BOGOMOLETS NATIONAL MEDICAL UNIVERSITY

Department of Analytical, Physical and colloid chemistry

METHODICAL INSTRUCTIONS TO INDIVIDUAL WORK ON STUDYING THE COURSE "GENERAL AND INORGANIC CHEMISTRY"

For pharmacy students

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CONTENT

1. Biogenic elements; biological role, application in medicine.

Table 1. The list of basic terms, parameters, definitions to the topic «Biogenic elements; biological role, application in medicine».

Terms	Content value
Electronic configuration of the atom	Record of electron distribution by energy levels and sublevels in the atom. Electrons populate atomic orbitals, starting with the lowest energy level. The sequence in the energy growth of the sublevels is as follows: $1s < 2s < 2p < 3s < 3p < 4s \leq 3d < 4p < 5s \leq 4d < 5p < 6s \leq 5d \leq 4f$ and so on.
Valence electrons	Electrons involved in chemical bonding. For s- and p-elements valence electrons are the electrons of the outer-level orbitals, and for d-elements the electrons of the s-orbitals of the outer layer and the d-orbitals of the penultimate layer.
Chemical bond	A set of interactions that binds individual atoms into molecules, ions, radicals, crystals. Depending on the nature of the electron density distribution between the interacting atoms, covalent, ionic, and metallic bonds are distinguished.
Electronegativity	The relative ability of element atoms to attract shared electron pairs.
The degree of oxidation	The hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic, with no covalent component. This is never exactly true for real bonds.
Redox reactions	Chemical reactions occurring with the change in the degree of oxidation of the atoms that are part of the reactants. The degree of oxidation is altered by the redistribution of electrons between the oxidizing atom and the reducing atom.
The reducing agent	A substance whose molecules or ions contain atoms capable of emitting electrons, for example: 1. Free metals, especially alkaline and alkaline earth. 2.Hydrogen, Carbon. 3.Compounds of non metals in the lowest oxidation states ($\overset{-2}{S}, \overset{-2}{Se}, \overset{-3}{N}, \overset{-3}{P}, \overset{-1}{I}, \overset{-1}{Cl}, \overset{-1}{Br}$). 4. Compounds of some metals in the lowest oxidation states ($\overset{+2}{Mn}, \overset{+3}{Cr}, \overset{+2}{Pb}$).

	5.Metal Hydrides (NaH, CaH_2). 6. Hydrogen peroxide.
The oxidizing agent	A substance whose molecules or ions contain atoms capable of attaching electrons, for example: 1. Free halogens (F_2, Cl_2, Br_2, I_2), Oxigen. 2.Nitric acid HNO_3 and Nitrogen oxides ($\overset{+5}{N}_2O_5, \overset{+4}{N}O_2, \overset{+1}{N}_2O$),concentrated sulfuric acid. $H_2\overset{+6}{S}O_4$. 3. Compounds of Halogens with a positive oxidation number. ($H\overset{+1}{Cl}O, H\overset{+3}{Cl}O_2, H\overset{+5}{Cl}O_3, H\overset{+7}{Cl}O_4$). 4. Compounds of some metals with a high degree of oxidation ($\overset{+7}{Mn}, \overset{+6}{Mn}, \overset{+6}{Cr}, \overset{+4}{Pb}$, etc.). 5.Hydrogen peroxide (H_2O_2), metal peroxides (Na_2O_2, KO_2, BaO_2) and so on.
Oxidation	loss of electrons $\overset{0}{Fe} - 3e \rightarrow \overset{+3}{Fe}$
Reduction	gain of electrons $\overset{+2}{Cu} + 2e \rightarrow \overset{0}{Cu}$
Electrolytic dissociation	The process of decomposition of a substance into ions when dissolved in water (and other solvents) or during melting.
Electrolytes	Substances, melts or solutions of which conduct an electric current due to dissociation into ions. Examples of electrolytes are acids, salts and bases.
Dissociation degree	Quantitative characterization of the dissociation process, which is equal to the ratio of the amount of electrolyte that has decomposed into ions n_i to the total amount of electrolyte in solution n_0: $\alpha = \frac{n_i}{n_0}$ The degree of dissociation depends on the nature of the substance, the nature of the solvent, the concentration of the substance and the temperature.
Strong electrolytes	Electrolytes, which are almost completely dissociated into ions in dilute aqueous solutions. Strong electrolytes are soluble bases (alkalis), strong mineral acids, and all soluble salts.
Weak electrolytes	Electrolytes, which even in dilute aqueous solutions do not completely dissociate into ions. Weak electrolytes include poorly soluble bases, amphoteric hydroxides, weak mineral

	acids, and low soluble salts. Weak electrolytes include almost all organic acids, water, ammonium hydroxide.
Acidity and alkalinity of solutions	In water (and in aqueous solutions) there is always a certain amount of $H^+$and OH^-ions formed as a result of reversible dissociation: $H_2O \leftrightarrows H^+ + OH^-$; $K_{\text{д}} = 1{,}8 \cdot 10^{-16} mol/l$ *Neutral* are called solutions in which the concentrations of ions H^+ and OH^- are equal. *Acidic* are called solutions in which the concentration of H^+ ions is greater than the concentration of OH^- ions. *Alkaline* are called solutions in which the concentration of H^+ ions is less than the concentration of OH^- ions.
Acid	An electrolyte, in the dissociation of which only cations H^+ are formed, example: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ $CH_3COOH \leftrightarrows H^+ + CH_3COO^-$
Strong acids	Acids that are strong electrolytes and dissociate almost completely in aqueous solutions. Strong acids include the following: H_2SO_4, $HNO_3, HCl, HBr, HI, HMnO_4, HClO_4$, H_2CrO_4
Bases	An electrolyte, the dissociation of which from only OH^-anions, example: $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$ $NH_3 \cdot H_2O \leftrightarrows NH_4^+ + OH^-$ Most bases are insoluble in water.
Strong bases (alkalis)	Bases that are strong electrolytes and dissociate in aqueous solutions almost completely. Strong bases include bases formed by alkaline and alkaline earth metals: $LiOH, NaOH, KOH, RbOH, CsOH, FrOH$ $Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$
Neutralization reaction	The reaction between a base and an acid whose product is salt and water, for example: $H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$ $H^+ + OH^- \rightarrow H_2O$
Salts	Salts – substances, which include acidic residues (anions) combined with cations of different origin (ions of metals, and groups, as NH_4^+, etc.). Salts that are soluble in water are strong electrolytes.
Hydrolysis of salts	The interaction of salt ions with water, in which the formation of week electrolite occurs, when this occurs, water spontaneously ionizes into hydroxide anions and hydronium cations. Hydrolysis undergoes salts formed: 1) weak base cation and strong acid anion; 2) a strong base cation and a weak acid anion;

	3) weak base cation and weak acid anion.
Degree of hydrolysis	Quantitative characterization of the hydrolysis process, which is equal to the ratio of the number of particles that have undergone hydrolysis $n_{г}$, to their number before hydrolysis n_0: $$\alpha_{г} = \frac{n_{г}}{n_0}$$

Algorithm for performing exercises on the subject of "Hydrolysis of salts"

1. Determine the solubility of the salt according to the solubility table.
2. Specify the strength of the base and the acids that form the salt. To conclude on the possibility of hydrolysis.
3. Record the dissociation equation for salt. Specify which salt ion will react with water.
4. Record the ionic and molecular equation of the hydrolysis reaction. In the case of multiply charged ions only for the first stage.
5. Determine the reaction of the medium of the solution of salt to be

a) acidic if the salt is formed by a strong acid and a weak base;
b) alkaline if the salt is formed by a strong base and a weak acid;
c) neutral (or close to neutral - slightly acidic, slightly alkaline) if the salt is formed by a weak base and a weak acid.

Examples of exercises

Example 1

Write the electronic formula of the chromium atom and ion Cr^{3+}.

Solution:

The order number of chromium in the periodic system of elements indicates the number of electrons in an atom (24).

Record the distribution of electrons by levels and sublevels of chromium atoms: $_{24}Cr$ $1s^22s^22p^63s^23p^63d^54s^1$

electronic ion formula Cr^{3+}:

Cr^{3+} $1s^22s^22p^63s^23p^63d^34s^0$.

Example 2

Electronic configuration $1s^22s^22p^63s^2\ 2p^64s^2$ corresponds to the atom:

a) Sodium　　b) Calcium　　c) Lithium　　d) Beryllium

Solution:

The order number of an element in the periodic system of elements indicates the number of electrons in an atom. Electronic configuration $1s^22s^22p^63s^22p^64s^2$ corresponds to an atom with a order number 20 (2+2+6+2+6+2=20), This is Calsium.

Example 3

Determine the degree of oxidation of the nitrogen in the substance: a) N_2O_4, b) HNO_3, c) $(NH_4)_2CO_3$.

***Solution*:**

a) The degree of oxidation of Nitrogen x, Oxigen -2. Based on the neutrality of the molecule, we make the equation:$2x + 4(-2) = 0$, hence $x = +4$, ie the degree of oxidation of nitrogen in N_2O_4 is +4.

b) The degree of oxidation of Nitrogen x, Hydrogen +1, Oxigen -2. Based on the neutrality of the molecule, we make the equation: $(+1) + x + 3(-2) = 0$, hence $x = +5$, ie the degree of oxidation of nitrogen in HNO_3 is +5.

c) The degree of oxidation of Hydrogen+1, Oxigen -2, Carbon in carbonates (salts of carbonic acid H_2CO_3) +4, Nitrogen x. We make the equation:
$2x + 2 \cdot 4(+1) + (+4) + 3(-2) = 0$, hence $x = -3$, that is, the degree of nitrogen oxidation in $(NH_4)_2CO_3$ is -3.

Example 4

Which of the reactions are redox:

a) $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$;
b) $Na_2O + 2\ HCl \rightarrow 2\ NaCl + H_2O$;
c) $H_2 + Cl_2 \rightarrow 2\ HCl$;
d) $Cl_2 + H_2O \rightarrow HClO + HCl$?

Solution:

We determine in which of these chemical equations the degrees of oxidation of atoms change:

a) $2\overset{0}{Na} + 2\overset{+1}{H}_2\overset{-2}{O} \rightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} + \overset{0}{H}_2$;

b) $\overset{+1}{Na}_2\overset{-2}{O} + 2\overset{+1}{H}\overset{-1}{Cl} \rightarrow 2\overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{H}_2\overset{-2}{O}$;

c) $\overset{0}{H}_2 + \overset{0}{Cl}_2 \rightarrow 2\overset{+1}{H}\overset{-1}{Cl}$;

d) $\overset{0}{Cl}_2 + \overset{+1}{H}_2\overset{-2}{O} \rightarrow \overset{+1}{H}\overset{+1}{Cl}\overset{-2}{O} + \overset{+1}{H}\overset{-1}{Cl}$.

The degrees of oxidation of the atoms change in the reactions a, c, d, therefore, they are redox.

Example 5

Specify the reducing agent and oxidizing agent in the reactions:

a) $8\ HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4\ H_2O$;
b) $2\ H_2S + H_2SO_3 \rightarrow 3\ S + 3\ H_2O$.

Solution:

The reducing agent gives away electrons during redox reactions, increasing its oxidation state. The oxidizing agent attaches electrons, reducing its oxidation state. Therefore, it is necessary to determine which atoms in these equations change the degree of oxidation:

a) $8\overset{+1}{H}\overset{-1}{I} + \overset{+1}{H}_2\overset{+6}{S}\overset{-2}{O}_4 \rightarrow 4\overset{0}{I}_2 + \overset{+1}{H}_2\overset{-2}{S} + 4\overset{+1}{H}_2\overset{-2}{O}$

$\overset{+1}{H}\,\overset{-1}{I}$ (iodide ion I^{-}) – reducing agent, H_2SO_4 (sulfate ion SO_4^{2-} or $\overset{+6}{S}$) – oxidizing agent.

b) $2\overset{+1}{H}_2\overset{-2}{S}+\overset{+1}{H}_2\overset{+4}{S}\overset{-2}{O}_3 \rightarrow 3\overset{0}{S}+3\overset{+1}{H}_2\overset{-2}{O}$

H_2S ($\overset{-2}{S}$) – reducing agent, H_2SO_3 (ion SO_3^{2-} or $\overset{+4}{S}$) – oxidizing agent.

Example 6

Identify the types of redox reactions:

a) $H_2 + Cl_2 \rightarrow 2HCl;$

b) $2KClO_3 \rightarrow 2KCl + 3O_2;$

c) $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2;$

d) $Cl_2 + H_2O \rightarrow HCl + HClO.$

Solution:

In reaction a: $\overset{0}{H}_2+\overset{0}{Cl}_2 \rightarrow 2\overset{+1}{H}\overset{-1}{Cl}$ the oxidant and the reducing agent are the elements of different molecules so the type of redox reaction is intermolecular..

In reaction b: $2K\overset{+5}{Cl}\overset{-2}{O}_3 \rightarrow 2K\overset{-1}{Cl}+3\overset{0}{O}_2$ the oxidizing agent and the reducing agent are the elements of the same compound so the type of redox reaction is intramolecular.

In reactions c: $2\overset{+4}{N}O_2+H_2O \rightarrow H\overset{+5}{N}O_3+H\overset{+3}{N}O_2$,

d: $\overset{0}{Cl}_2+H_2O \rightarrow H\overset{-1}{Cl}+H\overset{+1}{Cl}O$

the same element acts as an oxidizing agent and as a reducing agent is therefore a type of redox disproportionation reaction.

Example 7

In which of these substances manganese can show only oxidizing properties, and in which - only reductive: $KMnO_4$, MnO_2, Mn_2O_7, Mn, K_2MnO_4, MnO?

Solution:

Determine the degree of oxidation of manganese in these compounds: $K\overset{+7}{Mn}O_4, \overset{+4}{Mn}O_2, \overset{+7}{Mn}_2O_7, \overset{0}{Mn}, K_2\overset{+6}{Mn}O_4, \overset{+2}{Mn}O.$

The highest oxidation characteristic of manganese, +7 is found in the compounds $KMnO_4$, Mn_2O_7. Therefore, the manganese in these compounds can only be an oxidant, that is, to reduce its oxidation level. The smallest degree of oxidation $\overset{0}{Mn}$ is in simple matter. Therefore, metallic manganese can only be a reducing agent, increasing its degree of oxidation.

Example 8

Using the electronic balance method to select the coefficients in the redox reaction:

$H_2S + K_2Cr_2O_7 + H_2SO_4 \rightarrow S + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$;

Solution:

Write the scheme of reaction with the obtained degree of oxidation of the elements that perform them:

$$H_2\overset{-2}{S} + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \rightarrow \overset{0}{S} + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O;$$

Here H_2S is a reducing agent and $K_2Cr_2O_7$ is an oxidizing agent.

We formulate the electronic equations, taking into account that $K_2Cr_2O_7$ and $Cr_2(SO_4)_3$ quantities of substance 1 mol contain 2 mol of chromium:

$$\overset{-2}{S} - 2e^{-} \rightarrow \overset{0}{S}$$

$$2\overset{+6}{Cr} + 6e^{-} \rightarrow 2\overset{+3}{Cr}$$

We find the coefficients for the reducing agent, oxidant and products of their oxidation and reduction:

$$\begin{array}{l|c|l} \overset{-2}{S} - 2e^{-} \rightarrow \overset{0}{S} & & 3 \ \text{the reducing agent, the oxidation process} \\ & 6 & \\ 2\overset{+6}{Cr} + 6e^{-} \rightarrow 2\overset{+3}{Cr} & & 1 \ \text{oxidizer, the reduction process} \end{array}$$

The coefficients obtained for the H_2S and the product of its oxidation S, oxidizer $K_2Cr_2O_7$ and the product of its reduction $Cr_2(SO_4)_3$ are substituted into the reaction scheme:

$3\ H_2S + K_2Cr_2O_7 + H_2SO_4 \rightarrow 3\ S + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$;

The rest of the coefficients are selected in the following sequence:1) salt K_2SO_4, 2) acid H_2SO_4, 3) water. The final reaction equation is:

$3\ H_2S + K_2Cr_2O_7 + 4\ H_2SO_4 \rightarrow 3\ S + Cr_2(SO_4)_3 + K_2SO_4 + 7\ H_2O$;

To verify the correctness of the coefficients, we calculate the amount of oxygen in the left and right parts of the equation.

On the left: (7 + 4 · 4) mol = 23 mol

On the right: (3 · 4 + 4 + 7) mol = 23 mol

So the equation is spelled correctly.

Example 9

The neutralization equation misses the formula. Post it

$H_2SO_4 + 2KOH \quad = \quad ? \quad + 2\ H_2O$

Solution:

The neutralization reaction is the interaction of an acid with a base that produces salt and water. So the formula misses the salt formula.The number of substances in the left-hand side of the equation should be equal to the number of substances in the right-hand side of the equation, so $2K^{+}, SO_4^{2-}$ is missing in the right-hand side of the equation. In the neutralization equation, the formula K_2SO_4 (potassium sulfate) is omitted.

Example 10

To determine in which solutions of the following salts hydrolysis occurs:

ferric (III) nitrate
potassium nitrate
calcium chloride
sodium sulfate
sodium sulfite
argenum bromide
barium sulfate;
ammonium carbonate;
calcium carbonate.

Solution:

Analysis of the possibility of hydrolysis is carried out in accordance with the algorithm shown in table 1.

1) According to the solubility table, determine which of the salts are soluble in water and which are insoluble.

Water soluble salts:	*Water insoluble salts:*
ferric (III) nitrate $Fe(NO)_3$	bromide argument $AgBr$
potassium nitrate KNO_3	barium sulfate $BaSO_4$
calcium chloride $CaCl_2$	calcium carbonate $CaCO_3$
sodium sulfate Na_2SO_4	As these salts are insoluble in water, hydrolysis in aqueous solutions will not occur.
sodium sulfite Na_2SO_3	
ammonium carbonate $(NH_4)_2CO_3$	

2) Determine whether the soluble salts are a weak base cation or a weak acid anion.

$Fe(NO)_3$ – salt formed by a strong acid HNO_3 and a weak base $Fe(OH)_3$. Hydrolysis of the cation occurs

KNO_3 – salt formed by a strong acid HNO_3 and strong base KOH. Hydrolysis does not occur.

$CaCl_2$ – salt formed by a strong acid HCl and strong base $Ca(OH)_2$. Hydrolysis does not occur.

Na_2SO_4 – salt formed by a strong acid H_2SO_4 and strong base $NaOH$. Hydrolysis does not occur.

Na_2SO_3 – salt formed by a weak acid H_2SO_3 and strong base $NaOH$. Hydrolysis of the anion ccurs

$(NH_4)_2CO_3$ – salt formed by a weak acid H_2CO_3 and a weak base $NH_3.H_2O$. Hydrolysis of the anion and of the cation occurs at the same time.

Answer: Hydrolysis occurs in solutions of ferric (III) nitrate, sodium sulfite, ammonium carbonate.

Example 11

What is the reaction of the medium in an aqueous solution of barium chloride? Argue the answer.

Solution:

The medium of an aqueous salt solution may differ from the neutral one when hydrolysis of the salt occurs in the solution.

$BaCl_2$ – is a soluble salt formed by a strong acid HCl and a strong base $Ba(OH)_2$. Hydrolysis does not occur, so the medium in the solution of barium chloride is neutral.

Example 12

What is the reaction of the medium in an aqueous solution of potassium sulfite? Argue the answer.

Solution:

1) K_2SO_3– is a soluble salt formed by a weak acid H_2SO_3 and strong base KOH. This salt undergoes hydrolysis.
2) In an aqueous solution, the salt dissociates into ions:
$$K_2SO_3 \rightarrow 2K^+ + SO_3^{2-}$$
The anion SO_3^{2-} will react with water, since it is the weak electrolyte that corresponds to it.
3) The first stage of hydrolysis:
$$SO_3^{2-} + H_2O \leftrightarrows HSO_3^- + OH^- \qquad \text{reduced ionic equation}$$
$$K_2SO_3 + H_2O \leftrightarrows KHSO_3 + KOH \qquad \text{molecular equation}$$

Answer: The medium of the solution of potassium sulfite is alkaline, since the hydrolysis of the salt in the solution increases the amount of ions OH^-.

Example13

What is the reaction of the medium in an aqueous solution of magnesium chloride? Argue the answer.

Solution:

1) $MgCl_2$– is a soluble salt formed by a strong acid HCl and week base $Mg(OH)_2$. This salt undergoes hydrolysis.
2) In an aqueous solution, the salt dissociates into ions:
$$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$$
The cation Mg^{2+} will react with water, since it is the weak electrolyte that corresponds to it.
3) The first stage of hydrolysis:
$$Mg^{2+} + H_2O \leftrightarrows Mg(OH)^+ + H^+ \qquad \text{reduced ionic equation}$$
$$MgCl_2 + H_2O \leftrightarrows Mg(OH)Cl + HCl \qquad \text{molecular equation}$$

Answer: The medium of the solution of magnesium chloride is acidic, because as a result of hydrolysis of salt in the solution increases the amount of ions H^+ .

Example 14

What is the reaction of the medium in aqueous ammonium carbonate solution? Argue the answer.

Solution:

1) $(NH_4)_2CO_3$– is a soluble salt formed by the weak acid H_2CO_3 and the week base $NH_3 \cdot H_2O$. This salt undergoes hydrolysis.
2) In an aqueous solution, the salt dissociates into ions:
$$(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{2-}$$

Both ions will react with water.

3) The first stage of hydrolysis

$NH_4^+ + CO_3^{2-} + H_2O \leftrightarrows NH_3 \cdot H_2O + HCO_3^-$ reduced ionic equation

$(NH_4)_2CO_3 + H_2O \leftrightarrows NH_3 \cdot H_2O + NH_4HCO_3$ molecular equation

Answer: The medium of ammonium carbonate solution is close to neutral because two weak electrolytes are formed as a result of hydrolysis. To more accurately determine the reaction of the solution medium, a quantitative comparison of the strength of the hydrolysis products is required.

Example 15

Establish the correspondence between the salt formula and the ionic equation of hydrolysis of this salt. Salt NH_4CH_3COO

Ionic hydrolysis equation:

a) $CH_3COO^- + HOH \leftrightarrows CH_3COOH + OH^-$

b) $CH_3COO^- + NH_4^+ + HOH \leftrightarrows CH_3COOH + NH_3 \cdot H_2O$

c) $NH_4^+ + HOH \leftrightarrows NH_3 \cdot H_2O + H^+$

Solution:

Ammonium acetate NH_4CH_3COO – is a salt formed by a weak base $NH_3 \cdot H_2O$ and and week acid CH_3COOH. Therefore, both the cation (NH_4^+) and anion (CH_3COO^-) of the salt will react with water. The ionic hydrolysis equation of this salt is the equation b:

$CH_3COO^- + NH_4^+ + HOH \leftrightarrows CH_3COOH + NH_3 \cdot H_2O$.

Self-Test Exercises

1.1 Write the electron formulas of atoms of carbon, nitrogen, chlorine, potassium, aluminum, iron, copper.

1.2 Determine the degree of oxidation of the chlorine atom in the compounds HCl, Cl_2, $NaClO$, $KClO_3$, $HClO_4$. Which of these substances can be

a) oxidants only;

b) reducing agents only?

1.3 How many electrons does the oxidant receive as a result of the transformations:

a) $HNO_3 \rightarrow NO_2$ *f)* $H_2SO_4 \rightarrow SO_2$

b) $HNO_3 \rightarrow NO$ *g)* $H_2SO_4 \rightarrow S$

c) $HNO_3 \rightarrow N_2O$ *h)* $H_2SO_4 \rightarrow H_2S$

d) $HNO_3 \rightarrow N_2$ *i)* $KMnO_4 \rightarrow MnO_2$

e) $HNO_3 \rightarrow NH_4$ *j)* $KMnO_4 \rightarrow MnSO_4$?

1.4 The neutralization formula omits the salt formula. Post it

$H_2S + 2NaOH = \ ? \ + 2\,H_2O$

1.5 What is the reaction of the medium in an aqueous solution of sodium phosphate? Argue the answer.

1.6 What is the reaction of the medium in aqueous sodium acetate solution?Argue the answer.

1.7 What is the reaction of the medium in an aqueous solution of magnesium acetate?Argue the answer.

1.8 What is the reaction of the medium in an aqueous solution of aluminum chloride?Argue the answer.

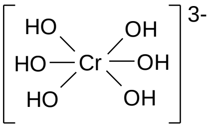
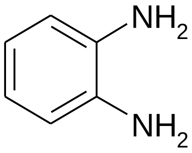
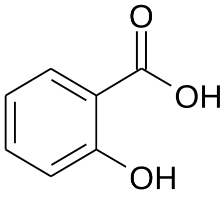
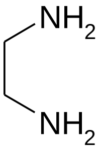
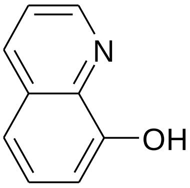
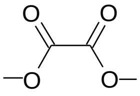
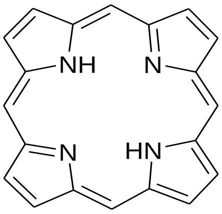
1.9 What is the reaction of the medium in an aqueous solution of potassium carbonate? Argue the answer.

1.10 What is the reaction of the medium in an aqueous solution of sodium sulfide?Argue the answer.

2. Complex formation in biological systems.

Table 2. List of basic terms, parameters, characteristics for the topic "Complex formation in biological systems".

Complex compounds (coordination compounds)	These are particles (neutral molecules or ions) that are formed as a result of attachment to a given ion (or atom), which is called a complexing agent (central atom, central ion) of neutral molecules or other ions called ligands.
Complexing agent (central atom, central ion)	Typical complexing agents are the atoms of the elements Cr, Co, Ni, Fe, Mn and cations Ag^{+}, Au^{+}, Cu^{+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pt^{2+}, Pt^{4+} and the like. Cations of *s*- and p- elements are also capable of complexing. These are the cations of the metals Be^{2+}, Al^{3+}, Sn^{2+}, Sn^{4+}, Pb^{2+} and the non-metals Si, B, P, N in certain oxidation state. Alkaline and alkaline earth metals exhibit the least ability to complex formation.
Ligands	Molecules of inorganic and organic compounds (H_2O, NH_3, CO) or ions (OH^-, CN^-, Cl^-, F^-, NO_2^-), that form donor-acceptor bonds (also coordination bonds) with complexing agent.The donor-acceptor bond is formed by a pair of electrons from one atom of ligand (the donor) and a free (unfilled) orbital from comlexing agent (the acceptor). For example: $[Pt(\mathbf{NH_3})_2Cl_2]$; $K[Ag(\mathbf{CN})_2]$; $Na_2[Zn(\mathbf{OH})_4]$; $[Cr(\mathbf{H_2O})_5\mathbf{Cl}]Cl_2$.
Coordination number	The number of σ bonds a central atom forms with the ligands. In the case of monodentant ligands is equal to the number of ligands coordinated around the complexing agent. The coordinate number of the central atom is often twice the absolute value of its degree of oxidation. The most common are complex compounds with c.n. 2, 4, 6. Examples of coordination compounds with c.n. 2: $K[Ag^{+}(CN)_{\mathbf{2}}]$; $[Ag^{+}(NH_3)_{\mathbf{2}}]Cl$; with c.n. 4: $[Ni(CO)_{\mathbf{4}}]$; $[Pt^{+2}(NH_3)_{\mathbf{2}}Cl_{\mathbf{2}}]$. with c.n. 6: $K_3[Fe^{+3}(CN)_{\mathbf{6}}]$; $[Cr^{+3}(H_2O)_{\mathbf{5}}Cl]Cl_2$.
Ligand denticity	The number of σ bonds by which a ligand is bonded to a central atom.
Monodentate ligands	They contain one donor atom and form only one bond with the complexing agent. For example, F^-, Cl^-, Br^-, I^-, CN^-, OH, NH_3, H_2O and the like. For example, in the complex compound $Na_3[Cr(\mathbf{OH})_6]$, each of the six

	ligands (OH^-) is bonded to the central atom (Cr^{3+}) by a single σ bond.  .
Bidentate ligands	They form two bonds with the central atom. Example:     Thus, in the complex compound $K_3[Fe(C_2O_4)_3]$ - the ligand  is bound to the central ion (Fe^{3+}) by two σ bonds.
Tetradentate ligands	Ligands containing four donor atoms and capable of forming four bonds with one central atom. For example, porphyrins and close in structure corrins.The simplest porphyrin - porphin: 
The inner sphere	Complexing agent and the ligands that surround it.
Cationic complexes	Complexes with positively charged inner sphere: $[Ag(NH_3)_2]^+$; $[Cr(H_2O)_6]^{3+}$; $[Zn(NH_3)_4]^{2+}$.
Anionic complexes	Complexes with negatively charged inner sphere: $[Al(OH)_6]^{3-}$; $[Fe(CN)_6]^{3-}$; $[Fe(CN)_6]^{4-}$.
Neutral complexes	Complexes with electroneutral inner sphere: $[Ni(CO)_4]$; $[Pt(NH_3)_2Cl_2]$, $[Fe(CO)_5]$.
The outer sphere	Most often these are alkali and alkaline earth metal cations and ammonium cation: $\mathbf{K}[Ag(CN)_2]$, or anions of acidic residues and OH^-: $[Ag(NH_3)_2]\mathbf{Cl}$, $[Zn(NH_3)_4](\mathbf{OH})_2$. Neutral complexes have no outer sphere: $[Pt(NH_3)_2Cl_2]^0$.
Charge of complex ion (inner sphere)	It equals the algebraic sum of the charges of the particles that form it. So in complex $K_3[Al(OH)_6]$:

	Al^{3+}– central ion; OH^-– ligands, coordination number Al^{3+}–6; $[Al(OH)_6]^{3-}$– inner sphere, its charge (+3)+6(-1)=-3; K^+– is the outer sphere, its charge is equal to the charge of the inner sphere with the opposite sign (+3).
The bound between the inner and outer sphere of the complex	Ionic: $K_3[Al(OH)_6] \rightarrow 3K^+ + [Al(OH)_6]^{3-}$; $K[Ag(CN)_2] \rightarrow K^+ + [Ag(CN)_2]^-$.
Ammine complexes	Ligands are NH_3 molecules or molecules containing–NH_2, =NH or ≡N, for example $[Ag(NH_3)_2]Cl$; $[Zn(NH_3)_4]Cl_2$; $[Cr(CH_3NH_2)_6](NO_3)_3$
Aquacomplexes	Ligands – molecules H_2O, for example $[Al(H_2O)_6]Cl_3$; $[Cr(H_2O)_6](NO_3)_3$.
Acid complexes	Ligands – acid residues, for example $K_3[Fe(CN)_6]$; $K[Ag(CN)_2]$.
Hydroxocomplexes	Ligands – ions OH^-, for example $Na_2[Zn(OH)_4]$; $K_3[Al(OH)_6]$
Polyhalides	Ligands – halogen molecules and complexing agent is a halogen ion, for example $K[I(I_2)]$; $K[I(Cl_2)]$.
The equation of formation of cationic complexes:	$Al(NO_3)_3 + 6H_2O \rightarrow [Al(H_2O)_6](NO_3)_3$; $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$.
Equation of formation of anionic complexes:	$3NaOH + Al(OH)_3 \rightarrow Na_3[Al(OH)_6]$; $4KCN + Fe(CN)_2 \rightarrow K_4[Fe(CN)_6]$.
Equation of formation of neutral complexes:	$PtCl_2 + 2NH_3 \rightarrow [Pt(NH_3)_2Cl_2]$, $Fe + 5CO \rightarrow [Fe(CO)_5]$
Hybridization of atomic orbitals	Interaction (mixing, equalization) of different types, but similar in energy, atomic orbitals of a given atom with the formation of hybrid orbitals of the same shape and energy. The type of hybridization is determined by the electronic configuration of the complexing agent, its coordination number, the nature and electronic structure of the ligands.
Geometric structure of complexes	The spatial arrangement of the ligands around the central atom is determined by the type of hybridization of the atomic orbitals of the central atom. See Table 3.

Table 3. Dependence of the geometric structure of the complexes on the coordination number and the oxidation state of the complexing agent.

Coordination number of central atom	The type of hybridization of the complexing agent AO	Geometric structure of complex ion	Complex ions
2	sp	linear	$[Ag(NH_3)_2]^+$; $[CuBr_2]^-$.
4	sp^3	tetrahedron	$[BeF_4]^{2-}$; $[Zn(NH_3)_4]^{2+}$.
	dsp^2	flat square	$[Pt(NH_3)_2Cl_2]$; $[Ni(CN)_4]^{2-}$
6	d^2sp^3	octahedron	$[Cr(OH)_6]^{3-}$
	sp^3d^2	octahedron	$[Al(OH)_6]^{3-}$

Examples of exercises

Example 1

Name: central ion, ligands, coordination number, oxidation state of complexing agent, type of hybridization of atomic orbitals of complexing agent, internal coordination sphere, outer sphere, elementary charge of complex ions, geometry of complex ions:

a) $[PtCl_2(NH_3)_2]$, b) $Na_3[Al(OH)_6]$.

Solution:

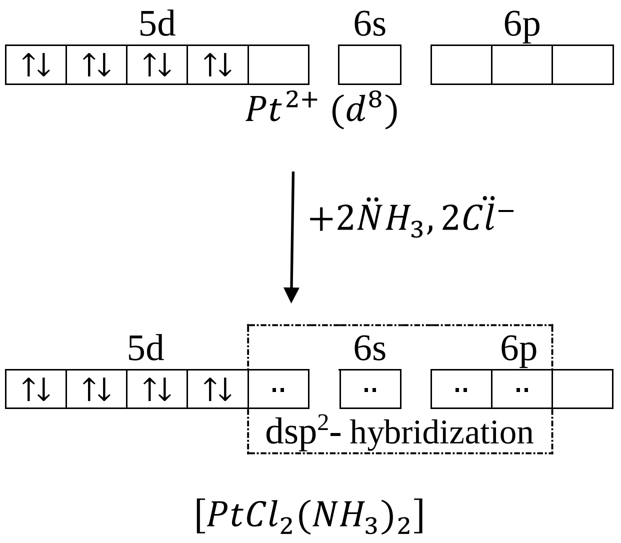
a) $[PtCl_2(NH_3)_2]$

central ion (complexing agent)	Pt^{+2}
ligands	Cl^-, NH_3
coordination number	4
the degree of oxidation of the complexing agent	+2
internal coordination sphere	$[PtCl_2(NH_3)_2]$
external sphere	-
elementary charge of complex ion	0
ligand dent	1,1
the type of hybridization of the orbitals of the complexing agent	dsp^2
geometry of complex ion	square

Formation of donor-acceptor bound in the complex $[PtCl_2(NH_3)_2]$*:*

The electronic formula of platinum atoms ${}_{78}Pt$ $5d^9\,6s^1 6p^0$
The electronic formula of platinum ion Pt^{2+} $5d^8\,6s^0 6p^0$

The Pt^{2+} ion has vacant orbitals (one 5d, one 6s, three 6p), to which four unallocated electron pairs of chlorine (2 Cl^-) and nitrogen (2 $\ddot{N}H_3$) pass:



This is done by dsp^2 hybridization of platinum atomic orbitals, the ligands are placed in the vertices of the square.

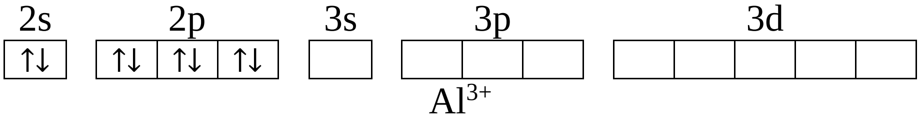
b) $Na_3[Al(OH)_6]$

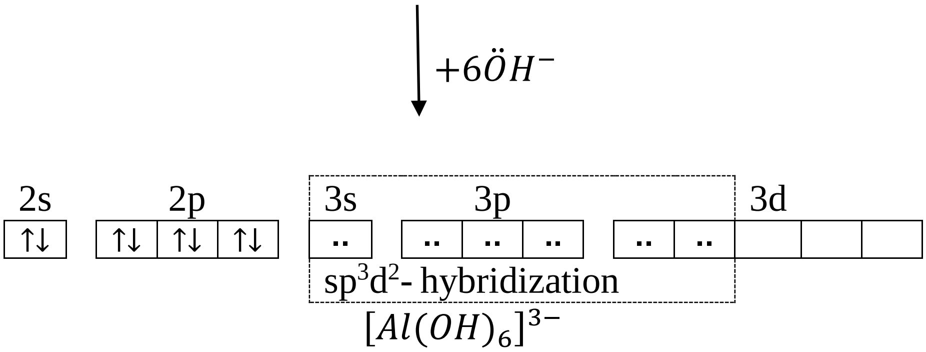
central ion (complexing agent)	Al^{3+}
ligands	OH^-
coordination number	6
the degree of oxidation of the complexing agent	+3
internal coordination sphere	$[Al(OH)_6]^{-3}$
external sphere	$3Na^+$
elementary charge of complex ion	-3
ligand dent	1
the type of hybridization of the orbitals of the complexing agent	sp^3d^2
geometry of complex ion	octahedral

Formation of a donor-acceptor bond in an ion $[Al(OH)_6]^{3-}$*:*

The electronic formula of an aluminum atom ${}_{13}Al$ $1s^2\,2s^2\,2p^6\,3s^2\,3p^1 3d^0$
Electronic formula of aluminum ion Al^{3+} $1s^2\,2s^2\,2p^6\,3s^0\,3p^0 3d^0$

The Al^{3+} ion has vacant orbitals (one 3s, three 3p and five 3d orbitals), to which six unallocated electron pairs of the oxygen atom of the ligand group OH^- pass. This involves sp^3d^2 hybridization and octahedral ligand placement.





Self test questions

Name: central ion, ligands, coordination number, oxidation state of complexing agent, type of hybridization of atomic orbitals of complexing agent, ligand dent, internal coordination sphere, outer sphere, elementary charge of complex ion, geometry of complex ion for bonding $K_2[Be(OH)_4]$; $K_2[HgI_4]$; $K[Ag(CN)_2]$; $[Zn(NH_3)_4]SO_4$; $K_3[AlF_6]$; $[Cr(H_2O)_6]Cl_3$. Put the answers in the table.

Complexes / Name it	$K_2[Be(OH)_4]$	$K_2[HgI_4]$	$K[Ag(CN)_2]$	$[Zn(NH_3)_4]SO_4$	$K_3[AlF_6]$	$[Cr(H_2O)_6]Cl_3$
central ion (complexing agent)						
ligands						
coordination number						
the degree of oxidation of the complexing agent						
internal coordination sphere						
external sphere						
elementary charge of complex ion						
ligand dent						
the type of hybridization of the orbitals of the complexing agent						
geometry of complex ion						

3.The quantities characterizing the quantitative composition of the solutions. Preparation of solutions

Table 4 . Methods for expressing the content of substances in solution

The value name	Mar king	formula	Units of measurement	Content value
Mass fraction of a substance in solution	$\omega(X)$	$\omega(X)=\frac{m(X)}{m(sol-n)}\cdot 100\%$ or $\omega(X)=\frac{m(X)}{m(sol-n)}$	% or dimensionless	The ratio of the mass of solute to the mass of solution
The volume fraction of a substance in solution	$\varphi(X)$	$\varphi(X)=\frac{V(X)}{V(sol-n)}\cdot 100\%$ or $\varphi(X)=\frac{V(X)}{V(sol-n)}$	% or dimensionless	The ratio of the volume of solute to the volume of solution
The molar fraction of a substance in solution	$\chi(X)$	$\chi(X)=\frac{n(X)}{\sum n_i}\cdot 100\%$ or $\chi(X)=\frac{n(X)}{\sum n_i}$	% or dimensionless	The ratio of the amount of substance of component X to the total amount of all substances in the system
Mass concentration	$\rho(X)$	$\rho(X)=\frac{m(X)}{V(sol-n)}$	$^{g}/_{l}$, $^{g}/_{m^3}$, $^{kg}/_{m^3}$, $^{g}/_{ml}$	The ratio of the mass of substance X contained in the solution to the volume of that solution
Molar concentration	$c(X)$	$c(X)=\frac{n(X)}{V(sol-n)}=$ $=\frac{m(X)}{M(X)\cdot V(sol-n)}$	$^{mol}/_{l}$	The ratio of the amount of substance X contained in the solution to the volume of that solution
The molar concentration of the equivalent	$c(\frac{1}{z}X)$	$c\left(\frac{1}{z}X\right)=\frac{n(\frac{1}{z}X)}{V(sol-n)}=$ $=\frac{m(x)}{M(\frac{1}{z}X)\cdot V(sol-n)}$	$^{mol}/_{l}$	The ratio of the amount of substance equivalent in solution to the volume of this solution

Molality	$b(x)$	$b(x) = \frac{n(x)}{m(solv)} = $ $= \frac{m(x)}{M(x) \cdot m(solv)}$	${}^{mol}/_{kg}$	The ratio of the amount of substance X contained in the solution to the weight of the solvent

$m(X) -$ mass of solute (g, kg);
$m(sol-n) -$ mass of the solution (equal to the sum of the masses of all the components of the solution) (g, kg);
$m(solv) -$ the mass of the solvent (g, kg);
$V(X) -$ volume of solute (l, ml);
$V(sol-n) -$ volume of solution (l, ml);
$M(X) -$ the molar mass of the substance $({}^{g}/_{mol})$;
$M(\frac{1}{z}X) -$ molar mass of substance equivalent $({}^{g}/_{mol})$;
$n(X) -$ amount of substance (mol);
$n(\frac{1}{z}X) -$ amount of substance equivalent (mol).

An equivalent is a conditional or real particle that is equivalent to one hydrogen ion in acid-base reactions or one electron in redox reactions.

The equivalence factor $\boldsymbol{f_{eq}} = \frac{\boldsymbol{1}}{\boldsymbol{z}}$ - is a number that shows which part of the real particle of the substance is equivalent to one hydrogen ion in acid-base reactions or one electron in redox reactions.

Z - is the number of moles of equivalents of a substance contained in 1 mol of this substance.

The molar mass of an equivalent substance is equal to the molar mass of that substance multiplied by the equivalence factor:

$$M\left(\frac{1}{z}X\right) = f_{eq} \cdot M(X) = \frac{M(X)}{z}$$

The amount of the substance is equal to the ratio of the mass of the substance to its molar mass:

$$n(X) = \frac{m(X)}{M(X)}$$

The amount of a substance equivalent, that is, a substance, the conventional unit of which is equivalent, is the ratio of the mass of the substance to the molar mass of the substance equivalent:

$$n\left(\frac{1}{z}X\right) = \frac{m(X)}{M(\frac{1}{z}X)}$$

Table 5. Links between ways of expressing substance in solution

Mass fraction	$\omega(X) = \frac{\rho(X)}{\rho(sol-n)} \cdot 100\% = \frac{c(X) \cdot M(X)}{\rho(sol-n)} \cdot 100\% = \frac{c\left(\frac{1}{z}X\right) \cdot M\left(\frac{1}{z}X\right)}{\rho(sol-n)} \cdot 100\%$
Mass concentration	$\rho(X) = \frac{\omega(X) \cdot \rho(sol-n)}{100\%} = M(X) \cdot c(X) = M(\frac{1}{z}X) \cdot c(\frac{1}{z}X)$
Molar concentration	$c(X) = \frac{\omega(X) \cdot \rho(sol-n)}{M(X) \cdot 100\%} = \frac{\rho(X)}{M(X)} = \frac{c\left(\frac{1}{z}X\right)}{z}$
The molar concentration of the equivalent	$c\left(\frac{1}{z}X\right) = \frac{\omega(X) \cdot \rho(sol-n)}{M\left(\frac{1}{z}X\right) \cdot 100\%} = \frac{\rho(X)}{M(\frac{1}{z}X)} = z \cdot c(X)$
Molality	If the mass fraction is dimensionless: $b(X) = \frac{\omega(X)}{M(X) \cdot (1-\omega(X))}$ If the mass fraction is expressed as a percentage: $b(X) = \frac{\omega(X)}{M(X) \cdot (100\% - \omega(X))}$
$\rho(sol-n)$ – density of the solution ($^g/_{ml}$, $^g/_{cm^3}$, $^{kg}/_{m^3}$).	

Examples of problem solving

Example 1

In medical practice, aqueous solutions of potassium permanganate of various concentrations are used. Calculate the mass of potassium permanganate and the volume of water (in l) required to prepare a 200 g solution with a mass fraction of $KMnO_4$ 2%.

Given:	Find:
$m(sol-n) = 200\ g$	$m(KMnO_4)-?$
$\omega(KMnO_4) = 2\%$	$V(H_2O)-?$
$\rho(H_2O) = 1\ ^g/_{ml}$	

Solution:

1) Determine the mass of potassium permanganate in solution:

$$\omega(KMnO_4) = \frac{m(KMnO_4)}{m(sol-n)} \cdot 100\% \ \Rightarrow \ m(KMnO_4) = \frac{\omega(KMnO_4) \cdot m(sol-n)}{100\%}$$

$$m(KMnO_4) = \frac{2\% \cdot 200g}{100\%} = 4g$$

2) Determine the mass of water in the solution, given that the mass of the solution is equal to the sum of the masses of potassium permanganate and water:

$m(sol-n) = m(H_2O) + m(KMnO_4) \Rightarrow m(H_2O) = m(sol-n) - m(KMnO_4)$

$m(H_2O) = 200g - 4g = 196g$

3) Calculate water volume:

$$V(H_2O) = \frac{m(H_2O)}{\rho(H_2O)} = \frac{196g}{1\,{}^{g}\!/_{ml}} = 196ml = 0{,}196l$$

Answer: $m(KMnO_4) = 4g$; $V(H_2O) = 0{,}196l$

Example 2

To 500 g of potassium chloride solution with a mass fraction KCl 5% added 300g of water. Determine the mass fraction of potassium chloride in the resulting solution.

Given:	**Find:**
$\omega_1(KCl) = 5\%$ $m_1(sol-n) = 500\ g$ $\Delta m(H_2O) = 300g$	$\omega_2(KCl) - ?$

Solution:

1) Determine the mass of potassium chloride contained in the stock solution:

$$\omega(KCl) = \frac{m(KCl)}{m(sol-n)} \cdot 100\% \quad \Rightarrow \quad m(KCl) = \frac{\omega_1(KCl) \cdot m_1(sol-n)}{100\%}$$

$$m(KCl) = \frac{5\% \cdot 500g}{100\%} = 25g$$

2) Determine the mass of the solution obtained after adding water to the stock solution:

$$m_2(sol-n) = m_1(sol-n) + \Delta m(H_2O) = 500g + 300g = 800g$$

3) Determine the mass fraction of potassium chloride in the resulting solution:

$$\omega_2(KCl) = \frac{m(KCl)}{m_2(sol-n)} \cdot 100\% = \frac{25g}{800g} \cdot 100\% = 3{,}125\%$$

Answer: $\omega_2(KCl) = 3{,}125\%$

Example 3

To 150 g of an alcoholic solution of iodine with a mass fraction of iodine of 3% was added 5 g of crystalline iodine. Calculate the mass fraction of iodine in the resulting solution.

Given:	**Find:**
$m_1(so-n) = 150\ g$ $\omega_1(I_2) = 3\%$ $\Delta m(I_2) = 5\ g$	$\omega_2(I_2)-?$

Solution:

1) Determine the mass of iodine contained in the stock solution:

$$\omega(I_2) = \frac{m(I_2)}{m(sol-n)} \cdot 100\% \quad \Rightarrow \quad m_1(I_2) = \frac{\omega_1(I_2) \cdot m_1(sol-n)}{100\%}$$

$$m_1(I_2) = \frac{3\% \cdot 150g}{100\%} = 4{,}5g$$

2) Determine the weight of iodine after adding an additional portion of iodine:

$$m_2(I_2) = m_1(I_2) + \Delta m(I_2) = 4{,}5g + 5g = 9{,}5g$$

3) Determine the weight of the solution after adding an additional portion of iodine:

$$m_2(sol-n) = m_1(sol-n) + \Delta m(I_2) = 150g + 5g = 155g$$

4) Calculate the mass fraction of iodine in the final solution:

$$\omega_2(I_2) = \frac{m_2(I_2)}{m_2(sol-n)} \cdot 100\% = \frac{9{,}5g}{155g} \cdot 100\% = 6{,}1\%$$

Answer: $\omega_2(I_2) = 6{,}1\%$

Example 4

Calculate the weight of water to be added to 50 g of potassium permanganate solution with a mass fraction of $KMnO_4$ 5%, to obtain a solution with a potassium permanganate mass fraction of 1%.

Given:	**Find:**
$m_1(sol-n) = 50\ g$ $\omega_1(KMnO_4) = 5\% = 0{,}05$ $\omega_2(KMnO_4) = 1\% = 0{,}01$	$\Delta m(H_2O)-?$

Solution:

1) Determine the mass of potassium permanganate contained in the stock solution:

$$\omega(KMnO_4) = \frac{m(KMnO_4)}{m(sol-n)} \cdot 100\% \ \Rightarrow m(KMnO_4) = \frac{\omega_1(KMnO_4) \cdot m_1(sol-n)}{100\%}$$

$$m(KMnO_4) = \frac{5\% \cdot 50g}{100\%} = 2{,}5g$$

2) Determine the mass of the solution in which 2.5 g of potassium permanganate have a mass fraction of 1%:

$$m_2(\text{р} - \text{ну}) = \frac{m(KMnO_4)}{\omega_2(KMnO_4)} \cdot 100\% = \frac{2{,}5g}{1\%} \cdot 100\% = 250g$$

3) Calculate the mass of water to be added to the stock solution:

$$\Delta m(H_2O) = m_2(sol-n) - m_1(sol-n) = 250g - 50g = 200g$$

Answer:$\Delta m(H_2O) = 200g$

Example 5

Calculate the mass of glucose to be added to 200 g of an aqueous solution with a mass fraction of glucose of 2% to obtain a solution with a mass fraction of glucose of 5%.

Given:	**Find:**
$m_1(\text{р} - \text{ну}) = 200\ g$ $\omega_1(C_6H_{12}O_6) = 2\%$ $\omega_2(C_6H_{12}O_6) = 5\%$	$\Delta m(C_6H_{12}O_6)$–?

Solution:

1) Determine the mass of glucose contained in the stock solution:$\omega(C_6H_{12}O_6) = \frac{m(C_6H_{12}O_6)}{m(\text{р}-\text{ну})} \cdot 100\%$

$$m_1(C_6H_{12}O_6) = \frac{\omega_1(C_6H_{12}O_6) \cdot m_1(sol-n)}{100\%}$$

$$m_1(C_6H_{12}O_6) = \frac{2\% \cdot 200g}{100\%} = 4g$$

2) Determine the weight of the extra portion of glucose:

$$m_2(C_6H_{12}O_6) = m_1(C_6H_{12}O_6) + \Delta m(C_6H_{12}O_6)$$

$$m_2(sol-n) = m_1(sol-n) + \Delta m(C_6H_{12}O_6)$$

$$\omega_2(C_6H_{12}O_6) = \frac{m_2(C_6H_{12}O_6)}{m_2(sol-n)} \cdot 100\% = \frac{m_1(C_6H_{12}O_6) + \Delta m(C_6H_{12}O_6)}{m_1(sol-n) + \Delta m(C_6H_{12}O_6)} \cdot 100\%$$

$$\frac{\omega_2(C_6H_{12}O_6)}{100\%} = \frac{m_1(C_6H_{12}O_6) + \Delta m(C_6H_{12}O_6)}{m_1(sol-n) + \Delta m(C_6H_{12}O_6)}$$

позначимо $\Delta m(C_6H_{12}O_6) = x$

$$\frac{5\%}{100\%} = \frac{4 + x}{200 + x}$$

$$0{,}05(200 + x) = 4 + x$$

$$10 + 0{,}05x = 4 + x$$

$$x - 0{,}05x = 10 - 4$$

$$0{,}95x = 6$$

$$x = 6{,}32 \quad ⇨ \quad \Delta m(C_6H_{12}O_6) = 6{,}32g$$

Answer: $\Delta m(C_6H_{12}O_6) = 6{,}32g$

Example 6

The 200 ml solution contains 8.55 g of barium hydroxide. Calculate mass concentration $\rho(Ba(OH)_2)$, molar concentration $c(Ba(OH)_2)$ and molar concentration of equivalent $c\left(\frac{1}{2}Ba(OH)_2\right)$. $M(Ba(OH)_2) = 171\,{}^{g}/_{mol}$.

Given:	**Find:**
$m(Ba(OH)_2) = 8{,}55\ g$	$\rho(Ba(OH)_2)$–?
$V(\text{р} - \text{ну}) = 200\ \text{м}l = 0{,}2\ l$	$c(Ba(OH)_2)$–?
$M(Ba(OH)_2) = 171\,{}^{g}/_{mol}$	$c\left(\frac{1}{2}Ba(OH)_2\right)$–?

Solution:

The formulas required for the calculations are shown in Table 4:

1) mass concentration:

$$\rho(Ba(OH)_2) = \frac{m(Ba(OH)_2)}{V(sol-n)} = \frac{8{,}55\ g}{0{,}2\ l} = 42{,}75\,{}^{g}/_{l}$$

2) molar concentration:

$$c(Ba(OH)_2) = \frac{m(Ba(OH)_2)}{M(Ba(OH)_2)\cdot V(sol-n)} = \frac{8{,}55\ g}{171\,{}^{g}/_{mol}\cdot 0{,}2l} = 0{,}25\,{}^{mol}/_{l}$$

3) molar concentration of equivalent:

$$c\left(\tfrac{1}{2}Ba(OH)_2\right) = \frac{m(Ba(OH)_2)}{M(\frac{1}{2}Ba(OH)_2)\cdot V(sol-n)} = \frac{8{,}55g}{\left(\frac{171}{2}\right){}^{g}/_{mol}\cdot 0{,}2l} = 0{,}5\,{}^{mol}/_{l}$$

Answer: $\rho(Ba(OH)_2) = 42{,}75\,{}^{g}/_{l}$;
$c(Ba(OH)_2) = 0{,}25\,{}^{mol}/_{l}$;
$c\left(\frac{1}{2}Ba(OH)_2\right) = 0{,}5\,{}^{mol}/_{l}$

Example 7

Potassium permanganate solutions are widely used in analytical practice. Calculate the mass of potassium permanganate required to prepare a 600 ml solution with a molar concentration of equivalent $\mathrm{c}\left(\frac{1}{5}KMnO_4\right) = 0{,}75\,{}^{mol}/_{l}$. $M(KMnO_4) = 158\,{}^{g}/_{mol}$

Given:	**Find:**
$V(sol-n) = 600\ \text{м}l = 0{,}6\ l$	$m(KMnO_4)$–?

c$\left(\frac{1}{5}KMnO_4\right) = 0{,}75\,{}^{mol}/_{l}$
$M(KMnO_4) = 158\,{}^{g}/_{mol}$

Solution:

$$c\left(\frac{1}{5}KMnO_4\right) = \frac{n(\frac{1}{5}KMnO_4)}{V(sol-n)} = \frac{m(KMnO_4)}{M(\frac{1}{5}KMnO_4)\cdot V(sol-n)}$$

$$m(KMnO_4) = c\left(\frac{1}{5}KMnO_4\right)\cdot\ M\left(\frac{1}{5}KMnO_4\right)\cdot V(sol-n)$$

$$m(KMnO_4) = 0{,}75\,{}^{mol}/_{l}\cdot\frac{158}{5}\,{}^{g}/_{mol}\cdot 0{,}6l = 14{,}22g$$

Answer: $m(KMnO_4) = 14{,}22g$

Example 8

What is the mass of potassium carbonate contained in 200 ml of the mass concentration solution K_2CO_3 $24{,}3\,{}^{g}/_{l}$?

Given:
$V(sol-n) = 200\text{ м}l = 0{,}2\ l$
$\rho(K_2CO_3) = 24{,}3\,{}^{g}/_{l}$

Find:
$m(K_2CO_3)-?$

Solution:

Write down the formula for calculating the mass concentration and express the mass of potassium carbonate from it:

$$\rho(K_2CO_3) = \frac{m(K_2CO_3)}{V(sol-n)} \quad\Rightarrow\quad m(K_2CO_3) = \rho(K_2CO_3)\cdot V(sol-n)$$

$$m(K_2CO_3) = 24{,}3\,{}^{g}/_{l}\cdot 0{,}2l = 4{,}86\ g$$

Answer: $m(K_2CO_3) = 4{,}86\ g$

Example 9

Calculate the molar concentration of HCl in a 36% hydrochloric acid solution if the density of the solution 1,18 $^{g}/_{\text{мl}}$.

Дано:
$w(HCl) = 36\%$
$\rho(sol-n) = 1{,}18\,{}^{g}/_{\text{м}l}$

Find:
$c(HCl)-?$

Solution:

The formula that relates the molar concentration to the mass fraction is given in the Table 5:

$$c(HCl) = \frac{\omega(HCl)\cdot\rho(sol-n)}{M(HCl)\cdot 100\%}$$

$$c(HCl) = \frac{36\% \cdot 1{,}18\,{}^{g}/{}_{\text{мl}}}{36{,}5\,{}^{g}/{}_{mol} \cdot 100\%} = 0{,}0116\,{}^{mol}/{}_{\text{мl}} = 11{,}6\,{}^{mol}/{}_{l}$$

Answer: $c(HCl) = 11{,}6\,{}^{mol}/{}_{l}$

Example 10

Calculate mass concentration, molar concentration and molar concentration of sodium carbonate equivalent in solution with mass fraction Na_2CO_3 11,6%, я what is the density of the solution 1,12 ${}^{g}/{}_{ml}$. $M(Na_2CO_3) = 106\,{}^{g}/{}_{mol}$

Given:	Find:
$\omega(Na_2CO_3) = 11{,}6\% = 0{,}116$	$\rho(Na_2CO_3)$–?
$\rho(sol-n) = 1{,}12\,{}^{g}/{}_{\text{мl}}$	$c(Na_2CO_3)$–?
$M(Na_2CO_3) = 106\,{}^{g}/{}_{mol}$	$c\left(\frac{1}{2}Na_2CO_3\right)$–?

Solution:

Formulas that relate mass fraction to mass concentration, molar concentration and molar concentration of equivalent are given in Table5:

1) mass concentration:

$$\rho(Na_2CO_3) = \omega(Na_2CO_3) \cdot \rho(sol-n)$$

$$\rho(Na_2CO_3) = 0{,}116 \cdot 1{,}12\,{}^{g}/{}_{\text{мl}} = 0{,}13\,{}^{g}/{}_{\text{мl}} = 130\,{}^{g}/{}_{l}$$

2) molar concentration:

$$c(Na_2CO_3) = \frac{\omega(Na_2CO_3) \cdot \rho(sol-n)}{M(Na_2CO_3)}$$

$$c(Na_2CO_3) = \frac{0{,}116 \cdot 1{,}12\,{}^{g}/{}_{\text{мl}}}{106\,{}^{g}/{}_{mol}} = 1{,}225 \cdot 10^{-3}\,{}^{mol}/{}_{\text{мl}} = 1{,}225\,{}^{mol}/{}_{l}$$

3) molar concentration of the equivalent:

$$c\left(\tfrac{1}{2}Na_2CO_3\right) = \frac{\omega(Na_2CO_3) \cdot \rho(sol-n)}{M\left(\frac{1}{2}Na_2CO_3\right)}$$

$$c\left(\tfrac{1}{2}Na_2CO_3\right) = \frac{0{,}116 \cdot 1{,}12\,{}^{g}/{}_{\text{мl}}}{\left(\frac{106}{2}\right){}^{g}/{}_{mol}} = 2{,}45 \cdot 10^{-3}\,{}^{mol}/{}_{\text{мl}} = 2{,}45\,{}^{mol}/{}_{l}$$

Answer:
$\rho(Na_2CO_3) = 130\,{}^{g}/{}_{l}$
$c(Na_2CO_3) = 1{,}225\,{}^{mol}/{}_{l}$
$c\left(\frac{1}{2}Na_2CO_3\right) = 2{,}45\,{}^{mol}/{}_{l}$

Self-test questions.

3.1 Baking soda (sodium bicarbonate) is a part of many culinary recipes and is also used to rinse your throat as a 2% solution. Calculate the weight of baking soda and the volume of water required to prepare 250g of such solution.

Answer:$m(NaHCO_3) = 5g\ V(H_2O) = 0{,}245l$

3.2 A solution with a mass fraction of glucose 5% in medicine is used to replenish the volume of fluid in the body and as a source of easily digestible valuable nutrients. Calculate the amount of glucose introduced into the body by infusing 250 ml of this solution. Density of solution $1{,}02\,{}^{g}/_{ml}$.

Answer: $m(C_6H_{12}O_6) = 12{,}75g$

3.3 An aqueous solution of sodium hypochlorite (NaClO) is characterized by a powerful bactericidal activity and oxidizing action and is used in dentistry for the medical treatment of root canals and disinfection of the tooth cavity. Calculate the mass of sodium hypochlorite contained in 30 ml of a solution with a NaClO mass fraction of 10%. The density of the solution $1{,}07\,{}^{g}/_{ml}$.

Answer: $m(NaClO) = 3{,}21g$

3.4 An aqueous solution of furacillin with a mass fraction of 0.02% is used externally as an antibacterial drug. How much of this solution can be made from one tablet containing 0.1g of furacillin? The density of the solution $1\,{}^{g}/_{ml}$.

Answer: $V(sol-n) = 500ml$

3.5 In medical practice, 0.9% sodium chloride solution is often used. Calculate the weight of water to be added to 200 g of a solution with a mass fraction of NaCl 5% to obtain a solution with a mass fraction of 0.9%.

Answer: $\Delta m(H_2O) = 911{,}1g$

3.6 Calculate the mass of calcium chloride to be added to 250 g of a solution with a mass fraction of $CaCl_2$ 3%, to obtain a solution with a mass fraction of $CaCl_2$ 10%.

Answer: $m(CaCl_2) = 19{,}44g$

3.7 In burns with alkalis, the affected area of the skin is washed with water for 5-10 min and then neutralized with a solution of acetic acid with a mass fraction of CH_3COOH 1%. What volume of acetic essence with a mass fraction of CH_3COOH 80% (essence density of 1.07 g/ml) should be taken to prepare 1 l of a 1% solution of acetic acid (density of solution $1\,{}^{g}/_{ml}$)?

Answer: $V(\text{essences}) = 11{,}68ml$

3.8 3% and 30% hydrogen peroxide solutions are used in medical practice. What volume of water should be added to a 5 ml solution with a mass fraction of H_2O_2 30%, to prepare a solution with a mass fraction H_2O_2 3%? Density of solutions $1\,{}^{g}/_{ml}$.

Answer: $V(H_2O) = 45ml$

3.9 What mass of potassium dichromate is required to prepare a 500 ml solution with a molar concentration of equivalent $c\left(\frac{1}{6}K_2Cr_2O_7\right) = 0{,}6\,{}^{mol}\!/_{l}$?
$M(K_2Cr_2O_7) = 294\,{}^{g}\!/_{mol.}$

Answer:$m(K_2Cr_2O_7) = 14{,}7g$

3.10 What mass of potassium dichromate is required to prepare a 500 ml solution with a molar concentration $0{,}975mol/l$? $M(KOH) = 56\,{}^{g}\!/_{mol.}$

Answer: $m(KOH) = 27{,}3g$

3.11 What is the weight of phosphoric acid contained in 300 ml of solution
a) with a molar concentration $c(H_3PO_4) = 0{,}2\,{}^{mol}\!/_{l}$;
b) with a molar concentration of equivalent $c\left(\frac{1}{3}H_3PO_4\right) = 0{,}2\,{}^{mol}\!/_{l}$?
$M(H_3PO_4) = 98\,{}^{g}\!/_{mol}$

Answer: а) $m(H_3PO_4) = 5{,}88g$;
б) $m(H_3PO_4) = 1{,}96g$

3.12 Calculate the mass fraction of hydrochloric acid in solution if the molar concentration $HClO_4$ $1{,}233\,{}^{mol}\!/_{l}$.
The density of the solution $1{,}07\,{}^{g}\!/_{ml}$; $M(HClO_4) = 100{,}5\,{}^{g}\!/_{mol.}$

Answer: $\omega(HClO_4) = 11{,}58\%$

3.13 Calculate the molar concentration of nitric acid solution with mass fraction HNO_3 30%. The density of the solution $1{,}18\,{}^{g}\!/_{ml}$; $M(HNO_3) = 63\,{}^{g}\!/_{mol.}$

Answer: $c(HNO_3) = 5{,}619\,{}^{mol}\!/_{l}$

3.14 Calculate the molar concentration of phosphate acid equivalent $c(\frac{1}{3}H_3PO_4)$ in solution with a mass fraction H_3PO_4 10,32%. The density of the solution $1{,}055\,{}^{g}\!/_{ml}$; $M(H_3PO_4) = 98\,{}^{g}\!/_{mol.}$

Answer: $c\left(\frac{1}{3}H_3PO_4\right) = 3{,}333\,{}^{\mathrm{mol}}\!/_{\mathrm{l}}$

3.15 To obtain ammonia in 500 g of water dissolved 54.75 g of ammonia. Calculate the mass fraction, mass concentration and molar concentration NH_3 in the solution obtained. The density of the solution $0{,}958\,{}^{g}\!/_{ml}$.

Answer: $\omega(NH_3) = 9{,}87\%$;
$\rho(NH_3) = 94{,}54\,{}^{g}\!/_{l}$;
$\mathrm{c}(NH_3) = 5{,}561\,{}^{mol}\!/_{l}$

3.16 Calcium chloride solution with mass fraction $CaCl_2$ 10% is used in medicine as anti-allergic and anti-inflammatory agent. Calculate the mass and molar concentrations of this solution. The density of the solution $1{,}083\,{}^{g}/_{ml}$, $M(CaCl_2) = 111\,{}^{g}/_{mol}$.

Answer: $\rho(CaCl_2) = 108{,}3\,{}^{g}/_{l}$;
$c(CaCl_2) = 0{,}975\,{}^{mol}/_{l}$

4. Acid-base balance in the body. pH of biological fluids

Table 6. Basic parameters and characteristics used to describe acid-base equilibrium in solution.

Parameter	**Marking**	**Content value**
Constant dissociation	$K_a = \frac{[H^+] \cdot [An^-]}{[HAn]}$ (1) $K_b = \frac{[OH^-] \cdot [Kt^+]}{[KtOH]}$ (2)	The equilibrium constant of the dissociation process equals the ratio of the product of equilibrium molar concentrations of dissociation products to the equilibrium molar concentration of the original component. For acid HAn, the dissociation of which in water gives the cation H^+ and the anion An^-, the dissociation constant K_a is expressed by equation (1). For the basis $KtOH$, the dissociation of which produces the anion OH^- and the cation Kt^+, the dissociation constant K_b is expressed by the equation (2).
The degree of dissociation	$\alpha = \frac{c_i}{c_0}$, where $c_i -$ is the concentration of molecules that have dissociated into ions; $c_0 -$ total concentration of dissolved molecules.	Quantitative characterization of the dissociation process, equal to the ratio of the amount of electrolyte decomposed into ions, to the total amount of electrolyte in solution. The degree of dissociation increases with the dilution of the solution, with increasing temperature of the solution.
Ostwald's Law	$K_d = \frac{c(X) \cdot \alpha^2}{1 - \alpha}$, at $\alpha \ll 1$ $\alpha \approx \sqrt{\frac{K_d}{c(X)}}$ or $\alpha \approx \sqrt{K_d \cdot V}$, where $V = \frac{1}{c(X)}$ - a value called dilution	The degree of dissociation of the weak binary electrolyte is inversely proportional to the square root of the molar concentration or directly proportional to the square root of the dilution. As the concentration of the solution decreases, the degree of dissociation of the weak electrolyte increases.
The activity of the ion	$a(x_i), {}^{mol}/_{l}$ $a(x_i) = f(x_i) \cdot c(x_i)$	The effective concentration of the x_i, ion, according to which it participates

		in the interactions occurring in solutions of strong electrolytes.
The activity factor of the ion	$f(x_i)$ at $f(x_i) = 1$ $a(x_i) = c(x_i)$	Characterizes the electrostatic bonding of ions and shows how many times the activity of an ion differs from its true concentration in solution. The magnitude of the activity coefficient depends on the ionic strength of the solution. The higher the ionic strength of the solution, the less important is the activity factor, and the greater the activity of the ion differs from the true concentration.
The ionic strength of the solution	$\mu = \frac{1}{2}\sum_{i=1}^{n}(z_i^2 b_i)$	Characterizes the electrostatic field intensity of all ions in solution. It equals the half-sum of the molarity products of each of the ions (b(X)) by its elementary charge squared (Z^2**)**.
Ionic product of water	$K_{H_2O} = [H^+][OH^-] = const,$ $[H^+][OH^-] = 1 \cdot 10^{-14}\, {}^{mol^2}/_{l^2}$ (at T=298K) $pH + pOH = 14$	The value is constant at the given temperature for water and any aqueous solutions, equal to the product of the concentration of hydrogen ions and hydroxide ions
Hydrogen index	$pH = -lg[H^+]$	Quantitative characterization of the acidity of the medium equal to the negative decimal logarithm of the active concentration of free hydrogen ions in solution
Hydroxide index	$pOH = -lg[OH^-]$	Quantitative characterization of the alkalinity of the medium equal to the negative decimal logarithm of the active concentration of free <u>OH^-</u> ions in solution.
The degree of hydrolysis	$\alpha_г = \frac{n_г}{n_0}$ or $\alpha_г = \frac{c_г}{c_0}$	Quantitative characterization of the hydrolysis process, which is equal to the ratio of the number of particles undergoing hydrolysis n_h, to their number before the beginning of hydrolysis n_0. The degree of hydrolysis increases with dilution of the solution and with increasing temperature.

The hydrolysis constant	hydrolysis by the anion: $K_h = \frac{[HAn][OH^-]}{[An^-]} = \frac{K_{H_2O}}{K_a}$ hydrolysis by cation: $K_h = \frac{[KtOH][H^+]}{[Kt^+]} = \frac{K_{H_2O}}{K_b}$ hydrolysis by cation and anion: $K_h = \frac{K_{H_2O}}{K_b\, K_a}$	Characterizes the state of equilibrium during hydrolysis.

Examples of problem solving

Example 1

Calculate the molar concentration of free ions H^+ and OH^- at temperature 25℃:
a) in a sulfuric acid solution with a molar concentration of $0{,}04\ mol/l$, if the degree of electrolyte dissociation is 100% ;
b) in a solution of acetic acid with a molar concentration of $0{,}04 mol/l$, if the degree of dissociation of the electrolyte is 2,1% .

Given:

$c(H_2SO_4) = 0{,}04\,{}^{mol}/_{l}$

$\alpha = 100\% = 1$

$c(CH_3COOH) = 0{,}04\,{}^{mol}/_{l}$

$\alpha = 2{,}1\% = 0{,}021$

Find:

$[H^+]-?$

$[OH^-]-?$

Solution:

The amount of free hydrogen ions formed by the dissociation of an acid in a solution depends on the degree of dissociation and the number of "acidic" protons in the acid molecule.

a) The dissociation of sulfuric acid is as follows:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

At 100% dissociation, each molecule H_2SO_4 breaks up, and two free H^+ ions are formed from each molecule.

1) Calculate the molar concentration of free ions H^+:

$$[H^+] = c(H_2SO_4) \cdot n \cdot \alpha = 0{,}04\,{}^{mol}/_{l} \cdot 2 \cdot 1 = 0{,}08 mol/l$$

where n – the number of protons in an acid molecule;
α - the degree of acid dissociation.

2) Calculate the molar concentration of free ions OH^-, using an ionic product of water:

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} = \frac{10^{-14}\, mol^2/l^2}{0{,}08\,{}^{mol}/_{l}} = 1{,}25 \cdot 10^{-13}\,{}^{mol}/_{l}$$

б) The dissociation of acetic acid occurs according to the scheme:

$$CH_3COOH \leftrightarrows H^+ + CH_3COO^-$$

One free H^+, ion is formed from one molecule during dissociation, but only 0,021 parts of all molecules present in the solution break up at ions at a given acid concentration.

1) Calculate the molar concentration of free ions H^+:

$$[H^+] = c(CH_3COOH) \cdot n \cdot \alpha = 0{,}04\,{}^{mol}/_{l} \cdot 1 \cdot 0{,}021 = 8{,}4 \cdot 10^{-4}\,{}^{mol}/_{l}$$

2) Calculate the molar concentration of free ions OH^-, using the ionic product of water:

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} = \frac{10^{-14}\,mol^2/l^2}{8{,}4 \cdot 10^{-4}\,{}^{mol}/_{l}} = 1{,}19 \cdot 10^{-11}\,{}^{mol}/_{l}$$

Answer: a) $[H^+] = 0{,}08\,{}^{mol}/_{l}$; $[OH^-] = 1{,}25 \cdot 10^{-13}\,{}^{mol}/_{l}$

b) $[H^+] = 8{,}4 \cdot 10^{-4}\,{}^{mol}/_{l}$; $[OH^-] = 1{,}19 \cdot 10^{-11}\,{}^{mol}/_{l}$

Example 2

Calculate the molar concentration of free ions H^+ and OH^- at temperature 25℃ in sodium hydroxide solution with molar concentration $0{,}005\,{}^{mol}/_{l}$, if the degree of dissociation of the electrolyte 100% .

Given:	**Find:**
$c(NaOH) = 0{,}005\,{}^{mol}/_{l}$	$[H^+]-?$
$\alpha = 100\% = 1$	$[OH^-]-?$

Solution:

The dissociation of sodium hydroxide occurs according to the scheme:

$$NaOH \rightarrow Na^+ + OH^-$$

When the degree of dissociation is 100% the molar concentration of free ions OH^- is equal to the molar concentration $NaOH$.

1) Calculate the molar concentration of free ions OH^-:

$$[OH^-] = c(NaOH) \cdot n \cdot \alpha = 0{,}005\,{}^{mol}/_{l} \cdot 1 \cdot 1 = 0{,}005\,{}^{mol}/_{l}$$

where

n – the number of OH- groups in the base,

α - the degree of dissociation of the base.

2) Calculate the molar concentration of free H^+, ions using the ionic product of water:

$$[H^+] = \frac{K_{H_2O}}{[OH^-]} = \frac{10^{-14}\,mol^2/l^2}{0{,}005\,{}^{mol}/_{l}} = 2 \cdot 10^{-12}\,{}^{mol}/_{l}$$

Answer: $[H^+] = 2 \cdot 10^{-12}\,{}^{mol}/_{l}$; $[OH^-] = 5 \cdot 10^{-3}\,{}^{mol}/_{l}$

Example 3

The molar concentration of free H^+ ions in venous blood is equal $4{,}365 \cdot 10^{-8}\,{}^{mol}/_{l}$. Calculate a) the concentration of free ions OH^-; b) pH and pOH of venous blood.

Given:	**Find:**
$[H^+] = 4{,}365 \cdot 10^{-12}\, {}^{mol}/{}_{l}$	a) $[OH^-]-?$
	b) $pH-?$
	$pOH-?$

Solution:

а) Розрахувати молярну концентрацію вільних іонів OH^-:

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} = \frac{10^{-14}\,\text{моль}^2/\text{л}^2}{4{,}365 \cdot 10^{-8}\,{}^{\text{моль}}/{}_{\text{л}}} = 2{,}29 \cdot 10^{-7}\,{}^{\text{моль}}/{}_{\text{л}}$$

б) Calculate the pH value :

$pH = -lg[H^+] = -\lg(4{,}365 \cdot 10^{-8}) = -(lg4{,}365 + lg10^{-8}) =$
$= -(0{,}640 - 8) = 7{,}36$

Calculate the pOH value using ion OH^-concentration values:

$pOH = -lg[OH^-] = -\lg(2{,}29 \cdot 10^{-7}) = -(lg2{,}29 + lg10^{-7}) =$
$= -(0{,}36 - 7) = 6{,}64$

If pH is known, then pOH is easier to find using the logarithmic form of the ionic product of water:

$$pH + pOH = 14$$
$$pOH = 14 - pH = 14 - 7{,}36 = 6{,}64$$

Answer: a) $[OH^-] = 2{,}29 \cdot 10^{-7}\, {}^{mol}/{}_{l}$;
b) $pH = 7{,}36$; $pOH = 6{,}64$.

Example 4

Mass fraction of sulfuric acid in a solution is 0.049%. Calculate the pH and pOH of the solution if the electrolyte dissociation degree is 100% and the solution density is 1 g/mL. How will the pH and pOH change if this solution is diluted a) 10 times; b) 100 times? $M(H_2SO_4) = 98\, {}^{g}/{}_{mol}$.

Given:	**Find:**
$\omega(H_2SO_4) = 0{,}049\%$	$pH-?$
$\rho(sol-n) = 1\, {}^{g}/{}_{ml}$	$pOH-?$
$\alpha = 100\% = 1$	
$M(H_2SO_4) = 98\, {}^{g}/{}_{mol}$.	

Solution:

1) Calculate the molar concentration of sulfuric acid using the formula in table 5:

$$c(H_2SO_4) = \frac{\omega(H_2SO_4) \cdot \rho(sol-n)}{M(H_2SO_4) \cdot 100\%} = \frac{0{,}049\% \cdot 1000\, {}^{g}/{}_{l}}{98\, {}^{g}/{}_{mol} \cdot 100\%} = 0{,}005\, {}^{mol}/{}_{l}$$

2) Calculate the molar concentration of free H^+ ions, considering that two hydrogen ions are formed by dissociation of one moleculeH_2SO_4:

$$[H^+] = c(H_2SO_4) \cdot n \cdot \alpha = 0{,}005\,{}^{mol}/_{l} \cdot 2 \cdot 1 = 0{,}01\,{}^{mol}/_{l}$$

3) Calculate pH:
$pH = -lg[H^+] = -lg0{,}01 = 2$

4) Calculate pOH:
$pOH = 14 - pH = 14 - 2 = 12$

5) When diluting this solution 10 times the molar concentrations of the solutes are reduced 10 times:

$$[H^+]_1 = \frac{[H^+]}{10} = \frac{10^{-2}\,{}^{mol}/_{l}}{10} = 10^{-3}\,{}^{mol}/_{l}$$

$$(pH)_1 = -lg[H^+]_1 = -lg10^{-3} = 3$$

$$(pOH)_1 = 14 - pH_1 = 14 - 3 = 11$$

6) When diluting this solution 100 times the molar concentrations of the solutes are reduced 100 times:

$$[H^+]_2 = \frac{[H^+]}{100} = \frac{10^{-2}\,{}^{mol}/_{l}}{100} = 10^{-4}\,{}^{mol}/_{l}$$

$$(pH)_2 = -lg[H^+]_2 = -lg10^{-4} = 4$$

$$(pOH)_2 = 14 - pH_2 = 14 - 4 = 10$$

Answer: in the original solution pH = 2, pOH = 12;
at dilution of this solution 10 times the pH rises by 1 and pOH decreases by 1;
when diluted with this solution 100 times the pH increases by 2 and pOH decreases by 2.

Example 5

Calculate the pH of a 1% acetic acid solution, given that the acid dissociation rate is 1.2% and the density of the solution $1\,{}^{g}/_{ml}$. $M(CH_3COOH) = 60\,{}^{g}/_{mol}$

Given:	**Find:**
$\omega(CH_3COOH) = 1\%$ $\rho(\text{р} - \text{ну}) = 1\,{}^{g}/_{ml}$ $\alpha = 1{,}2\% = 0{,}012$ $M(CH_3COOH) = 60\,{}^{g}/_{mol}$	$pH-?$

Solution:

The dissociation of acetic acid is as follows:

$$CH_3COOH \leftrightarrows H^+ + CH_3COO^-$$

1) Calculate the molar concentration of acetic acid:

$$c(CH_3COOH) = \frac{\omega(CH_3COOH) \cdot \rho(sol-n)}{M(CH_3COOH) \cdot 100\%} = \frac{1\% \cdot 1000\, {}^{g}/_{l}}{60\, {}^{g}/_{mol} \cdot 100\%} = 0{,}167\, {}^{mol}/_{l}$$

2) Calculate the molar concentration of free H^+ given that the dissociation of one molecule CH_3COOH forms one proton and only 0.012 part of all acid molecules splits into ions:

$$[H^+] = c(CH_3COOH) \cdot n \cdot \alpha = 0{,}167\, {}^{mol}/_{l} \cdot 1 \cdot 0{,}012 = 2 \cdot 10^{-3}\, {}^{mol}/_{l}$$

3) Calculate the pH value:
$pH = -lg[H^+] = -lg(2 \cdot 10^{-3}) = 2{,}7$

Answer: $pH = 2{,}7$

Example 6

The mass concentration of calcium hydroxide in the solution is equal 0,037g/l. Calculate the pH of the solution given the degree of electrolyte dissociation 100%. $M(Ca(OH)_2) = 74\, {}^{g}/_{mol}$

Given:	**Find:**
$\rho(Ca(OH)_2) = 0{,}037\, {}^{g}/_{l}$ $\alpha = 100\% = 1$ $M(Ca(OH)_2) = 74\, {}^{g}/_{mol}$	$pH-?$

Solution:

Calcium hydroxide dissociation occurs according to the scheme:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

1) Calculate the molar concentration $Ca(OH)_2$:

$$c(Ca(OH)_2) = \frac{\rho(Ca(OH)_2)}{M(Ca(OH)_2)} = \frac{0{,}037\, {}^{g}/_{l}}{74\, {}^{mol}/_{l}} = 5 \cdot 10^{-4}\, {}^{mol}/_{l}$$

2) Calculate the molar concentration of free ions OH^-:
$[OH^-] = c(Ca(OH)_2) \cdot n \cdot \alpha = 5 \cdot 10^{-4}\, {}^{mol}/_{l} \cdot 2 \cdot 1 = 10^{-3}\, {}^{mol}/_{l}$

3) Calculate the pOH value :
$pOH = -lg[OH^-] = -lg10^{-3} = 3$

4) Calculate the pH value :
$pH = 14 - pOH = 14 - 3 = 11$

Answer: $pH = 11$

Example 7

The hydrogen indicator of formic acid solution is 2.56. Determine the mass fraction of HCOOH in the solution, given that the dissociation rate of the electrolyte is 6.1% and the density of the solution $1\, {}^{g}/_{ml}$. $M(HCOOH) = 46\, {}^{g}/_{mol}$.

Given:
$pH = 2{,}56$
$\alpha = 6{,}1\% = 0{,}061$
$\rho(\text{р} - \text{ну}) = 1\,{}^{g}/_{ml}$
$M(HCOOH) = 46\,{}^{g}/_{mol}$

Find:
$c(HCOOH) - ?$

Solution:

Formic acid dissociation occurs according to the scheme:

$$HCOO\boldsymbol{H} \leftrightarrows H^{+} + HCOO^{-}$$

1) Using the pH value to calculate the molar concentration of free ions H^{+}:

$$[H^{+}] = 10^{-pH} = 10^{-2,56} = 2{,}754 \cdot 10^{-3}({}^{mol}/_{l})$$

2) Given that the number of free H^{+} ions is related to the total acid concentration in the solution and depends on the degree of dissociation of the acid molecules, find the molar concentration $HCOOH$:

$$c(HCOOH) = \frac{[H^{+}]}{n \cdot \alpha} = \frac{2{,}754 \cdot 10^{-3}\,{}^{mol}/_{l}}{1 \cdot 0{,}061} = 0{,}045\,{}^{mol}/_{l}$$

(n – the amount in the acid molecule of "acidic" protons)

3) Calculate the mass fraction of formic acid:

$$\omega(HCOOH) = \frac{c(HCOOH) \cdot M(HCOOH)}{\rho(\text{р} - \text{ну})} \cdot 100\%$$

$$\omega(HCOOH) = \frac{0{,}045\,{}^{mol}/_{l} \cdot 46\,{}^{g}/_{mol}}{1000\,{}^{g}/_{l}} \cdot 100\% = 0{,}2\%$$

Answer: $\omega(HCOOH) = 0{,}2\%$

Example 8

What is the mass of sulfuric acid contained in 400 ml of solution if the pH value of this solution is 1. Degree of electrolyte dissociation 100%. $M(H_2SO_4) = 98\,{}^{g}/_{mol}$

Given:
$V(sol - n) = 400ml = 0{,}4l$
$pH = 1$
$\alpha = 100\% = 1$
$M(H_2SO_4) = 98\,{}^{g}/_{mol}$

Find:
$m(H_2SO_4) - ?$

Solution:

1) Using the pH value to calculate the molar concentration of free ions H^{+}:
$[H^{+}] = 10^{-pH} = 10^{-1}\,{}^{mol}/_{l}$

2) Calculate the molar concentration H_2SO_4:

$$c(H_2SO_4) = \frac{[H^{+}]}{n \cdot \alpha} = \frac{10^{-1}\,{}^{mol}/_{l}}{2 \cdot 1} = 0{,}05\,{}^{mol}/_{l}$$

3) Find the mass of H_2SO_4, contained in 400 ml of this solution:

$$m(H_2SO_4) = M(H_2SO_4) \cdot c(H_2SO_4) \cdot V(sol-n)$$

$$m(H_2SO_4) = 98\,{}^{g}/_{mol} \cdot 0{,}05\,{}^{mol}/_{l} \cdot 0{,}4л = 1{,}96g$$

Answer: $m(H_2SO_4) = 1{,}96g$

Example 9

Calculate the mass of potassium hydroxide required to prepare 250 ml of solution with pH = 13, given that the degree of electrolyte dissociation 100%. $M(KOH) = 56\,{}^{g}/_{mol}.$

Given:	**Find:**
$V(sol-n) = 250ml = 0{,}25l$ $pH = 13$ $\alpha = 100\% = 1$ $M(KOH) = 56\,{}^{g}/_{mol}$	$m(KOH)-?$

Solution:

1) From pH to go to pOH:

$$pOH = 14 - pH = 14 - 13 = 1$$

2) Find the molar concentration of free ions OH^-:

$$[OH^-] = 10^{-pOH} = 10^{-1}\,{}^{mol}/_{l}$$

3) Знайти загальну молярну концентрацію KOH, використовуючи її зв'язок з молярною концентрацією вільних іонів OH^-:

$$c(KOH) = \frac{[OH^-]}{n \cdot \alpha} = \frac{10^{-1}\,{}^{mol}/_{l}}{1 \cdot 1} = 10^{-1}\,{}^{mol}/_{l}$$

4) Calculate the mass of KOH sample required to prepare this solution:

$$m(KOH) = M(KOH) \cdot C(KOH) \cdot V(sol-n)$$

$$m(KOH) = 56\,{}^{g}/_{mol} \cdot 10^{-1}\,{}^{mol}/_{l} \cdot 0{,}25l = 1{,}4g$$

Answer: $m(KOH) = 1{,}4g$

Example 10

The hydrogen index of the solution of barium hydroxide is 13. Determine the mass fraction of $Ba(OH)_2$ in the solution, given that the degree of dissociation of the electrolyte is 100% and the density of the solution 1g/ml. $M(Ba(OH)_2) = 171\,{}^{g}/_{mol}$

Given:	**Find:**
$pH = 13$ $\alpha = 100\% = 1$ $M(Ba(OH)_2) = 171\,{}^{g}/_{mol}$ $\rho(\text{р} - \text{ну}) = 1\,{}^{g}/_{ml}$	$\omega(Ba(OH)_2)-?$

Solution:

1) From pH to go to pOH:
   $pOH = 14 - pH = 14 - 13 = 1$
2) Find the molar concentration of free ions OH^-:
   $[OH^-] = 10^{-pOH} = 10^{-1}\, {}^{mol}/_{l}$
3) Calculate the total molar concentration $Ba(OH)_2$:
   $$c(Ba(OH)_2) = \frac{[OH^-]}{n \cdot \alpha} = \frac{10^{-1}\, {}^{mol}/_{l}}{2 \cdot 1} = 0{,}05\, {}^{mol}/_{l}$$
   ($n = 2$ – the number of OH- groups)
4) The formula that relates the mass fraction to the molar concentration is given in Table 5:
   $$\omega(Ba(OH)_2) = \frac{c(Ba(OH)_2) \cdot M(Ba(OH)_2) \cdot 100\%}{\rho(sol-n)}$$
   $$\omega(Ba(OH)_2) = \frac{0{,}05\, {}^{mol}/_{l} \cdot 171\, {}^{g}/_{mol} \cdot 100\%}{1000\, {}^{g}/_{l}} = 0{,}855\%$$

Answer: $\omega(Ba(OH)_2) = 0{,}855\%$

Example 11

Write the reaction equation of the first stage of hydrolysis and calculate the hydrolysis constant for the following salts:

а) $AlCl_3,\ K_{д_3}(Al(OH)_3) = 1{,}38 \cdot 10^{-9}\, {}^{mol}/_{l}$;
б) $HCOONa,\ K_д(HCOOH) = 1{,}77 \cdot 10^{-4}\, {}^{mol}/_{l}$;
в) $(NH_4)_2CO_3,\ K_{д2}(H_2CO_3) = 4{,}69 \cdot 10^{-11}\, {}^{mol}/_{l}$,
$K_д(NH_3 \cdot H_2O) = 1{,}75 \cdot 10^{-5}\, {}^{mol}/_{l}$.

Given:	**Find:**
$K_{д_3}(Al(OH)_3) = 1{,}38 \cdot 10^{-9}\, {}^{mol}/_{l}$	$K_{г1}(AlCl_3)$–?
$K_д(HCOOH) = 1{,}77 \cdot 10^{-4}\, {}^{mol}/_{l}$	$K_{г1}(HCOONa)$–?
$K_{д2}(H_2CO_3) = 4{,}69 \cdot 10^{-11}\, {}^{mol}/_{l}$	$K_{г1}((NH_4)_2CO_3)$–?
$K_д(NH_3 \cdot H_2O) = 1{,}75 \cdot 10^{-5}\, {}^{mol}/_{l}$	

Solution:

a) $AlCl_3$ - is a soluble salt formed by the weak base $Al(OH)_3$ and the strong acid HCl. Hydrolysis occurs by cation. Equation I stages of hydrolysis:
$$AlCl_3 + H_2O \leftrightarrows Al(OH)Cl + HCl$$
$$Al^{3+} + H_2O \leftrightarrows Al(OH)^{2+} + H^+$$
The hydrolysis constant is calculated by the formula:

$$K_h = \frac{K_{H_2O}}{K_b},$$

where K_{H_2O} ionic product of water, K_b - the dissociation constant of the weak basis

$$K_{h1}(AlCl_3) = \frac{K_{H_2O}}{K_{d_3}(Al(OH)_3)} = \frac{10^{-14}\, mol^2/l^2}{1{,}38 \cdot 10^{-9}\, {}^{mol}/_{l}} = 7{,}25 \cdot 10^{-6}\, {}^{mol}/_{l}$$

b) $HCOONa$ - it is a soluble salt formed by a strong NaOH base and a weak HCOOH acid. Hydrolysis occurs on the anion. Hydrolysis equation:

$$HCOONa + H_2O \leftrightarrows HCOOH + NaOH$$
$$HCOO^- + H_2O \leftrightarrows HCOOH + OH^-$$

The hydrolysis constant is calculated by the formula

$$K_h = \frac{K_{H_2O}}{K_a},$$

where K_{H_2O} ion product of water, K_a - is the dissociation constant of weak acid

$$K_h(HCOONa) = \frac{K_{H_2O}}{K_d(HCOOH)} = \frac{10^{-14}\, mol^2/l^2}{1{,}77 \cdot 10^{-4}\, {}^{mol}/_{l}} = 5{,}65 \cdot 10^{-11}\, {}^{mol}/_{l}$$

c) $(NH_4)_2CO_3$- it is a soluble salt formed by a weak base $NH_3 \cdot H_2O$ and a weak acid H_2CO_3. Hydrolysis occurs by cation and anion. Equation I stages of hydrolysis:

$$(NH_4)_2CO_3 + H_2O \leftrightarrows NH_4HCO_3 + NH_3 \cdot H_2O$$
$$NH_4^+ + CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + NH_3 \cdot H_2O$$

The hydrolysis constant is calculated by the formula

$$K_{г} = \frac{K_{H_2O}}{K_a K_b},$$

where K_{H_2O} ionic product of water, K_a - dissociation constant of weak acid; K_b - the dissociation constant of the weak base

$$K_{h1}((NH_4)_2CO_3) = \frac{K_{H_2O}}{K_{d2}(H_2CO_3) \cdot K_d(NH_3 \cdot H_2O)} =$$
$$= \frac{10^{-14}\, mol^2/l^2}{4{,}69 \cdot 10^{-11}\, {}^{mol}/_{l} \cdot 1{,}75 \cdot 10^{-5}} = 12{,}2$$

Answer: $K_{h1}(AlCl_3) = 7{,}25 \cdot 10^{-6}\, {}^{mol}/_{l}$;

$K_h(HCOONa) = 5{,}65 \cdot 10^{-11}\, {}^{mol}/_{l}$;

$K_{h1}((NH_4)_2CO_3) = 12{,}2$.

Self-test questions

4.1 Calculate the molar concentration of free H^+ and OH^- ions at temperature 25°C:
a) in a solution of trichloroacetic acid (Cl_3CCOOH) with a molar concentration of $0{,}003\, {}^{mol}/_{l}$, if the degree of dissociation of the electrolyte 89%;

b) in cyanidic acid (HCN) solution with a molar concentration $0{,}003\,^{mol}/_{l}$, if the degree of dissociation of the electrolyte 0,5%;
c) in a solution of barium hydroxide ($Ba(OH)_2$) with a molar concentration $0{,}003\,^{mol}/_{l}$, if the degree of dissociation of the electrolyte 100%;
d) in a solution of ammonia ($NH_3 \cdot H_2O$) with a molar concentration of NH_3 $0{,}003\,^{mol}/_{l}$, if the degree of dissociation of the electrolyte 7,5% .

Answer: a) $[H^+] = 2{,}67 \cdot 10^{-3}\,^{mol}/_{l}$; $[OH^-] = 3{,}745 \cdot 10^{-12}\,^{mol}/_{l}$;
b) $[H^+] = 1{,}5 \cdot 10^{-5}\,^{mol}/_{l}$; $[OH^-] = 6{,}67 \cdot 10^{-9}\,^{mol}/_{l}$;
c) $[H^+] = 1{,}67 \cdot 10^{-12}\,^{mol}/_{l}$; $[OH^-] = 6 \cdot 10^{-3}\,^{mol}/_{l}$;
d) $[H^+] = 4{,}44 \cdot 10^{-11}\,^{mol}/_{l}$; $[OH^-] = 2{,}25 \cdot 10^{-4}\,^{mol}/_{l}$.

4.2 Calculate *pH* and *pOH* for solutions:
a) with a molar concentration of free ions H^+ $3{,}5 \cdot 10^{-3}\,^{mol}/_{l}$;
b) with a molar concentration of free ions OH^- $5{,}4 \cdot 10^{-2}\,^{mol}/_{l}$.

Answer: а) $pH = 2{,}46; pOH = 11{,}54$;
б) $pH = 12{,}73; pOH = 1{,}27$.

4.3 Calculate the pH for solutions of a) nitric acid (HNO_3) with a molar concentration $10^{-3}\,^{mol}/_{l}$; b) barium hydroxide ($Ba(OH)_2$) with a molar concentration $0{,}5 \cdot 10^{-2}\,^{mol}/_{l}$, if the degree of electrolyte dissociation is 100%. How will the pH of these solutions change when diluted 100 times?

Answer: a) $pH = 3$, will increase by 2;
b) $pH = 12$, will decrease by 2

4.4 Calculate the pH value of a 6% acetic acid solution, given that the acid dissociation rate is 0.5% and the density of the solution $1\,^{g}/_{ml}$.
$M(CH_3COOH) = 60\,^{g}/_{mol}$

Answer: $pH = 2{,}3$

4.5 Calculate the pH of the solution with a barium hydroxide mass fraction of 0.02%, given that the electrolyte dissociation rate is 100% and the density of the solution $1\,^{g}/_{ml}$. $M(Ba(OH)_2) = 171\,^{g}/_{mol}$

Answer: $pH = 11{,}37$

4.6 Calculate the molar concentration of free H^+ and OH^- ions in the secretion of the pancreas with pH 7,7.

Answer: $[H^+] = 2 \cdot 10^{-8}\,^{mol}/_{l}$;
$[OH^-] = 5 \cdot 10^{-7}\,^{mol}/_{l}$

4.7 Calculate the mass of hydrochloric acid contained in 300 ml of solution at pH = 2, given that the degree of dissociation of the electrolyte 100%.

$M(HCl) = 36{,}5\, ^{g}/_{mol}$

Answer: $m(HCl) = 0{,}1095g$

4.8 Calculate the mass fraction of sulfuric acid in solution with pH = 2 if the degree of electrolyte dissociation is 100%.
The density of the solution $1^{g}/_{ml}$; $M(H_2SO_4) = 98\, ^{g}/_{mol}$

Answer: $\omega(H_2SO_4) = 0{,}049\%$

4.9 Calculate the mass of barium hydroxide required to prepare 250 ml of solution at pH = 13, given that the degree of electrolyte dissociation 100%. $M(Ba(OH)_2) = 171\, ^{g}/_{mol}$.

Answer: $m(Ba(OH)_2) = 2{,}1375г$

4.10 Calculate the mass fraction of ammonia (NH_3) in aqueous solution if the pH of this solution is 11,8. The degree of dissociation $NH_3 \cdot H_2O$ 23%; density of the solution $0{,}998^{g}/_{ml}$; $M(NH_3) = 17\, ^{g}/_{mol}$

Answer: $\omega(NH_3) = 0{,}047\%$

4.11 The hydrogen index of the solution of barium hydroxide is 12. Calculate the mass concentration of $Ba(OH)_2$ in solution, given that the degree of dissociation of the electrolyte 100%. $M(Ba(OH)_2) = 171\, ^{g}/_{mol}$.

Answer: $\rho(Ba(OH)_2) = 0{,}855\, ^{g}/_{l}$

4.12 Write the reaction equation of the first stage of hydrolysis and calculate the hydrolysis constant for the following salts:
a) $MgCl_2$, if $K_{d2}(Mg(OH)_2 = 2{,}5 \cdot 10^{-3}\, ^{mol}/_{l}$;
b)K_3PO_4, if $K_{d_3}(H_3PO_4) = 1{,}26 \cdot 10^{-12}\, ^{mol}/_{l}$;
c) $Mg(CH_3COO)_2$, if $K_{d2}(Mg(OH)_2 = 2{,}5 \cdot 10^{-3}\, ^{mol}/_{l}$,
$K_d(CH_3COOH) = 1{,}75 \cdot 10^{-5}\, ^{mol}/_{l}$.

Answer: а) $K_{h1}(MgCl_2) = 4 \cdot 10^{-12}\, ^{mol}/_{l}$;
б) $K_{h1}(K_3PO_4) = 7{,}94 \cdot 10^{-3}\, ^{mol}/_{l}$;
в) $K_{h1}(Mg(CH_3COO)_2) = 2{,}28 \cdot 10^{-7\text{-}}\, ^{mol}/_{l}$.

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

Basic thermodynamic quantities

Parameter	**Designation, unit of measurement**	**Semantic meaning**
Internal energy	U, $J, кJ$	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, $J, кJ, cal, кcal$	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, $J, кJ$	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

		(compression) of the system, equal to $A = p(V_2 - V_1) = p\Delta V$ The system performs expansion work (A> 0), the external environment performs compression work on the system (A <0).
Enthalpy	$H,$ $J, кJ;$ $H = U + pV$ $\Delta H = \Delta U + p\Delta V$	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.
Thermal effect of a chemical reaction	$Q,$ $кJ\ or\ кJ/mol,$ $cal\ or\ кcal/mol$ thermal effect of isochoric process $(V = const)$: $Q_V = \Delta U$ thermal effect of the isobaric process $(p = const)$: $Q_P = \Delta H$	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 kJ) or to 1 mol of any i-th participant of the reaction (measured in kJ / mol of the i-th substance).
Standard enthalpy of reaction	$\Delta H^0_{298},$ $кJor\ кJ/mol$	Thermal effect of isobaric-isothermal process, attributed to standard thermodynamic conditions: p = 101325 Pa = 1 atm = 760 mm Hg ,, which means the index "0" on the top right; T = 298.15 K, indicating the index "298" at the bottom right. 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.
Standard enthalpy of substance formation	$\Delta H^0_{f298}\,(sub., state\ of\ m.$ $кJ/mol$	Thermal effect (standard enthalpy ΔH^0_{f298}) of the reaction of formation of 1 mol of a given complex substance from the corresponding amount of simple substances in standard conditions. The standard enthalpy of formation of any simple substance in its most thermodynamically stable aggregate and allotropic state is 0.

Standard enthalpy of combustion of matter	$\Delta H^0_{c.298}\,(sub., st. of\ m.)$, $\text{к}J/mol$	Thermal effect (standard enthalpy $\Delta H^0_{c.298}$) 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, $\frac{J}{\text{К}}\ or\ \frac{J}{mol\cdot \text{К}}$; $\Delta S = S_2 - S_1$ 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^0_{298}, $^{J}/_{(\text{К}\cdot mol)}$	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 TΔS 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, $J, \text{к}J$, $G = H - TS$ $\Delta G = \Delta H - T\Delta S$	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	$\Delta G^0_{f298}(sub., st. of\ m.)$ $\text{к}J/mol$	The standard Gibbs energy is the formation of 1 mol of this compound from simple substances under standard thermodynamic conditions.

Free Helmholtz energy	F, $J, \text{кJ}$, $F = U - TS$ $\Delta F = \Delta U - T\Delta S$	Generalized thermodynamic function of the system state, which takes into account the energy and disorder of the system in isochoric-isothermal conditions (V, T = const). Another name is isochoric-isothermal potential. The free Helmholtz energy shows what part of ΔU is converted to work.
Caloric content of food	кJ/g or кcal/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.

$$\boxed{Q = \Delta U + A}$$

The second law of thermodynamics.

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

$$\boxed{\Delta S > 0}$$

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 = const) or isochoric-isothermal (V, T = const) conditions. The criterion for the direction of the spontaneous process in these cases is the sign of the change in the Gibbs energyΔG (in the case of isobaric-isothermal processes) or the Helmholtz energyΔF (in the case of isochoric-isothermal processes)

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

Analysis of the equation ΔG = ΔH-TΔS 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 TΔS. 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 (ΔH <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 (ΔS> 0). Possible options:

$\begin{cases} \Delta H < 0 \\ \Delta S > 0 \end{cases}$	In this case ΔG <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 ΔG <0 if | ΔH |> | TΔS |, the reaction is thermodynamically possible at a relatively low temperature.
$\begin{cases} \Delta H > 0 \\ \Delta S > 0 \end{cases}$	In this case ΔG <0 if | ΔH | <| TΔS |, 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:
$$\Delta H = \sum_i n_i (\Delta H_i)_{f.}^{prod.} - \sum_j n_j \left(\Delta H_j\right)_{f.}^{reag.}$$
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:
$$\Delta H = \sum_i n_i (\Delta H_i)_{c.}^{reag.} - \sum_j n_j \left(\Delta H_j\right)_{c.}^{prod.}$$

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:	**Find:**
$\Delta H_c(c.) = -17\ кJ/g$ $\Delta H_c(p.) = -17\ кJ/g$ $\Delta H_c(f.) = -39{,}9\ кJ/g$ $\omega(c.) = 2{,}7\% = 0{,}027$ $\omega(p.) = 2{,}6\% = 0{,}026$ $\omega(f.) = 25\% = 0{,}25$ $m(sour\ cream) = 250g$	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:

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

$$\Delta H_c(s.c.) = 0{,}027 \cdot (-17\,^{кJ}/_{g}) + 0{,}026 \cdot (-17\,^{кJ}/_{g}) + 0{,}25 \cdot (-39{,}9\,^{кJ}/_{g}) =$$
$$= -10{,}876\,^{кJ}/_{g}$$

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 $10{,}876\,^{кJ}/_{g}$, and the caloric content of 250 g of sour cream:

$$250g \cdot 10{,}876\,^{кJ}/_{g} = 2719кJ = 650кcal$$

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:

$\Delta H_c(c.) = -17\,кJ/g$
$\Delta H_c(p.) = -17\,кJ/g$
$\Delta H_c(f.) = -39{,}9\,кJ/g$
$\omega(в.) = 65{,}4\% = 0{,}654$
$\omega(б.) = 11{,}8\% = 0{,}118$
$\omega(ж.) = 5{,}8\% = 0{,}058$
$m(H_2O) = 720g$
$\Delta H^0_{ev.}(H_2\mathrm{O}) = 41\,^{\mathrm{кJ}}/_{\mathrm{mol}}$

Find:

$m(oatm.) - ?$

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:

$$Q = n(H_2O) \cdot \Delta H^0_{ev.}(H_2\mathrm{O}) = \frac{\mathrm{m(H_2O)}}{\mathrm{M(H_2O)}} \cdot \Delta H^0_{ev.}(H_2\mathrm{O})$$

$$Q = \frac{720g}{18\,g/mol} \cdot 41\,^{\mathrm{кJ}}/_{\mathrm{mol}} = 1640кJ$$

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:

$$\boxed{\Delta H_{c.}(oatm.) = \sum \omega(x) \cdot \Delta H_c(x)}$$

$$\Delta H_{c.}(oatm.) = 0{,}654 \cdot (-17\,^{кJ}/_{g}) + 0{,}118 \cdot (-17\,^{кJ}/_{g}) + 0{,}058 \cdot (-39{,}9\,^{кJ}/_{g}) =$$
$$= -13{,}182\,^{кJ}/_{g}$$

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

$$m(oatm.) = \frac{1640кJ}{13,182\,^{кJ}/_{g}} = 124,4\ g$$

Answer: $m(oatm.) = 124,4g$

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:	**Find:**
standard conditions.	ΔS^0_{298} – ? ΔH^0_{298}–? ΔG^0_{298} – ?

Solution:

Write the reaction equation:

$$2N_2O_{(g)} + O_{2(g)} \rightarrow 4NO_{(g)}$$

Write reference data:

$S^0_{298}(N_2O_{(g)}) = 220,0\frac{J}{mol\cdot К}$ $\qquad \Delta H^0_{f.298}(N_2O_{(g)}) = 81,6\ кJ/mol$

$S^0_{298}(O_{2(g)}) = 205,2\frac{J}{mol\cdot К}$ $\qquad \Delta H^0_{f.298}(NO_{(g)}) = 91,3\,кJ/mol$

$S^0_{298}(NO_{(g)}) = 210,8\frac{J}{mol\cdot К}$ $\qquad \Delta G^0_{f.298}(N_2O_{(g)}) = 103,7\ кJ/mol$

$\Delta G^0_{f.298}(NO_{(g)}) = 87,6\ кJ/mol$

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:*

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

$$\Delta S^0_{298} = 4\cdot S^0_{298}(NO_{(g)}) - [2\cdot S^0_{298}(N_2O_{(g)}) + S^0_{298}(O_{2(g)})]$$

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

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:*

$$\Delta H^0_{298} = 4\cdot \Delta H^0_{f.298}(NO_{(g)}) - [2\cdot \Delta H^0_{f.298}(N_2O_{(g)}) + \Delta H^0_{f.298}((O_{2(g)})]$$

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

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

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

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

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:

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

$$\Delta G_{298}^0 = 4 \cdot \Delta G_{f.298}^0 \left(NO_{(g)}\right) - \left[2 \cdot \Delta G_{f.298}^0 \left(N_2O_{(g)}\right) + \Delta G_{f.298}^0 ((O_{2(g)})\right]$$

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

Answer:

$$\Delta S_{298}^0 = 198 J/K$$
$$\Delta H_{298}^0 = 202\text{к}J$$
$$\Delta G_{298}^0 = 143\text{к}J$$

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

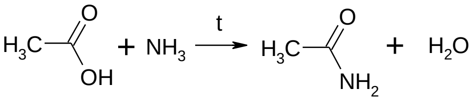
Example 4

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:	**Find:**
standard conditions	ΔH_{298}^0- ?

Solution:

Write the reaction equation:



Write reference data:

$\Delta H^0_{c.298}\left(CH_3COOH_{(l)}\right) = -874{,}2\ \text{к}J/mol$

$\Delta H^0_{c.298}\left(NH_{3(g)}\right) = -382{,}8\ \text{к}J/mol$

$\Delta H^0_{c.298}\left(CH_3CONH_{2(l)}\right) = -1184{,}6\,\text{к}J/mol$

$\Delta H^0_{c.298}(H_2O) = 0$

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:

$$\Delta H^0_{298} = [\Delta H^0_{c.298}(CH_3COOH) + \Delta H^0_{c.298}(NH_3)] - [\Delta H^0_{c.298}(CH_3CONH_2) + \Delta H^0_{c.298}(H_2O)]$$

$$\Delta H^0_{298} = [-874{,}2\text{к}J + (-382{,}8\text{к}J)] — [-1184{,}6\text{к}J + 0] = -72{,}4\text{к}J$$

Answer: $\Delta H^0_{298} = -72{,}4\text{к}J$

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:	**Find:**
$m(C_2H_5OC_2H_5) = 100g$	$Q-?$

Solution:

Write the equation of the combustion reaction of diethyl ether:

$$C_2H_5OC_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

Write reference data:

$$\Delta H^0_{c.298}\,(C_2H_5OC_2H_5) = -2723{,}9\,\text{к}J/mol$$

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

$$Q = -\Delta H^0_{c.298}\,(C_2H_5OC_2H_5)\cdot n(C_2H_5OC_2H_5) = -\Delta H^0_{c.298}\,(C_2H_5OC_2H_5)\frac{m(C_2H_5OC_2H_5)}{M(C_2H_5OC_2H_5)}$$

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

Answer: $Q = 3680{,}9\text{к}J$

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:
$m(p.) = 47\ g$
$m(f.) = 59\ g$
$m(cheese) = 200g$
caloric content of proteins = 17кJ/g
caloric content of fats = 39,9 кJ/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:

$$47\text{г}\cdot 17\ {}^{\text{к}J}/_{g} + 59\text{г}\cdot 39{,}9\ {}^{\text{к}J}/_{g} = 3153{,}1\text{к}J$$

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

$$\frac{3153{,}1\text{к}J}{200g} = 15{,}76\ {}^{\text{к}J}/_{g}$$

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

$$\frac{3153{,}1}{4{,}184} = 844{,}4\ \text{к}cal \qquad \frac{15{,}76}{4{,}184} = 3{,}77\ {}^{\text{к}cal}/_{g}$$

Answer: a) caloric content of 200 g of cheese is 3153,1 кJ (або 844,4 кcal);
b) caloric content of cheese in terms of g of product is equal to 15,76 кJ/g (or 3,77 кcal/g)

Self-test questions

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

1) $2HBr_{(g)} + Cl_{2(g)} \leftrightarrows 2HCl_{(g)} + Br_{2(l)}$

2) $2Pb(NO_3)_{2(s)} \leftrightarrows 2\,PbO_{(s.)} + 4NO_{2(g)}$
$+ \mathrm{O}_{2(g)}$

3) $Cl_{2(g)} + H_{2(g)} \leftrightarrows 2HCl_{(g)}$

4) $NH_{3(g)} + HCl_{(g)} \leftrightarrows NH_4\mathrm{Cl}_{(s)}$

5) $CO_{(g)} + O_{3(g)} \leftrightarrows CO_{2(g)} + O_{2(g)}$

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)
$\Delta S^0_{298}, {}^{J}/_{K}$	-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)
$\Delta H^0_{298}, кJ$	-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^0_{298} та ΔH^0_{298}, calculated in Problems 1.2 and 1.3.

Answer:

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

1.5 Calculate the thermal effect of the photosynthesis reaction

$$6CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(s.)} + 6O_{2(g)},$$

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?

Anser: $\Delta G = 2818{,}6кJ$

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

$$C_6H_{12}O_{6(s-n)} \rightarrow 2CH_3CH(OH)COOH_{(s-n)},$$

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.

Answer: $\Delta S^0_{298} = 174{,}5\,J/K$
$\Delta H^0_{298} = -108{,}2$ кJ
$\Delta G^0_{298} = -160{,}2$ кJ

1.7 Calculate the standard enthalpy of the ethylene hydrogenation reaction

$$C_2H_4 + H_2 \rightarrow C_2H_6,$$

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

Answer: $\Delta H^0_{298} = -136{,}3$ кJ

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

$$C_6H_{12}O_{6(s.)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)},$$

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

Answer: $Q = 778{,}5$кJ

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

$$C_{12}H_{22}O_{11(s.)} + 12O_{2(g)} \rightarrow 12CO_{2(g)} + 11H_2O_{(l)},$$

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

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

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.

Answer: a) 5500кJ
б) 22 кJ/g

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.

Answer: 306,84кJ (73,34кcal)

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.

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: $m = 408\ g$

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, %**				**кcal****
	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.

6. Kinetics of biochemical reactions

Basic kinetic quantities

Parameter	**Marking, Unit**	**Semantic meaning**
Average reaction rate	$v, mol/(l \cdot s)$ for reaction $A + B \rightarrow AB$: $v = -\frac{\Delta c_A}{\Delta \tau}$ або $v = \frac{\Delta c_{AB}}{\Delta \tau}$	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: *at a constant temperature, the rate of the chemical reaction is directly proportional to the product of the molar concentrations of the reagents.*
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	k, reaction order — dimension k 0 — $\frac{mol}{l \cdot s}$ 1-st — c^{-1} 2-nd — $\frac{l}{mol \cdot s}$ 3-d — $\frac{l^2}{mol^2 \cdot s}$	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	differential form: $-\frac{dc}{dt} = kc$ integral form: $lnc = lnc_0 - kt$, where: $c = c_0 \cdot e^{-kt}$, $k = \frac{1}{t} ln \frac{c_0}{c}$ or $k = \frac{ln2}{\tau_{1/2}}$; the transition from natural to decimal logarithm gives: $k = \frac{2{,}3}{t} lg \frac{c_0}{c}$ and $k = \frac{2{,}3 \cdot lg2}{\tau_{1/2}}$	The integral form of the equation expresses the linear dependence of the variables lnc and t. k – 1st order reaction rate constant; c_0 - the concentration of the starting material at the initial time; c – the concentration of the substance at time t; t - the time elapsed since the beginning of the reaction.
Vant-Goff Rule	$v_2 = v_1 \cdot \gamma^{\frac{T_2 - T_1}{10}}$, $k_2 = k_1 \cdot \gamma^{\frac{T_2 - T_1}{10}}$, 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.	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	$k = A \cdot e^{-\frac{E_a}{RT}},$ $lnk = lnA - \frac{E_a}{RT}$ $ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ or $ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$	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 - 0.75 mol / l .

$$C_2H_5Br + NaOH \xrightarrow{C_2H_5OH,T} C_2H_4 + NaBr + H_2O$$

Given:	**Find:**
$c_1(C_2H_5Br)$ =0,1 mol/l	v–?
$c_2(C_2H_5Br)$ =0,075 mol/l	
$t_1 = 1min = 60\ s$	
$t_2 = 20min = 1200\ s$	

Solution:

Write the reaction equation:

$$C_2H_5Br + NaOH \xrightarrow{C_2H_5OH,T} C_2H_4 + NaBr + H_2O$$

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

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

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

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:

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

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

b) The reaction rate does not depend on the concentration of products, in this case NO2 (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 → AB is bimolecular. Initial concentrations of substances are as follows:

c_0 (A) = 2.5 mol, c_0 (B) = 1.5 mol. The reaction rate constant k = 0.8l⁄(mol · 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:	**Find:**
$c_0(A) = 2{,}5\,mol/l$	$c(A)-?$

$c_0(B) = 1{,}5\, mol/l$
$c(B) = 1{,}5\, mol/l$
$k = 0{,}8\, л/(mol \cdot s)$

$v - ?$

Solution:

a) The rate of bimolecular reaction A + B → 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

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

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

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

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:

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

and the reaction rate at this time is equal to:

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

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

Example 4

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

Given:
$\gamma = 4$
$\Delta t = 50°\mathrm{C}$

Find:
$\frac{k_2}{k_1} - ?$

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:	**Find:**
$\gamma = 2$	$\Delta t-?$
$\frac{v_2}{v_1} = 32$	

Solution:

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

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

$$lg32 = \frac{\Delta t}{10} lg2$$

$$\frac{\Delta t}{10} = \frac{lg32}{lg2}$$

$$\Delta t = 10\frac{lg32}{lg2} = 50$$

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:	**Find:**
$\frac{v_2}{v_1} = 20$	$\gamma-?$
$t_1 = 20°\mathrm{C}$	
$t_2 = 50°\mathrm{C}$	

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:
$\rho_0(C_{12}H_{22}O_{11}) = 100\,g/l$
$m(C_6H_{12}O_6) = 3{,}96g$
$V(s-n) = 1l$
$t = 5\ h.$

Find:
a) k–?
b) $\tau_{1/2}$–?

Solution:

Write the reaction equation:

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

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:

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

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:

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

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 $V(s-n) = 1l$):

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

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

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

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

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

$$\tau_{1/2} = \frac{2{,}3 \cdot lg2}{k} = \frac{2{,}3 \cdot lg2}{0{,}0156h^{-1}} = 44{,}4h$$

Answer: a) $k = 0{,}0156h^{-1}$ (or $4{,}35 \cdot 10^{-6}s^{-1}$);
b) $\tau_{1/2} = 44{,}4h$

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:

$m_0 = 0{,}1g$ | $t-?$
$m_{\text{вив.}} = 0{,}99m_0 = 0{,}099g$
$\tau_{1/2} = 80h$

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:

$$k = \frac{2{,}3 \cdot lg2}{\tau_{1/2}} = \frac{2{,}3 \cdot lg2}{80h} = 8{,}65 \cdot 10^{-3} h^{-1}$$

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: $\approx 22\ days$

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

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 → AB.

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

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

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

$$C_2H_4Br \rightarrow C_2H_4 + HBr,$$

if a) the pressure in the system is halved; b) reduce the HBr concentration by 2 times; c) reduce the concentration of C_2H_4Br 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

$$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH.$$

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 C_2H_5OH times.

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

2.6 Homogeneous gas-phase reaction $\mathrm{A + 2B \rightarrow AB_2}$ 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 = 0.084l/ (mol (s)) at 25 ° C. The initial concentrations are as follows: $c_0(CH_3COOC_2H_5)$ = 0.05 mol/l; $c_0(OH^-)$ = 0.1 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 mol/l.

Answer: $v_0 = 4{,}2 \cdot 10^{-4}\, mol/(l \cdot s)$;
$v = 1{,}2 \cdot 10^{-4}\, mol/(l \cdot s)$;
$c(CH_3COOC_2H_5) = 0{,}02\, mol/l.$

2.8 In the gas reaction of the 2nd order A + B → AB, the initial concentrations of substances are equal to 0.5 mol/l and 1.2 mol/l, respectively. The initial reaction rate is $1{,}2 \cdot 10^{-3}\, mol/(l \cdot s)$.. Calculate the rate constant and the reaction rate at the moment when the concentration of substance B is 1 mol/l

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

2.9 The reaction 2A + B → AB is trimolecular. The initial concentrations of substances are as follows: $c_0(A) = 2{,}5\, mol/l,\ c_0(B) = 1{,}5\, mol/l.$ The reaction rate constant $k = 0{,}8\, l^2/(mol^2 \cdot s)$. 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: $c(A) = 0{,}5\, mol/l$;
$v = 0{,}2\, mol/(l \cdot s)$.

2.10 How many times will the rate constant of a chemical reaction increase with increasing temperature from 0 ° C to 70 ° C if γ = 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 $1{,}2 \cdot 10^{-3}\, mol/(l \cdot s)$ (γ = 3).

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

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

Answer: $\Delta t = 40℃$

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

Answer: $t = 60℃$

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 $1{,}8 \cdot 10^{-5}\, mol/(l \cdot s)$ and $1{,}152 \cdot 10^{-3}\, mol/(l \cdot s)$ respectively.

Answer: $\gamma = 2$

2.16 The temperature coefficient of the gas reaction 2A + B → 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) $k = 2{,}54 \cdot 10^{-4} s^{-1}$);
б) $\tau_{1/2} = 45{,}4 min$.

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 20oC 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 25oC is equal to $2 \cdot 10^{-6} h^{-1}$.

Answer: 0.48% of the original amount

7. 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)	For the reaction $\mathrm{aA} + \mathrm{bB} \leftrightarrows cC + dD$ $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b},$ $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b},$ where the square brackets denote the equilibrium concentrations of the participants in the reaction (in mol / l).	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.
Dissociation constant	For acid: $HAn \leftrightarrows H^+ + An^-$ $K_a = \frac{[H^+] \cdot [An^-]}{[HAn]}$ For the basics: $KtOH \leftrightarrows Kt^+ + OH^-$	Dissociation constant For acid: For the basics: An equilibrium constant describing the dissociation of a weak

	$K_b = \frac{[OH^-] \cdot [Kt^+]}{[KtOH]}$	electrolyte is used to quantify the electrolyte force.
Instability constant	$MeL_n \leftrightarrows Me + nL$ $K_{inst.} = \frac{[Me] \cdot [L]^n}{[MeL_n]}$	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	$Kt_nAn_m \leftrightarrows nKt^{m+} + mAn^{n-}$ $SP = [Kt^{m+}]^n \cdot [An^{n-}]^m$	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:

a) $2HBr_{(g)} + Cl_{2(g)} \leftrightarrows 2HCl_{(g)} + Br_{2(l)}, \quad \Delta H < 0;$

b) $Fe_2(SO_4)_{3(s)} \leftrightarrows Fe_2O_{3(s)} + 3SO_{3(g)}, \quad \Delta H > 0;$

c) $H_{2(g)} + S_{(l)} \leftrightarrows H_2S_{(g)}; \ \Delta H < 0 .$

Solution:

a) $2HBr_{(g)} + Cl_{2(g)} \leftrightarrows 2HCl_{(g)} + Br_{2(l)}, \quad \Delta H < 0;$

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

$$2HBr_{(g)} + Cl_{2(g)} \leftrightarrows 2HCl_{(g)} + Br_{2(l)}$$

3mol 2mol

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).

b) $Fe_2(SO_4)_{3(s)} \leftrightarrows Fe_2O_{3(s)} + 3SO_{3(g)}, \quad \Delta H > 0;$

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

$$Fe_2(SO_4)_{3(s)} \leftrightarrows Fe_2O_{3(s)} + 3SO_{3(g)}$$

0 mol 3 mol

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).

c) $H_{2(g)} + S_{(l)} \leftrightarrows H_2S_{(g)}; \ \Delta H < 0 .$

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:

$$H_{2(g)} + S_{(l)} \leftrightarrows H_2S_{(g)}$$

1mol 1mol

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

$$CH_{4(g)} + 2H_2S_{(g)} \leftrightarrows CS_{2(g)} + 4H_{2(g)}$$

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) $NH_{3(g)} + HCl_{(g)} \leftrightarrows NH_4\mathrm{Cl}_{(s)}, \quad \Delta H < 0;$

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

Solution:

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

a) $NH_{3(g)} + HCl_{(g)} \leftrightarrows NH_4\mathrm{Cl}_{(s)}, \quad \Delta H < 0;$

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

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) $N_{2(g)} + O_{2(g)} \leftrightarrows 2NO_{(g)};$

b) $C_{(s)} + 2H_{2(g)} \leftrightarrows CH_{4(g)};$

c) $HF_{(so-n)} \leftrightarrows H^+_{(so-n)} + F^-_{(so-n)}.$

Solution:

a) $N_{2(g)} + O_{2(g)} \leftrightarrows 2NO_{(g)}$;

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 - N_2 and O_2 - in the denominator:

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

b) $C_{(s)} + 2H_{2(g)} \leftrightarrows CH_{4(g)}$;

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 H_2 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 - CH_4 - in the numerator, the concentration of the starting material - H_2 - in the denominator:

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

c) $HF_{(so-n)} \leftrightarrows H^{+}_{(so-n)} + F^{-}_{(so-n)}$.

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: $[Ag(SCN)_2]^-$, $[Ag(CN)_2]^-$, $[Ag(S_2O_3)_2]^{3-}$, $[Ag(NH_3)_2]^+$. 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):

$$[Ag(SCN)_2]^- \leftrightarrows Ag^+ + 2SCN^- \qquad K_{inst}([Ag(SCN)_2]^-) = \frac{[Ag^+]\cdot[SCN^-]^2}{[Ag(SCN)_2]^-};$$

$$[Ag(CN)_2]^- \leftrightarrows Ag^+ + 2CN^- \qquad K_{inst}([Ag(CN)_2]^-) = \frac{[Ag^+]\cdot[CN^-]^2}{[Ag(CN)_2]^-};$$

$$[Ag(S_2O_3)_2]^{3-} \leftrightarrows Ag^+ + 2S_2O_3^{2-} \qquad K_{inst}([Ag(S_2O_3)_2]^{3-}) = \frac{[Ag^+]\cdot[S_2O_3^{2-}]^2}{[Ag(S_2O_3)_2]^{3-}};$$

$$[Ag(NH_3)_2]^+ \leftrightarrows Ag^+ + 2NH_3 \qquad K_{inst}([Ag(NH_3)_2]^+) = \frac{[Ag^+]\cdot[NH_3]^2}{[Ag(NH_3)_2]^+}.$$

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

$$K_{inst}([Ag(SCN)_2]^-) = 5{,}89\cdot10^{-9}\,mol^2/l^2\,;$$

$$K_{inst}([Ag(CN)_2]^-) = 1\cdot10^{-21}\,mol^2/l\text{л}^2\,;$$

$$K_{inst}([Ag(S_2O_3)_2]^{3-}) = 3{,}47\cdot10^{-14}\,mol^2/l^2\,;$$

$$K_{inst}([Ag(NH_3)_2]^+) = 1{,}0\cdot10^{-7}\,mol^2/l^2.$$

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:

$$Mg_3(PO_4)_2, Ca_3(PO_4)_2,\ Sr_3(PO_4)_2.$$

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):

$$/.SP(Mg_3(PO_4)_2) = 1{,}04\cdot10^{-24}\,mol^5/l^5\,;$$

$$SP(Ca_3(PO_4)_2) = 2{,}07\cdot10^{-33}\,mol^5/l^5\,;$$

$$SP(Sr_3(PO_4)_2) = 1{,}0\cdot10^{-31}\,mol^5/l^5.$$

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 solubiities of the compounds are given in Annex 4:

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

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

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

Because

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

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

then

$Ag^+ + Br^- \rightarrow AgBr\downarrow$,

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

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

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 $c(Ca^{2+}) = 1{,}0 \cdot 10^{-3}\, mol/l$ to precipitate $CaHPO_4$?With respect to the concentration of hydrophosphate ions, it is in the blood plasma $c(HPO_4^{2-}) = 2{,}9 \cdot 10^{-4}\, mol/l.$

Given:	**Find:**
$c(Ca^{2+}) = 1{,}0 \cdot 10^{-3}\, mol/l$ $c(HPO_4^{2-}) = 2{,}9 \cdot 10^{-4}\, mol/l$	*Q-?*

Solution:

Record the reaction equation:

$$Ca^{2+} + HPO_4^{2-} \leftrightarrows CaHPO_4\,;$$

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

$$SP(CaHPO_4) = \ 2{,}7 \cdot 10^{-7} \frac{mol^2}{l^2}$$

Calculate the product of concentrations

$$ДК = \mathrm{c(Ca^{2+}) \cdot c(HPO_4^{-})} = 1{,}0 \cdot 10^{-3}\, {}^{mol}/_{l} \cdot 2{,}9 \cdot 10^{-4}\, {}^{mol}/_{l}$$
$$= 2{,}9 \cdot 10^{-7}\, {}^{mol^2}/_{l^2}\,;$$

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

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

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:	**Find:**
$c_0(AgNO_3) = 0{,}02\, mol/l$	$Q-?$

$c_0(H_2SO_4) = 0{,}02\ mol/l$
$V(AgNO_3) = V(H_2SO_4)$

Solution:

1.Record the reaction equation:

$2AgNO_3 + H_2SO_4 \rightarrow Ag_2SO_4 \downarrow + 2HNO_3;$

$2Ag^+ + SO_4^{2-} \leftrightarrows Ag_2SO_4 \downarrow$ *(heterogeneous equilibrium).*

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):

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

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

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

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

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:

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

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

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

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

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

.

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

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

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 $5.35 \cdot 10^{-13}$ mol²/l². M (AgBr) = 188g/mol.

Given:	**Find:**
$SP(AgBr) = 5{,}35 \cdot 10^{-13}\, mol^2/l^2$ $M(AgBr) = 188 g/mol$	$\rho(AgBr) - ?$

Solution:

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

$$AgBr_{(pres)} \leftrightarrows Ag^+_{(sol-n)} + Br^-_{(sol-n)};$$

$$SP(AgBr) = [Ag^+][Br^-].$$

2. Calculate the molar concentration of AgBr in saturated solution:

$$[Ag^+] = [Br^-] = c(AgBr)$$

$$SP(AgBr) = [Ag^+][Br^-] = c^2(AgBr)$$

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

2. Calculate mass concentration $AgBr$:

$$\rho(AgBr) = M(AgBr) \cdot c(AgBr)$$

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

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

Example 12

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

Given:	**Find:**
$\rho(Ag_2SO_4) = 3{,}12\, {g}/{l}$	$Q(Ag_2SO_4) - ?$

Solution:

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

$$Ag_2SO_{4(pres)} \leftrightarrows 2Ag^+_{(sol-n)} + SO^{2-}_{4(sol-n)};$$

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

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 :

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

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

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

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

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

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

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.

1) $CO_{(g)} + 2H_{2(g)} \leftrightarrows CH_3OH_{(g)}$, Δ H < 0;

2) $N_{2(g)} + O_{2(g)} \leftrightarrows 2NO_{(g)}$, Δ H > 0;

3) $2SO_{2(g)} + O_{2(g)} \leftrightarrows 2SO_{3(\text{g})}$, Δ H < 0;

4) $3Fe_{(s)} + 4H_2O_{(g)} \leftrightarrows Fe_3O_{4(s)} + 4H_{2(\text{г})}$, Δ H > 0;

5) $CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}, \quad \Delta \mathrm{H} > 0;$

6) $CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}, \quad \Delta H < 0;$

7) $H_{2(g)} + I_{2(g)} \leftrightarrows 2HI_{(g)}, \quad \Delta H < 0;$

8) $2NaHCO_{3(s)} \leftrightarrows Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}, \quad \Delta \mathrm{H} > 0;$

9) $MnO_{2(s)} + 2H_{2(g)} \leftrightarrows MnO_{(s)} + 2H_2O_{(g)}, \quad \Delta \mathrm{H} > 0;$

10) $NH_{3(g)} + CO_{2(g)} + H_2O_{(g)} \leftrightarrows NH_4HCO_{3(s)}, \quad \Delta H < 0.$

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: $Q = 2 \cdot 10^{-7}\, mol^2/l^2$
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 ρ($CaCO_3$)= 2,0·10^{-3} g/l lead to the formation of $CaCO_3$ precipitate? M ($CaCO_3$) = 100 g / mol.

Answer: $Q = 4 \cdot 10^{-10}\, mol^2/l^2$
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 (CdC_2O_4) = 200 g / mol.

Answer: $Q = 9 \cdot 10^{-8}\, mol^2/l^2$
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 (BaF_2) = 175 g / mol.

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

3.12 Will precipitate $Ag_2C_2O_4$ with increasing mass concentration of $Ag_2C_2O_4$ in solution to 0.06 g /l. M ($Ag_2C_2O_4$) = 304g / mol.

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

3.13 Will a precipitate be formed when mixing equal volumes of $Pb(NO_3)_2$ and $CaCl_2$ solutions with a molar concentration of 0.03 mol / l?

Answer: $Q = 3{,}375 \cdot 10^{-6}\, mol^3/l^3$
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: $Q = 2{,}5 \cdot 10^{-5}\, mol^2/l^2$
precipitate is formed

3.15 Will a precipitate of equal volumes of $Ca(NO_3)_2$and Na_2SO_4 solutions with a molar concentration of 0.01 mol / l be precipitated?

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

3.16 Calculate the mass concentration of Nickel sulfide ρ (NiS) in saturated solution. M (NiS) = 91 g / mol.

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

3.17 Calculate the mass concentration of PbI_2 in saturated solution.
M (PbI_2) = 461g / mol.

Answer: $\rho(PbI_2) = 0{,}986\, g/l$

3.18 Calculate the mass concentration of $SrSO_4$ in saturated solution.
M ($SrSO_4$) = 184g / mol.

Answer: $\rho(SrSO_4) = 0{,}108\, g/l$

3.19 Calculate the mass concentration of Ag_2CO_3 in saturated solution. M (Ag_2CO_3) = 276 g / mol.

Answer: $\rho(Ag_2CO_3) = 0{,}056\ g/l$

Addition.

1. Thermodynamic properties of some substances

ΔH^0_{298} - standard enthalpy of substance formation, кJ/mol;

S^0_{298}- standard entropy of matter, J/(mol·К);

ΔG^0_{298} - standard change of Gibbs energy in the formation of a complex substance from simple substances, кJ/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^0_{298}, $\text{к}J/mol$	S^0_{298}, $J\text{Дж}/(mol \cdot \text{К})$	ΔG^0_{298}, $\text{к}J\text{Дж}/mol$
Br_2	l	0	152,2	0
CO_2	g	-383,5	213,8	-394,4
CO	g	-110,5	197,7	-137,2
Cl_2	g	0	223,1	0
H_2	g	0	130,7	0
HBr	g	-36,3	198,7	-53,4
HCl	g	-92,3	186,9	-95,3
H_2O	g	-241,8	188,8	-228,6
H_2O	l	-285,8	70,0	-237,1
H_2O_2	g	-187,8	109,6	-120,4
N_2	g	0	191,6	0
NH_3	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	s	-2222	360	-1545
H_2O_2	g	-187,8	109,6	-120,4
N_2	g	0	191,6	0
NH_3	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

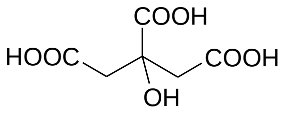
Substance	state	$\Delta H^0_{c.298}$, $кJ/mol$
H_2	g	-285,8
NH_3	g	-382,8
CH_4	g	-890,8
C_2H_4	g	-1411,2
C_2H_6	g	-1560,7
$C_2H_5OC_2H_5$	l	-2723,9
$C_6H_{12}O_6$ (glucose)	c	-2802,5
$C_{12}H_{22}O_{11}$ (saccharose)	c	-5639,7
CH_3COOH	l	-874,2
CH_3CONH_2	lp	-1184,6

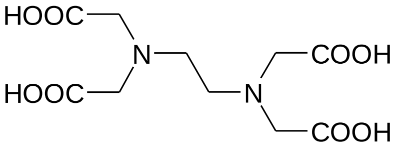
3.Instability constants of complex ions

$К_{inst}$ – the constant of complete dissociation of the complex ion in aqueous solution at 20-30ºC:

$$ML_n \leftrightarrows M + nL$$

$$К_{inst} = \frac{[M] \cdot [L]^n}{[ML_n]}$$





H_3Cit – citric acid; H_4Edta – ethylenediaminetetraacetic acid;
Cit^{3-} – citrate anion. $Edta^{4-}$ – ethylenediaminetetraacetate.

Complex	$\mathbf{K_{inst}}$	**Complex**	$\mathbf{K_{inst}}$
$[Ag(SCN)_2]^-$	$3,89 \cdot 10^{-9}$	$[Fe(C_2O_4)_3]^{3-}$	$6,31 \cdot 10^{-21}$
$[Ag(CN)_2]^-$	$1 \cdot 10^{-21}$	$[FeF_6]^{3-}$	$7,94 \cdot 10^{-17}$
$[Ag(S_2O_3)_2]^{3-}$	$3,47 \cdot 10^{-14}$	$[Fe(SCN)_6]^{3-}$	$5,89 \cdot 10^{-4}$
$[Ag(NH_3)_2]^+$	$1,0 \cdot 10^{-7}$	$[Fe(CN)_6]^{3-}$	$1,0 \cdot 10^{-42}$
$[CaCit]^-$	$6,75 \cdot 10^{-4}$	$[HgEdta]^{2-}$	$1,6 \cdot 10^{-22}$
$[CaEdta]^{2-}$	$2,58 \cdot 10^{-11}$	$[PbEdta]^{2-}$	$5,0 \cdot 10^{-14}$
$[Ca(P_2O_7)]^{2-}$	$2,5 \cdot 10^{-6}$	$[CdEdta]^{2-}$	$3,47 \cdot 10^{-17}$
$[Ca(P_3O_9)]^-$	$3,55 \cdot 10^{-4}$		
$[Ca(P_4O_{12})]^{2-}$	$3,8 \cdot 10^{-6}$		

4. The solubility products of some sparingly soluble electrolytes at 25ºC

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. 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≤a≤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:

$$0{,}01 = 10^{-2}$$
$$0{,}0001 = 10^{-4}$$
$$100000 = 10^5$$
$$0{,}000054 = 5{,}4 \cdot 10^{-5}$$
$$12000000 = 1{,}2 \cdot 10^7$$

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..., 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: $log_b b = 1$ $(lg10 = 1)$
4) The logarithm of the product is equal to the sum of the logarithms: $\mathrm{log_b}(a \cdot c) = log_b a + log_b c$ $(\mathrm{lg}(a \cdot c) = lga + lgc)$
5) The logarithm of the fraction is equal to the difference of the logarithms: $log_b \frac{a}{c} = log_b a - log_b c$ $(lg \frac{a}{c} = lga - lgc)$
6) The logarithm of the number a to the power of n is equal to the logarithm of the number a multiplied by n: $log_b a^n = n \cdot log_b a$ $(lga^n = n \cdot lga\ ;\ \ lg10^n = n)$

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:

$$lg283500 = \mathrm{lg}(2{,}835 \cdot 10^5) \approx \mathrm{lg}(2{,}8 \cdot 10^5) = lg2{,}8 + lg10^5 = 0{,}447 + 5 = 5{,}447$$

Examples:

$$lg0{,}00283 = lg(2{,}83 \cdot 10^{-3}) \approx lg(2{,}8 \cdot 10^{-3}) = lg2{,}8 + lg10^{-3} = 0{,}447 + (-3) = -2{,}553$$

$$lg0{,}000006 = lg(6 \cdot 10^{-6}) = lg6 + lg10^{-6} = 0{,}778 + (-6) = -5{,}222$$

$$lg0{,}000368 = lg(3{,}68 \cdot 10^{-4}) \approx lg(3{,}7 \cdot 10^{-4}) = lg3{,}7 + lg10^{-4} = 0{,}568 + (-4) = = -3{,}432$$

$$lg0{,}0561 = lg(5{,}61 \cdot 10^{-2}) \approx \mathrm{lg}(5{,}6 \cdot 10^{-2}) = lg5{,}6 + lg10^{-2} = 0{,}748 + (-2) = -1{,}252$$

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*

$$\boldsymbol{lg(n,m) = 0,xyz} \qquad \boldsymbol{10^{0,xyz} = n,m}$$