot 10^{-4} \frac{J \cdot m}{mol}$

5.12* Calculate the amount of adsorption of organic acid from an aqueous solution on activated carbon, if $K = 0.46$ l / g, $C_p = 10$ mmol / l, $1/n = 0.25$.

Answer: $\Gamma = 253$ mmol/g

5.13* Calculate the amount of adsorption (Γ) of valeric acid from aqueous solution, if it is known that $C_p = 0.4$ mol / l, the surface activity is $6,4 \cdot 10^{-4}$ J • mol⁻¹, $T = 293$ K.

Answer: $\Gamma = 2,6 \cdot 10^{-5}$ mol/m²

5.14* Find the maximum adsorption of a substance at the water-air interface at the Langmuir equation, if at an equilibrium molar concentration of the substance equal to 0.02 mol / l the adsorption is $4 \cdot 10^{-3}$ mol / m², and $K = 0.8$.

Answer: $\Gamma_{\max} = 1,681$ mol/m²

5.15* Calculate the area occupied by the surfactant molecule if the limiting adsorption $\Gamma_{\max} = 8,3 \cdot 10^{-6}$ mol / m².

Answer: $S_0 = 20 \cdot 10^{-20}$ m²

5.16* Calculate the length of the surfactant molecule if $\Gamma_{\max} = 8,5 \cdot 10^{-6}$ mol / m², $M(x) = 0.074$ kg / mol, $\rho = 800$ kg / m³.

Answer: $l_0 = 7,76 \cdot 10^{-10}$ m

5.17* Calculate the length of a molecule of butyric acid, if the area occupied by one molecule in the surface layer $S_0 = 3,2 \cdot 10^{-19}$ m², $\rho = 978$ kg / m³, $M(x) = 0.088$ kg / mol.

Answer: $l_0 = 4,68 \cdot 10^{-10}$ m

6. Preparation, purification and properties of colloidal solutions

List of basic terms

Term	Content value
Dispersion	is the degree of grinding of the substance. $D = 1/d$ where D - the degree of dispersion, M^{-1} d - diameter of the city, μ .
Dispersed	are systems in which one substance (dispersed phase) in the crushed state is evenly distributed among the particles of another substance (dispersion medium). The main feature of dispersed systems is the presence of the phase distribution surface, ie heterogeneity.
Coarse dispersed systems	The particle size is $10^{-7} - 10^{-4} \mu$. (suspensions, emulsions, powders, aerosols)
Fine systems	The particle size is $10^{-9} - 10^{-7} \mu$. (colloidal solutions, sols)
Molecular-disperse systems	The particle size is less than $10^{-9} \mu$. (true (molecular and ionic) solutions) Such solutions no longer have a phase separation surface and do not belong to dispersed systems.
Lyophilic systems (reversible)	systems in which the dispersed particles strongly interact with the solvent. When the solvent is water, they can be called hydrophilic systems.
Sol	Sol (colloidal solution) is an ultramicroheterogenic dispersion system. Aerosols are systems with a gas dispersion medium. Lyosols - with a liquid dispersion medium. Hydrosols - with aqueous dispersion medium.
Suspension	a dispersion system with a liquid dispersion medium and a solid dispersion phase.
Emulsion	a dispersion system with a liquid dispersion medium and a liquid dispersion phase. «First-class» emulsions are «oil-in-water» emulsions; «Second-clas» emulsions are «water-in-oil» emulsions.
Lyophilic systems (reversible)	systems in which the dispersed particles strongly interact with the solvent. When the solvent is water, they can be called hydrophilic systems.
Dispersion method of obtaining colloidal solutions	is to grind the substance to small particles. -mechanical way (ball mills, ultrasound); -chemical dispersion (peptization): the precipitate of the substance is transferred to the colloidal state by the addition of surfactants: soaps, proteins.

Condensation method for obtaining colloidal solutions	physical condensation: - evaporation of the solvent, resulting in condensation of the solid phase; - replacement of the solvent, for example, when pouring an alcoholic solution of cholesterol into water; chemical condensation - the use of reactions in which sediments are formed from small particles.
Dialysis	is the removal of low molecular weight impurities by diffusion through a semipermeable membrane.
Hemodialysis	The principles of dialysis are used in the apparatus "artificial kidney", where the flow of blood is passed through artificial semipermeable membranes. On one side of the membrane circulates the compensation fluid and on the other - the patient's blood. As a result, excess amounts of metabolites and toxins that accumulate in kidney diseases pass into the compensating fluid.
Electrodialysis	If impurities are only electrolytes, an electric field can be created to accelerate dialysis, which accelerates the transition of ions.
Ultrafiltration	Filter the colloidal solution through a semipermeable membrane at high pressure. In this case, the colloidal particles are trapped by the membrane, and impurities leave the colloidal solution.
Osmotic pressure	Vant-Goff equation: $\pi_{\text{ocm}} = \frac{v}{N_A} RT$ where R - gas constant; T - temperature; NA - Avogadro number; v - particulate concentration. eighths (colloidal solutions) < eighths (true solutions)
Sedimentation	deposition of particles by the force of gravity.
Optical properties of colloidal solutions	The passage of light through the colloidal system causes three optical effects: absorption, reflection and scattering.
The phenomenon of opalescence of colloidal solutions	The scattering of rays is manifested in the form of a matte glow of a blue hue when illuminated by lateral light.
The Tindal effect	when passing a parallel beam of light through a colloidal solution, a scattered light cone (Tindal cone) is observed.
Electro osmosis	the phenomenon of movement of the dispersion medium (ie solvent) relative to the stationary dispersed phase.
Electrophoresis	the phenomenon of the movement of colloidal particles relative to the dispersion medium (solvent), under the influence of direct electric current.

Broomstick	electrically neutral particle of the dispersed phase with the surrounding double electric layer.
Aggregate	consists of several hundred or thousands of atoms (m), is a microcrystalline soluble compound (referred to as “↓” in the reaction equation). Example: $AgNO_3 + KI \rightarrow AgI\downarrow + KNO_3$ $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Potential determining ion	ion capable of selective adsorption on the surface of the unit. Selective adsorption occurs according to Panetta-Faience rule: these are the ions that are part of the crystal lattice (or isomorphic to it) of the aggregate. Example: If the reaction occurs in excess of KI, then the ions I^- , their number n , will be adsorbed on the surface of the AgI aggregate. Iodide ions determine the potential and charge of the surface. $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
The nucleus of a colloidal particle.	The unit together with the potentialdetermining ions Example: $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Counterions	ions of opposite sign to the nucleus, which under the action of electrostatic forces are attracted to the nucleus, compensating for the charge of the nucleus. Their number is equal to the number of potentialdefinition ions (n). $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Adsorption layer	Potentialdetermining ions and part of counterions ($n-x$), which are closest to the nucleus. Example: $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Granule (colloidal particle)	The nucleus together with the adsorption layer of counterions. The sign of its charge is determined by the sign of the charge potential of determining ions. Example: $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Diffuse layer	The remaining x counterion ions that neutralize the charge of the granules and which are less strongly bound to the nucleus (electrostatic forces only) are diffused under the influence of thermal motion in the liquid phase. $\{m[AgI] nI^-(n-x)K^+\}^{x-} xK^+$
Zeta potential (ζ) or electrokinetic potential	The presence of a phase separation surface between the adsorption and diffuse layers of the micelles causes the formation of a zeta potential, which is the difference between the total charge of the potential of the determining ions and the charge of the counterions in the adsorption layer. The electrokinetic potential is measured by the speed of movement of the granules of a colloidal particle in an electric field by electrophoresis.

Isoelectric state	If the total charge potential of determining ions is equal to the charge of counterions, then the ζ potential is zero and the micelle is in the isoelectric state. Example: $\{m[AgI] nI^{-n} K^{+}\}^0$
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Examples of exercises

Example 1

How will the intensity of the scattered light in the colloidal system change if the wavelength of the incident light is halved?

The solution is:

The intensity of the scattered light (I) is inversely proportional to the wavelength of light in the fourth degree (λ^4): If the wavelength of the incident light is halved, then

$$I = k \frac{I_0 n V^2}{\lambda^4}$$

Since the intensity of the scattered light is inversely proportional to the wavelength of the light, then the scattered light intensity (I) will increase 16 times.

Example 2

Explain the structure and composition of the micelles sol AgI formed by the interaction of the nitrate argementum in solution with excess potassium iodide.

The solution is:



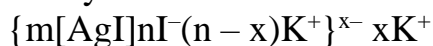
The basis of the colloidal particle is the electroneutral aggregate, consisting of several hundred or thousands of atoms, is a microcrystals of poorly soluble compound (in our case AgI).

The reaction will occur in excess of KI, then the potentialdetermining ions, Paneta-Faience's rule is iodine ions, because they complete the AgI crystalline lattice, which is why they are ,not potassium ions, form the potentialdetermining layer, their number n.

Iodide ions are potentialdefinition, determine the potential and charge of the surface. The aggregate together with the potentialdetermining ions is called the nucleus of a colloidal particle. Under the action of electrostatic forces, an opposite sign, the counterion, is attracted n ions to the nucleus, which offset the core charge. In this case, this role is played by K^+ ions.

The part of the counterions (n-x), which are closest located to the nucleus, are in the fluid layer and create an adsorption layer. The nucleus, together with the adsorption layer of counterions, is called a granule (or colloidal particle). The rest x of the counterions, which neutralize the surface charge and are less strongly bound to the nucleus (electrostatic forces only), are located under the influence of thermal motion in the liquid phase. Therefore, this layer is called diffuse.

The granule together with the diffuse layer is called micelles. The structure of the micelles can be represented by the formula:



Example 3

What structure will micelles sol have the argentine iodide obtained from AgNO_3 and KI solutions: a) for excess potassium iodide; b) for excess nitrate argentine? In which micelles the granule will move to the cathode at electrophoresis?

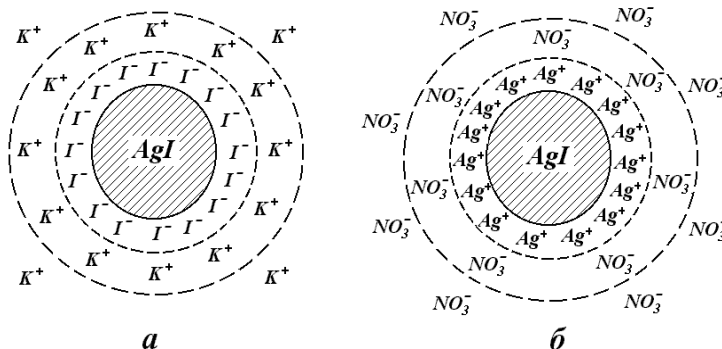
The solution is:

The micelle argentine iodide is formed by the following reaction: $\text{AgNO}_3 + \text{KI} \rightarrow \text{KNO}_3 + \text{AgI} \downarrow$

a) In solution with excess KI the structure of the micelles will be as follows: $\{m[\text{AgI}]n\text{I}^-(n-x)\text{K}^+\}^{x-} x\text{K}^+$ (explanation of example 2)

b) In solution with excess AgNO_3 : The micelles nucleus is formed from low soluble AgI . On its surface, they begin in accordance with the Panet - Faience selective adsorption rule, adsorbed Ag^+ ions, which are in solution in excess which can go to the completion of an AgI crystal. They create a positive charge of the nucleus and are potential determinants. Negatively charged ions join this layer $(n-x)\text{NO}_3^-$, that form the adsorption layer. Part of the ions $(x)\text{NO}_3^-$ forms a diffuse layer.

The structure of the micelles will be as follows: $\{m[\text{AgI}] \cdot n\text{Ag}^+(n-x)\text{NO}_3^-\}^{x+} x\text{NO}_3^-$



a) Negatively charged granule $\{m[\text{AgI}] n\text{I}^-(n-x)\text{K}^+\}^{x-} x\text{K}^+$.

b) Positively charged granule $\{m[\text{AgI}] n\text{Ag}^+(n-x)\text{NO}_3^-\}^{x+} x\text{NO}_3^-$

In electrophoresis in micelles $\{m[\text{AgI}] \cdot n\text{Ag}^+(n-x)\text{NO}_3^-\}^{x+} x\text{NO}_3^-$ the granule will move to the cathode because it is positively charged.

Example 4

To a cathode or anode by electrophoresis counterions diffuse layer will move in the micelles $\{m[\text{AgI}] n\text{Ag}^+(n-x)\text{NO}_3^-\}^{x+} x\text{NO}_3^-$?

The solution is:

The diffuse layer is formed by counterions $x\text{NO}_3^-$, hence the diffuse layer is negative charged and therefore, during electrophoresis, $x\text{NO}_3^-$ ions will move to the anode.

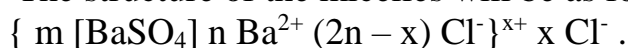
Example 5

Write the formula of micelles and granules (in the isoelectric state) obtained in excess BaCl_2 : $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 = \text{BaSO}_4\downarrow + 2\text{NaCl}$;

The solution is:

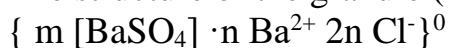
Low soluble barium sulfate forms a crystalline aggregate, which consists of m BaSO_4 . On the surface of the aggregate adsorbed n ions Ba^{2+} (as in excess BaCl_2). From the dissociation equation $\text{BaCl}_2 \rightarrow n \text{Ba}^{2+} + 2n \text{Cl}^-$ it follows, that $n \text{Ba}^{2+}$ responds $2n \text{Cl}^-$. It is connected to the kernel surface $(2n-x)$ ions Cl^- . The rest of the counterions $(x) \text{Cl}^-$ are placed in the diffuse layer.

The structure of the micelles will be as follows:



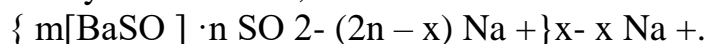
If the granule is in an isoelectric state, then the total charge potentialdetermining ions is equal to the charge of counterions. On the surface the aggregate is adsorbed $n \text{Ba}^{2+}$ ions. It is connected to the kernel surface $2n$ chloride of Cl^- ions, diffuse layer is absent.

The structure of the granule (in the isoelectric state) will be:



Example 6

Sol BaSO_4 was obtained by draining the same volumes of solutions BaCl_2 draining the same volumes of BaCl_2 solutions with a molar concentration of 0.005 mol/l and Na_2SO_4 with a molar concentration of 0.02 mol/l. What ions form a diffuse layer? The solution is: Barium sulfate micelles are formed by the following reaction: $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 = \text{BaSO}_4\downarrow + 2\text{NaCl}$ Low soluble barium sulfate forms a crystalline aggregate, consisting of $m \text{BaSO}_4$. On its surface, they begin in accordance with the Panet - Faience selective adsorption rule, adsorb $n \text{SO}_4^{2-}$ ions, which are in solution in excess (since the molar concentration of Na_2SO_4 is more) and who can go for BaSO_4 completion. They create a negative charge of the kernel and are potentialdeterminants. To this layer joins oppositely charged $(2n-x)$ ions Na^+ , that form the adsorption layer. The rest of the counterions $(x) \text{Na}^+$ are placed in the diffuse layer. Therefore, $x \text{Na}^+$ ions form a diffuse layer of micelles:

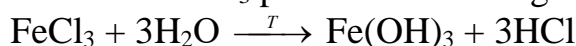


Example 7

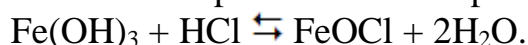
What is the formula of the micelle sol obtained by the hydrolysis reaction of the ferrum (III) chloride, given that the potentialdetermining ions are FeO^+ ions?

The solution is:

The hydrolysis reaction of FeCl_3 proceeds according to the scheme:



The nucleus of micelles becomes slightly soluble $\text{Fe}(\text{OH})_3$, surface molecules which interact with HCl and form the product of incomplete hydrolysis of FeOCl :



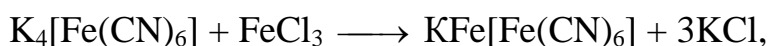
FeOCl molecules dissociate:



The FeO^+ ions formed stabilize the colloidal particle, adsorbed on its surface. The structure of the micelle sol ferum (III) hydroxide: $\{m [\text{Fe}(\text{OH})_3] n\text{FeO}^+ (n-x) \text{Cl}^-\}^{x+} x\text{Cl}^-$.

Example 8

What formula will the micelle sol of the Berlin lazure $\text{KFe}[\text{Fe}(\text{CN})_6]$ obtained by the reaction:



if during electrophoresis does the granule move to the anode?

The solution is:

If, during electrophoresis, the granule is moved to the anode, this means that the granule is negatively charged. The sign of its charge is determined by the sign of the charge potential definition ion.

If the reaction occurs in excess of FeCl_3 , then Fe^{3+} ions will be adsorbed on the surface of the $\text{KFe}[\text{Fe}(\text{CN})_6]$ aggregate (Selective adsorption occurs according to Panetta-Faience rule: these are the ions that belong to composition of the crystal lattice of the aggregate). Fe^{3+} ions are potential determinants, they create a positive charge for the nucleus and granules.

If the reaction occurs in excess $\text{K}_4[\text{Fe}(\text{CN})_6]$, then on the surface $\text{KFe}[\text{Fe}(\text{CN})_6]$ aggregates will adsorb $[\text{Fe}(\text{CN})_6]^{4-}$ (Selective adsorption occurs according to Panetta-Faience rule: these are the ions that make up the crystal lattice of the aggregate.). Ions $[\text{Fe}(\text{CN})_6]^{4-}$ create a negative charge of the nucleus and the granules, that is, the potential determinants.

Thus, the formula micelles sol of the Berlin azure in excess $\text{K}_4[\text{Fe}(\text{CN})_6]$ has the formula : $\{m \text{KFe}[\text{Fe}(\text{CN})_6] n[\text{Fe}(\text{CN})_6]^{4-} (4n-x) \text{K}^+ \}^{x-} x \text{K}^+$.

Example 9

Explain why inflammation causes erythrocytes to clump and settle .

The solution is:

In inflammatory processes in the blood plasma increases the content of proteins of the acute phase - fibrinogen, immunoglobulins and others. These proteins are adsorbed on the surface of red blood cells, which reduces their zeta potential. Factors leading to a decrease in zeta potential increase the likelihood of cell adhesion with each other and affect the rate of erythrocyte sedimentation due to gravity.

Self-test questions

6.1 What is the formula of the micelle of the Berlin azure $\text{KFe}[\text{Fe}(\text{CN})_6]$ obtained by the reaction: $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{FeCl}_3 \longrightarrow \text{KFe}[\text{Fe}(\text{CN})_6] + 3\text{KCl}$, if during electrophoresis the granule moves to the cathode?

6.2 The counterions of the diffuse layer in the micelle are moved to the cathode or anode during electrophoresis $\{m \text{KFe}[\text{Fe}(\text{CN})_6] n\text{Fe}^{3+} (3n-x) \text{Cl}^- \}^{x+} x \text{Cl}^-$?

6.3 What volume of a solution of $(\text{NH}_4)_2\text{S}$ with a molar concentration of 0.02 mol/l must be added to a solution of ZnCl_2 with a molar concentration of 0.02 mol / l to form a ZnS sol with a negatively charged granule?

6.4 Write the formula of the micelle of the sol obtained by the interaction of solutions of K_2SiO_3 and HCl , if the counterions in an electric field move to the cathode.

6.5 Write the formula of micelles and granules (in the isoelectric state) of the AgCl sol obtained in excess a) FeCl_3 , b) AgNO_3 .

6.6 What is the sign of the charge of a granule of CaSO_4 sol obtained by mixing equal volumes of CaCl_2 solutions with a molar concentration of 0.0025 mol / l and H_2SO_4 with a molar concentration of 0.02 mol / l.

6.7 Write the formula of the micelle and granules (in the isoelectric state) of the ZnS sol obtained in excess a) $(\text{NH}_4)_2\text{S}$, b) ZnCl_2 .

6.8 Write the formula of the micelle and granules (in the isoelectric state) of the sol AgBr obtained in excess a) NaBr , b) AgNO_3 .

6.9 Sol argentum bromide was obtained by the interaction of solutions of AgNO_3 and NaBr (excess). To which electrode will the sol particles move?

6.10 The ZnS sol was obtained by mixing equal volumes of $(\text{NH}_4)_2\text{S}$ solutions with a molar concentration of 0.002 mol / l and ZnCl_2 with a molar concentration of 0.02 mol / l. Which ions form a diffuse layer?

6.11 The ZnS sol was obtained by mixing equal volumes of $(\text{NH}_4)_2\text{S}$ solutions with a molar concentration of 0.2 mol / l and ZnCl_2 with a molar concentration of 0.02 mol / l. Which ions form a diffuse layer?

6.12 What volume of K_2SiO_3 solution with a molar concentration of 0.02 mol / l must be added to a solution of HCl with a molar concentration of 0.02 mol / l to form a sol of H_2SiO_3 with a negatively charged granule?

7. Coagulation of colloidal solutions. Properties of biopolymer solutions.

List of basic terms

Term	Semantic meaning
Coagulation of colloid solutions	the process of aggregation (sticking) of solid particles.
Schulze-Hardy rule	the coagulating action is inherent in the ion of the electrolyte, the charge of which is opposite to the charge of the colloidal particle (granule), and its coagulating action is stronger the higher its charge.
Coagulation threshold $C_c\left(\frac{1}{z}x\right)$	the minimum molar concentration of the electrolyte at which coagulation of the colloidal solution occurs. $C_c\left(\frac{1}{z}x\right) = \frac{C\left(\frac{1}{z}x\right) \cdot V_{(el-t)}}{V_{(sol)}}, \text{ mmol/l}$ $C\left(\frac{1}{z}x\right)$ – molar concentration of electrolyte equivalent; $V_{(sol)}$ – volume of sol; $V_{(el-t)}$ – electrolyte volume.
Coagulating power $V_c(x)$	the value inverse of the coagulation threshold, $V_c(x) = \frac{1}{C_c\left(\frac{1}{z}x\right)}, \text{ l/mmol.}$
DLFO theory	the coagulation threshold is inversely proportional to the charge of the coagulating ion in the sixth degree (for heavily charged sol particles).
Colloidal protection	stabilization of lyophobic dispersed systems by means of HMC which are adsorbed on a surface of particles and interfere with their sticking together.
Protective number	is equal to the mass (in mg) of dry macromolecular substance, which is able to protect 10 ml of sol from coagulation by adding to it 1 ml of sodium chloride solution with a mass fraction of 10% NaCl.
Macromolecular compounds (HMC) Polymers	substances with a molecular weight greater than 10,000 relative units of mass. Macromolecules are made up of a large number of repeating units (monomers).
Swelling	spontaneous penetration of low molecular weight fluid into the environment of HMC molecules and the associated displacement of the links, and then the chains of macromolecules. In the first stage, solvate shells are formed from solvent molecules ($\Delta H < 0$). In the second stage, the solvent molecules diffuse into the voids between the links and chains of macromolecules ($\Delta H = 0$), which is

	accompanied by a significant increase in the volume of the system. Dissolution of the HMC is a spontaneous process ($\Delta G < 0$).
Unlimited swelling	swelling, which ends with complete dissolution of the polymer and the formation of a molecular solution.
Limited swelling	the swelling goes to a certain limit and ends with the formation of gels containing a spatial grid of polymer chains filled with solvent molecules.
Thixotropy	Gels and jelly particles which are bound by weak intermolecular forces (hydrogen bonds, Van der Waals forces, hydrophobic interactions) are able to liquefy under mechanical influence, and then at rest - to tremble again (isothermal process).
Syneresis	the process of spontaneous division of jelly into two phases. With the release of liquid, the gels decrease in volume and become less transparent.
Coacervation	process of unauthorized association of water covers of several particles, without merging of the particles.
Salting	the process of precipitation of proteins from solution under the action of water-absorbing substances. These are alkali metal and ammonium salts, the ions of which form their own large hydrate shells (Li^+ , Na^+ , K^+ , SO_4^{-2} , PO_4^{3-} , CH_3COO^-)
Isoelectric point of protein	this is the pH value at which the protein molecule is in the isoelectric state, ie when the number of positive charges on the molecule is equal to the number of negative charges. $\text{H}_2\text{N}-\text{R}-\text{COOH} \rightarrow \text{H}_3\text{N}^+-\text{R}-\text{COO}^-$ (bipolar ion)
Methods for determining IEP	<ol style="list-style-type: none"> 1) by electrophoretic mobility of protein: in a solution whose pH is equal to IEP, electrophoresis is not observed; 2) by the intensity of turbidity of the HMC solution with the addition of salts: the maximum turbidity is observed in the solution, the pH of which is as close as possible to the IEP; 3) by the intensity of edema: minimal edema is observed in the solution, the pH of which is as close as possible to the IEP; 4) by the rate of gem formation: the maximum rate of gem formation is observed in a solution whose pH is as close as possible to the IEP.
Osmotic pressure of HMC solutions	<p>Haller's equation: $\pi = \frac{\rho(\text{X})}{\text{M}(\text{X})} \cdot \text{R} \cdot \text{T} + \text{k} \cdot \rho^2(\text{X}),$</p> <p>$\rho(\text{X})$ – mass concentration HMC; R – universal gas constant, T – temperature,</p>

	k – a constant that depends on the properties of the HMC and the solvent (in the case of macromolecules having a globular shape, k = 0).
Oncotic pressure	Part (0.5%) of the total osmotic pressure of blood plasma due to the presence of proteins in the blood. Oncotic blood plasma pressure is equal to $3,5 \cdot 10^3 - 3,9 \cdot 10^3$ Pa.
Donnan's balance	<p>A mobile equilibrium is established between the content of small cations and anions in the middle of the cell and in the intercellular fluid, but in such a way that the concentration of ions in the middle of the cell will always be higher than in the intercellular fluid due to those ions that bind to protein molecules. As a result, the osmotic pressure in the cell is slightly higher, which creates a certain turgor. This membrane equilibrium is described by the Donnan equation:</p> $X = \frac{C_3^2}{C_B + 2C_3}$ <p>C_o -the initial molar concentration of low molecular weight electrolyte in solution outside the cell; C_i - initial molar concentration of high molecular weight electrolyte inside the cell; X is the decrease in the molar concentration of the electrolyte that has passed from the external solution into the cell.</p>
If $C_o \gg C_i$	<p>you can neglect the term C_i, than: $\chi = \frac{C_o^2}{2C_o} = \frac{C_o}{2}$.</p> <p>Uniform distribution of ions on both sides of the membrane.</p>
If $C_o = C_i$	<p>than $\chi = \frac{C_o^2}{3C_o} = \frac{C_o}{3}$. A third of the number of ions from the external solution can pass into the middle of the cell.</p>
If $C_o \ll C_i$	<p>you can neglect the term C_o, than: $\chi = \frac{C_o^2}{C_i}$</p> <p>$X \approx 0$, that is, the passage of ions across the membrane in small quantities.</p>

Examples of exercises

Example 1

When coagulating the sol with electrolytes, the following values of coagulation thresholds (mmol / l) were obtained: $c_c(\text{KNO}_3) = 50,0$; $c_c(1/2\text{MgCl}_2) = 0,8$; $c_c(\text{NaBr}) = 49,0$.

Which of the following electrolytes has the greatest coagulating ability?

Specify the coagulating ion.

What is the sign of the charge of the particles (granules) of this sol?

Solution:

The value inverse of the coagulation threshold is called the coagulating ability:

$$V_c(x) = \frac{1}{C_c\left(\frac{1}{z}x\right)}, \text{ l/mmol.}$$

$$V_c(KNO_3) = \frac{1}{50} = 0.02 \text{ l/mmol;}$$

$$V_c(MgCl_2) = \frac{1}{0.8} = 1.25 \text{ l/mmol;}$$

$$V_c(NaBr) = \frac{1}{49.0} = 0.0204 \text{ l/mmol.}$$

has the greatest coagulating ability.

Since the coagulating effect is stronger the higher the ion charge (Schulze-Hardy rule), we compare the magnitude of the charges of anions and cations:

Anions (NO_3^- ; Cl^- ; Br^-): charges are the same.

Cations (K^+ , Mg^{2+} , Na^+): ion has the highest charge Mg^{2+} .

Since the anions in all electrolytes are single-charged, the ions - coagulants are cations. The highest charge has the Mg^{2+} , ion, so it is a coagulating ion.

The coagulating action is inherent in the ion of the electrolyte, the charge of which is opposite to the charge of the colloidal particle (granule), (Schulze-Hardy rule), respectively, the charge of the granule of this sol is negative.

Example 2

Sol AgI was obtained with an excess of $AgNO_3$. Which of the following coagulating electrolytes will have the lowest coagulation threshold: KCl , $FeSO_4$, $Al(NO_3)_3$?

Solution:

On the surface of the AgI aggregate, Ag^+ ions are adsorbed, which are in solution in excess. They create a positive charge of the nucleus and granules and are potentially determining.

The coagulating action is inherent in the electrolyte ion, the charge of which is opposite to the charge of the colloidal particle (granule), (Schulze-Hardy rule), respectively, the charge of the coagulating ion is negative.

The coagulating effect is stronger the higher the ion charge (Schulze-Hardy rule).

The highest charge among the anions (Cl^- , SO_4^{2-} , NO_3^-) has the anion SO_4^{2-} , so it is a coagulating ion.

Therefore, the electrolyte $FeSO_4$ has the greatest coagulating ability.

Because the coagulation ability is inversely proportional to the coagulation threshold, $FeSO_4$ will have the lowest coagulation threshold.

Example 3

What is the sign of the charge of the granules of sol, if the coagulation of sol electrolytes $c_c\left(\frac{1}{2}MgSO_4\right) > c_c\left(\frac{1}{3}Al(NO_3)_3\right)$?

Solutoin:

Compare the magnitude of the charges of anions and cations:

Anions (NO_3^- ; SO_4^{2-}): the ion has the highest charge SO_4^{2-} .

Cations (Al^{3+} , Mg^{2+}): the ion has the highest charge Al^{3+} .

Since $\text{Al}(\text{NO}_3)_3$ has a lower coagulation threshold, it accordingly has a higher coagulating ability and the coagulating ion is an ion Al^{3+} .

The coagulating action is inherent in the electrolyte ion, the charge of which is opposite to the charge of the granule (Schulze-Hardy rule), respectively, the charge of the granule of this sol is negative.

Example 4

Coagulation of 4 l of iron (III) hydroxide sol took place by adding to it 0.4 l of magnesium sulfate solution with a molar concentration equivalent to 0.0025 mol / l. Calculate the coagulation threshold.

Solution:

Determine the coagulation threshold:

$$C_c\left(\frac{1}{z}x\right) = \frac{C\left(\frac{1}{z}x\right) \cdot V_{(el-t)}}{V_{(sol)}} = \frac{0.0025 \cdot 0.4}{4} = 2.5 \cdot 10^{-4} \text{ МОЛЬ/Л.}$$

Example 5

The coagulating capacity of magnesium ions relative to the iron (III) hydroxide sol is 62.5 l / mmol. Calculate the minimum molar concentration of the equivalent electrolyte MgSO_4 , which causes coagulation of the sol $\text{Fe}(\text{OH})_3$.

Solution:

Coagulating ability - the value inverse of the coagulation threshold:

$$V_c(x) = \frac{1}{C_c\left(\frac{1}{z}x\right)}, \text{ Coagulation threshold is the minimum molar concentration of}$$

electrolyte at which coagulation of a colloidal solution occurs.

$$C_c\left(\frac{1}{z}x\right) = \frac{1}{V_c(x)} = \frac{1}{62.5} = 0.016 \text{ mmol/l.}$$

Example 6

Arrange the ions Cs^+ , Li^+ , K^+ , Na^+ , Rb^+ in a number of growth of their coagulating action.

Solution:

In a number of inorganic ions with the same charge, the coagulating effect is greater the larger the ion radius (ions with larger radii are less hydrated).

$\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ $\xrightarrow{\text{growth of coagulating action}}$

Example 7

Using the values of the golden number (in mg), select the HMC, which will have the greatest protective effect to increase the aggregative stability of the pharmaceutical drug: gelatin - 0.01; dextrin - 20.0; saponin - 115.0; egg albumin - 2.5.

Solution:

The golden number is the minimum mass of the HMC, which protects from coagulation 10 ml of red gold ash by adding 1 ml of sodium chloride solution with a mass fraction of 10%.

Gelatin has the lowest gold number - 0.01, so gelatin will have the greatest protective effect.

Example 8

The isoelectric point of the protein is 6.6. The protein is in a buffer solution with $[H^+] = 10^{-8}$ mol / l. Which electrode will the protein move to during electrophoresis?

Solution:

pH buffer solution $pH = -\lg[H^+] = -\lg(10^{-8}) = 8$.

If the IEP protein is 6.6, then at pH = 8.00 (alkaline medium) macroions will have a negative charge:

$H_3N^+-R-COO^- + OH^- \rightarrow H_2N-R-COO^- + H_2O$ (protein anion in an alkaline medium) and the protein will move to the anode.

Example 9

The isoelectric point of the protein is 4.5. The protein is in a buffer solution with $[H^+] = 10^{-3}$ mol / l. Which electrode will the protein move to during electrophoresis?

Solution:

pH buffer solution $pH = -\lg[H^+] = -\lg(10^{-3}) = 3$.

If the IEP protein is 4.5, then at pH = 3.00 (acidic environment) macroions will have a positive charge:

$H_3N^+-R-COO^- + H^+ \rightarrow H_3N^+-R-COOH$ (protein cation in an acidic environment) and the protein will move to the cathode.

Example 10

IEP casein 4.50, to which electrode will the protein move during electrophoresis at pH = 4.5?

Solution:

If the IEP of the protein is 4.5, then at pH = 4.5 electrophoresis is not observed, because in the isoelectric state the protein molecule is electroneutral (the number of positive charges on the molecule is equal to the number of negative charges: $H_2N-R-COOH \rightarrow H_3N^+-R-COO^-$).

Self test questions

7.1 When coagulating the sol with electrolytes, the following values of coagulation thresholds (mmol / l) were obtained: $c_c(KCl) = 20,50$; $c_c(1/2Na_2SO_4) = 0,32$. Determine the sign of the charge of the colloidal particle (granules) of the sol.

7.2 The coagulation threshold $c_c(1/2CaCl_2) = 0,69$ mmol / l relative to the sol AgI. What volume of calcium chloride solution with a molar concentration equivalent to 0.5 mol / l causes coagulation of 100 ml of sol?

Answer: $v(\text{CaCl}_2) = 0,15 \cdot 10^{-3} \text{ l}$.

7.3 The coagulation threshold of electrolytes relative to the sol increases in the sequence: $c_c(\frac{1}{3}(\text{NH}_4)_3\text{PO}_4) < c_c(\frac{1}{2}(\text{NH}_4)_2\text{SO}_4) < c_c(\text{NH}_4\text{NO}_3)$. What is the sign of the charge of the sol granules?

7.4 Coagulation of 500 ml of iron (III) hydroxide sol took place by adding to it 70 ml of sodium chloride solution with a molar concentration equivalent to 0.02 mol / l. Calculate the coagulation threshold.

Answer: $c_c = 2.8 \text{ mmol/l}$.

7.5 The coagulating capacity of phosphate ions relative to the aluminum hydroxide sol is 20.0 l / mmol. Calculate the minimum molar concentration of the electrolyte that causes coagulation of the sol $\text{Al}(\text{OH})_3$.

Answer: $c_c = 0,05 \text{ mmol/l}$.

7.6 Using the values of the iron number (in mg), select the HMC, which will have the greatest protective effect to increase the aggregative stability of the pharmaceutical drug: gelatin - 5.0; gum arabic - 25.0; dextrin - 20.0; egg albumin - 15.0.

7.7 The isoelectric point of insulin is 6.0. Insulin is in a buffer solution with $[\text{H}^+] = 10^{-8} \text{ mol/l}$. Which electrode will the insulin move to during electrophoresis?

7.8 To which electrode will β -lactoglobulin move during electrophoresis in a buffer solution with $[\text{H}^+] = 10^{-3} \text{ mol / l}$, if at $\text{pH} = 5.2$ β -lactoglobulin remains at the start?

7.9 The IEP of casein is 4.50, globulin is 7.0, and collagen is 4.0. How can these proteins be separated by electrophoresis? Explain the answer.

Answer: During electrophoresis at $\text{pH} = 4,5$.

7.10 To which electrode will the protein move during electrophoresis, if its IEP 4 and $\text{pH} = 5.2$?

7.11 If the IEP protein is 3.50, which functional groups predominate in the neutral medium?

7.12 If the IEP protein is 7.40, which functional groups predominate in the neutral medium?

Additions

1. Thermodynamic properties of some substances

ΔH_{298}^0 - standard enthalpy of substance formation, kJ/mol;

S_{298}^0 - standard entropy of matter, J/(mol·K);

ΔG_{298}^0 - standard change of Gibbs energy in the formation of a complex substance from simple substances, kJ/mol;

s is a solid state, l is a liquid state, g is a gaseous state, and aq is a substance in aqueous solution.

Substance	state	ΔH_{298}^0 , kJ/mol	S_{298}^0 , JДж/(mol · K)	ΔG_{298}^0 , kJДж/mol
<i>Br₂</i>	l	0	152,2	0
<i>CO₂</i>	g	-383,5	213,8	-394,4
<i>CO</i>	g	-110,5	197,7	-137,2
<i>Cl₂</i>	g	0	223,1	0
<i>H₂</i>	g	0	130,7	0
<i>HBr</i>	g	-36,3	198,7	-53,4
<i>HCl</i>	g	-92,3	186,9	-95,3
<i>H₂O</i>	g	-241,8	188,8	-228,6
<i>H₂O</i>	l	-285,8	70,0	-237,1
<i>H₂O₂</i>	g	-187,8	109,6	-120,4
<i>N₂</i>	g	0	191,6	0
<i>NH₃</i>	g	-45,9	192,8	-16,4
<i>NH₄Cl</i>	s	-314,4	94,6	-202,9
<i>NH₄NO₃</i>	s	-365,6	151,1	-183,9
<i>NO</i>	g	91,3	210,8	87,6
<i>N₂O</i>	g	81,6	220,0	103,7
<i>NO₂</i>	g	33,2	240,1	51,3
<i>O₂</i>	g	0	205,2	0
<i>O₃</i>	g	142,7	238,9	163,2
<i>Pb(NO₃)₂</i>	g	-451,8	213,9	
<i>PbO</i>	g	70,3	240,0	
<i>C₂H₅OC₂H₅</i>	l	-279,5	172,4	
<i>CH₃OCH₂CH₂CH₃</i>	l	-266,0	262,9	
phthalic acid	s	-782,0	207,9	
phthalic anhydride	s	-460,1	180	
L – lactic acid	aq	-686	222	-539
D – glucose	s	-1274,5	212,1	-910,0
D – glucose	aq	-1263,8	269,5	-917,0
Saccharose	s	-2222	360	-1545
<i>H₂O₂</i>	g	-187,8	109,6	-120,4
<i>N₂</i>	g	0	191,6	0
<i>NH₃</i>	g	-45,9	192,8	-16,4

NH_4Cl	s	-314,4	94,6	-202,9
NH_4NO_3	s	-365,6	151,1	-183,9
NO	g	91,3	210,8	87,6
N_2O	g	81,6	220,0	103,7
NO_2	g	33,2	240,1	51,3
O_2	g	0	205,2	0
O_3	g	142,7	238,9	163,2
$Pb(NO_3)_2$	g	-451,8	213,9	
PbO	g	70,3	240,0	
$C_2H_5OC_2H_5$	l	-279,5	172,4	
$CH_3OCH_2CH_2CH_3$	l	-266,0	262,9	
phthalic acid	s	-782,0	207,9	
phthalic anhydride	s	-460,1	180	
L – lactic acid	aq	-686	222	-539
D – glucose	s	-1274,5	212,1	-910,0
D – glucose	aq	-1263,8	269,5	-917,0
Saccharose	STB	-2222	360	-1545

2. Heat of combustion of some substances

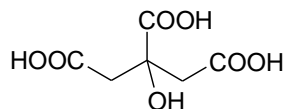
Substance	state	$\Delta H_{c,298}^0$, kJ/mol
H_2	g	-285,8
NH_3	g	-382,8
CH_4	g	-890,8
C_2H_4	g	-1411,2
C_2H_6	g	-1560,7
$C_2H_5OC_2H_5$	l	-2723,9
$C_6H_{12}O_6$ (glucose)	c	-2802,5
$C_{12}H_{22}O_{11}$ (saccharose)	c	-5639,7
CH_3COOH	l	-874,2
CH_3CONH_2	lp	-1184,6

3. Instability constants of complex ions

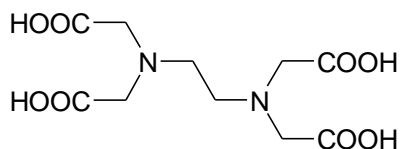
K_{inst} – the constant of complete dissociation of the complex ion in aqueous solution at 20-30°C:

$$ML_n \rightleftharpoons M + nL$$

$$K_{inst} = \frac{[M] \cdot [L]^n}{[ML_n]}$$



H₃Cit – citric acid;
Cit³⁻ – citrate anion.



H₄Edta – ethylenediaminetetraacetic acid;
Edta⁴⁻ – ethylenediaminetetraacetate.

Complex	K _{inst}	Complex	K _{inst}
[Ag(SCN) ₂] ⁻	3,89 · 10 ⁻⁹	[Fe(C ₂ O ₄) ₃] ³⁻	6,31 · 10 ⁻²¹
[Ag(CN) ₂] ⁻	1 · 10 ⁻²¹	[FeF ₆] ³⁻	7,94 · 10 ⁻¹⁷
[Ag(S ₂ O ₃) ₂] ³⁻	3,47 · 10 ⁻¹⁴	[Fe(SCN) ₆] ³⁻	5,89 · 10 ⁻⁴
[Ag(NH ₃) ₂] ⁺	1,0 · 10 ⁻⁷	[Fe(CN) ₆] ³⁻	1,0 · 10 ⁻⁴²
[CaCit] ⁻	6,75 · 10 ⁻⁴	[HgEdta] ²⁻	1,6 · 10 ⁻²²
[CaEdta] ²⁻	2,58 · 10 ⁻¹¹	[PbEdta] ²⁻	5,0 · 10 ⁻¹⁴
[Ca(P ₂ O ₇)] ²⁻	2,5 · 10 ⁻⁶	[CdEdta] ²⁻	3,47 · 10 ⁻¹⁷
[Ca(P ₃ O ₉)] ⁻	3,55 · 10 ⁻⁴		
[Ca(P ₄ O ₁₂)] ²⁻	3,8 · 10 ⁻⁶		

4. The solubility products of some sparingly soluble electrolytes at 25°C

Substance	SP	Substance	SP
$AlPO_4$	$9,84 \cdot 10^{-21}$	MgC_2O_4	$4,83 \cdot 10^{-6}$
$AgBr$	$5,35 \cdot 10^{-13}$	$Mg_3(PO_4)_2$	$1,04 \cdot 10^{-24}$
$AgCN$	$5,97 \cdot 10^{-17}$	MnC_2O_4	$1,70 \cdot 10^{-7}$
$AgCl$	$1,77 \cdot 10^{-10}$	MnS	$1,1 \cdot 10^{-13}$
AgI	$8,52 \cdot 10^{-17}$	$Ni_3(PO_4)_2$	$4,74 \cdot 10^{-32}$
$Ag_2C_2O_4$	$5,40 \cdot 10^{-12}$	NiS	$9,3 \cdot 10^{-22}$
Ag_2CO_3	$8,46 \cdot 10^{-12}$	$PbBr_2$	$6,6 \cdot 10^{-6}$
Ag_2SO_4	$1,2 \cdot 10^{-5}$	$PbCO_3$	$7,4 \cdot 10^{-14}$
BaC_2O_4	$1,1 \cdot 10^{-7}$	$PbCl_2$	$1,7 \cdot 10^{-5}$
$Ba_3(PO_4)_2$	$6,0 \cdot 10^{-39}$	PbI_2	$9,8 \cdot 10^{-9}$
$BaSO_4$	$1,08 \cdot 10^{-10}$	PbC_2O_4	$9 \cdot 10^{-10}$
BaF_2	$1,84 \cdot 10^{-7}$	$PbSO_4$	$2,53 \cdot 10^{-8}$
$CaCO_3$	$3,36 \cdot 10^{-9}$	PbS	$8,7 \cdot 10^{-29}$
CaC_2O_4	$2,32 \cdot 10^{-9}$	$SrCO_3$	$5,6 \cdot 10^{-10}$
$Ca_3(PO_4)_2$	$2,07 \cdot 10^{-33}$	SrC_2O_4	$5,6 \cdot 10^{-8}$
$CaHPO_4$	$2,2 \cdot 10^{-7}$	$Sr_3(PO_4)_2$	$1,0 \cdot 10^{-31}$
$CaSO_4$	$4,93 \cdot 10^{-5}$	$SrSO_4$	$3,44 \cdot 10^{-7}$
CaF_2	$3,45 \cdot 10^{-11}$	SrF_2	$4,33 \cdot 10^{-9}$
$CdCO_3$	$1,0 \cdot 10^{-12}$	FeS	$3,4 \cdot 10^{-17}$
CdC_2O_4	$1,42 \cdot 10^{-8}$	$FeCO_3$	$3,13 \cdot 10^{-11}$

5. Standard electrode potentials in aqueous solutions at 25°C

Semi-reaction	E^0, V
$Ag^+ + e^- \rightleftharpoons Ag$	0,800
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	-0,403
$Co^{2+} + 2e^- \rightleftharpoons Co$	-0,28
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1,92
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0,744
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	-0,407
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1,232
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	0,340
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0,447
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0,771
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1,776
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0,695
$I_2 + 2e^- \rightleftharpoons 2I^-$	0,5355
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	-1,185
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons 5Mn^{2+} + 4H_2O$	1,507
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0,257
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0,1375
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0,151
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0,760

6. Some mathematical information

1. Floating point numbers

A floating point is a form of representing numbers in which the number is stored as a mantissa and an exponent. The number n can be expressed as follows:

$$n = a \cdot b^m$$

where:

- a – mantissa (expresses the value of a number without taking into account the order; as a rule, the value of the mantissa is chosen so that $1 \leq a \leq 10$)
- b – basis (most often 10 is used as a basis);
- m – order (expresses the degree of the basis of the number by which the mantissa is multiplied).

This way of representing numbers is convenient when working with very large or very small numbers. Examples:

$$\begin{aligned}0,01 &= 10^{-2} \\0,0001 &= 10^{-4} \\100000 &= 10^5 \\0,000054 &= 5,4 \cdot 10^{-5} \\12000000 &= 1,2 \cdot 10^7\end{aligned}$$

2. Some properties of degree indicators

Equation	Example
$a^n \cdot a^m = a^{n+m}$	$10^{-4} \cdot 10^{-5} = 10^{-9}$
$\frac{a^n}{a^m} = a^{n-m}$	$\frac{10^{-3}}{10^{-6}} = 10^3$
$(a^n)^m = a^{n \cdot m}$	$(10^4)^2 = 10^8$

Any number to the power of 0 is equal to one, except $0^0 = 0$, $0^n = 0$.

3. The logarithm of the number a on the basis of b is called the exponent of the power n , to which you need to raise the number b to get a .

Record $\log_b a = n$ equivalent to a record $b^n = a$

Most often used:

- decimal logarithm (basis 10, designation \lg);
- natural logarithm (basis $e = 2.7183\dots$, designation \ln).

4. Some properties of logarithms

- 1) Logarithms of numbers greater than one are positive, and numbers less than one are negative.
- 2) The logarithm of the number 1 on any basis is equal to 0: $\log_b 1 = 0$
- 3) Логарифм числа, рівного основі, дорівнює 1: $\log_b b = 1$ ($\lg 10 = 1$)
- 4) The logarithm of the product is equal to the sum of the logarithms:
 $\log_b (a \cdot c) = \log_b a + \log_b c$ ($\lg(a \cdot c) = \lg a + \lg c$)
- 5) The logarithm of the fraction is equal to the difference of the logarithms:
 $\log_b \frac{a}{c} = \log_b a - \log_b c$ ($\lg \frac{a}{c} = \lg a - \lg c$)

- 6) The logarithm of the number a to the power of n is equal to the logarithm of the number a multiplied by n : $\log_b a^n = n \cdot \log_b a$ ($\lg a^n = n \cdot \lg a$; $\lg 10^n = n$)

5. Finding the decimal logarithm of a number using the logarithm table.

In order to use the table to find the decimal logarithm of a number, you must first find its order, ie give the number as:

$$283500 = 2,835 \cdot 10^5 \text{ (fifth order)}$$

Round the number to two significant digits:

$$2,835 \cdot 10^5 \approx 2,8 \cdot 10^5$$

At the intersection of row 2 and column 0.8 (see Table 9) find the value and add to it the order of the number:

$$\lg 283500 = \lg(2,835 \cdot 10^5) \approx \lg(2,8 \cdot 10^5) = \lg 2,8 + \lg 10^5 = 0,447 + 5 = 5,447$$

Examples:

$$\begin{aligned} \lg 0,00283 &= \lg(2,83 \cdot 10^{-3}) \approx \lg(2,8 \cdot 10^{-3}) = \lg 2,8 + \lg 10^{-3} = 0,447 + (-3) \\ &= -2,553 \end{aligned}$$

$$\lg 0,000006 = \lg(6 \cdot 10^{-6}) = \lg 6 + \lg 10^{-6} = 0,778 + (-6) = -5,222$$

$$\begin{aligned} \lg 0,000368 &= \lg(3,68 \cdot 10^{-4}) \approx \lg(3,7 \cdot 10^{-4}) = \lg 3,7 + \lg 10^{-4} = 0,568 + (-4) = \\ &= -3,432 \end{aligned}$$

$$\lg 0,0561 = \lg(5,61 \cdot 10^{-2}) \approx \lg(5,6 \cdot 10^{-2}) = \lg 5,6 + \lg 10^{-2} = 0,748 + (-2) = -1,252$$

6. Finding a number on a decimal logarithm using a table

In order to use the table to find the decimal antilogarithm of a positive number (raise 10 to a positive power), you must first present the exponent in the form of the sum of integers and fractions:

$$2,93423 = 2 + 0,93423$$

Round the fractional part to three significant digits:

$$0,93423 \approx 0,934$$

Find the nearest number in the logarithm table and add the values of the corresponding row and column (see Table 9):

$$8 + 0,6 = 8,6$$

Multiply the value obtained by 10 to the power of the integer of the original number:

$$10^{2,93423} \approx 10^2 \cdot 10^{0,934} \approx 10^2 \cdot 8,6 = 860$$

If you need to raise 10 to a negative power, you must first provide a power exponent in the form of the sum of the negative integer part and the positive fractional part:

$$-1,05782 = -2 + 0,94218$$

And then act similarly:

$$10^{-1,05782} \approx 10^{0,942} \cdot 10^{-2} = 8,7 \cdot 10^{-2} = 0,087$$

Examples:

$$10^{-5,483} = 10^{0,517} \cdot 10^{-6} \approx 3,3 \cdot 10^{-6}$$

$$10^{-3,947} = 10^{0,053} \cdot 10^{-4} \approx 1,1 \cdot 10^{-4}$$

$$10^{-9,54} = 10^{0,56} \cdot 10^{-10} \approx 3,6 \cdot 10^{-10}$$

$$10^{-7,401} = 10^{0,599} \cdot 10^{-8} \approx 4 \cdot 10^{-8}$$

$$10^{-2,457} = 10^{0,543} \cdot 10^{-3} \approx 3,5 \cdot 10^{-3}$$

Table of decimal logarithms

0,m n	0,0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
1	0,000	041	079	114	146	176	204	230	255	279
2	301	322	342	362	380	398	415	431	447	462
3	477	491	505	519	532	544	556	568	580	591
4	602	613	623	634	644	653	663	672	681	690
5	699	708	716	724	732	740	748	756	763	771
6	778	785	792	799	806	813	820	826	833	839
7	845	851	857	863	869	875	881	887	892	898
8	903	909	914	919	924	929	935	940	945	949
9	954	959	964	969	973	978	982	987	991	996
$lg(n, m) = 0,xyz$						$10^{0,xyz} = n, m$				