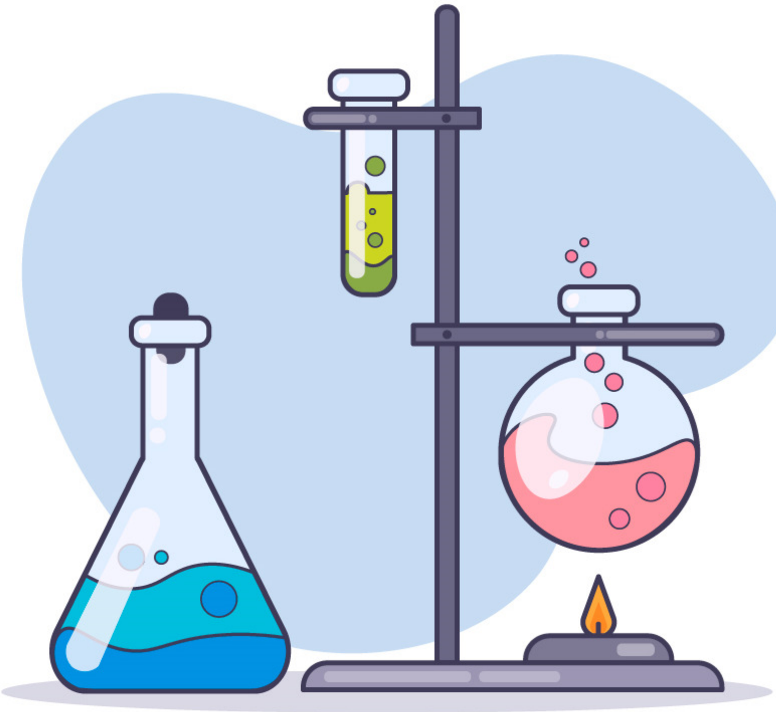
UNIVERSITATEA
DE MEDICINĂ ŞI FARMACIE
„VICTOR BABEŞ“ DIN TIMIŞOARA

RALUCA POP **MIHAIELA ANDONI**



PRACTICAL LABORATORY FOR GENERAL AND INORGANIC CHEMISTRY

GHIDURI ŞI ÎNDRUMĂTOARE
DE LABORATOR

Editura „Victor Babeş”
Timişoara, 2023

The book is addressed to first-year students at the Faculty of Pharmacy and aims to familiarize them with fundamental notions of chemistry: acid-base reactions, redox reactions, concentration of solutions. Both the theoretical notions and the experiments lead to the acquisition by students of the basic laboratory operations and techniques. Also, experiments that illustrate the chemical properties of some compounds with applications in the pharmaceutical industry are included.

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SUMMARY

CHAPTER 1. LABORATORY PROCEDURES

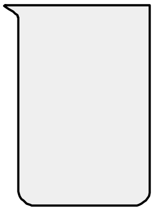
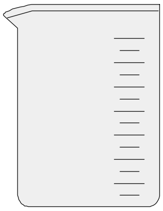
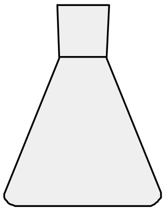
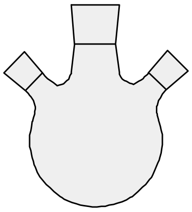
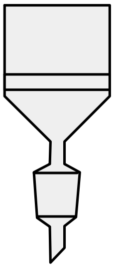
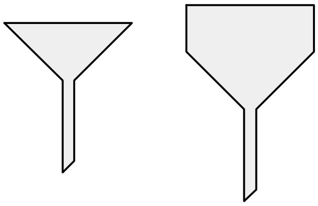
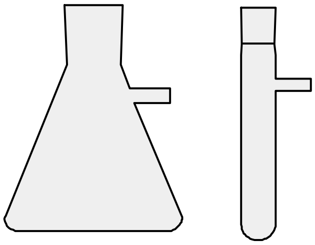
1.1. Laboratory safety instructions

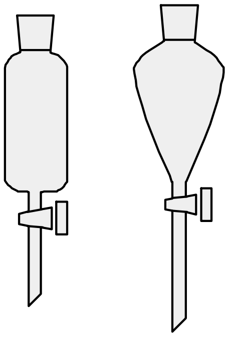
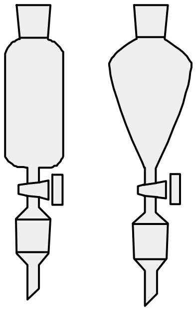
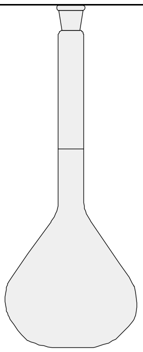
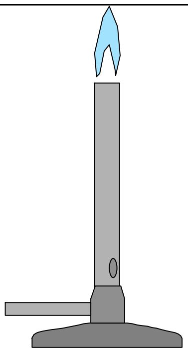
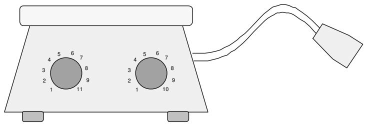
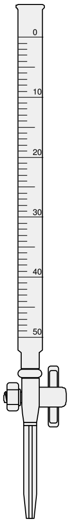
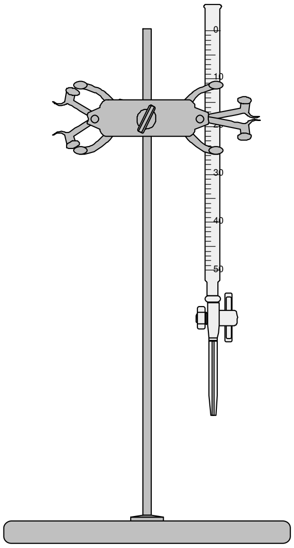
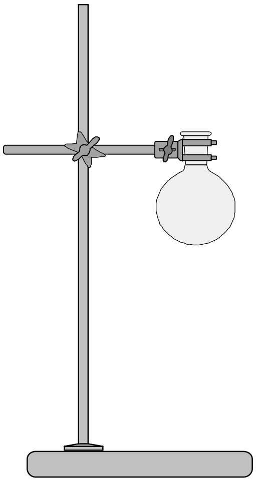
1. Preparation for an experiment is always done by reading the instructions in the manual before entering the laboratory. Do not modify an experience until you receive the teacher's approval.
2. Do only the experiments assigned or approved by the teacher. Unauthorized experimentation is prohibited.
3. Check the labels on any reagent bottle before using the content of the bottle.
4. Never use reagents from unlabeled containers.
5. All chemicals are toxic to some degree. Never taste a substance or solution.
6. Avoid inhaling toxic fumes.
7. When working with volatile substances or strong acids and bases, always work under the fume hood.
8. Keeping and eating food in the laboratory is prohibited.
9. During laboratory hours it is mandatory to wear the gown. When indicated, use the fume hood and safety glasses.
10. All the used reagents are recovered in a suitable vessel at the end of the session.
11. Report any accident, even a minor injury, to the teacher.
12. Experiments in progress are never left unattended.

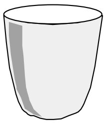
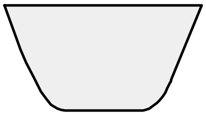
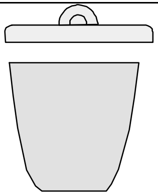
13. Always work with small amounts of reagents. Unused reagents are never put back into the container from which they were taken.

14. After completing the experiments, wash the used laboratory utensils and clean the work table.

CHAPTER 2. VESSELS AND UTENSILS USED IN THE CHEMISTRY LABORATORY

		
Berzelius beaker	Berzelius graduated beaker	Erlenmeyer flask
		
round bottom flask	round bottom flask	round bottom flask
		
Büchner funnel	funnels	vacuum flask

		
separatory funnel	drip funnels	volumetric flask
		
Bunsen burner	tripod stand	magnetic stirrer
		
burette	burette with stand	stand

		
crucible	mortar	crucible with lid

CHAPTER 3. BASIC OPERATIONS

3.1. Volume measurement [2]

➢ Using a pipette to measure volumes

Measure approximately 400 mL of distilled water into a clean Berzelius beaker and let it sit for 15 minutes at room temperature.

Check that the volumetric pipette is clean by filling it up to the mark with distilled water and then emptying it. If water drops remain on the walls of the pipette, it means that it has not been properly cleaned.

Measure and write down the mass of a clean Erlenmeyer flask (125 mL).

Measure 10 mL of water from the Berzelius beaker and insert it into the Erlenmeyer flask. Measure and record the mass of the Erlenmeyer flask in which the 10 mL of water was introduced.

The last two operations are repeated 3 times, without emptying the flask between determinations.

Calculate the mass of water for each of the 3 determinations and determine the density of water in each of the 3 cases.

➢ Using a flask for measuring volumes

Measure and record the mass of a clean 100 or 150 mL Berzelius beaker. It is necessary to use a graduated glass beaker.

Measure 50 ml of water at room temperature using the beaker.

Measure and record the mass of the glass of water.

Empty the beaker and measure again 50 mL of water at room temperature. Repeat the last two steps at least one more time.

Knowing the mass of water and the measured volume of water, calculate the density of water for each measurement.

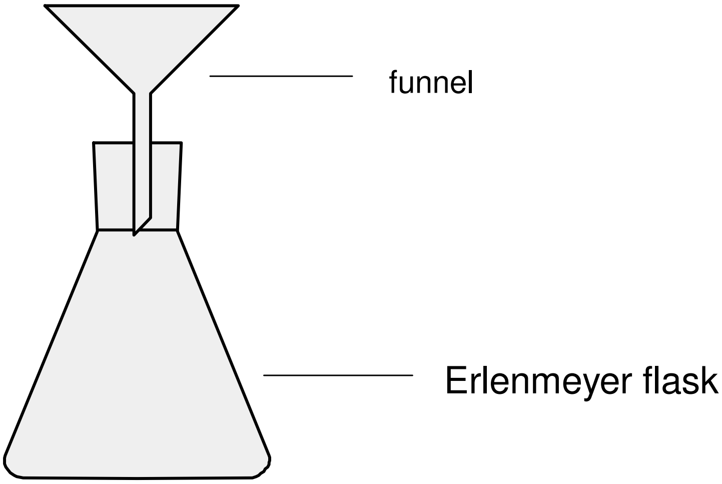
3.2. Filtration

It is a technique used to remove solid impurities from a solution or to separate a solid compound from a solution. The two types of filtration widely used in chemistry laboratories are gravity filtration and vacuum filtration.

➢ Gravity filtration

This type of filtration is used to remove solid impurities from a solution; impurities can be, for example, a drying agent or a by-product.
To perform this type of filtration, the following laboratory utensils are required:

- Glass funnel
- Erlenmeyer flask
- Filter paper
- stand
- clamps and holders

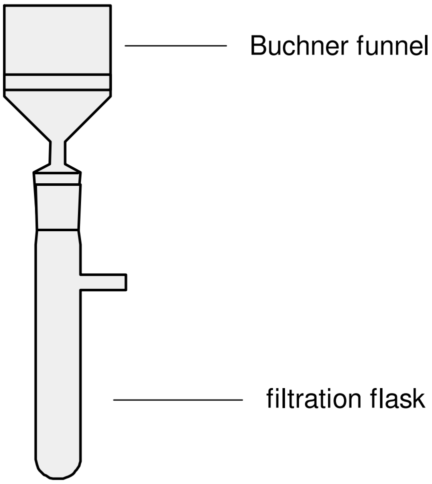


➢ Vaccum filtration

This type of filtration is used when it is desired to collect the solid compound (for example, the separation of crystals obtained after recrystallization). Vacuum filtration is faster than gravity filtration due to the low pressure applied to the solution being filtered.

The laboratory utensils required for vacuum filtration are:

- Buchner funnel
- Filtration flask
- Filter paper
- Vacuum tube



Stages of vacuum filtration

1. Fixing the filter flask;
2. Fixing the Buchner funnel;
3. Choosing a filter paper of the right size, which does not exceed the edges of the Buchner funnel;
4. Connect the filter bowl to the vacuum tube.

5. The filter paper is moistened with a small amount of solvent (the same solvent used in the solution to be filtered). The vacuum source is turned on and the adhesion of the filter paper to the Buchner funnel is checked.

6. The mixture to be filtered is poured into the center of the Buchner funnel.

7. The precipitate collected on the filter paper is washed with a small amount of solvent to remove impurities dissolved in the filtrate.

8. Disconnect the filter bowl from the vacuum flask.

9. The obtained precipitate is dried at room temperature, on a watch glass.

CHAPTER 4. PURIFICATION METHODS OF CHEMICAL COMPOUNDS

4.1. Distillation

Distillation is a common method of purifying liquids and separating mixtures of liquids into their individual components. It is applicable to liquid mixtures cahracterized by large differences between the boiling temperatures of the components (usually, mixtures in which one component is hardly volatile and the other slightly volatile).

The distillation process involves heating a liquid to the boiling point, followed by its condensation and collection.

Experiment 1. Water distillation [3]

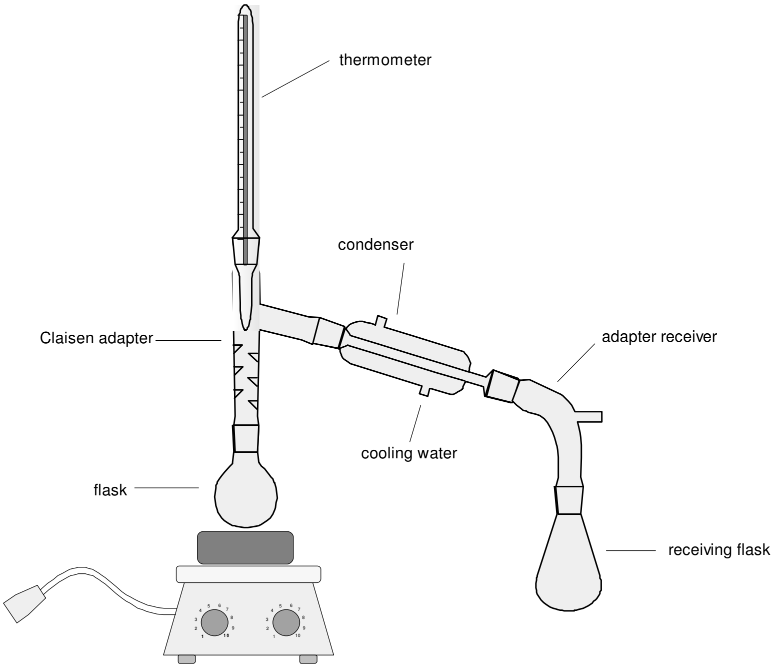


Figure 1. Distillation process in laboratory

Required equipment:
- round bottom flask
- condenser
- thermometer
- adapter for the receiving flask
- Erlenmeyer flask
- heat source

Work method: measure 100 mL of tap water and determine its pH with the help of indicator paper. The installation shown in the figure below is carried out and the evolution of the temperature is followed (distillation will start at ~100°C). The first collected fraction is discarded, and for the rest of the collected distilled water, the pH is determined again. The results obtained are compared and the differences between the two pH values are explained.

4.2. Extraction

Liquid-liquid extraction is a process of purification/separation of the components of a mixture based on their different solubilities in two immiscible solvents. Usually, one of the solvents is water, and the other is an organic solvent (methylene chloride, ethyl ether or ethyl acetate are frequently used).

Stages of liquid-liquid extraction

1. Fixing the separating funnel with a ring clamp to a stand. The separatory funnel valve must be closed.

2. The liquid to be extracted is introduced into the separatory funnel, followed by the extraction solvent.

3. Attach the stopper of the dropping funnel and shake for a few seconds.

4. Leave for a few minutes at room temperature to separate the two layers.

5. After the clear separation of the two layers, remove the plug and open the drain valve. Collect the first separated layer (the lower one) in a Berzelius beaker.

6. If necessary, collect the second layer (the upper one) remaining in the separation funnel.

Experiment 2. I_2 extraction from iodine tincture [3]

Work method: 30 mL of distilled water and 5 mL of iodine tincture are introduced into an Erlenmeyer flask. Stir gently and then add 20 mL of CCl_4. Fix the stopper of the separatory funnel and shake gently for a few seconds. Place the funnel back in the stand and leave it at room temperature for a few minutes, until the two layers are clearly separated. Remove the stopper of the separatory funnel and collect the lower layer (CCl_4, the one containing I_2) in a Berzelius beaker.

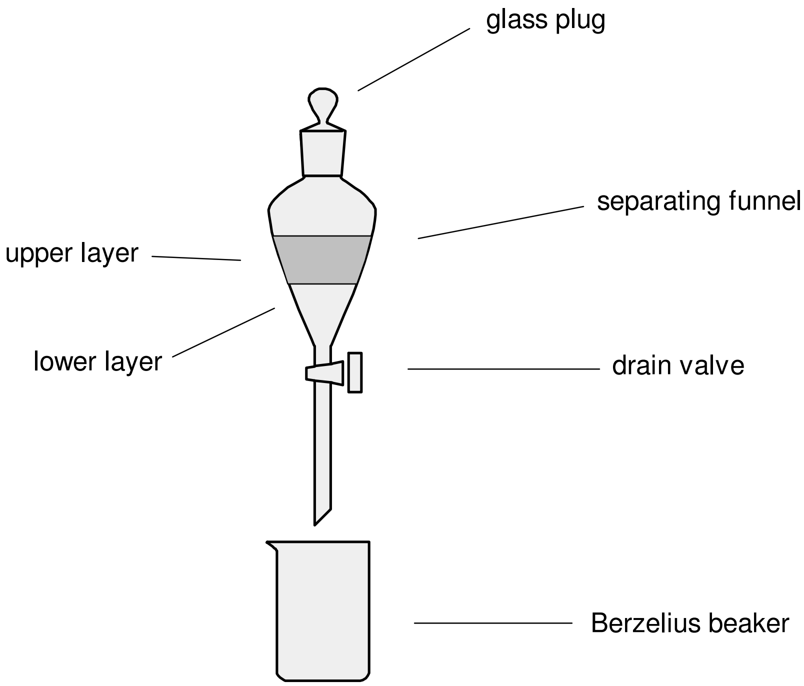


Figure 2. Liquid-liquid extraction process

4.3. Recrystallization

Recrystallization is a common method of purifying a compound, based on the fact that the solubility of a solid compound increases with increasing temperature.

Working method: the solid compound is dissolved in the minimum required amount of solvent (for this, the solvent is added in small portions) with heating, obtaining a saturated solution. The next operation is the hot filtration of the solution, in order to remove impurities, and the filtrate is allowed to cool at room temperature. Once the temperature of the filtrate decreases, crystals begin to appear, which will be filtered and left to dry at room temperature.

Experiment 3. $Na_2SO_4{\cdot}7H_2O$ recrystallization

Working method: Dissolve 25 g of $Na_2SO_4{\cdot}7H_2O$ in the minimum required amount of solvent (approximately 40 mL of water) and heat until the entire amount of salt has dissolved. Add activated carbon and filter the obtained solution while warm. The filtrate is allowed to cool at room temperature, then the filter vessel is placed in a water and ice bath. The formed sodium sulfate crystals will be separated by filtration on a Büchner funnel, washed 2-3 times with distilled water and dried in an oven.

CHAPTER 5. CLASSIFICATION AND NOMENCLATURE OF INORGANIC COMPOUNDS

Inorganic compounds can be divided into four categories: **acids, bases, oxides and salts**.

Since the rules for naming inorganic compounds take into account the oxidation state of the constituent atoms, we will first discuss the oxidation state and the rules for establishing it.

5.1. Oxidation state

Definition: The oxidation state (hereinafter denoted O.S.) represents a number assigned to an element in a chemical compound; indicates the number of electrons given/accepted by the respective atom.

Rules for establishing the oxidation state

1. Free atoms and atoms in molecules formed by identical elements have an oxidation state equal to zero.

Examples: $Ca^0 + S^0 \rightarrow CaS$

$H_2^0 + Cl_2^0 \rightarrow 2HCl$

2. **In compounds, the elements of groups I_A, II_A and III_A always have a positive oxidation state, equal to the number of the group they belong to.**

Examples: $Na^{+1}Cl$

$Ca^{+2}S$

$Al^{+3}Br_3$

3. In compounds, the fluorine atom always has a negative oxidation state, O.S. = -1 (it is the element with the highest electronegativity in the periodic table).

Examples: NaF^{-1}
HF^{-1}
$F_2^{-1}O$

4. In most compounds, the hydrogen atom has an oxidation state O.S. = +1.

Examples: $H^{+1}Cl$
$H^{+1}ClO_4$.

Exception: in metal hydrides, the H atom will have oxidation state O.S. = -1 (since metals always have a positive oxidation state).

Examples: $Na^{+1}H^{-1}$
$Al^{+3}H_3^{-1}$

5. In most compounds, the oxygen atom will have O.S. = -2.

Examples: CaO^{-2}
H_2O^{-2}

Exceptions:

a. in compounds of oxygen with fluorine, oxygen will have a positive oxidation state because it is less electronegative than fluorine.
Examples: $F_2^{-1}O^{+2}$

b. in peroxides, the oxygen atom has O.S. = -1
Examples: $H_2^{+1}O_2^{-1}$; $Ba^{+2}O_2^{-1}$.

6. In a neutral compound, the sum of the oxidation states of the constituent atoms must equal zero.

By applying this rule, the oxidation states corresponding to atoms that can have several oxidation numbers can also be determined.

Examples: $H^{+1}ClO_4^{-2}$ → O.S. (H) + O.S. (Cl) + 4 · O.S. (O) = 0

+1 + O.S. (Cl) + 4 · (-2) = 0

→ + O.S. (Cl) = +7

7. In an ionic compound, the sum of the oxidation states of the constituent atoms must equal the charge of the respective ion.

Examples:

1. CO_3^{2-}: O.S. (C) + 3 · O.S. (O) = -2

O.S. (C) + 3 · (-2) = -2

→ + OS.. (Cl) = +4

2. NH_4^+: O.S. (N) + 4 · O.S. (H) = +1

O.S. (N) + 4 · (+1) = +1

→ + O.S. (N) = -3

Elements from groups IV$_A$, V$_A$, VI$_A$ and VII$_A$, as well as elements from secondary groups, can have several oxidation states. We will present in the following table the possible oxidation states of the elements from the main groups IV$_A$, V$_A$, VI$_A$ and VII$_A$:

Table 1. Oxidation states of elements from groups IV$_A$, V$_A$, VI$_A$ and VII$_A$

Oxidation state	**Group IV$_A$**	**Group V$_A$**	**Group VI$_A$**	**Group VII$_A$**
maximum O.S.	+4	+5	+6	+7
intermediate O.S.	+2	+3	+4	+5
		+1	+2	+3
				+1
minimum O.S.	-4	-3	-2	-1

maximum O.S.= maximum oxidation state = number of the group
minimum O.S. = minimum oxidation state = number of the group - 8
intermediate O.S. = it is determined by subtracting 2 units from the value of the maximum oxidation state

5.2. Nomenclature of inorganic compounds

5.2.1. Acids

Definition: acids are substances that contain one or more hydrogen atoms, which dissociate in aqueous solution with the release of protons (H^+).

$$HX \rightleftarrows H^+ + X^- \text{ (1)}$$

In aqueous environment, protons and water form hydronium ions H_3O^+:

$$H^+ + H_2O \rightleftarrows H_3O^+ \text{ (2)}$$

Taking into account relations (1) and (2), it can be said that acids are substances that, in an aqueous environment, form hydronium ions.

$$HX + H_2O \rightleftarrows H_3\,O^+ + X^- \text{ (3)}$$

Classification of acids

1. Depending on their composition, acids can be classified into hydracids and oxoacids.

1.1. Hydracids (H_nX)

where**:** n = 8 – the number of the group to which element X belongs
X = non-metal with minimum oxidation state

Definition: Hydracides are compounds that contain one or more hydrogen atoms and a non-metal atom.

Examples: HCl, H_2S, H_2Se.

Naming: hydro X + ic acid

Examples:
HCl → hydrochloric acid
HBr → hydrobromic acid

1.2. Oxoacids (H_nXO_y)

where: X - non-metal at maximum or intermediate oxidation state

Oxoacids are compounds that, in addition to hydrogen and non-metal atoms, also contain one or more oxygen atoms.

Examples: HNO_3, H_2SO_4, $HClO_4$, H_3PO_4.

The oxoacids are named according to the oxidation state of the non-metal X. Thus, if in the respective oxoacid the oxidation state of non-metal X is themaximum oxidation state, its name will be:

Naming: X + ic acid

Examples:	H_2CO_3	carbonic acid
	HNO_3	nitric acid
	H_2SO_4	sulfuric acid
	H_3PO_4	phosphoric acid

If the oxidation state of the non-metal X is an intermediate oxidation state, its name will be:

Naming: X + ous acid

Examples:	HNO_2	nitrous acid
	H_2SO_3	sulfurous acid
	H_3PO_3	phosphorous acid

In the case of oxoacids where the non-metal is an element from group VIIA, the names are established as follows:

O.S. = +7	per +	X + ic acid	($HClO_4$ – acid perchloric)
O.S. = +5		X+ ic acid	($HClO_3$ – acid chloric)
O.S. = +3		X + ous acid	($HClO_2$ – acid chlorous)
O.S. = +1	hypo +	X + ous acid	($HClO$ – acid hypochlorous)

2. Depending on the number of hydrogen atoms in the molecule, acids are classified as monoprotic (one hydrogen atom), diprotic (two hydrogen atoms) or triprotic (three hydrogen atoms in the molecule).

Examples: HCl – monoprotic; H_2S – diprotic, H_3PO_4 – triprotic.

5.2.2. Bases

Definition: bases are substances that contain one or more hydroxyl groups (OH), which they set free in aqueous solutions in the form of hydroxide ions (HO^-).

$$MOH \rightleftarrows M^+ + HO^- \quad (4)$$

General formula: $M(OH)_n$, where: M – metal
n – valence of the metal

Naming: M hydroxide

Exemple: NaOH – sodium hydroxide
$Al(OH)_3$ – aluminum hydroxide

In the case of transition metal hydroxides, the valence of the metal in the respective compound is also indicated.

Examples:

$Fe(OH)_2$	– iron (II) hydroxide
$Fe(OH)_3$	– iron(III) hydroxide
CuOH	– copper (I) hydroxide
$Cu(OH)_2$	– copper (II) hydroxide

5.2.3. Oxides

Definition: Oxides are binary compounds of oxygen with various metals or non-metals.

Oxides classification

According to their behavior in the reaction with water, oxides are classified into acidic oxides, basic oxides and neutral oxides.

1. **Acidic oxides** are those that, through the reaction with water, form acids.

Examples: SO_2, CO_2, SO_3, P_2O_5 form the following acids: H_2SO_3, H_2CO_3, H_2SO_4 and H_3PO_4.

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

2. **Basic oxides are oxides that, by reacting with water, form hydroxides.**

Examples: Na_2O, CaO, MgO, BaO form NaOH, $Ca(OH)_2$, $Mg(OH)_2$ and $Ba(OH)_2$.

$$Na_2O + H_2O \rightarrow 2NaOH$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$MgO + H_2O \rightarrow Mg(OH)_2$$
$$BaO + H_2O \rightarrow Ba(OH)_2$$

3. **Neutral oxides are those that do not form either acids or bases by reacting with water.**

Examples: CO, N_2O.
General formula: E_2O, where E –monovalent element

Naming: E oxyde
Examples: Na_2O – sodium oxyde
Al_2O_3 – aluminum oxyde

In the case of transition metal oxides, the valence of the metal in the respective compound is also indicated.

Examples: FeO – iron(II) oxyde
Fe_2O_3 – iron(III) oxyde
CuO – copper(II) oxyde
Cu_2O – copper(I) oxyde

5.2.4. Salts

Definition: Salts are substances obtained by the reaction between an acid and a base.

General formula:

M_xE_y, for salts originating from hydracids (NaCl, Na_2S);
M_xEO_y, for salts originating from oxycids (Na_2SO_3, $Ca(NO_3)_2$).

The name of the salts is based on the name of the conjugate base of the acid (anion), respectively of the cation.

If the anion derives from a hydracide, the name of the salt will be:

Metal E + ide

Examples:

NaBr – sodium bromide
K_2S – potassium sulfide
$MnCl_2$ – manganese chloride

If the anion derives from an oxoacid in which the nonmetal has the maximum oxidation state, the name of the salt will be:

Metal E + ate

Examples:

Na_2SO_4 – sodium sulfate
$CaCO_3$ – calcium carbonate
$KClO_4$ – potassium perchlorate

If the anion derives from an oxyacid in which the nonmetal has intermediate oxidation state, the name of the salt will be:

Naming: metal E + ite

Examples: Na_2SO_3 – sodium sulfite
KNO_2 – sodium nitrite
NaClO – sodium hypochlorite

CHAPTER 6. SOLUTIONS. CONCENTRATION OF SOLUTIONS

A **solution** is a homogeneous mixture of two or more substances that are found in varying proportions. The component present in greater quantity is called the **solvent**, and the other component is called the **solute** (dissolved substance). Thus, in the case of an aqueous solution of potassium iodide, we will say that potassium iodide is the solute (the dissolved substance) and water is the solvent (the solvent). The most common solvent is water, so in the following we will discuss solutions in which the solvent is water.

The amount of substance dissolved in a certain amount of solvent represents the concentration of the respective solution.

The main ways of expressing the concentration of a solution are the following:

6.1. Percent concentration – c_p (%)

The percentage concentration shows how many parts of the solute are found dissolved in 100 g of solution.

$C_p = \frac{m_d}{m_s} \cdot 100$; where: m_d – mass of dissolved substance (solute) (g)

m_s – mass of the solution (g)

For example, a 25% KI solution means 25 g of KI dissolved in 100 g solution. Or, taking into account that the mass of the solution (m_s) is equal to the mass of the solute (m_d) and the mass of the solvent (m_{H2O}), a 25% KI solution means 25 g of KI dissolved in 75 g of H_2O.

$$m_s = m_d + m_{H2O}$$

6.2. Molar concentration – C_M (mol/L)

Molar concentration shows the number of moles of solute that are dissolved in one liter of solution.

$C_M = \frac{m_d}{M \cdot V_s}$; where: m_d – mass of dissolved substance (solute) (g)

M – molecular weight of the substance (g/mol)
V_s – volume of the solution (L)

Knowing that the number of moles is calculated as the ratio between the dissolved mass and the molecular weight of a substance (m_d/M), the molar concentration expression becomes:

$C_M = \frac{\nu}{V_s}$; where: υ – number of moles ($\nu = \frac{m_d}{M}$)

For example, a 2M KI solution means 2 moles of KI dissolved in one liter of solution.

6.3. Normal concentration – C_N (gram equivalent/L)

The normal concentration shows the number of gram-equivalents of solute that are dissolved in one liter of solution.

$C_N = \frac{m_d}{E_g \cdot V_s}$; where: m_d – mass of dissolved substance (solute) (g)

E_g – gram equivalent (g/mol)
V_s – volume of solution (L)

In order to calculate the normal concentration of a solution, the gram-equivalent of the dissolved substance must be determined.

The gram-equivalent is calculated using the following relationship:

$E_g = \frac{M}{x}$; where: M – molecular weight of the substance (g/mol)

x – depending on the nature of the dissolved substance

Table 2. Calculation of gram-equivalent for acids, bases, oxides, salts

Dissolved substance	x	Examples
Acid, H_nX	x = n, number of hydrogen atoms of the acid	$E_g(HCl) = \frac{M_{HCl}}{1}$; $E_g(H_2SO_4) = \frac{M_{H2SO4}}{2}$
Base, $M(OH)_m$	x = m, number of OH groups of the base	$E_g(Al(OH)_3) = \frac{M_{Al(OH)3}}{3}$; $E_g(Ca(OH)_2) = \frac{M_{Ca(OH)2}}{2}$
Salts, B_zA_y **Oxides, E_zO_y**	x = y·z	$E_g(CaCl_2) = \frac{M_{CaCl2}}{2 \cdot 1}$; $E_g(Al_2(SO_4)_3) = \frac{M_{Al2(SO4)3}}{3 \cdot 2}$

The relationship between Cp and C_M, respectively Cp and C_N

Knowing that the density of a solution is given by the relation: $\rho = \frac{m_s}{V_s}$; ρ – density (g/cm^3), it follows that:

$$C_M = \frac{C_p \cdot \rho \cdot 10}{M}; C_N = \frac{C_p \cdot \rho \cdot 10}{E_g} \quad (5)$$

6.4. Exercises and problems

1. Calculate the mass of KOH and the volume of distilled water required to prepare 500 g of KOH solution 8%.

$\mu_{KOH} = 56$ g/mol
$\rho_{H2O} = 1$ g/mL

2. 200 mL of 2M HCl solution is diluted with 800 mL of distilled water. Calculate the molar concentration of the final solution.

3. Prepare 100 mL of $Mg(OH)_2$ 3N solution. Calculate:
a) Mass of magnesium hydroxide required to prepare the solution
b) Molar and percentage concentration of the solution

μ $Mg(OH)_2$ = 58 g/mol
ρ solution = 1.075 g/mL

4. Dissolve 28 g of KOH in distilled water, obtaining 400 mL of solution. Calculate the percent and molar concentration of the solution.

ρ solution = 1.035 g/mL

5. Calculate the amount of water that must be added to 200 g of 10% NaCl solution to obtain a 4% NaCl solution.

6. Calculate the amounts of H_2SO_4 80% and H_2SO_4 10% needed to obtain 350 g of H_2SO_4 30% solution.

7. Calculate the amount of NaCl that must be added to 200 g of 4% NaCl solution to obtain a 10% NaCl solution.

8. Calculate the volume of H_2SO_4 solution of concentration 59.7% (d=1.5 g/cm^3) which is necessary to obtain 500 mL of 0.1M H_2SO_4 solution.

9. The method of obtaining $CuSO_4$ in the laboratory is:

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

a) Calculate the amount of $CuSO_4$ that is obtained, knowing that 196 g of 75% $Cu(OH)_2$ solution reacts with 196 g of H_2SO_4;
b) Calculate the percentage concentration of the $CuSO_4$ solution that is obtained after the reaction from point a).

10. Determine the initial amount of $FeCl_3 \cdot 6H_2O$, knowing that x grams of anhydrous substance were obtained by drying it and 99 g of water were removed.

11. Calculate the molar concentration of a mixture consisting of 100 mL of 2M HNO_3, 100 mL of 1N HNO_3 and 100 mL of water.

12. Calculate the volume of 2M NaOH solution needed to neutralize a 200 g solution of 32% H_2SO_4.

13. React a 2M NaOH solution with a 1M HCl solution. Determine the relationship between V_{NaOH} and V_{HCl} for the reaction to be complete.

14. Calculate the amount of salt obtained by the reaction between 100 g $Ca(OH)_2$ 15% and 20 g H_2SO_4 5%.

15. Calculate the amounts of $Al(OH)_3$ and HCl needed to obtain 300 mL of 1.5M $AlCl_3$, knowing that the HCl is in excess of 0.5 mol over the required amount.

16. Calculate the final molar concentration of a NaOH solution that is obtained by mixing 100 g of 1M NaOH, 50 mL of 20% NaOH and 50 mL of 2N NaOH.

17. Determine the mass of water that must be removed from 250 g of $FeCl_3 \cdot 6H_2O$ solution, to obtain a 40% concentration solution.

18. What is the composition of the final solution resulting from the reaction of 100 mL of 5M HCl with 200 mL of 2M $Mg(OH)_2$?

19. a) Calculate the percentage concentration of the $FeSO_4$ solution that is obtained by mixing 417 g of $FeSO_4{\cdot}7H_2O$ with 100 ml of $FeSO_4$ of 2M concentration and density 1.2 g/cm^3.
b) Starting from the final solution calculated in point a), calculate the mass of H_2O that must be evaporated to obtain a 60% concentration solution.
c) Calculate the volume of the $FeSO_4$ solution obtained at point b), knowing that the solution has a concentration of 3.25M.

20. The method of obtaining $CuSO_4$ in the laboratory is:

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

a) calculate the amount of $CuSO_4$ that is obtained, knowing that react 245 g of 60% $Cu(OH)_2$ solution with 200 ml of 5M H_2SO_4;
b) what is the amount of $CuSO_4{\cdot}5H_2O$ that corresponds to the $CuSO_4$ obtained in the reaction;
c) what is the amount of $CuSO_4$ obtained from the reaction, if 500 ml $Cu(OH)_2$ 4N reacts with the same amount of H_2SO_4 (200 ml H_2SO_4 5M).

21. The method of obtaining Na_2SO_4 in the laboratory is:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

a) calculate the amount of Na_2SO_4 that is obtained by the reaction between 250 ml of 8M NaOH and 122.5 g of 80% H_2SO_4 solution;
b) knowing that the solubility of Na_2SO_4 at 20ºC is 14 g Na_2SO_4/100 g H_2O, calculate the amount of water in which the Na_2SO_4 obtained in point a) must be dissolved to obtain a saturated solution at 20ºC;
c) calculate the percentage, molar and normal concentration of the obtained saturated solution.

22. For the preparation of a $MgCO_3$ solution with a concentration of 3.5 M and a density of 1,176 g/cm3, solutions of $MgCO_3$ 70% and $MgCO_3$ 10% are used.
a) Calculate the mass of $MgCO_3$ 70% and $MgCO_3$ 10% solutions, respectively, which are needed to prepare 600 g of $MgCO_3$ 3.5M solution.
b) Knowing that the solubility of $MgCO_3$ at 70°C is 33.3 g $MgCO_3$/100 g H_2O, determine if the solution obtained at point a) is saturated at the temperature of 70°C.
c) Calculate the amount of $MgCO_3$ that must be added to the 600 g of $MgCO_3$ solution to obtain a final concentration of 35%.

23. The method of obtaining $CuSO_4$ in the laboratory is:

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$

a) calculate the amount of $CuSO_4$ that is obtained, knowing that react 147 g $Cu(OH)_2$ with 200 ml H_2SO_4 5M;

b) what is the amount of $CuSO_4$ obtained from the reaction, if 500 ml $Cu(OH)_2$ 2M reacts with the same amount of H_2SO_4 (200 ml H_2SO_4 5M).

24. The method of obtaining Na_2SO_4 in the laboratory is:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

a) calculate the amount of Na_2SO_4 that is obtained by the reaction between 250 ml of 8M NaOH and 98 g of H_2SO_4 solution;

b) calculate the percentage concentration of the Na_2SO_4 solution obtained after the reaction.

7. PH OF AQUEOUS SOLUTIONS

7.1. Acids and bases [4]

Definitions of acids

Arrhenius: an acid is a compound that dissociates in aqueous medium with the formation of H^+.
Brønsted: an acid is a proton donor (H^+).
Lewis: an acid is an electron acceptor.

Definitions of bases

Arrhenius: a base is a compound that dissociates in aqueous medium with formation of HO^-.
Brønsted: a base is a compound that accepts protons.
Lewis: a base is an electron donor.

Acids and bases can be divided into two categories:
-hard acids and hard bases
-soft acids and soft bases

Strong acids are completely ionized in aqueous solution, where they form the hydronium ion (H_3O^+) and an anion (conjugate base A^-).

$$HA + H_2O \rightarrow A^- + H_3O^+$$

Examples: HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4 (in the first ionization step).

Weak acids are partially ionized in aqueous solution; thus, in addition to the H_3O^+ ions and the conjugate base A^-, there will always be non-ionized HA acid.

$$HA + H_2O \rightleftharpoons A- + H_3O^+$$

Examples: organic acids, HF, HNO_2, H_3PO_4, H_2CO_3.

Analogously, in the case of bases we will have:

- strong, fully ionized bases: NaOH, KOH, $Ba(OH)_2$.
- weak, partially ionized bases: NH_3, $Mg(OH)_2$, $Cu(OH)_2$.

7.2. Calculation of the pH of a solution

The ionization reaction of water is:

$$H_2O + H_2O = H_3O^+ + HO^-$$

The ionization constant associated with this reaction is given by the relation (1):

$K_w = [H_3O^+]\cdot[HO^-] = 10^{-14}$ (1)

pH is a way of expressing the molar concentration of H_3O^+ ions in an aqueous solution. Thus, the pH of a solution is defined by the relationship:

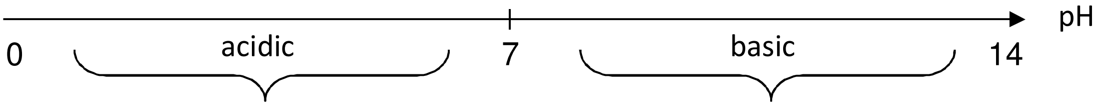
$pH = -\log[H_3O^+]$ (2)

Analogously, $pOH = -\log[HO^-]$ (3)

If we logarithmize equation (1), we obtain the following relationship:

$pH + pOH = pK_w = 14$

If pH = pOH = 7, the solution will be neutral.
If pH < 7, the solution will have an acidic character.
If pH > 7, the solution will have a basic character.



7.3. The pH of strong acid solutions

As mentioned before, strong acids are completely ionized in aqueous solution. The reaction that describes the behavior of a strong acid in aqueous solution is:

$$HA + H_2O \rightarrow A^- + H_3O^+$$

Knowing that:

(1) $pH = -\log[H_3O^+]$
(2) $[H_3O^+] = [A^-] = [HA]$,

The pH of a strong acid solution will be calculated with the relationship:

$\boxed{\mathbf{pH = -log[HA]}}$

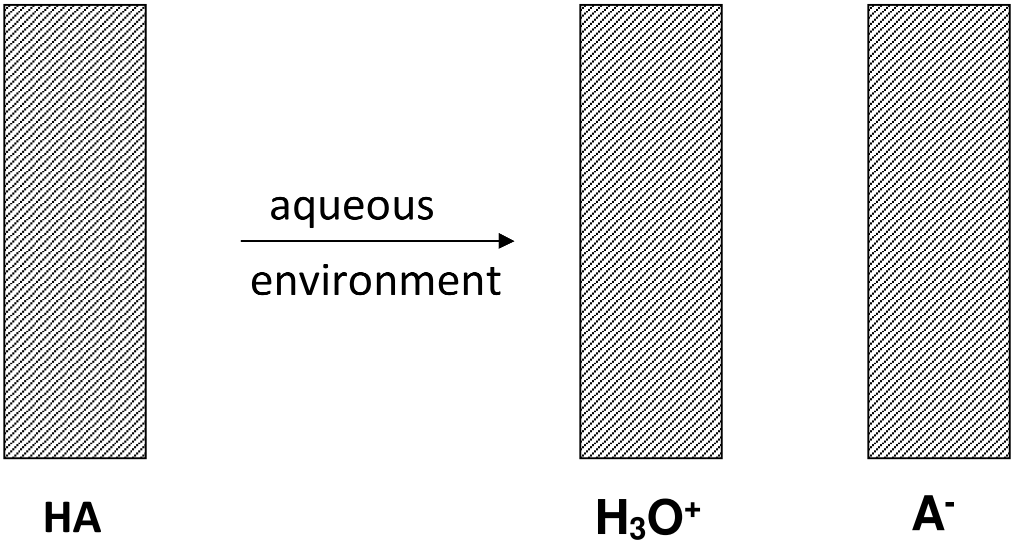


Figure 3. Dissociation of a strong acid

Analogously, in the case of a strong base, the formula for calculating pOH is:

$\boxed{\mathbf{pOH = -log[BOH]}}$

7.4. The pH of weak acid solutions

In this case, we must take into account that the acid will not be completely dissociated in aqueous medium.

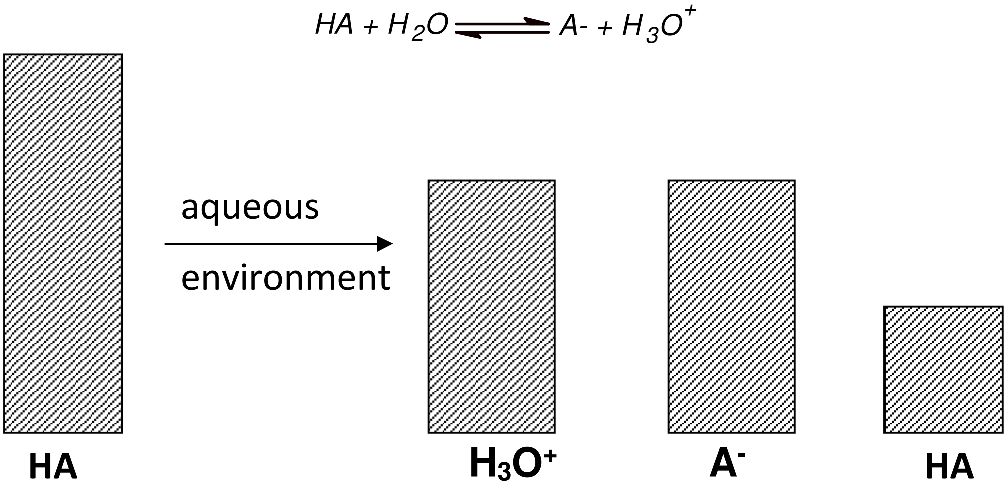


Figure 4. Dissociation of a weak acid

The equilibrium constant associated with the reaction is:

$$K_a = \frac{\left[H_3O^+\right] \cdot \left[A^-\right]}{\left[HA\right]},$$

where: K_a – acidity constant of HA acid

Knowing that $[H_3O^+]$ = [A-] → $\left[H_3O^+\right] = \sqrt{K_a \cdot [HA]}$

By logarithmizing the above relationship, the formula for calculating the pH of a weak acid becomes:

$$\boxed{pH = \frac{1}{2}\left(pK_a - \log[HA]\right)}$$

Analogously, the pOH of a weak base will be calculated with the relationship:

$$\boxed{pOH = \frac{1}{2}\left(pK_b - \log\left[BOH\right]\right)}$$

The relationship between the acidity constant (K_a) of a weak acid and the basicity constant (K_b) of its conjugate base:

$$K_a(HA) \cdot K_b(A^-) = 10^{-14}$$

or

$$pK_a + pK_b = 14$$

The higher the acidity constant K_a (i.e. the lower the pK_a), the stronger the acid.

7.5. Exercises

1. Calculate the pH of the following solutions:
- HNO_2 0.01M
- LiOH 0.05M
- $LiNO_2$ 0.01M

K_a (HNO_2/NO_2^-) = $4.0x10^{-4}$

2. Calculate the pH of the following solutions:
- HClO 0.015M
- $Ba(OH)_2$ 0.1M
- $Ba(ClO)_2$ 0.001M

K_a (HClO/ClO-) = $3x10^{-8}$

3. An aqueous solution of HI contain:
a) H_3O^+, I^-, HI
b) H_3O^+, I^-
c) HI/I^-

4. An aqueous solution of HNO_2 contain:
a) NO_2^- și HO^-
b) HNO_2, NO_2^-, H_3O^+
c) NO_2^-, H_3O^+

5. An aqueous solution of $Cu(OH)_2$ contain:
a) Cu^{2+}, HO^-
b) Cu^{2+}, HO^- și $Cu(OH)_2$
c) Cu^{2+}, H_3O^+

6. An aqueous solution of RbOH contain:
a) Rb^+, HO^-
b) Rb^+, HO^- și RbOH
c) Rb^+, H_3O^+

7. Calculate the pH of a 100 ml HNO_2 solution needed to neutralize 200 ml 1% NaOH solution.
$M_{HNO2} = 47g/mol$; $M_{NaOH} = 40g/mol$
$\rho_{NaOH10\%} = 1.15g/ml$
$K_a(HNO_2/NO_2^-) = 5 \cdot 10^{-4}$

8. Calculate the pH of a 100 ml HF solution needed to neutralize 200 ml 1% NaOH solution.
$M_{HF} = 20g/mol$; $M_{NaOH} = 40g/mol$
$\rho_{NaOH10\%} = 1.15g/ml$
$K_a(HF/F^-) = 6,8 \cdot 10^{-4}$

9. Calculate the pH of a 100 ml HF solution needed to neutralize 200 ml of 1% NaOH solution.
$M_{HF} = 20g/mol$; $M_{NaOH} = 40g/mol$
$\rho_{NaOH10\%} = 1.15g/ml$
$K_a(HF/F^-) = 6,8 \cdot 10^{-4}$

10. Calculate the pH of a solution of 200 g NH_3 of initial concentration 10%, after it is diluted with 100 ml H_2O.
$M_{NH3} = 17g/mol$
$\rho_{NH3} = 0,75g/ml$
$K_a(NH_4^+/NH_3) = 5,5 \cdot 10^{-10}$

11. Calculate the pH of a solution made by mixing 200 ml of 2.8% KOH with 100 ml of 0.5N HCl.
M_{KOH}=56 g/mol
ρ_{KOH}=1,05 g/ml
5b. Calculate the pH of an NH_3 solution of the same molar concentration as that of the KOH solution. $K_a(NH_4^+/NH_3)=5,5 \cdot 10^{-10}$

12. Calculate the pH of a solution obtained by mixing 400 ml of 2% NaOH with 100 ml of 0.5N HCl.
M_{NaOH}= 40 g/mol
P_{NaOH}=1,1 g/ml
12b. Calculate the pH of an NH_3 solution of the same molar concentration as that of the NaOH solution.
$K_a(NH_4^+/NH_3)=5,5 \cdot 10^{-10}$

CHAPTER 8. HYDROLYSIS OF SALTS

When a salt is dissolved in water, the ions that form it can react with the water; these hydrolysis reactions of the anions/cations give the respective salt solution a neutral, acidic or basic character.

Consider a salt with the general formula MA, which is obtained by a neutralization reaction of the type:

$$\mathbf{MOH + HA \rightarrow MA + H_2O}$$

Depending on the nature of the base and acid involved in the reaction, salts can be classified into four categories:

1. Salts originating from a strong base and a strong acid

Examples: NaCl, NaI, $MgBr_2$, KNO_3, $KClO_4$

In this case, the cation of the salt (M^+) is a very weak acid and the anion (A^-) is a very weak base. As previously discussed, very weak acids and bases do not hydrolyze, which means that the solution of these salts will be a neutral solution.

$$M^+ + H_2O \nrightarrow$$
$$A^- + H_2O \nrightarrow$$

In this case, the pH value of the salt solutions must be pH = 7 (theoretical); practically, the pH value is equal to the pH value of the distilled water with which the respective solution was prepared.

2. Salts originating from a strong base and a weak acid

Examples: NaF, $NaNO_2$, $Mg(ClO)_2$, K_3PO_4

In this case, the cation of the salt (M^+) is a very weak acid and the anion (A^-) is a weak base. Only the waek base can react with water, which means that the solution of these salts will be a basic solution.

$$M^+ + H_2O \nrightarrow$$
$$A^- + H_2O \rightleftarrows HA + HO^-$$

The formula for calculating the pH will be the following:

$$pOH = \frac{1}{2}(pK_b - logC_{sare})$$

$$pH = 14 - pOH$$

3. Salts originating from a weak base and a strong acid

Examples: $AlCl_3$, CuI_2, $Fe(NO_3)_3$, NH_4Br

In this case, the cation of the salt (M^+) is a weak acid and the anion (A^-) is a very weak base. Only the weak acid can react with water, which means that the solution of these salts will be an acidic solution.

$$M^+ + H_2O \rightleftarrows MOH + H^+$$
$$A^- + H_2O \nrightarrow$$

The formula for calculating the pH will be the following:

$$pH = \frac{1}{2}(pK_a - logC_{sare})$$

4. Salts originating from a weak base and a weak acid

Examples: NH_4F, CH_3COONa

In this case, the cation of the salt (M^+) is a weak acid and the anion (A^-) is a very weak base. Both the weak base and the weak acid can react with water, the acidic or basic character of the solution being given by the ratio between K_a and K_b associated with the two reactions:

$$M^+ + H_2O \rightleftarrows MOH + H^+ \qquad (1) \qquad K_{a(1)}$$
$$A^- + H_2O \rightleftarrows HA + HO^- \qquad (2) \qquad K_{b(2)}$$

If $K_a > K_b$, the solution will be acidic.
If $K_a < K_b$, the solution will be basic.
If $K_a = K_b$, the solution will be neutral.

The formula for calculating the pH will be the following:

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{pK_{a1} + (14 - pK_{b2})}{2}$$

Acidity constants, K_a

K_a (CH_3COOH/CH_3COO^-)	$1.7 \cdot 10^{-5}$
K_a (H_2CO_3/HCO_3^-)	$4.3 \cdot 10^{-7}$
K_a (HCO_3^-/CO_3^{2-})	$4.8 \cdot 10^{-11}$
K_a ($HClO/ClO^-$)	$3.5 \cdot 10^{-8}$
K_a (H_2S/HS^-)	$8.9 \cdot 10^{-8}$
K_a (HS^-/S^{2-})	$1.2 \cdot 10^{-13}$
K_a (HNO_2/NO_2^-)	$4.5 \cdot 10^{-4}$
K_a ($H_3PO_4/H_2PO_4^-$)	$6.9 \cdot 10^{-3}$
K_a ($H_2PO_4^-/HPO_4^{2-}$)	$6.2 \cdot 10^{-8}$
K_a (HPO_4^{2-}/PO_4^{3-})	$4.8 \cdot 10^{-13}$

The type of hydrolysis of salt solutions is summarized in the following table:

Table 3. Hydrolysis of salts

Salt (MA)	**Cation (M^+)**	**Anion (A^-)**	**Hydrolysis**
	very weak acid	very weak base	neutral
	very weak acid	weak base	basic
	weak acid	very weak base	acidic
	weak acid	weak base	depending on the ratio between K_a and K_b

Exercises

Specify the approximate value (>7, <7, =7) of the pH of the following salt solutions:

Na_3PO_4

Na_2SO_4

NH_4Br

$FeCl_3$

NH_4NO_3

$Ca(NO_3)_2$

$CuSO_4$

K_2CO_3

K_2SO_4

$Al(NO_3)_3$

$NaBr$

$HCOONa$

CHAPTER 9. LABORATORY EXPERIMENTS

L1. Experimental and theoretical determination of the pH of some salt solutions

1. Prepare 50 mL of 0.15 M concentration solution for the following salts: CH_3COONa, $KClO_3$, $CuSO_4$, Na_2SO_3, NH_4Cl, NH_4NO_3.

Work method: prepare 6 Berzelius beakers and label them accordingly. Weigh the amount of each salt required to prepare the 0.1M concentration solution and put it in the respective Berzelius beaker, and dissolved it in 50 mL of distilled water.

2. Determine, with the help of indicator paper, the experimental pH of the prepared solutions and write down the obtained values.

3. Calculate the theoretical pH of the 6 salt solutions, knowing the following values $K_a(K_b)$:

$K_a(CH_3COOH/CH_3COO^-)=1.76\cdot 10^{-5}$; $K_b(CH_3COO^-/CH_3COOH)=5{,}68\cdot 10^{-10}$
$K_a(Cu^{2+}/Cu^+)=5\cdot 10^{-7}$;
$K_a(HSO_4^-/SO_4^{2-})=1{,}2\cdot 10^{-2}$; $K_b(SO_4^{2-}/HSO_4^-)=8{,}3\cdot 10^{-13}$
$K_a(HSO_3^-/SO_3^{2-})=6\cdot 10^{-8}$; $K_b(SO_3^{2-}/HSO_3^-)=1.66\cdot 10^{-7}$
$K_a(NH_4^+/NH_3)= 5{,}65\cdot 10^{-10}$

4. The obtained results are noted in the following table:

Solution 0.1M	**Experimental pH**	**Theoretical pH**
CH_3COONa		
$KClO_3$		
NH_4NO_3		
Na_2SO_3		
$CuSO_4$		
NH_4Cl		

5. Explain, for each of the six cases, the obtained results.

CH_3COONa -

$KClO_3$ -

NH_4NO_3 -

Na_2SO_3 -

$CuSO_4$ -

NH_4Cl -

L2. Determination of the acidity constant K_a of acetic acid by the conductometric method

The conductivity of an electrolyte solution is a measure of its ability to conduct electricity.

Electrolyte: any substance that, dissolved in a solvent (usually water), dissociates to form ions.
Strong electrolytes: strong acids and bases, salts
Weak electrolytes: weak acids and bases

The unit of measure (S.I.) of conductivity is S/m (Siemens/meter).

To measure the conductivity of an electrolyte solution, a voltage is applied to the electrode immersed in that solution; the ions will move in the solution, making it possible for the electric current to pass through the solution. Thus, the conductivity of an electrolyte solution depends on the number of ions present in the solution (so it varies depending on the concentration).

The molar conductivity of a weak acid (Λ_M) is given by the expression:

$$\Lambda_M = \frac{\Lambda}{c},$$

where Λ is the conductivity of the weak acid, and c is its molar concentration.

The degree of dissociation α is given by the relation:

$$\alpha = \frac{\Lambda_M}{\Lambda_0},$$

where Λ_0 represents the molar conductivity at infinite dilutions.

The acidity constant of acetic acid is:

$$K_a = \frac{[H^+][CH3COO^-]}{[CH3COOH]} = \frac{(\alpha c)^2}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

Work method

Add 1 mL of 1M CH_3COOH to 60 mL of water and measure the conductivity after each addition of acetic acid.

V (CH_3COOH 1M) mL	$C_{CH3COOH}$ (mol/L)	Conductivity (µS/cm)	Molar conductivity (µS/cm·M)	Molar fraction (α)	K_a/pK_a
1					
2					
3					
4					
5					
6					
7					

The average value of K_a/pK_a is: ………..

L3. Determination of the water content of a hydrate [5]

Work method

1. A watch glass is placed on a round clamp, which is heated for about 5 minutes, after which it is removed with the help of a wooden clamp and allowed to cool to room temperature. The dry watch glass is weighed on the analytical balance.

2. Weigh approximately 2.5 g of $CuSO_4 \cdot 5H_2O$ directly onto the watch glass, then dry for 5 minutes using the method described in the previous point. After cooling, weigh the watch glass and its contents again and note their mass.

3. The drying of the watch glass and its contents is repeated until no more water evaporates (until a constant mass is obtained).

4. Calculate the amount of water that has been removed from the crystal hydrate and calculate its water content (in mass percent).

The mass of the watch glass (after it has been dried):

....

The mass of the watch glass and the initial crystal hydrate:

....

The mass of the watch glass and the crystal hydrate after the first drying operation:

....

The mass of the watch glass and the crystal hydrate after the second drying operation:

....

The mass of the watch glass and the crystal hydrate after the ..... drying operation:

....

The mass of the watch glass and the crystal hydrate after the ..... drying operation:

....

The mass of the watch glass and the crystal hydrate after the ..... drying operation:
....

Crystal hydrate mass (before drying):
....

Crystal hydrate mass (after drying):
....

Theoretical water content (% mass) of $CuSO_4 \cdot 5H_2O$:
....

Practical water content (% mass) of $CuSO_4 \cdot 5H_2O$:
....

L4. Determination of the NaCl concentration of a saline solution using silver ions [6]

The conductivity of an electrolyte solution is a measure of its ability to conduct electricity.

Electrolyte: any substance that, dissolved in a solvent (usually water), dissociates to form ions.

Strong electrolytes: strong acids and strong bases, salts

Weak electrolytes: weak acids and weak bases

The unit of measure (S.I.) of conductivity is S/m (Siemens/meter).

To measure the conductivity of an electrolyte solution, a voltage is applied to the electrode immersed in that solution; the ions will move in the solution, making it possible for the electric current to pass through the solution. Thus, the conductivity of an electrolyte solution depends on the number of ions present in the solution (so it varies depending on the concentration).

Work method

Measure 10 mL physiological serum with a pipette and put it in a 200 mL Berzelius beaker. Add another 90 mL of distilled water, measured using a cylinder. The conductivity of the obtained solution is measured. Add 2 mL of 0.1M $AgNO_3$ solution and measure the conductivity after each addition. 22 mL of 0.1M $AgNO_3$ solution (12 conductance readings) will be added (in total). Graph the dependence conductivity=f(V), where V is the volume of $AgNO_3$ added to the saline solution.

Experimental results

$AgNO_3$ volume (mL)	0	2	4	6	8	10
Conductivity						

$AgNO_3$ volume (mL)	12	14	15	16	18	20	22
Conductivity							

The dependence conductivity=f(V) is graphically represented, and the equivalence point is considered to be the intersection of the tangents to the graph.

The reaction that occurs is:

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$
$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl\downarrow + Na^+ + NO_3^-$

Determine (on the basis of the graph) the volume of $AgNO_3$ necessary for dosing Cl ions, then calculate the corresponding number of moles of $AgNO_3$. Knowing the number of moles of $AgNO_3$ that reacted with NaCl, calculate the number of moles of NaCl in the solution and its molar concentration.

L5. Experimental determination of pH

The objective of the work: measuring the pH of some solutions with the help of the pH-meter and comparing with the theoretical values.

Work method

1. React 10 mL of 0.1M HCl with 20 mL of 0.4% NaOH. Measure the pH of the obtained solution using the pH meter. Calculate the theoretical pH value and compare it with the experimental value.

2. React 10 mL 0.1M HCl with 10 mL 0.4% NaOH. Measure the pH of the obtained solution using the pH meter. Calculate the theoretical pH value and compare it with the experimental value.

3. React 20 mL of 0.1M HCl with 10 mL of 0.4% NaOH. Measure the pH of the obtained solution using the pH meter. Calculate the theoretical pH value and compare it with the experimental value.

- Calculate the number of moles of HCl and NaOH that react, in each of the 3 cases.
- Determine in which of the 3 experiments the reaction between HCl and NaOH is complete.
- Calculate the pH of the final solution for the 3 reactions.

L6. Determination of sodium chloride solubility [2]

The factors that influence solubility

1. Temperature: if the dissolution process takes place with energy absorption (endothermic), the solubilization of the substance is favored by the increase in temperature. Conversely, if dissolution is an exothermic process (occurring with energy release), solubilization is favored by low temperatures.
2. Size of the molecules: large molecules (those with more atoms or a higher molecular mass) will have a lower solubility because they can hardly be solvated by the solvent molecules.
3. Polarity: polar compounds dissolve in polar solvents, non-polar compounds dissolve in non-polar solvents.

A saturated solution at a certain temperature contains the maximum amount of substance that can be dissolved in that solvent at that temperature. Once the temperature drops, part of the initially dissolved substance will start to precipitate.

Work method: Weigh (to two decimal places) approximately 9 g of NaCl, which are introduced into a 50 mL test tube together with 20 mL of distilled water. The tube is heated on a water bath until the crystals are completely dissolved (up to about 80°C). If at this temperature there is still undissolved solid substance, add 1 mL of distilled water and heat again to 80°C. After the entire amount of NaCl has dissolved, the solution is allowed to cool to room temperature. Note the temperature at which NaCl crystals begin to form again. Add another 2 mL of water, reheat the solution until the crystals dissolve again and let it cool again for a few minutes. Note the temperature at which crystals start to appear again.

Salt	NaCl	V (mL)	20	20 + 1	20 + 1 + 2
Weight (g)		T (°C)			

L7. Determination of the neutralizing capacity of antacid type tablets [2]

Work method

Prepare 400 mL of hydrochloric acid solution with a concentration of ≈0.6 M, starting from a solution of hydrochloric acid with a concentration of 5 M. The solution thus obtained is stored in a 500 mL Erlenmeyer flask.

Determination of the exact concentration of the prepared hydrochloric acid solution:

Transfer 10 mL of the prepared hydrochloric acid solution into an Erlenmeyer beaker and add 20 mL of distilled water. Fill a 50 mL burette with a 0.15 M sodium hydroxide solution. In the Erlenmeyer beaker containing the hydrochloric acid solution, add 2-3 drops of phenolphthalein and titrate until the color of the indicator changes. Note the volume of sodium hydroxide that was used for the titration and calculate the exact concentration of the hydrochloric acid solution.

Analysis of antacid type tablets

Crush two antacid tablets in a porcelain mortar and weigh the resulting mass, which is quantitatively transferred into a 250 mL Erlenmeyer flask. Then add 25 mL of distilled water and 25 mL of the hydrochloric acid solution whose concentration was previously established. The mixture thus obtained is boiled for 5 minutes, after which it is allowed to cool to room temperature. The added hydrochloric acid has the role of dissolving the tablets and reacting completely with the existing basic compounds. The pH of the final solution is determined with pH paper. After the obtained solution has cooled, add 5 drops of methyl orange and titrate with the sodium hydroxide solution that was also used for the exact determination of the hydrochloric acid concentration. The color shift is: red (acid), gray, green (basic).

CHAPTER 10. OXIDO-REDUCTION REACTIONS

Oxido-reduction reactions (Redox reactions)

They are reactions in which the oxidation state of atoms changes.

Oxidation: reaction that proceeds with the loss of electrons (oxidation state increases)
Reduction: reaction that proceeds with the acceptance of electrons (oxidation state decreases)

Oxidizing species: the one that accepts electrons
Reducing species: the one that donates electrons

To explain the fact that in a redox reaction the oxidizing species is reduced and the reducing species is oxidized, the following analogy can be used: as we pour the contents of a full container into an empty one, the empty container fills (and becomes full), and the full container becomes empty. Thus, the full container can be considered the oxidizer, and the empty container - the reducer, and the transferred liquid represents the transfer of electrons [7,8].

$$\begin{array}{lcll} Ox_1 + ne^- & \rightleftharpoons & Red_1 & \quad \text{reduction} \\ Red_2 & \rightleftharpoons & Ox_2 + ne^- & \quad \text{oxidation} \\ \hline Ox_1 + Red_2 & \longrightarrow & Red_1 + Ox_2 & \quad \text{global reaction} \end{array}$$

Acidic medium:

$$Ox_1 + ne^- + mH^+ \rightleftharpoons Red_1 + zH_2O$$

Alkaline medium:

$$Ox_1 + ne^- + mH_2O \rightleftharpoons Red_1 + zHO^-$$

! S.O. ↑ - oxidation – reducing agent
! S.O. ↓ - reduction – oxidating agent

Experiment 1

Redox reactions – the reactivity of metals

The reactivity series of metals is shown in the figure below:

Pt Au Ag Hg Cu H Pb Sn Ni Fe Zn Al Mg Na

$\longrightarrow$

Consider the reaction:

$M + M_1X \rightarrow MX + M_1$

This can only occur if the M metal is more reactive than the M_1 metal.

The objective of the work: comparison of copper reactivity in the reaction with Ag^+ and Pb^{2+} ions

Work method

Two test tubes are prepared in which 5 mL of $AgNO_3$ and $Pb(NO_3)_2$ solutions are introduced. A piece of copper is inserted into each test tube and left at room temperature for 5 minutes.

Write down the observations and complete the chemical reaction (where applicable).

(1) $Cu + AgNO_3 \rightarrow$

(2) $Cu + Pb(NO_3)_2 \rightarrow$

Reaction (1): Cu has the role of …………………… and Ag^+ is ………………

Reaction (2): Cu has the role of ……………………, and Pb^{2+} is ……………..

Experiment 2

Oxidation states of manganese (Mn)

2A.

Work method: A few drops of potassium permanganate solution are introduced into a test tube, acidified with 2-3 drops of sulfuric acid (or alkalized with a few drops of sodium hydroxide) and a few drops of sodium sulfite are added.

$MnO_4^- + SO_3^{2-}$	Color (initial)	Color (final)	Products	Oxidation state of manganese (Mn)
Acidic	violet		$Mn^{2+} + SO_4^{2-}$	
Alkaline	violet		$MnO_2 + SO_4^{2-}$	

The reactions that occur are the following:

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

$$MnO_4^- + SO_3^{2-} + H_2O \rightarrow MnO_2 + SO_4^{2-} + HO^-$$

Balance the reactions (based on the redox couples) and establish the role of MnO_4^-, respectively of SO_3^{2-}.

2B.

Work method: A few drops of potassium permanganate solution are introduced into a test tube, acidified with 2-3 drops of sulfuric acid (or alkalized with a few drops of sodium hydroxide) and a few drops of potassium iodide are added.

$MnO_4^- + I^-$	Color (initial)	Color (final)	Products	Oxidation state of manganese (Mn)
Acidic	violet		$Mn^{2+} + I_2$	
Alkaline	violet		$MnO_4^{2-} + IO_3^-$	

The reactions that occur are the following:

$$MnO_4^- + I^- + H^+ \rightarrow Mn^{2+} + I_2 + H_2O$$

$$MnO_4^- + I^- + HO^- \rightarrow MnO_4^{2-} + IO_3^- + H_2O$$

Balance the reactions (based on the redox couples) and establish the role of MnO_4^-, respectively of I^-.

Experiment 3. Redox behavior of iodine compounds [9]

Work method: In a 250 mL Erlenmeyer beaker, add 100 mL of distilled water, 5 mL of 0.1M H_2SO_3 and 5 mL of starch solution. Each group of students adds different volumes of HIO_3 (ranging from 4 mL to 11 mL) and notes the corresponding observations.

Preparation of solutions:

100 mL H_2SO_3 0.1M is prepared from 50 mL $NaHSO_3$ 0.2M and 50 mL H_2SO_4 0.1M;

100 mL HIO_3 0.1M is prepared from 50 mL KIO_3 0.1M to 50 mL H_2SO_4 0.5M;

Starch solution: 10 g starch/250 mL water.

The reactions that occur are the following:

$$H_2SO_3 + HIO_3 \rightarrow 3H_2SO_4 + HI$$

$$5HI + HIO_3 \rightarrow \underset{\text{blue}}{3I_2} + 3H_2O \quad \text{(+ starch)}$$

$$H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + \underset{\text{colorless}}{2HI}$$

Determine the redox couples for each of the 3 reactions and determine the oxidizing and reducing species, respectively.

CHAPTER 11. SYNTHESIS OF INORGANIC COMPOUNDS

11.1. Synthesis of copper(I) iodide [2]

Work method: weigh 2 g of Cu and dissolve in the required amount of nitric acid. The obtained solution is partially neutralized (up to pH = 4) with aqueous ammonia solution. The obtained solution is boiled for a few minutes to remove the nitrogen dioxide formed, then cooled to room temperature. Prepare an iodide-thiosulfate solution with the following composition: 36.5 g KI and 28.0 g $Na_2S_2O_3 \cdot 5H_20$, which are brought to a volume of 100 mL. For an initial copper sample of ~2g, ~25 mL of iodide-thiosulfate solution is required. The iodide-thiosulfate solution is introduced into the burette and added in drops to the reaction mixture, immediately observing the formation of a brown-brown precipitate. When the entire amount of copper has reacted, there is a color change from brown → light yellow.

The reactions that occur are:

$$\mathbf{Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2NO_2\uparrow + 2H_2O}$$

$$\mathbf{2Cu^{2+} + 2I^- + 2S_2O_3^{2-} \rightarrow 2CuI\downarrow + S_4O_6^{2-}}$$

Iodide transforms Cu^{2+} ions into CuI, but there is a risk that the precipitate formed is contaminated with I_2. For this reason, the thiosulfate solution is needed, which will reduce elemental iodine I_2 to iodide I^-, soluble in the reaction mixture.

The obtained reaction mixture is filtered, washing the precipitate several times to remove all soluble impurities. The precipitate is removed from the filter and dried until all traces of water are removed.

11.2. Synthesis of alum [10]

Weigh approximately 0.5 g pieces of Al, which are inserted into a 50 mL Berzelius beaker; add 5 mL of water and 4.0 mL of concentrated sulfuric acid. The solution thus obtained is heated to boiling (not too strong) and water is added if the volume of the solution decreases too much. Continue heating for 30 minutes (or less if Al is no longer observed in the reaction mass). The reaction mixture is cooled and a small amount of water is added. The filtrate is poured into a 50 mL beaker, placed in an ice bath. 4.0 mL of 10M KOH is added to the filtrate with stirring, maintaining the acid pH of the solution (check with pH paper). If the pH of the solution becomes alkaline, adjust it with a few drops of concentrated sulfuric acid. The reaction mixture is again brought to a boil until the solid dissolves. After its complete dissolution, the glass is placed again in the ice bath; crystals will begin to form within minutes. The reaction mixture is filtered on a Büchner funnel, and the precipitate is washed on the filter with a small amount of methanol. The obtained product is weighed on a watch bottle and the yield is calculated.

Steps of synthesis:

- dissolving the aluminum:
  $Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$
- neutralization of excess acid:
  $H_2SO_4 + KOH \rightarrow K_2SO_4 + H_2O$
- precipitation of the product:
  $KAl(SO_4)_2 + H_2O \rightarrow KAl(SO_4)_2 \cdot 9H_2O$
- global reaction:
  $Al + H_2SO_4 + KOH + H_2O \rightarrow KAl(SO_4)2 \cdot 9H_2O + H_2$

11.3. Synthesis of copper sulfate ($CuSO_4$) [2]

11.3.1. Obtaining a solution of copper nitrate $Cu(NO_3)_2$

Work method

Weigh approximately 0.5 g of copper wire and insert it into an Erlenmeyer flask. Measure 4 mL of nitric acid using a graduated cylinder and pour over the copper wire, gently shaking the Erlenmeyer flask to facilitate the dissolution of the copper. After dissolving the entire amount of copper, add 100 mL of distilled water.

The reaction that takes place is:

$$4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

	Technical mass (g)	Pure compound mass (g)	Volume (mL)	Mole number	Yield (%)
Nitric acid					
Copper					
Copper nitrate (theoretical)					
Copper nitrate (practic)					

11.3.2. Synthesis of copper hydroxide (II)

Work method

Over the previously obtained copper(II) nitrate solution, a 6M sodium hydroxide solution is added in stages (until the formation of a precipitate is no longer observed - approximately 20 mL). The solution obtained is filtered, and the precipitate obtained is washed with distilled water on the filter funnel.

$$Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3$$

	Technical mass (g)	Pure compound mass (g)	Volume (mL)	Mole number	Yield (%)
Copper nitrate					
Sodium hydroxide					
Copper hydroxide (theoretical)					
Copper hydroxide (practic)					

11.3.3. Synthesis of copper sulfate

Work method

The copper(II) hydroxide obtained in the previous step reacts with a 3M H_2SO_4 solution (sulfuric acid is added until the formation of a precipitate is no longer observed). The obtained copper sulfate is filtered and weighed, considering its humidity to be 30%.

$$\mathbf{Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O}$$

	Technical mass (g)	Pure compound mass (g)	Volume (mL)	Mole number	Yield (%)
Copper hydroxide					
Sulfuric acid					
Copper sulfate (theoretical)					
Copper sulfate (practic)					

CHAPTER 12. CHEMICAL PROPERTIES OF NON-METALS [11,12]

12.1. Group VIIA

General presentation

- Halogen ↔ **Salt generator**

Non-metallic character

- **Ground state: diatomic molecules X_2**

F_2	Cl_2	Br_2	I_2
gas	**gas**	**liquid**	**solid**
yellow	**green**	**red-brown**	**purple**

At – product of some nuclear reactions, was identified in the series of natural disaggregation of U and Th.

- **Electron configuration**:

F – $[He]2s^2 2p^5$
Cl – $[Ne]3s^2 3p^5$
Br – $[Ar]3d^{10}4s^2 4p^5$
I – $[Kr]4d^{10}5s^2 5p^5$
At – $[Xe]4f^{14}5d^{10}6s^2 6p^5$

7 valence electron ··· → **+ 1 electron** for achieving the stable octet configuration → **higher reactivity than the other non-metallic groups of the periodic system**

→ they are only found as chemical compounds, never in elemental form.

Halogen	Oxidation states of halogens (in compounds)
F	**-1 (always)**
Cl	**-1**, +1, +3, +5, +7
Br	**-1**, +1, +3, +5, +7
I	**-1**, +1, +3, +5, +7

- **Fluorine,** the most electronegative element of the periodic system, forms combinations with the other elements only at the -1 oxidation state.

- **Chlorine, bromine and iodine** form combinations in positive oxidation states only with the two more electronegative elements, O and N.

Obtaining and uses of halogens

Fluorine, F_2

It is obtained only by electrolysis of a solution of KF in anhydrous HF (KHF_2):

$$2KHF_2 \xrightarrow[70\ -\ 100\ \text{grd. C}]{\text{electrolysis}} H_2 + F_2 + 2KF$$

~ 20% of modern drugs contain fluorine; a single F atom can influence the chemical properties of the pharmaceutical compound and the way it acts.

The effect of the fluorine atom:

- Carbon-fluorine bond stability; fluoridation increases its metabolism time
- The increase in lipophilicity, due to the hydrophobic nature of the carbon-fluorine bond

Examples

Antidepressants – fluorinated molecules that selectively limit serotonin content
Quinolones – fluorinated antibiotics with a broad spectrum of action
Anesthetic drugs - long action time, insoluble in blood

Chlorine, Cl_2

Obtaining methods

- Electrolysis of an aqueous solution of sodium chloride

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$$

- By oxidizing Cl^- with various oxidizing agents: MnO_2, MnO_4^-, ClO_3^-

$$2Cl^- + MnO_2 + 4H^+ \rightarrow Cl_2 + Mn^{2+} + 2H_2O$$

$$5Cl^- + MnO_4^- + 8H^+ \rightarrow 5/2Cl_2 + Mn^{2+} + 4H_2O$$

$$5Cl^- + ClO_3^- + 6H^+ \rightarrow 3Cl_2 + 2H_2O$$

- By thermal dissociation of noble metal chlorides

Uses

- **Intermediate in the pharmaceutical industry –** 2/3 of the pharmaceutical compounds were obtained by using chlorinated derivatives
- **Disinfectant**

Bromine, Br_2

Obtaining

- By electrolysis of an aqueous solution of Br^-

$$2NaBr + 2H_2O \rightarrow Br_2 + H_2 + 2NaOH$$

- Oxidation of Br^- with Cl_2

$$Br^- + 1/2Cl_2 \rightarrow Br_2 + Cl^-$$

- Oxidation of Br^- with other oxidizing agents

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

Applications

- Quite rarely found in pharmaceutical compounds
- **Vasodilators:** nicergoline
- **Sedatives:** bratyzolam
- **Antiseptics:** merbromine

Iodine, I_2

Obtaining

- Iodide oxidation with chlorine

$$I^- + 1/2Cl_2 \rightarrow I_2 + Cl^-$$

- Iodide oxidation with weak oxidizing agents

$$2I^- + O_3 + H_2O \rightarrow I_2 + O_2 + 2HO^-$$

$$2I^- + H_2O_2 \rightarrow I_2 + 2H_2O$$

- Reducing the iodate IO_3^- with SO_2 in aqueous solution

$$2IO_3^- + 5SO_2 + 4H_2O \rightarrow I_2 + 2HSO_4^- + 3H_2SO_4$$

Applications

- Saturated solution of KI (SSKI) for the treatment of thyrotoxicosis
- **Biologic role**: constituent of thyroid hormones T4 (thyroxine) and T3 (triiodothyronine)

Halogens at minimum oxidation state (O.S.= -1)

Halides

1. Ionic halides

To characterize the ionic halogens from the acid-base, redox and reactivity point of view, we will use solutions of the following substances:

- NaF (sodium fluoride): toxic compound; in extremely small quantities it has a beneficial role in preventing dental caries;
- NaCl (sodium chloride): compound necessary in numerous biological processes, but present in excess leads to an increase in blood pressure;
- KBr (potassium bromide): found in various tissues;

- NaI (sodium iodide): compound necessary for the proper functioning of the thyroid gland.

Preparation of halide solutions: prepare 100 mL of halide solution (NaF, NaCl, KBr and NaI) of 0.1M concentration. The solutions are stored in properly labeled Erlenmeyer flasks.

Necessary laboratory equipment and utensils:
- analytical balance
- 100 mL volumetric flask
- Erlenmeyer flasks
- stirring rod

Experiment 1. Theoretical and experimental determination of the pH of halogen solutions

The pH of the 4 prepared solutions is first determined with the help of indicator paper, then with the help of the pH-meter. The obtained results are noted in the following table, as well as the value determined by calculating the pH.

$K_a(HF/F^-) = 6.6*10^{-4}$

	NaF	NaCl	KBr	NaI
pH (indicator paper)				
pH (pH-meter)				
theoretical pH				

Experiment 2. Identification reaction of ionic halides

Work method: 2-3 mL of the prepared halogen solutions are introduced into 4 test tubes, after which a few drops of $AgNO_3$ or $Ca(NO_3)_2$ solution are added.

! Complete the reactions below and characterize the reaction products obtained.

$NaF + AgNO_3 \rightarrow AgF + NaNO_3$

…………

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

…………

$KBr + AgNO_3 \rightarrow AgBr + KNO_3$

…………

$NaI + AgNO_3 \rightarrow AgI + NaNO_3$

…………

$2NaF + Ca(NO_3)_2 \rightarrow CaF_2 + 2NaNO_3$

……………

$2NaCl + Ca(NO_3)_2 \rightarrow CaCl_2 + 2NaNO_3$

……………

$2KBr + Ca(NO_3)_2 \rightarrow CaBr_2 + 2KNO_3$

……………

$2NaI + Ca(NO_3)_2 \rightarrow CaI_2 + 2NaNO_3$

……………

Redox behavior

Due to the minimum oxidation state -1, the halide ions are exclusively reducing agents. The reducing character increases with the atomic number Z of the 4 halogens. Thus, F^- is the weakest reducer.

Experiment 3. Stability of halide ions towards O_2 physically dissolved in aqueous solution

$$X^- + O_2 \rightarrow X_2 + H_2O \quad \text{(acidic medium)}$$

The redox couples that are taken into account are:

$$1/2I_2 + 1e^- \rightarrow I^- \quad | *4$$
$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

$$4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O$$

The protons required for the process are provided by the reaction:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

Observations

Under standard conditions, the species susceptible to oxidation is iodide I^-. Thus, if a freshly prepared KI solution is colorless, over time and in an open system the solution turns yellow due to the oxidation of I^- to I_2. For this reason, the iodide solution is prepared fresh and stored in dark glass containers.

Experiment 4. Reaction of solid halides with concentrated H_2SO_4

The principle of the work: The same oxidizer is reduced to a lower oxidation state the stronger the reducing agent.

Work method: 3-4 mL of NaCl, KBr and KI solution are introduced into 3 test tubes, to which they are added 2-3 mL H_2SO_4.

The observations are recorded in the following table:

	+ H_2SO_4	Reaction products	Observations
NaCl			
KBr		Br_2, SO_2	
NaI		I_2, H_2S	

Oxidation state zero (O.S.= 0)

Experiment 5. Methods of obtaining halogens at O.S. = 0

Work method: 5 mL of KX and 5 mL of KXO are introduced into a test tube, both solutions having a concentration of 1M. The reaction takes place in an acidic medium, provided by the 5 mL of 1M HCl added to the test tube.

The general reaction is:

$$X^- + XO_3^- + H^+ \rightarrow X_2 + H_2O$$

Observations

1. Write the reactions for X = Cl, Br, I and the observations related to the experiments in question.

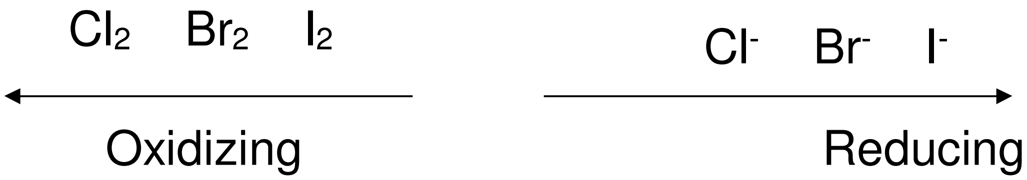
2. What do you observe in the case of the reaction between KCl and $KClO_3$ in 0.1M HCl?

3. Repeat the reaction between KCl and $KClO_3$, using concentrated HCl as the reaction medium. What do you notice?

Experiment 6. Interhalogen exchange reactions

The principle of the work: an oxidant can be reduced under standard conditions only by a stronger reducing agent than its conjugate.

$$1/2E_2 + E'^- \rightarrow E^- + 1/2E'_2$$



Work method:

- To 5 mL of chlorine water solution, add a few mL of KBr solution. The color of the reaction mixture, initially yellow-green, becomes yellow-brown. Write the equation for the reaction that takes place.
- To 5 mL of bromine water solution, add a few mL of KI solution. The color of the reaction mixture, initially yellow-brown, becomes reddish-brown. Write the equation for the reaction that takes place.

Experiment 7. Redox disproportionation of halogens in alkaline environment

Principle of work: redox disproportionation reaction is a reaction in which a species containing an atom in an intermediate oxidation state reacts with itself, resulting in two species in which the given atom has a lower or higher oxidation state than the original one.

General reaction: $3X_2 + 6HO^- \rightarrow X^- + XO_3^- + H_2O$

Work method: to 5 mL of $KI \cdot I_2$ solution, add a few mL of NaOH solution, until the reaction mixture becomes colorless.

! Write the equation of the reaction that took place.

12.2. Group VI_A

General properties

- **Electron configuration**:

O – $[He]2s^22p^4$
S – $[Ne]3s^23p^4$
Se – $[Ar]3d^{10}4s^24p^4$
Te – $[Kr]4d^{10}5s^25p^4$
Po – $[Xe]4f^{14}5d^{10}6s^26p^4$

- **Oxidation states of chalcogens in compunds:**

O	-2, +2 (+2: only in compound with fluorine)
S	-2, +2, +4, +6
Se	-2, +2, +4, +6
Te	-2, +2, +4, +6

Oxygen

Oxidation state zero; O.S. = 0 (O_2)

Redox balances for the molecule O_2

O_2 – oxidant in acidic medium
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

O_2 – oxidant in alkaline medium
$O_2 + 4e^- + 2H_2O \rightarrow 4HO^-$

Oxidation state -2 (minimum oxidation state) O.S. = -2

Water – complexing and precipitation agent for divalent M(II) cations, which usually have a coordination number of 4 or 6

Precipitation reagent

$[M(OH_2)_4]^{2+} + 2HO^- \rightarrow M(OH)_2(OH_2)_2 + 2H_2O$

$[M(OH_2)_6]^{2+} + 2HO^- \rightarrow M(OH)_2(OH_2)_4 + 2H_2O$

Chelating reagent

$M(OH)_2(OH2)_2 + 2HO^- \rightarrow [M(OH)_4]^{2-} + 2H_2O$

$M(OH)_2(OH2)_4 + 2HO^- \rightarrow [M(OH)_4(OH2)_2]^{2-} + 2H_2O$

! Not all hydroxides of divalent cations dissolve by hydroxocomplexation (Cu and Ni cations do not dissolve, unlike the Zn cation).

Water – complexing and precipitation agent for trivalent M(III) cations, which usually have a coordination number of 6

Precipitation reagent

$[M(OH_2)_6]^{3+} + 3HO^- \rightarrow M(OH)_3(OH_2)_3 + 3H_2O$

Chelating reagent

$M(OH)_3(OH_2)_3 + 3HO^- \rightarrow [M(OH)_4]^{2-} + 2H_2O$

$M(OH)_3(OH_2)_3 + HO^- \rightarrow [M(OH)_4(OH_2)_2]^- + H_2O$

! Not all hydroxides of divalent cations dissolve by hydroxocomplexation (Fe cations do not dissolve, unlike the Al cation).

Experiment 1. HO^- ion as precipitating and complexing agent for divalent cations

Work method: 2-3 mL of $CuSO_4$ or $ZnSO_4$ solution are introduced into two test tubes. Add the 0.1M NaOH solution dropwise and with stirring until the corresponding hydroxides precipitate. Continue adding the 0.1M NaOH solution in excess, noting in which of the two cases the dissolution of the precipitate by hydroxocomplexation took place.

! Write the equations of the reactions that took place.

Experiment 2. HO^- ion - precipitating and chelating agent for trivalent cations

2-3 mL of $Al_2(SO_4)_3$, respectively $Fe_2(SO_4)_3$ solution are introduced into two test tubes. Add the 0.1M NaOH solution dropwise and with stirring until the corresponding hydroxides precipitate. The excess addition of the 0.1M NaOH solution is continued, noting in which of the two cases the dissolution of the precipitate by hydroxocomplexation took place.

! Write the equations of the reactions that took place.

Redox behavior

Experiment 3: H_2O, reducing agent in acidic medium

Work method: 2-3 mL of $KMnO_4$ solution, 1 mL of water and 1-2 mL of diluted H_2SO_4 solution are introduced into a test tube. A color variation from purple to brown is observed.

The reaction that takes place is the following:

$$\underset{\text{purple}}{4MnO_4^-} + 4H^+ \rightarrow \underset{\text{brown}}{4MnO_2} + 3O_2 + 2H_2O$$

Experiment 4: HO^- ion, reducing agent in alkaline environment

Work method: 2-3 mL of KMnO4 solution, 1 mL of water and 1-2 mL of NaOH solution are introduced into a test tube. A color variation from purple to green is observed.

The reaction that takes place is the following:

$$\underset{\text{purple}}{4MnO_4^-} + 4HO^- \rightarrow \underset{\text{green}}{4MnO_4^{2-}} + O_2 + 2H_2O$$

Oxides, EO (Oxidation states O.S. = -2)

The elements of groups I_A, II_A and III_A form oxides in which the oxidation state of the metal coincides with the number of the group to which it belongs. The rest of the elements from groups IV_A, V_A, VI_A, VII_A, as well as transition metals, can form oxides in which the respective element will have several oxidation states.

Depending on the nature of the E-O bond, oxides are classified into oxides with an ionic structure and oxides with a covalent structure.

Oxides with an ionic structure are basic oxides, forming the corresponding hydroxides in aqueous solutions.

$EO + H_2O \rightarrow E(OH)_2$; E is a group I_A or II_A element

Oxides with a covalent structure are acidic oxides, forming the corresponding oxoacids in aqueous solutions.

$EO_2 + H_2O \rightarrow H_2EO_3$

Experiment 5.

Work method: Put a few milligrams of CaO in a test tube and add 2-3 mL of distilled water. Measure the pH using indicator paper.

Experiment 6.

Work method: A few milligrams of Al_2O_3 are introduced into a test tube and 2-3 mL of distilled water are added. Measure the pH using indicator paper.

! Explain the results obtained and write the equation of the chemical reaction (where appropriate).

Sulfur compounds at minimum oxidation state O.S.= -2 (H_2S, S^{2-})

Redox behavior

The sulfur atom in hydrogen sulfide (O.S.=-2) can be oxidized to S, SO_2 or SO_4^{2-} depending on the nature of the oxidant used in the reaction, its concentration and the pH of the reaction medium.

Experiment 7. Redox behavior of hydrogen sulfide H_2S

Principle of the work: highlighting the reducing character of H_2S in an acidic environment

Work method: In a test tube, I_2 is obtained by the reaction between KI and KIO_3 in an acidic environment, provided by H_2SO_4. Na_2S is added, which in the acidic reaction medium will release hydrogen sulphide H_2S. The formation of colloidal sulfur S is immediately observed.

Global reaction: **$H_2S + I_2 \rightarrow S + 2HI$**

Experiment 8. Redox behavior of H_2S

Principle of the work: highlighting the reducing character of H_2S in an acidic environment

Work method: Br_2 is obtained in a test tube by the reaction between KBr and $KBrO_3$ in an acidic environment, provided by HNO_3. Na_2S is added, which in the acidic reaction medium will release hydrogen sulphide H_2S. H_2S will be oxidized to SO_4^{2-}, the sulfate ion being identified by adding a few drops of $BaCl_2$ solution to the reaction mixture, obtaining $BaSO_4$ (white precipitate).

Global reaction: **$H_2S + 4Br_2 + 4H_2O \rightarrow H_2SO_4 + 8HBr$**

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{white precipitate}}{BaSO_4\downarrow} + 2HCl$$

Oxidation state -1 (O.S. = -1)

Hydrogen peroxide, H_2O_2

Inorganic peroxides can be classified into two categories:

- peroxides with ionic structure (alkaline and alkaline-earth metal peroxides);
- peroxides with a covalent structure (hydrogen peroxide).

Acid-base behavior

H_2O_2 has a weak acid character, which is due to the more pronounced descreening of the two H atoms (which are each bound to a strongly electronegative O atom, unlike H_2O).

$$H_2O_2 + H_2O = HO_2^- + H_3O^+ \qquad pK_a = 12$$

Experiment 9.

Measure the pH of the following solutions using indicator paper:
a) H_2O_2 3%
b) H_2O_2 6%
c) H_2O_2 12%
d) H_2O_2 30%

Compare the results with those obtained by theoretical calculation.

Redox behavior

In H_2O_2, the oxygen atom has oxidation state O.S. = -1, which means that:

- can be reduced to O.S. = -2 (oxidizing character)

- can be oxidized at O.S. = 0 (reducing character)

The redox couples corresponding to the oxidizing and reducing character are the following:

Oxidizing character - acidic environment

$H_2O_2 + 2e^- + 2H^+ = 2H_2O$

Oxidizing character – basic environment

$H_2O_2 + 2e^- = 2HO^-$

Reducing character - acidic environment

$O_2 + 2e^- + 2H_2O = H_2O_2 + 2HO^-$

Reducing character - basic environment

$O_2 + 2e^- + 2H^+ = H_2O_2$

Experiment 10. Redox behavior of H_2O_2

Work method: 2-3 mL of $MnSO_4$ solution, 2 mL of H_2O_2 6% and a few drops of NaOH solution are introduced into a test tube until a brown precipitate (MnO_2) is obtained.

Determine the role of H_2O_2 in the redox reaction that took place and write its equation.

Experiment 11. Redox behavior of H_2O_2

Mod de lucru: 3-4 mL of $KMnO_4$ solution, a few drops of H_2SO_4 solution and 2-3 mL of H_2O_2 are introduced into a test tube. A variation in the color of the reaction mixture from violet → colorless will be immediately observed.

Determine the role of H_2O_2 in the redox reaction that took place and write its equation.

Experiment 12. Redox behavior of H_2O_2

Work method: 3-4 mL of $KMnO_4$ solution, a few drops of H_2SO_4 solution and 2-3 mL of H_2O_2 are introduced into a test tube. A variation in the color of the reaction mixture from violet → colorless will be immediately observed.

Determine the role of H_2O_2 in the redox reaction that took place and write its equation.

Sulfur compounds at oxidation state +4 (H_2SO_3, SO_3^{2-})

Being in an intermediate oxidation state, sulfurous acid and sulfites are redox ampholytes.

- oxidizes to SO_4^{2-} (reducing character)
- are reduced to S, H_2S, S^{2-} (oxidizing character)

Practically, only the reductive character is important.

Experiment 13. Redox behavior of sulfite SO_3^{2-}

Principle of the work: highlighting the reducing character of SO_3^{2-}

Work method: 2-3 mL of $KMnO_4$ solution and 3-4 mL of diluted HNO_3 are introduced into a test tube. Add the Na_2SO_3 solution drop by drop and stirring until the purple color disappears. The formation of SO_4^{2-} is checked by adding a few drops of $BaCl_2$, when a white precipitate should be obtained.

Experiment 14. Redox behavior of sulfite SO_3^{2-}

Principle of the work: highlighting the reducing character of SO_3^{2-}

Work method: 2-3 mL of $K_2Cr_2O_7$ solution and 3-4 mL of diluted H_2SO_4 are introduced into a test tube. Add the Na_2SO_3 solution in drops and stirring until it turns orange to from green.

! Based on the redox couples, write the equations of the chemical reactions that take place.

Oxidation state +6 (maximum oxidation state) of sulfur

H_2SO_4 –diprotic acid
- strong acid in the first ionization step
- weak acid in the second ionization step

Redox behavior

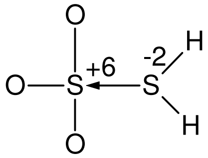
Oxidation state +6 is the maximum oxidation state, which means that H_2SO_4 and SO_4^{2-} are exclusively oxidizing agents.

The table below shows the reactants and products of the reactions of sulfuric acid with Br_2, respectively I_2. Based on it, write the equations of the reactions that take place in each of the two cases.

Reaction	Reagents		Products	
(1)	H_2SO_4	Br_2	SO_2	Br^-
(2)	H_2SO_4	I_2	S	I^-

Average oxidation state of sulfur +2

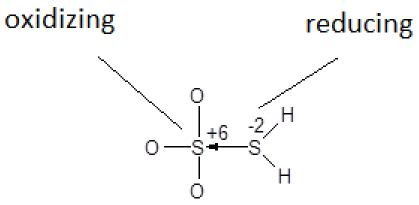
$H_2S_2O_3$, $S_2O_3^{2-}$ (Thiosulfuric acid, thiosulfate)



Acid-base behavior

The pair of electrons in the S-S bond is attracted to the sulfur atom at oxidation state +6 due to its high charge density, which causes the electron density of the S(-2) atom to decrease, which tries to recover its negative charge by attracting electrons from the sulfur-hydrogen S-H bond. For this reason, the hydrogen atom will be strongly deshielded and easily removed, which means that in the first step of deprotonation, thiosulfuric acid is a strong acid.

Redox behavior



Theoretically, thiosulfuric acid (and thiosulfates) are redox ampholytes. Practically, however, only the reducing function is manifested, because the access of reducing agents to S(+6) is hindered by the presence of the 3 neighboring oxygen atoms. Instead, the access of oxidants to the marginal S(-2) atom is much easier, so the reducing character of thiosulfuric acid (respectively thiosulfates) predominates.

The character of redox ampholyte is manifested only intramolecularly when S(+6) and S(-2) interact, S(+6) being reduced to S(+4), and S(-2) being oxidized to S(0). For this reason, the thiosulphuric acid solution is unstable, colloidal S is deposited over time.

$$H_2S_2O_3 \rightarrow SO_2 + S + H_2O$$

! Write the redox couples corresponding to the decomposition reaction of thiosulfuric acid.

Work 15. Redox behavior of $H_2S_2O_3$

Principle of the work: $H_2S_2O_3$ – intramolecular redox ampholyte

Work method: To 2-3 mL of $Na_2S_2O_3$ solution, add 2-3 mL of HCl solution while stirring. The reaction mixture is kept at room temperature for a few minutes, observing the formation of white-yellowish (colloidal) sulfur S.

Work 16. Redox behavior of $H_2S_2O_3$

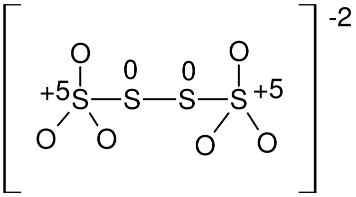
Principle of the work: $H_2S_2O_3$ – reducing agent

Work method: In a test tube, prepare I_2 (I_3^- reddish brown) from 2 mL of KI solution, 2 mL of KIO_3 and 2-3 mL of HCl. Add the $Na_2S_2O_3$ solution in drops and with stirring until the disappearance of gray I_2 (respectively I_3^- reddish-brown).

General reaction: **$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$**

tetrathionate

In tetrathionate ($S_4O_6^{2-}$) the oxidation state of the S atom is +2.5 (average oxidation state), due to the tetrathionate structure:



12.3. Group V_A

- **Electron configuration**:

N – $[He]2s^2 2p^3$

P – $[Ne]3s^2 3p^3$

As – $[Ar]3d^{10} 4s^2 4p^3$

Sb – $[Kr]4d^{10} 5s^2 5p^3$

Bi – $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$

- **Oxidation states of V_A group elements in compounds:**

N	-3; -2; -1; 0; +2; +3; +5
P	-3; 0; +3; +5
As	-3; 0; +3; +5
Sb	-3; 0; +3; +5
Bi	-3; 0; +3; +5

Oxidation state -3 (Minimum oxidation state)

The most important compound in which nitrogen has oxidation state -3 is ammonia NH_3. In aqueous solution, ammonia is a weak base:

$$\mathbf{NH_3 + H_2O \rightarrow NH_4^+ + HO^-} \quad K_b = 1.8 \cdot 10^{-5}$$

Experiment 1.

Work method: Measure the pH of a solution of NH_3 2N and compare it with the pH of solutions of NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ of the same concentration;

Knowing that $K_b(NH_3) = 1.8 \cdot 10^{-5}$, compare the experimental results with those obtained by calculation.

Experiment 2. NH_3 – chelating agent

Work method: 5 mL of $AgNO_3$ solution is introduced into a test tube, to which 5 mL of NH_3 solution is added. The resulting precipitate is separated, then excess NH_3 solution is added to it until it dissolves.

! Write the equations of the chemical reactions that take place and characterize the reaction products.

Experiment 3. NH_3 – chelating agent

Work method: 5 mL of $CuSO_4$ solution (respectively $ZnSO_4$ and $NiCl_2$) is introduced into a test tube, to which 5 mL of NH_3 solution is added. The resulting precipitate is separated, then excess NH_3 solution is added to it until it dissolves.

! Write the equations of the chemical reactions that take place and characterize the reaction products.

Compounds in which the nitrogen atom has the minimum oxidation state O.S. = -3 → ammonium salts

Thermal decomposition of ammonium salts

Ammonium salts sublimate when heated (do not melt); sublimation is apparent, because the vapors do not contain molecules of $NH_4^+A^-$, but a mixture of NH_3 and HA which recombines upon cooling.

Case 1

If the anion A^- is a weak reducer, there is no redox interaction with N(-3), and the decomposition reaction is:

$$NH_4A \rightarrow NH_3 + HA \quad (HA: HF, HCl, HBr, HI, H_2S)$$

Case 2

If the acid HA is an acid of lower mass, it leaves the system more easily and the equilibrium shifts to the right:

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$$

Case 3

If HA is a strong oxidant, it will interact with N(-3), giving a redox reaction:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Experiment 4. Thermal decomposition of ammonium salts

Work method: Insert a spatula tip of NH_4Cl into a crucible and heat for 1-2 minutes. Place a slide on which a drop of Nessler's reagent has been placed on top of the crucible.

Experiment 5. Thermal decomposition of ammonium salts

Work method: A spatula tip of $(NH_4)_2CO_3$ is inserted into a crucible and heated for 1-2 minutes. Place a slide on which a drop of solution has been placed on top of the crucible $Ba(OH)_2$.

Oxidation state +3

As it is an intermediate oxidation state, the compounds in which the nitrogen atom has the +3 oxidation state (nitric acid, respectively nitrogen oxides) can be both oxidizing and reducing (they are redox ampholytes).

Experiment 6: redox disproportionation of nitrite ion NO_2^- in acidic medium

Work method: 3-4 mL of $NaNO_2$ solution is introduced into a test tube, to which a few drops of diluted H_2SO_4 are added until the release of brown gas is observed (NO_2, resulting from the oxidation of intermediate NO).

Observation: acidification cannot be done with HCl because Cl^- is a stronger reducer than NO_2^- and it is substituted for it (HNO_3 behaves analogously).

General reaction: $NO_2^- \rightarrow NO_3^- + NO$

Exercise: based on the two redox couples presented previously, write the overall redox reaction. Determine the coefficients of each reactant and reaction product.

Experiment 7: oxidation of NO_2^- with Br_2, MnO_4^- şi $Cr_2O_7^{2-}$ in acidic environment

Reagents		Acidic medium (H^+)	Reaction products	
NO_2^-	Br_2		NO_3^-	Br^-
NO_2^-	MnO_4^-		NO_3^-	Mn^{2+}
NO_2^-	$Cr_2O_7^{2-}$		NO_3^-	Cr^{3+}

Work method: 5 mL of KNO_2 solution, 5 mL of $KMnO_4$ ($K_2Cr_2O_7$) solution and 2-3 mL of H_2SO_4 solution are introduced into a test tube. In the case of the reaction with Br_2, it is obtained from 2 mL of KBr solution and 2 mL of $KBrO_3$ solution acidulated with diluted H_2SO_4. Write down the observations in each of the three cases and complete the redox reactions.

Oxidation state +5 (Nitric acid, nitrates)

Experiment 8. Reducing HNO_3 with chloride Cl^-

Work method: 2 mL of HNO_3(c) is added to a solution of 6 mL of HCl(c). The contents of the test tube (colorless) are heated until the solution turns yellow (due to the formation of Cl_2).

Redox couples: Cl^-/Cl_2; NO_3^-/NO_2^-

Exercise: based on the two redox couples presented previously, write the overall redox reaction. Determine the coefficients of each reactant and the reaction products.

Experiment 9. Reduction reaction with bromine Br^-

Work method: 3-4 mL of HNO_3(c) is added to a 3 mL KBr solution. The colorless contents of the test tube are heated until the solution turns yellow-brown (due to the formation of Br_2).

Redox couples: Br^-/Br_2; NO_3^-/NO_2^-

Exercise: based on the two redox couples presented previously, write the overall redox reaction. Determine the coefficients of each reactant and the reaction products.

Experiment 10. Reduction reaction with iodine I^-

Work method: 3-4 mL of HNO_3(c) is added to a solution of 3 mL of KI. Iodide is a stronger reducing agent than chloride and bromide, so heating the reaction mixture is not necessary. The formation of I_2 (grey-violet) is observed first; by adding excess HNO_3, the formed I_2 reacts further, forming HIO_3 (colorless solution).

Redox couples: I^-/IO_3^-; NO_3^-/NO

Exercise: based on the two redox couples presented previously, write the overall redox reaction. Determine the coefficients of each reactant and reaction product.

Applications

Three HNO_3 solutions of different concentrations (c1<c2<c3) react with a H_2S solution.

The reactions that take place are the following:

HNO_3 (c1) + $H_2S \rightarrow NO + S + H_2O$

HNO_3 (c2) + $H_2S \rightarrow NO + SO_2 + H_2O$

HNO_3 (c3) + $H_2S \rightarrow NO + SO_4^{2-}$

Explain the variation of the oxidizing character of HNO_3 depending on its concentration. Determine, with the help of redox couples, the coefficients of the reactants and reaction products.

Experiment 11. Reduction in basic environment of nitrate ion NO_3^-

The oxidizing character of NO_3^- in a basic environment is highlighted through the following reactions:

Reagents		Alkaline environment (HO-)	Reaction products	
NO_3^-	Mn^{2+} (colorless)		NO_2^-	MnO_2 (brown)
NO_3^-	Cr^{3+} (green)		NO_2^-	$CrO_4$2- (yellow)
NO_3^-	Al (silver)		NH_3	$Al(OH)_3$

Working method: 5 mL of KNO_3 solution, 5 mL of $MnCl_2$ solution (respectively 5 mL of $Cr_2(SO_4)_3$, a tip of Al powder spatula) and 2-3 mL of NaOH solution are introduced into a test tube. Write down the observations in each of the three cases and complete the redox reactions.

CHAPTER 13. METALS

For the preparation of solutions in which the metal is aquacation, a slightly soluble salt is used (preferably, nitrates of the respective metals).

$M_mA_n \rightarrow [M(OH_2)_x]^{n+}$

Acid-base reactions

1. Reaction with strong bases (hydroxides)
- proceeds with the precipitation of the hydroxide of the corresponding metal

$$[M(OH_2)x]^{n+} + nHO^- \rightarrow M(OH)_n(OH_2)_{x-n}\downarrow + nH_2O$$

2. The complexation reaction

$$[M(OH_2)_x]^{n+} + L \rightarrow [ML_x]^{n+}$$

13.1. Group IV_A metals (Sn, Pb)

Maximum oxidation state = +4
Intermediate oxidation state = +2

Preparation of solutions $[M(OH_2)_4]^{2+}$

Experiment 1. Preparation of solutions $[Sn(OH_2)_4]^{2+}$

Work method: dissolve a few mg of $SnCl_2$ in distilled water; a hardly soluble hydrolysis product (inorganic polymer) is obtained.

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl$$

This polymer can only be destroyed in the presence of concentrated HCl, when hot, when the overall reaction is as follows:

$$SnCl_2 + H_2O = [Sn(OH_2)_4]^{2+} + 2Cl^-$$

Sn(II), a strong reducing agent, is oxidized in aqueous solution by O_2 dissolved in water. The reactions that take place are the following:

$Sn^{2+} = Sn^{4+} + 2e^-$
$\frac{1}{2} O_2 + 2e^- + 2H^+ = H_2O$

$Sn^{2+} + \frac{1}{2} O_2 + 2H^+ \rightarrow Sn^{4+} + H_2O$

Therefore, once prepared, the Sn(II) solution will be kept in the presence of Sn^0, because Sn^0 will reduce Sn^{4+}:

$Sn^{4+} + 2e^- = Sn^{2+}$
$Sn^0 = Sn^{2+} + 2e^-$

$Sn^{4+} + Sn^0 \rightarrow 2Sn^{2+}$

Experiment 2. Preparation of solutions $[Pb(OH_2)_4]^{2+}$

Work method: Pb(II) solutions are much easier to prepare than those of tin, it being sufficient to dissolve a few miligrames $Pb(NO_3)_2$ or $Pb(CH_3COO)_2$ in distilled water.

Experiment 3. Reaction with strong bases, precipitation of hydroxides and verification of amphoteric carácter

Work method: 2-3 mL of Pb(II) or Sn(II) solution are introduced into two test tubes, to which the diluted NaOH solution is added in n one of the test tubes, add the diluted HNO3 solution in portions until the precipitate is solubilized, and in the other add 30% NaOH solution.

$[Sn(OH_2)_4]^{2+} + 2HO^- \rightarrow Sn(OH)_2(OH_2)_2 + 2H_2O$

$Sn(OH)_2(OH_2)_2 + 2H_3O^+ \rightarrow [Sn(OH_2)_4]^{2+} + 2H_2O$

$Sn(OH)_2(OH_2)_2 + 2HO^- \rightarrow [Sn(OH)_4]^{2-} + 2H_2O$

! Write the appropriate reactions for $[Pb(OH_2)_4]^{2+}$.

Experiment 4. $PbSO_4$ precipitation and solubilization by hydroxocomplexation

Work method: 2-3 mL of $Pb(NO_3)_2$ solution is introduced into a test tube to which a few drops of H_2SO_4 diluted solution are added.

$$\mathbf{Pb(NO_3)_2 + H_2SO_4 \rightarrow \underset{\text{White precipitate}}{PbSO_4\downarrow} + 2HNO_3}$$

30% NaOH solution is added to the formed precipitate until it is solubilized:

$$\mathbf{PbSO_4 + 4NaOH \rightarrow [Pb(OH)_4]^{2-} + 2Na_2SO_4}$$

Experiment 5. $PbCrO_4$ precipitation and solubilization by hydroxocomplexation

Work method: 2-3 mL of $Pb(NO_3)_2$ solution is introduced into a test tube to which a few drops of K_2CrO_4 diluted solution are added.

$$\mathbf{Pb(NO_3)_2 + K_2CrO_4 \rightarrow \underset{\text{Yellow precipitate}}{PbCrO_4\downarrow} + 2KNO_3}$$

30% NaOH solution is added to the formed precipitate until it is solubilized:

$$\mathbf{PbCrO_4 + 4NaOH \rightarrow [Pb(OH)_4]^{2-} + 2Na_2CrO_4}$$

Experiment 6. Precipitation of Pb(II) halides and solubilization by halogen complexation

Work method: 2-3 mL of $Pb(NO_3)_2$ solution is introduced into a test tube to which a few drops of NaCl solution are added.

$$\mathbf{Pb(NO_3)_2 + 2NaCl \rightarrow \underset{\text{White precipitate}}{PbCl_2\downarrow} + 2NaNO_3}$$

30% NaOH solution is added to the formed precipitate until it is solubilized:

$$\mathbf{PbCl_2 + NaCl(exces) \rightarrow Na_2[PbCl_4]}$$

Redox reactions of group IV_A metals

Sn^{2+} - strong reducer
Pb^{4+} - strong oxidant

Experiment 7. Reducing MnO_4^- with Sn^{2+}.

Work method: 2-3 mL of oxidant ($KMnO_4$) and acidic $SnCl_2$ solution are introduced into a test tube until the color turns violet → colorless.

The global reaction is:

$$\mathbf{2KMnO_4 + 5SnCl_2 + 16\,HCl \rightarrow 2MnCl_2 + 5SnCl_4 + 2KCl + 8H_2O}$$

! Write the redox couples corresponding to the global reaction.

Experiment 8. Oxidation of iodide with PbO_2 in acid medium

Mod de lucru: 2-3 mL of KI solution, 2-3 mL of HNO_3 and PbO_2 solution are introduced into a test tube. The I_2 formed in the reaction is extracted into CCl_4.

The global reaction is:

$$\mathbf{PbO_2 + 4HI \rightarrow PbI_2 + I_2 + 2H_2O}$$

13.2. The reactions of chromium (Cr) (VIb)

Electron configuration: $[_{18}Ar]3d^5 4s^1$

Maximum oxidation state (Cr) = +6
Intermediate oxidation state (Cr) = +3

Experiment 9. Reaction with strong bases; precipitation of $Cr(OH)_3$.

Work method: 2-3 drops of $Cr_2(SO_4)_3$ solution are introduced into a test tube and a few drops of NaOH solution are added until the corresponding precipitate is obtained.

$$\mathbf{[Cr(OH_2)_6]^{3+} + 3NaOH \rightarrow Cr(OH)_3(OH_2)_3\downarrow + 3H_2O}$$

Experiment 10. The reaction with weak bases; precipitation of $Cr(OH)_3$ and complexation with NH_3.

Work method: 2-3 drops of $Cr_2(SO_4)_3$ solution are introduced into a test tube and a few drops of NH_3 solution are added until the corresponding precipitate is obtained. By adding NH_3 in excess, the precipitate obtained dissolves.

$$[Cr(OH_2)_6]^{3+} + 3NH_3 \rightarrow Cr(OH)_3(OH_2)_3\downarrow + 3NH_4^+$$

$$Cr(OH)_3(OH_2)_3\downarrow + 3NH_3 \rightarrow [Cr(NH_3)_6]^{3+} + 3HO^- + 3H_2O$$

Redox behavior

Experiment 11. Equilibrium $CrO_4^{2-} \leftrightarrow Cr_2O_7^{2-}$ in aqueous solution

Work method: 3-4 mL of $K_2Cr_2O_7$ (orange) and K_2CrO_4 (yellow) solutions are introduced into 2 test tubes. Add in drops NaOH solution, respectively H_2SO_4 until the corresponding color change. It can be returned to the initial state by adding H_2SO_4 solution, respectively NaOH.

$$(1)\ 2CrO_4^{2-} + 2H_3O^+ \leftrightarrow Cr_2O_7^{2-} + 3H_2O$$
$$(2)\ Cr_2O_7^{2-} + 2HO^- \leftrightarrow 2CrO_4^{2-} + H_2O$$

Experiment 12. $Cr_2O_7^{2-}$ - oxidant in acidic environment

Work method: add 2-3 mL of H_2SO_4 solution and reducing agent solution to 2-3 mL of $K_2Cr_2O_7$ solution, until the corresponding color change.

In acidic environment, $Cr_2O_7^{2-}$ is a strong oxidizing agent:

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

Oxidising agent	Reducing agent	Reaction products		Change of color
$Cr_2O_7^{2-}$	I^-	Cr^{3+}		orange → ....
	H_2O_2			
	SO_3^{2-}			
	NO_2^-			
	$S_2O_3^{2-}$			

13.3. Reactions of manganese (Mn) (VII_b)

Electron configuration: $[_{18}Ar]3d^5 4s^2$

Maximum oxidation state = +7
Intermediate oxidation state = +2; +3; +4; +6

Acid-base behavior

Experiment 13. Hydrolysis behavior of $MnSO_4$

Work method: 5 mg of $MnSO_4$ and 5 mL of water are introduced into a test tube. The pH of the obtained solution is measured both with the help of the pH-meter and with indicator paper.

The global reaction is:

$$\mathbf{MnSO_4 + water \rightarrow \underset{\text{weak acid}}{[Mn(OH_2)_6]^{2+}} + \underset{\text{weak base}}{SO_4^{2-}aq}}$$

$$\mathbf{[Mn(OH_2)_6]^{2+} + H_2O = [Mn(OH)(OH_2)_5]^+ + H_3O^+} \quad pKa = 10.1$$

$$\mathbf{SO_4^{2-} + H_2O = HSO_4^- + HO^-} \quad Ka = 2$$

Experiment 14. Reaction with strong bases; precipitation of $Mn(OH)_2$

Work method: 2-3 drops of $MnSO_4$ solution are introduced into a test tube and a few drops of NaOH solution are added until the corresponding precipitate is obtained.

$$\mathbf{[Mn(OH_2)_6]^{2+} + 2NaOH \rightarrow Mn(OH)_2(OH_2)_4\downarrow + 2H_2O}$$

Experiment 15. The reaction with weak bases; precipitation of $Mn(OH)_2$.

Work method: 2-3 drops of $MnSO_4$ solution are introduced into a test tube and a few drops of NH_3 solution are added until the corresponding precipitate is obtained.

$$\mathbf{[Mn(OH_2)_6]^{2+} + 2NH_3 \rightarrow Mn(OH)_2(OH_2)_4\downarrow + 2NH_4^+}$$

Redox behavior

Experiment 16. The obtaining of MnO_2 in laboratory

Work method: 2-3 mL $MnSO_4$ and 2-3 mL $KMnO_4$ are introduced into a test tube; separate the obtained brown precipitate (MnO_2).

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + 2H_2SO_4 + K_2SO_4$$

Experiment 16. MnO_2 – oxidising agent in acidic environment

Work method: The previously obtained MnO_2 is acidified with 3-4 mL of H_2SO_4 solution and a reducing agent solution is added until the precipitate disappears and the corresponding color change occurs.

$$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$$

Oxidising agent	Reducing agent	Reaction products		Change of color
MnO_2	I^-	Mn^{2+}		...... → yellow-brownish
	H_2O_2		O_2	
	SO_3^{2-}		SO_4^{2-}	
	$H_2C_2O_4$		CO_2	

Experiment 17. Reduction of MnO_4^- to MnO_4^{2-}

Work method: to 4-5 mL of $KMnO_4$ solution add one NaOH granule; it is gently heated on a water bath, obtaining MnO_4^{2-} (green).

$$2KMnO_4 + 2NaOH \rightarrow K_2MnO_4 + Na_2MnO_4 + ½\,O_2 + H_2O$$

Experiment 18. „Step by step” reduction of permanganate MnO_4^- to Mn^{2+} in the presence of iodide I^-

Work method: 4-5 mL of $KMnO_4$ solution is alkalized with 3 mL of 30% NaOH solution, after which 3-4 mL of KI solution is added. A green solution ($MnO_4$2-) is immediately obtained, to which a few drops of acetic acid solution are added until MnO_2 precipitates. It is further acidified with H_2SO_4 until the precipitate "solubilizes" and Mn^{2+} is obtained.

(1) $MnO_4^- + I^- \rightarrow MnO_4^{2-} + IO_3^-$
(2) $MnO_4^{2-} + I^- \rightarrow MnO_2 + IO_3^-$
(3) $MnO_2 + I^- \rightarrow Mn^{2+} + I_2$

Experiment 19. Permanganate MnO_4^- as oxidising agent in acidic environment

Work method: to 2-3 mL of $KMnO_4$ solution, add 2-3 mL of diluted H_2SO_4 and reducing agent solution, until the appropriate color change.

In acidic environment, MnO_4^- is a strong oxidizer:

$$MnO_4^- + 5e^- + 8H^+ = 2Mn^{2+} + 4H_2O$$

Oxidising agent	Reducing agent	Reaction products		Change of color
MnO_4^-	I^-	Mn^{2+}		Purple → ....
	H_2O_2			
	$H_2C_2O_4$			
	NO_2^-			
	$S_2O_3^{2-}$			

CHAPTER 14. INORGANIC COMPOUNDS WITH PHARMACEUTICAL ACTION

14.1. Alkaline metals

Lithium compounds

Li_2CO_3 (Lithium carbonate) [13]

- Used in the treatment of bipolar disorder;
- It acts by inhibiting the activity of protein-kinase C, which has a high activity in the case of various manias.

Obtaining methods

- by the reaction of lithium peroxide with carbon dioxide:

$$2Li_2O_2 + 2CO_2 \rightarrow 2Li_2CO_3 + O_2$$

Physical and chemical properties

- solid compound, high melting point
- white powder
- forms basic solutions
- hardly soluble in water

Sodium compounds [14]

Na^+ is the main cation in extracellular fluids, representing ~90-95% of cations present in plasma and interstitial fluid.

Sodium compounds with pharmacological action:

$NaHCO_3$ (Sodium bicarbonate)

- Antacid

Physical and chemical properties

- Solid compound
- White powder
- Water soluble
- forms basic solutions

Obtaining methods: Solvay process

$$NaCl(aq) + NH_3(aq) + CO_2(s) + H_2O \rightarrow NH_4Cl(aq) + NaHCO_3(s)$$

$Na_2HPO_4 \cdot 12H_2O$ (Disodium phosphate)

- laxative

Physical and chemical properties

- white granules
- forms basic solutions
- water soluble

Obtaining methods

$$H_3PO_4 + 2\ NaOH \rightarrow Na_2HPO_4 + 2\ H_2O$$

Sodium citrate

- anticoagulant for the blood to be stored
- urinary alkalinizer
- white crystalline powder
- high solubility in water

NaF (Sodium fluoride)

- preventive role of dental cavities; it is used in the form of gel or solution.
- greenish-white solid compound
- low solubility in water

NaCl (Sodium chloride)

important role in osmotic and acid-base equilibrium

$Na_2S_2O_7$ (Sodium thiosulfate)

- it is used intravenously as an antidote for cyanide poisoning
- topical antifungal agent
- white crystalline compound
- high solubility in water

Potassium compounds

KI (Potassium iodide)

- expectorant and decongestant in the treatment of asthma, chronic bronchitis
- white crystals
- over time the color may turn yellow, due to the following reaction:

$$4\ KI + 2\ CO_2 + O_2 \rightarrow 2\ K_2CO_3 + 2\ I_2$$

$KMnO_4$ (Potassium permanganate)

- used in the treatment of fungal infections and dermatological conditions
- gray-violet solid
- high solubility in water

KCl (Potassium chloride)

- used to prevent and treat low levels of pottasium
- white crystalline compound
- high solubility in water

14.2. Alkaline earth metals

Magnesium compounds

MgO (magnesium oxide)

- antacid, laxative

$MgCO_3$ (Magnesium carbonate) [15]

- antacid, alkaline buffer in pharmaceutical preparations. It is also one of the ingredients of toothpaste.

Physical properties

- white solid compound, hygroscopic
- low solubility in water.

Obtaining methods

$$MgCl_2(aq) + 2NaHCO_3(aq) \rightarrow MgCO_3(s) + 2NaCl(aq) + H_2O(l) + CO_2(g)$$

$MgSO_4$ (magnesium sulfate) [16]

- laxative
- solid crystalline compound, white color

Obtaining methods

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

$Ca_3(PO_4)_2$ (Calcium phosphate)

- inactive compound, used in pharmaceutical formulations
- white powder
- low water solubility

$CaCl_2$ (calcium chloride) [17]

- intravenous infusion
- role of increasing the level of Ca in the body and ensuring the proper functioning of the heart when the level of K is too high.
- white, hygroscopic powder
- soluble in water

Obtaining methods

$2\,NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

$Ca(OH)_2$ (Calcium hydroxide)

compound with astringent action, used in topical lotions

Obtaining methods

$CaO + H_2O \rightarrow Ca(OH)_2$

$BaSO_4$ (barium sulfate)

contrast agent

Obtaining methods

$Ba(NO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HNO_3$

Physical and chemical properties

- white crystalline compound
- low water solubility

14.3. Other metals

$Al(OH)_3$ (Aluminum hydroxide) [18]

- antacid
- white amorphous poder
- water insoluble

$CuSO_4$ (copper sulfate) [19]

- antiseptic, antifungal agent, treatment of copper deficiency
- white-grey anhydrous crystalline compound
- crystal hydrate: blue-green crystalline compound

Obtaining methods

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

$AgNO_3$ (Silver nitrate) [20]

- crystalline compound (high toxicity)
- antiseptic and astringent properties

Obtaining method

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO$$

Iodine tincture (I_2 2.5%, KI 2.5%) [21]

- cutaneous use, local antiseptic

$FeSO_4$ (iron(II) sulfate) [22]

- for the prevention and treatment of iron deficiency, anemia.
- white crystals (anhydrous)
- white-yellow crystals (monohydrate)
- blue-green crystals (heptahydrate)

Obtaining method

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

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