Ministry of Health of the Republic of Belarus
Educational institution
"Gomel State Medical University"

Department of General and Bioorganic Chemistry

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METHODOLOGICAL MANUAL
for conducting the laboratory class
in the academic discipline "Medical chemistry"
for students
the first-year of the Faculty of International Students (FIS),
studying in the specialty 7-07-0911-01 "Medical business"

Topic 4: Theory of redox reactions

Time: 2 hours

Approved at the meeting of the Department
of General and Bioorganic Chemistry
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THE TRAINING AND EDUCATIONAL GOAL, TASKS, MOTIVATION TO STUDY THE TOPIC

Training purpose:

– formation of students' basic professional competence for solving diagnostic, research and other tasks of professional activity based on knowledge about the general concept of redox reaction;

– formation of skills and abilities to make up the equations of the redox reactions, as well as to balance these equations by the ion-electron (half reaction) method;

– familiarization with the influence of the pH of the medium on the oxidizing ability of substances.

Educational goal:

– to develop your personal, spiritual potential;

– to form the qualities of a patriot and a citizen who is ready to actively participate in the economic, industrial, socio-cultural and social life of the country;

– learn to observe academic and labor discipline, the norms of medical ethics and deontology;

– to realize the social significance of their future professional activities.

Tasks:

As a result of the training session, the student should

know:

– fundamentals of redox reactions;
– the most important oxidizing and reducing agents used in laboratory practice;
– types of redox reactions;
– methods that are used to balance redox reactions;
– oxidizing properties of $KMnO_4$ in different media;

be able to:

– find the oxidation numbers of elements in molecules and ions;
– make up equations of redox reactions;
– specify the oxidizer and the reducer;
– determine the type of redox reaction;
– balance redox reactions by the ion-electron (half reaction) method;

possess:

– skills in finding the oxidation numbers of atoms of elements in molecules and ions;
– skills in balancing equations of redox reactions.

Motivation to study the topic:

Redox processes play an important role in the metabolism and energy exchange occurring in humans and animals.

Redox reactions are necessary links in a complex chain of both anabolic (formation of structural elements of a living organism) and catabolic processes (reactions of decomposition of substances-substrates: proteins, fats and carbohydrates), but their role as the main sources of energy for a living organism is especially great. With the help of redox reactions in the body, some toxic substances formed during metabolism are destroyed.

Pharmaceutical properties of some medical products are directly related to their redox properties.

NECESSARY EQUIPMENT

1. Methodological manual for students on the topic "Theory of redox reactions".
2. Training tables:
a) Periodic Table of chemical elements by D.I. Mendeleev;
b) table of solubility of acids, bases and salts.
3. Reference materials of basic physico-chemical constants.
4. Chemical reagents and equipment necessary for laboratory work.

CONTROL QUESTIONS ON THE TOPIC OF THE CLASS

1. Fundamentals of redox reactions. The most important oxidizing and reducing agents. Types of redox reactions.

2. Balancing of redox reactions using the half-reaction method.

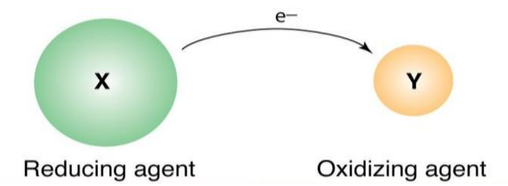
3. Influence of the pH of medium on the oxidizing ability of substances (oxidizing properties of $KMnO_4$ in various media).

COURSE OF THE CLASS

The theoretical part

1. FUNDAMENTALS OF REDOX REACTIONS. THE MOST IMPORTANT OXIDIZING AND REDUCING AGENTS. TYPES OF REDOX REACTIONS

Oxidation-reduction reactions (redox reactions) are reactions in which electrons are transferred from one species (reducing agent or reductant) to another (oxidizing agent or oxidant):



Reducing agents are electrons donors while **oxidizing agents** are electrons acceptors.

The most important reducing agents are:
▪ metals and some nonmetals (H_2, C);
▪ some oxides (CO, NO, N_2O, SO_2);
▪ some acids (H_2S, H_2SO_3, HCl, HBr, HI);
▪ salts of these acids;
▪ most organic compounds.

The most important oxidizing agents are:
▪ some nonmetals: O_2, O_3, F_2, Cl_2, Br_2, I_2;
▪ H_2SO_4 (concentrated), HNO_3;
▪ some salts ($KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, $FeCl_3$, $CuCl_2$).

Oxidation is the loss of electrons; **reduction** is the gain of electrons. Oxidation and reduction always run together in a joint process. In any redox reaction, the number of electrons lost by the reductant is equal the number of electrons gained by the oxidant.

Redox reactions are processes in which the oxidation numbers of the atoms change. The change in oxidation number is associated with a gain or loss of electrons.

Oxidation number (oxidation state) is the charge that an atom would have if the compound in which it was found was ionic.

Compounds with the lowest oxidation number of the element can only be reducing agents (Me^{0}, $N^{-3}H_3$, H_2S^{-2}, HCl^{-1}, HBr^{-1}, HI^{-1}). Compounds with the highest oxidation number of the element can only be oxidizing agents ($KMn^{+7}O_4$, $K_2Cr^{+6}{}_2O_7$, $KCl^{+7}O_4$, $HN^{+5}O_3$, $H_2S^{+6}O_{4(conc.)}$). If an element is in an intermediate oxidation state, then, depending on the conditions, it can act as both an oxidizer and a reducing agent [1].

For example:

$H_2S^{+6}O_4$ is only an oxidizer, $H_2S^{+4}O_3$ is either an oxidizer or a reducing agent, depending on the conditions, H_2S^{-2} is only a reducing agent.

The types of redox reactions are:

▪ *Intermolecular reactions* – oxidizing and reducing agents are different substances:

$$K_2Cr^{+6}{}_2O_{7(oxidant)} + 6KI^{-2}{}_{(reductant)} + 7H_2SO_4 \rightarrow Cr^{+3}{}_2(SO_4)_3 + 3I_2^{0} + 4K_2SO_4 + 7H_2O$$

▪ *Intramolecular reactions* – oxidizing and reducing agents are atoms in a molecule of one substance:

$$2Cu(NO_3)_2 \xrightarrow{t} 2CuO + 4NO_2 + O_2 \quad N^{+5} \text{ – oxidant, } O^{-2} \text{ – reductant.}$$

▪ *Disproportionation reactions* – the same element in the molecule is both oxidized and reduced in a process:

$$3Cl_2^{0} + 6KOH \xrightarrow{t} 5KCl^{-1} + KCl^{+5}O_3 + 3H_2O$$

2. BALANCING OF REDOX REACTIONS USING THE HALF-REACTION METHOD

Two types of methods are applied to balance redox reactions:

1) electron balance method (oxidation number change method) is based on determining the number of lost and gained electrons, taking in account the comparison of atoms' oxidation numbers in reactants' and products' molecules; it may be used for balancing of any chemical reaction;

2) ion-electron (half reaction) method may be applied to balance redox reactions, which run in aqueous solutions.

Balancing of redox reactions using the half-reaction method

Since reduction is impossible without oxidation and vice versa, the redox reaction can be described as two half-reactions, one of which represents the oxidation process and the other the reduction process. Each half-reaction is balanced separately (in terms of masses and charges), and then both half-reactions are summed to get a general balanced equation.

In half-reactions:

▪ only particles that have changed their charge or composition are taken into account;

▪ formulas of strong electrolytes, readily soluble in water, are written in the form of ions;

▪ formulas of weak electrolytes, nonelectrolytes and hard soluble electrolytes are written in the form of molecules;

▪ for reactions in an *acidic medium:*

water molecules (H_2O) are used to balance the O atoms;
protons (H^+) are used to balance the H atoms;

▪ for reactions in a *basic medium*:

hydroxide ions are used to balance the O atoms (*as a rule, two OH^- are added to balance one O atom);*

H_2O molecules are used to balance hydrogen atoms [1-3].

In redox reactions, H_2O_2 can be both an oxidizer and a reducing agent. Depending on the nature of the medium, the following transformations of hydrogen peroxide are possible:

▪ *H_2O_2 is an oxidizer:*

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (in an acidic medium);

$H_2O_2 + 2e^- \rightarrow 2OH^-$ (in a basic medium).

▪ *H_2O_2 is a reducing agent:*

$H_2O_2 - 2e^- \rightarrow 2H^+ + O_2$ (in an acidic medium);

$H_2O_2 + 2OH^- - 2e^- \rightarrow 2H_2O + O_2$ (in a basic medium).

The equivalence factor for oxidizing and reducing agents (f_e) is calculated as:

$$f_e(X) = \frac{1}{Z} \leq 1$$

Z is the number of electrons gained or lost by one molecule or one ion.

Example 1. Write the equation of the interaction between potassium dichromate and hydrogen sulfide in an acidic medium. Balance the redox reaction using the half-reaction method.

1.1 We write a molecular scheme of the reaction in an acidic medium:

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

1.2 We write this equation in ion-molecular form. To do this, it is necessary to represent all strong electrolytes in the form of ions, and leave weak electrolytes, gases and hardly soluble substances in the form of molecules. Strong electrolytes include all good soluble salts, some acids (HCl, HNO_3, H_2SO_4, etc.), alkalis ($LiOH$, $NaOH$, KOH, etc.). The oxidation numbers of atoms are not used, but take into account the charges of real ions and the nature of the medium in which the redox process occurs:

$2K^+ + Cr_2O_7^{2-} + H_2S + 2H^+ + SO_4^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + S^0 + 2K^+ + SO_4^{2-} + H_2O$

1.3 We determine the particles that have changed their charge or composition:

Reduction process: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Oxidation process: $H_2S \rightarrow S^0$

1.4 As the reaction occurs in acidic medium, to balance oxygen we use H_2O; to balance hydrogen we use H^+:

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$H_2S \rightarrow S^0 + 2H^+$

1.5 To balance the charges in the half-reactions we have to use electrons:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$$H_2S - 2e^- \rightarrow S^0 + 2H^+$$

1.6 To have the same number of electrons in both half-reactions, the second equation must be multiplied by 3, and then sum up the equations:

$$\begin{array}{l|cl} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O & 1 & f_e = 1/6 \\ H_2S - 2e^- \rightarrow S^0 + 2H^+ & 3 & f_e = 1/2 \\ \hline \end{array}$$

$$Cr_2O_7^{2-} + 14H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S^0 + 6H^+$$

After the canceling out of the same particles in the left and right sides of the equation, we obtain a total ion-molecular equation that reflects the meaning of the chemical reaction:

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S^0$$

1.7 We transfer the obtained coefficients to the molecular equation of the reaction:

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

Example 2. Write the equation of reaction of the interaction of potassium dichromate with sodium sulfide in a basic medium. Balance the redox reaction using the half-reaction method.

2.1 Molecular scheme of the reaction in a basic medium:

$$K_2Cr_2O_7 + Na_2S + KOH \rightarrow K_3[Cr(OH)_6] + Na_2SO_3$$

2.2 We make up half-reactions of oxidation and reduction processes and write down the complete ion equation:

$$\begin{array}{l|cl} Cr_2O_7^{2-} + 7H_2O + 6e^- \rightarrow 2[Cr(OH)_6]^{3-} + 2OH^- & 1 & f_e = 1/6 \\ S^{2-} + 6OH^- - 6e^- \rightarrow SO_3^{2-} + 3H_2O & 1 & f_e = 1/6 \\ \hline \end{array}$$

$$Cr_2O_7^{2-} + \cancelto{4}{7H_2O} + S^{2-} + \cancelto{4}{6OH^-} \rightarrow 2[Cr(OH)_6]^{3-} + \cancel{2OH^-} + SO_3^{2-} + \cancel{3H_2O}$$

2.3 We write down the molecular equation of the reaction:

$$K_2Cr_2O_7 + 4H_2O + Na_2S + 4KOH \rightarrow 2K_3[Cr(OH)_6] + Na_2SO_3$$

Example 3. Write the equation of reaction of the interaction of potassium dichromate with sodium sulfide in a neutral medium. Balance the redox reaction using the half-reaction method.

2.1 Molecular scheme of the reaction in a neutral medium:

$$K_2Cr_2O_7 + Na_2S + H_2O \rightarrow Na_2SO_4 + KOH + Cr(OH)_3\downarrow$$

2.2 We make up half-reactions of oxidation and reduction processes and write down the complete ion equation:

$$\begin{array}{l|cl} Cr_2O_7^{2-} + 7H_2O + 6e^- \rightarrow 2Cr(OH)_3 + 8OH^- & 4 & f_e = 1/6 \\ S^{2-} + 8OH^- - 8e^- \rightarrow SO_4^{2-} + 4H_2O & 3 & f_e = 1/8 \\ \hline \end{array}$$

$$4Cr_2O_7^{2-} + 28H_2O + 3S^{2-} + 24OH^- \rightarrow 8Cr(OH)_3 + 32OH^- + 3SO_4^{2-} + 12H_2O$$

2.3 We write down the molecular equation of the reaction:

$$4K_2Cr_2O_7 + 3Na_2S + 16H_2O \rightarrow 3Na_2SO_4 + 8KOH + 8Cr(OH)_3\downarrow$$

3. INFLUENCE OF THE pH OF MEDIUM ON THE OXIDIZING ABILITY OF SUBSTANCES (OXIDIZING PROPERTIES OF $KMnO_4$ IN VARIOUS MEDIA)

Oxidation-reduction reactions can occur in various media: acidic (excess of H^+ ions), neutral (H_2O) and alkaline (excess of OH^- ions). Depending on the character of the medium, the character of the reaction between the same substances may change. The medium affects the change of the oxidation numbers of atoms.

A classic example illustrating the influence of the medium on the nature of the redox reactions is the reduction of $KMnO_4$. Potassium permanganate is a strong oxidizer, and its oxidizing ability depends on the character of the medium.

Mn^{7+} ions exhibit the greatest oxidizing ability in an acidic medium, reducing to Mn^{2+} ions, somewhat less – in a neutral medium, in which they are reduced to MnO_2, and minimal – in a basic one, reducing to the MnO_4^{2-} manganate ion [1-3].

Let's consider ion-electron schemes on the example of oxidation of sodium sulfite with potassium permanganate in various media.

Acidic medium:

$$2KMnO_4 + 5Na_2SO_3 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 3H_2O$$

$$\begin{array}{l|l l}
MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O & 2 & f_e = 1/5 \\
SO_3^{2-} + H_2O - 2e^- \rightarrow SO_4^{2-} + 2H^+ & 5 & f_e = 1/2 \\
\hline
\end{array}$$

$$2MnO_4^- + \overset{6}{\cancel{16H^+}} + 5SO_3^{2-} + \cancel{5H_2O} \rightarrow 2Mn^{2+} + \overset{3}{\cancel{8H_2O}} + 5SO_4^{2-} + \cancel{10H^+}$$

Basic medium:

$$2KMnO_4 + Na_2SO_3 + 2KOH \rightarrow 2K_2MnO_4 + Na_2SO_4 + H_2O$$

$$\begin{array}{l|l l}
MnO_4^- + e^- \rightarrow MnO_4^{2-} & 2 & f_e = 1 \\
SO_3^{2-} + 2OH^- - 2e^- \rightarrow SO_4^{2-} + H_2O & 1 & f_e = 1/2 \\
\hline
\end{array}$$

$$2MnO_4^- + SO_3^{2-} + 2OH^- \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O$$

Neutral medium:

$$2KMnO_4 + 3Na_2SO_3 + H_2O \rightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH$$

$$\begin{array}{l|l l}
MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- & 2 & f_e = 1/3 \\
SO_3^{2-} + 2OH^- - 2e^- \rightarrow SO_4^{2-} + H_2O & 3 & f_e = 1/2 \\
\hline
\end{array}$$

$$2MnO_4^- + \overset{1}{\cancel{4H_2O}} + 3SO_3^{2-} + \cancel{6OH^-} \rightarrow 2MnO_2 + \overset{2}{\cancel{8OH^-}} + 3SO_4^{2-} + \cancel{3H_2O}$$

The practical part

Safety instructions before laboratory work.

LABORATORY WORK

The influence of the pH of the medium on the course of redox reactions

In three test tubes, add 3-4 drops of $KMnO_4$ solution. In the first test tube, add 2-3 drops of H_2SO_4 solution ($pH < 7$), in the second – 2-3 drops of H_2O ($pH \approx 7$), and in the third – 2-3 drops of NaOH solution ($pH > 7$). Then add a few crystals of KNO_2 or Na_2SO_3 to each of the test tubes. Mix the contents of the test tubes thoroughly with a glass stick. Note the change in the color of the solutions in all test tubes.

Report form:

1. Write the equations of the corresponding reactions, taking into account that the reddish violet color is characteristic of the MnO_4^- ion, green – for the MnO_4^{2-} ion, colorless – for the Mn^{2+} ion, the brown precipitate is MnO_2.

2. Balance the redox reactions using ion-electron (half reaction) method.

Control over the assimilation of the topic

It is conducted in the form of written independent work of students.

METHODOLOGICAL RECOMMENDATIONS FOR THE ORGANIZATION AND PERFORMING OF INDEPENDENT WORK OF STUDENT (IWS)

The time allotted for independent work can be used by students for:

– preparation for laboratory classes;
– taking notes of educational literature;
– performing tasks for self-control of knowledge;
– preparation of thematic reports, abstracts, presentations.

The main methods of organizing independent work:

– studying topics and problems that are not covered in the classroom;
– writing an abstract and making a presentation;
– performing tasks for self-control of knowledge.

List of tasks of IWS:

1. Arrange the following species in order of increasing oxidation number of the sulfur atom: a) H_2S; b) S_8; c) H_2SO_4; d) SO_2.

2. Which of the following are redox reactions?

a) $NH_3 + HCl \rightarrow NH_4Cl$; b) $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$;
c) $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$; d) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$.

3. Balance the following redox reactions using the half-reaction method:

a) $KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$;
b) $KMnO_4 + KNO_2 + H_2SO_4 \rightarrow MnSO_4 + KNO_3 + K_2SO_4 + H_2O$;
c) $KMnO_4 + KNO_2 + H_2O \rightarrow MnO_2 + KNO_3 + KOH$;
d) $KMnO_4 + KNO_2 + KOH \rightarrow K_2MnO_4 + KNO_3 + H_2O$;
e) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + K_2SO_4 + H_2O$;
f) $KMnO_4 + H_2S + H_2SO_4 \rightarrow MnSO_4 + S + K_2SO_4 + H_2O$;
g) $KMnO_4 + HCl_{conc.} \rightarrow MnCl_2 + Cl_2 + KCl + H_2O$;
h) $K_2Cr_2O_7 + Na_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + K_2SO_4 + H_2O$;
i) $K_2Cr_2O_7 + NO + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + HNO_3 + K_2SO_4 + H_2O$;
j) $Cl_2 + KOH \xrightarrow{t} KCl + KClO_3 + H_2O$

2. Calculate the mass of $KMnO_4$ required to prepare 1 liter of potassium permanganate solution with normality equals 0.1 mol/l, for use in permanganometric titration as an oxidizer in accordance with the half-reaction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Answer: 3.16 g

The control of the IWS is carried out in the form of:

– evaluation of an oral answer to a question, message, report or presentation;

– individual conversation.

LIST OF SOURCES USED

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2. Основы химии для иностранных студентов = Essential chemistry for foreign students : учебно-методическое пособие / С. В. Ткачёв [и др.]. – 5-е изд. – Минск : БГМУ, 2018. – 168 с. – Режим доступа: http://rep.bsmu.by:8080/handle/BSMU/21054.

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